



**Preparation, Characterization and Photocatalytic Application of  $\text{TiO}_2$   
Supported on Zeolites for Textile Wastewater Treatment**

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This is to certify that the thesis prepared by Kiros Guesh, **entitled: “*Preparation, Characterization and Photocatalytic Application of TiO<sub>2</sub> Supported on Zeolites for Textile Wastewater Treatment*”** submitted in fulfillment of the requirements of degree of Doctor of Philosophy (Inorganic Chemistry) complies with the regulation of the University and meets the accepted standards with respect to originality and quality.

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## ABSTRACT

### **Preparation, Characterization and Photocatalytic Application of TiO<sub>2</sub> Supported on Zeolites for Textile Wastewater Treatment**

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Addis Ababa University, 2016

In this PhD research, potential of Ethiopian natural zeolite for photocatalytic application has been assessed and 10, 20, 40 wt% TiO<sub>2</sub> supported on selected synthetic zeolite materials have been systematically prepared. Different treatment conditions both on the zeolite surface and TiO<sub>2</sub> have been attempted. Selected zeolites were treated at different conditions to make their surface chemistry suitable for TiO<sub>2</sub> support. The properties of supported TiO<sub>2</sub> were also tuned by changing the synthesis conditions. Furthermore, metal and nonmetal co-doped TiO<sub>2</sub> supported on zeolites have been prepared.

The prepared samples were characterized by X-ray diffraction (XRD), elemental analysis (ICP-OES), Thermogravimetric Analysis (TGA), N<sub>2</sub> adsorption-desorption isotherms, UV-Vis Diffuse Reflectance Spectroscopy (UV-Vis DRS), Scanning Electron Microscopy (SEM/EDS), Scanning Transmission Electron Microscopy with High Angular Annular Dark Field detector (STEM/HAADF), Electron Energy Loss Spectroscopy (STEM/EELS), Photoluminescence (PL) Spectroscopy and X-ray Photoelectron Spectroscopy (XPS). Crystalline TiO<sub>2</sub> with particle sizes ranging from 6 nm to 9 nm and semi- amorphous TiO<sub>2</sub> were prepared supported on zeolites. The supported TiO<sub>2</sub> showed higher light absorption coefficient and lower photoluminescence emissions than the pristine TiO<sub>2</sub> nanoparticles.

Photocatalytic activity of the samples was tested for the degradation of MO, a stable and non biodegradable azo dye. The reusability of the photocatalysts prepared and leaching extent of  $\text{Ti}^{4+}$  species during the photocatalytic reaction have been determined for selected samples. Photocatalytic treatment of real wastewaters from a textile factory in Ethiopia has been tested using selected synthetic photocatalysts.

The supported  $\text{TiO}_2$  nanoparticles showed higher photocatalytic activity than the pristine  $\text{TiO}_2$  nanoparticles. The enhanced photocatalytic activity of the supported  $\text{TiO}_2$  system is attributed to the dual role of the zeolite on enhancing adsorption capacity of the composite and brought some electronic changes on the  $\text{TiO}_2$  to lower photogenerated electron hole recombination rate. Leaching prevention and reusability are the added values of the zeolites in the photocatalytic reaction tested. Furthermore, the photocatalytic activity of the semi-amorphous  $\text{TiO}_2$  brings new features of  $\text{TiO}_2$  based photocatalysis, which needs further investigations.

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### **List Abbreviations**

|         |                                                          |
|---------|----------------------------------------------------------|
| BET     | Brunauer Emmett Teller                                   |
| DRS     | Diffuse Reflectance Spectroscopy                         |
| EDS     | Energy Dispersion Spectroscopy                           |
| EELS    | Electron Energy Loss Spectroscopy                        |
| EEPA    | Ethiopian Environmental Protection Authority             |
| ETIDI   | Ethiopian Textile Industry Development Institute         |
| FFT     | Fast Fourier Transform                                   |
| HAADF   | High Angular Annular Dark Field                          |
| ICP-MS  | Inductively Coupled Plasma Mass Spectrophotometry        |
| ICP-OES | Inductively Coupled Plasma Optical Emission Spectroscopy |
| MO      | Methyl Orange                                            |
| PL      | Photoluminescence                                        |
| SEM     | Scanning Electron Microscopy                             |
| STEM    | Scanning Transmission Electron Microscope                |
| TGA     | Thermogravimetric Analysis                               |
| TORm    | Mass Normalized Turnover Rate                            |
| XPS     | X-ray Photoelectron Spectroscopy                         |
| XRD     | X-Ray Diffraction                                        |

## **1. Background of the Study**

Photocatalysis by solid semiconductor photocatalysts has attracted much attention in the last 4 decades since 1972 when Fujishima and Honda [1] observed electrochemical photolysis of water on  $\text{TiO}_2$  semiconductor electrode, although such attempts are dated back to the second decade of the 20<sup>th</sup> century[2-6]. Photocatalysis has continued being an interesting area of research devoted to alleviating large number of global challenges[7]. It has shown to be a promising way for degradation of various pollutants such as dyes, pesticides and pharmaceuticals [8-15]. It is also being used in photoelectrochemical conversion in green chemical synthesis [16-26],  $\text{CO}_2$  photoreduction to yield organic fuels[27] and water photolysis to produce molecular hydrogen as energy carrier (source of clean energy)[28-32]. These are all current strategic research areas.

### **1.1. $\text{TiO}_2$ Based Photocatalysis: Fundamentals**

Among the many tested photocatalysts,  $\text{TiO}_2$  is found to be superb owing to its higher photocatalytic activity, suitable band position, reasonable price and photo stability [8, 25, 33]. According to the band theory, each solid can be characterized by two energetic bands: a valence band, VB, which possesses lower energy, completely or partially filled with electrons (at least at 0 K); and a conduction band, CB, with higher energy, empty at 0 K. The energetic distance between them ranges between 0.7-3.5 eV for semiconductors and is called a forbidden band or band gap energy,  $E_g$ . The distance between the valence and conduction bands determines the electronic properties of the solid such as electrical conduction and optical properties. Photocatalysis over  $\text{TiO}_2$ , solid semiconductor photocatalysts, is initiated by the absorption of a photon with energy equal to or greater

than the band gap of the semiconductor [9, 32, 34]. The absorption leads to a charge separation due to promotion of an electron ( $e^-$ ) from the valence band of the semiconductor photocatalyst to the conduction band, thus generating a hole ( $h^+$ ) in the valence band and an electron in the conduction band [32]. The ultimate goal of the process is to have a reaction between the activated electrons with an oxidant to produce a reduced product, and also a reaction between the generated holes with a reducer to produce an oxidized product. The photogenerated electrons could reduce adsorbed organic molecules through carbanions ( $R^-$ ) or react with electron acceptors such as  $O_2$  adsorbed on the surface of the photocatalyst reducing it to superoxide radical anion  $O_2^{\cdot-}$ . The photogenerated holes can oxidize the organic molecule to form carbocation intermediate ( $R^+$ ), or react with  $OH^-$  or  $H_2O$  oxidizing them into  $OH^\bullet$  radicals. Together with other highly oxidant species (peroxide radicals), they are reported to be responsible for the heterogeneous  $TiO_2$  photodecomposition of organic substrates such as dyes. The resulting  $^\bullet OH$  radical, being a very strong oxidizing agent (standard redox potential +2.8 eV) can oxidize most organic compounds to the mineral end-products. According to this, the relevant reactions at the semiconductor surface causing the degradation of dyes and other organic can be expressed as in Figure 1.

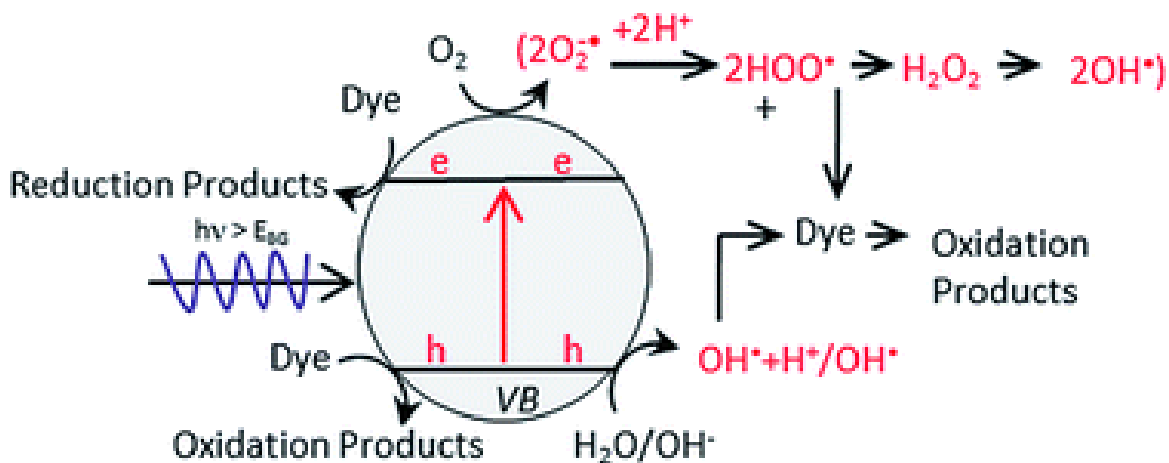


Figure 1: Photocatalytic degradation mechanism of dyes[35]

## 1.2. Synthesis Methods of TiO<sub>2</sub>

A variety of synthesis methods such as sol-gel[36-39], hydrothermal [40-42], solvothermal [43, 44] and sonochemical have been developed so far for the synthesis of TiO<sub>2</sub> nanoparticles [7]. Sol-gel method is a versatile process used in the production of several kind of materials. In a typical sol-gel process, a colloidal suspension, or a sol, is formed from the hydrolysis and polymerization reactions of the precursors, which are usually inorganic metal salts or metal organic compounds such as metal alkoxides. This process normally proceeds via a hydrolysis step of titanium (IV) alkoxide followed by condensation [45, 46]. Since this method is a solution process, it allows flexibility in parameter control with the aim of tailoring the structural characteristics such as composition homogeneity, grain size, particle morphology and porosity. In sol-gel method, a sol of amorphous TiO<sub>2</sub> is formed after hydrolysis of the TiO<sub>2</sub> precursor, which can be calcined to obtain anatase TiO<sub>2</sub>. If titanium alkoxide is used as a precursor, high temperature calcination is required for the removal of organics as well as for the

crystallization of  $\text{TiO}_2$  sol. If inorganic salts are used as precursors (e.g.  $\text{TiCl}_4$ ), then repeated washing is required for removing the inorganic species before calcinations. Sol–gel preparation of nano  $\text{TiO}_2$ , characterization and its photocatalytic activity have been reported in the literature. For example Su *et al.*, (2004) prepared the  $\text{TiO}_2$  sols by the hydrolysis and condensation of titanium (IV) *n*-butoxide in *iso*-propyl alcohol. In order to control the reaction kinetics, acetylacetone (acac) was used as a chemical additive to moderate the reaction rate. They calcined the sol from 400 to 700 °C to obtain the desired crystalline phase state. The microstructural and chemical properties of  $\text{TiO}_2$ , obtained by a sol–gel procedure were studied. They examined the photocatalytic activity of the as-prepared  $\text{TiO}_2$  for the photodecomposition of salicylic acid. They found that the anatase phase dominated the salicylic acid decomposition.

Hydrothermal synthesis is normally conducted in autoclaves with or without Teflon liners under controlled temperature and/or pressure with reactions in aqueous solutions. The temperature can be elevated above the boiling point of water, reaching the pressure of vapor saturation. The temperature and the amount of solution added to the autoclave largely determine the internal pressure produced. It is a method that is widely used for the production of small particles. For example Kolenko *et al.*, (2004) [40] prepared nanocrystalline titania with particle size ranging between 20–50 nm and specific surface area 20–80  $\text{m}^2\text{g}^{-1}$  by hydrothermal treatment of aqueous  $\text{TiOSO}_4$ ,  $\text{H}_2\text{TiO}(\text{C}_2\text{O}_4)_2$ , and  $\text{TiO}(\text{NO}_3)_2$  solutions followed by calcination. They studied the photocatalytic behavior of the synthesized  $\text{TiO}_2$  powders in photodegradation of phenol in water and they explored the optimal characteristics of the materials. They reported that best photocatalytic activity

was observed for a mixture of rutile (15%) and anatase (85%) prepared by high-temperature hydrolysis of aqueous  $\text{TiOSO}_4$  solution.

The solvothermal method is almost identical to the hydrothermal method except that the solvent used here is non aqueous. However, the temperature can be elevated much higher than that in hydrothermal method, since a variety of organic solvents with high boiling points can be chosen. The solvothermal method normally has better control than hydrothermal methods of the size and shape distributions and the crystallinity of the  $\text{TiO}_2$  nanoparticles. The solvothermal method has been found to be a versatile method for the synthesis of a variety of nanoparticles with narrow size distribution. For example, Kim *et al.*, (2003) [43] synthesized nanocrystalline  $\text{TiO}_2$  by surfactant-aided solvothermal synthetic method in toluene solutions. They used Titanium isopropoxide (TIP) as a Titanium (IV) precursor, which decomposed at high temperature in the surfactant-dissolved solution followed by thermal treatment at 250 °C for 20 h in an autoclave. The authors reported that  $\text{TiO}_2$  nanocrystalline particles with average size of 6 nm were synthesized.

### **1.3. $\text{TiO}_2$ based photocatalysis: Current Limitations**

Although  $\text{TiO}_2$  photocatalyst is the best photocatalyst so far, it has apparent challenges in its practical application (Figure 2).

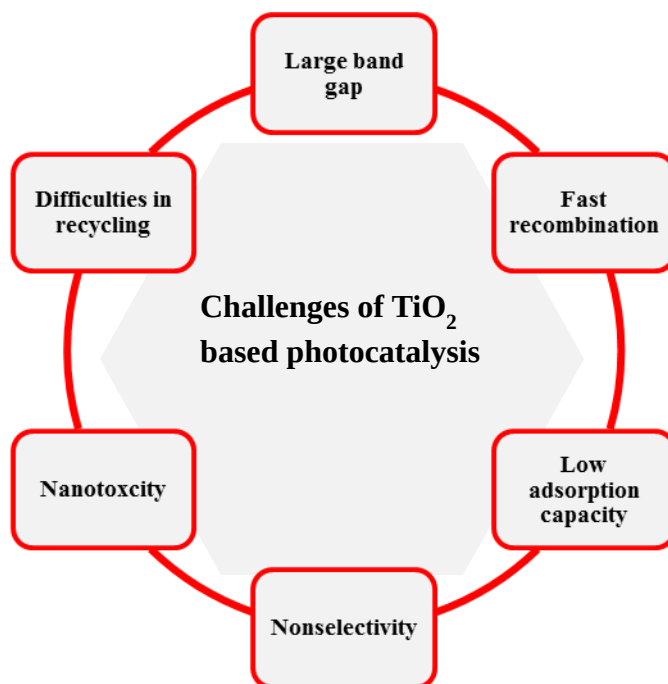


Figure 2: Limitations of TiO<sub>2</sub> Based photocatalysis

As shown in Figure 1, the first prerequisite for photocatalysis is that the material should create electron – hole pair upon absorption of certain amount of light energy which is equal or greater than the band gap energy ( $E_g$ ). The  $E_g$  of TiO<sub>2</sub> is 3.2 eV meaning it needs UV light irradiation in its light driven applications. Utilization of UV light is costly, environmentally unsafe and is very limited in the solar spectrum, almost less than 6%. To exploit the more abundant source of light energy coming from the sun, incorporation of certain changes within the semiconductor system is necessary in order to make it suitable for efficient utilization of visible light energy. Narrowing the large band gap of TiO<sub>2</sub> (3.2 eV) is therefore the challenging component of TiO<sub>2</sub> based photocatalysis [47-49]. Once the electron – hole pair is created upon absorbing light energy, the electron-hole pair will either be transferred to the adsorbed target molecules (interfacial electron hole transfer) or they will recombine emitting the absorbed energy. For effective photocatalysis, the

created electron-hole pair should be dissociated and transferred to the adsorbed species. However, the electron-hole pair recombination is faster than the interface electron-hole transfer, which decreases the photoactivity. Therefore, to delay this recombination some changes must be done on the surface and/or electronic properties of the semiconductor [34, 47-49]. Different approaches such as metallic doping [50, 51], nonmetallic doping [52-54], co-doping [55-57], and dye sensitization [58] have been attempted to narrow the band gap of  $\text{TiO}_2$  and delay the fast recombination rate of photogenerated electron-hole pairs. However, the metallic doping sometimes act as recombination centers, the nonmetallic doping narrows the band gap energy, but it is at the expense of the redox potential of the valence band of the semiconductor, and the dye synthesizing has a limitation of recyclability since the dye degrades itself within the first cycle. It was also reported that doped  $\text{TiO}_2$  is thermally unstable [8].

Besides these electronic challenges mentioned above,  $\text{TiO}_2$  is poor in adsorption [47, 59, 60] and nonselective [61-63] of the target molecule.  $\text{TiO}_2$  is super hydrophilic leading to poor affinity towards hydrophobic organic pollutants. Thus the adsorption is low, resulting in slow photocatalytic degradation rates [63] because the rate of photocatalysis is a function of the adsorption of the target molecule to be degraded.  $\text{TiO}_2$  is also known for its nonselective photocatalytic degradation via complete oxidation or complete reduction. In this regard, selectivity is important when dealing with a mixture, which contains compounds that need to be degraded and compounds that need to be recovered [61-63].

Aside the electronic and surface challenges explained in the above paragraphs, the fate of nanoparticles in general and TiO<sub>2</sub> nanoparticles in particular are not well studied when released to the environment. Recently, research reports are indicating the toxicity of TiO<sub>2</sub> in its nanosized regime [64-67]. For example Zhu *et al.*, (2010) [64] conducted a comprehensive toxicity assessment, including modified acute (72 hours) and chronic (21 days) toxicity tests as well as TiO<sub>2</sub> nanoparticles accumulation analysis using *Daphnia magna* as a model organism. They found that TiO<sub>2</sub> nanoparticles caused high toxicity when the exposure time extended to 72 h. Moreover, upon chronic exposure to TiO<sub>2</sub> nanoparticles for 21 days, *daphnia* displayed severe growth retardation and mortality, as well as reproductive defects. Significant amount of TiO<sub>2</sub> nanoparticles was also found accumulated in *daphnia*. Jin *et al.*, (2010) also reported that Ti had a direct combination with some protein or DNA after TiO<sub>2</sub> nanoparticles enter into a cell, which could also lead to cellular toxicity[65]. Very recently, the potential neurotoxicity of titanium dioxide nanoparticles has been reviewed by Song *et al.*, (2015) and indicated potential risk of TiO<sub>2</sub> nanoparticles [66]. Furthermore, Mao *et al.*, (2015) employed a human neuroblastoma cell line (SH-SY5Y) to study the effects of TiO<sub>2</sub> nanoparticles on neurological systems and found out noticeable cell morphology change and dysfunction of microtubule dynamics, due to the entrance of TiO<sub>2</sub> nanoparticles [67]. Therefore, the nanotoxicity issue of TiO<sub>2</sub> should be considered in every photocatalytic applications by preventing leaching of TiO<sub>2</sub> nanoparticles. Thus, TiO<sub>2</sub> has to be supported (immobilized) on supporting materials for practical applications.

#### 1.4. TiO<sub>2</sub> supported on Zeolites

There has been intensive research work devoted in searching for suitable substrates to support TiO<sub>2</sub> nanoparticles. Zeolites are good candidates due to their photochemical stability, transparency to UV–Visible radiation above 240 nm wavelength, uniform pores and channels, large surface areas and tunable hydrophilic/hydrophobic surface properties [59, 60, 68-72]. Zeolites are hydrated alumino-silicate minerals composed of linked alumina (AlO<sub>4</sub>) and silica (SiO<sub>4</sub>) tetrahedra. The tetrahedra combine to form rings, cages and other secondary building units that create cavities of defined size and shape. Cations of Group I and II metals – commonly sodium, magnesium and potassium are found in gaps in the structure and balance out the excess negative charge. As a result, the elemental composition of zeolites can be easily tuned. Additionally, a wide range of structures are possible. According to IUPAC classification of porous materials, zeolites are microporous solids with pore size less than 2 nm.

According the International Zeolite Association online database (<http://www.iza-structure.org/databases/>), to date 229 zeolite framework types have been synthesized and fully characterized and the number is increasing every year. Each framework type refers to many zeolites that are structurally related but differ in their exact elemental composition. The difference in elemental composition renders differences like hydrophobicity, acid base properties and cation exchange behaviors, which are important parameters in zeolite based applications. For example, Zeolite Y is a synthetic aluminosilicates that is structurally equivalent to the natural faujasite (IZA code FAU). It is a three dimensional zeolite with large cavities present in the structure that are

interconnected by 12 member ring (MR) channels, which means that there are 12 cations ( $\text{Si}^{4+}$  and  $\text{Al}^{3+}$ ) and 12  $\text{O}_2^-$  anions present in the ring (Figure 3). There are large numbers of zeolites with this structure but different  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio and different counter cation. For example, CBV 400 and CBV 760 are both Zeolite Y with FAU framework structure with the same counter ion,  $\text{H}^+$ , but they differ in the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio which is 5.1 and 60, respectively. Similarly, CBV100 and CBV 400 are both zeolite Y with FAU framework type with the same  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio which is 5.1, but they differ with the counter cation,  $\text{NH}_4^+$  and  $\text{H}^+$ , respectively.

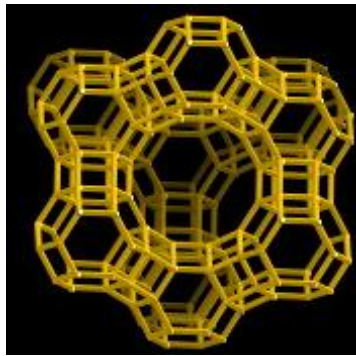


Figure 3: Faujasite (FAU) framework structure along the [111]

The same is also true for CBV 10A and CBV 21A, both possess MOR framework type (Figure 4) but with different  $\text{SiO}_2/\text{Al}_2\text{O}_3$  and counter ion.

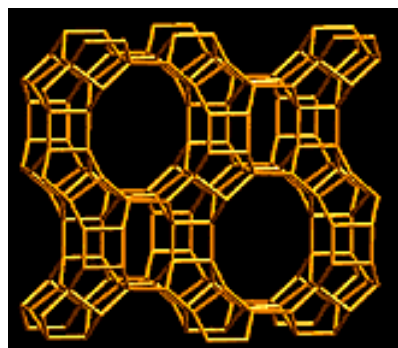


Figure 4: Mordenite (MOR) framework structure along the [001]

Over the years, zeolites have become an extremely important class of industrial catalyst. They are widely used in the petrochemical sector to prepare hydrocarbons through cracking, alkylation and isomerisation. Different synthetic routes and top down treatment strategies such as acid, steam, and base treatment are more readily implemented at an industrial scale to tune the chemistry of zeolites for pre designed applications [73-75]. In TiO<sub>2</sub> based photocatalysis, zeolites are commonly used as supports. Two aims are behind this approach, the use of the cavities of the zeolites as a confined space for the synthesis of small nanoparticles, or the tunable chemistry of the surface that allows controlling the hydrophilicity/hydrophobicity and thus the adsorption of a particular target molecule.

Li *et al.*, (2005) [76] investigated the surface interaction of TiO<sub>2</sub> on natural clinoptilolite and measured the photocatalytic degradation rate of methyl orange (MO), a model stable azo dye, in aqueous system to compare the photocatalytic activities of different photocatalysts. The authors reported that the TiO<sub>2</sub> particles loaded on zeolite are 50 nm, smaller than the pure TiO<sub>2</sub> (80 nm), and bonded to the zeolite via Ti-O-Si and Ti-O-Al bonds, which are formed by the reaction of TiO<sub>2</sub> with surface –OH of the zeolite during the synthesis and calcination at 200 °C. They reported that the bond energy is strong enough to keep the TiO<sub>2</sub> attached to the zeolite surface during the photocatalytic decomposing reaction; however, leaching results were not reported. The TiO<sub>2</sub>–clinoptilolite system showed better performance (24 min quicker for 95% degradation of MO) than the pure TiO<sub>2</sub> due to higher adsorption of the composite.

Shankar *et al.*, (2006) [77] used Zeolites HY, H $\beta$  and HZSM-5 with different physico-chemical properties as support for TiO<sub>2</sub> to survey their influence in the adsorption, dispersion and electronic structure of the final photocatalysts. The adsorption capacity of HY zeolite was found to be high and hence chosen by the authors for further modification to continue the investigation. They studied the photodegradation kinetics of 2, 4-dichlorophenoxyacetic acid (2,4-D) in aqueous solution and it was found that the reaction proceeds via pseudo first order kinetics. They conducted the photomineralization studies on all three zeolites with 1 wt% TiO<sub>2</sub>/HY, which demonstrated high adsorption and speculated that it has low light scattering. Its photocatalytic activity was found to be higher for photomineralization of 2, 4-D compared to pure TiO<sub>2</sub>. It takes 600 min for the pure TiO<sub>2</sub> to completely degrade for 2,4-D and 480 min for the 1 wt% TiO<sub>2</sub>/HY. Comparison of relative photonic efficiencies demonstrated that supported photocatalysts exhibited higher activity than Degussa P-25, Baker & Adamson, Tioxide and Fluka AG commercial photocatalysts. However, the photocatalytic materials were not fully characterized and the pH of the treatment was adjusted to the optimum of the catalyst behaviour (pH 3).

Petkowicz *et al.*, (2009) [78] reported the use of zeolite NaA as a support for the *in situ* generation of titania by impregnation with TiCl<sub>4</sub>, followed by calcination at 400 °C for 4 hours. The supported photocatalysts were evaluated for their activity in the photodecomposition of methylene blue (MB). According to these authors, zeolite TiO<sub>2</sub>-supported catalysts prepared by the impregnation of TiCl<sub>4</sub> are a simple means to produce active photocatalysts. The advantage of such supported photocatalysts, in comparison to

commercial TiO<sub>2</sub>, is mainly its grain size, which, in turn, renders it easier to separate and reuse. They reported that zeolite NaA was simply an inert support without affecting the Titania band gap.

In order to maximize the photocatalytic performance of the commercial TiO<sub>2</sub> powders as well as reduce the preparation cost, Takeuchi *et al.*, (2009)[79] prepared TiO<sub>2</sub> nanoparticles by mechanical blending of TiO<sub>2</sub> with the hydrophobic MOR zeolite in a simple preparation method. They evaluated the photocatalytic activity of the blended TiO<sub>2</sub>/MOR systems for the complete oxidation of gaseous acetaldehyde with O<sub>2</sub> under UV light irradiation. The authors reported that the hydrophobic zeolite powders efficiently gathered the gaseous acetaldehyde molecules within their cavities and supplied them onto the TiO<sub>2</sub> surface, enhancing the reactivity.

Li You-ji and Chen Wei (2011) prepared nanocrystalline TiO<sub>2</sub>–zeolite surface (TZS) composites by a novel technique, i.e., sol–gel method. They examined the behavior of TZS in the photocatalytic degradation of Rhodamine B (RhB) dye under UV-light as a function of pH, light intensity, irradiation time, TiO<sub>2</sub> coating ratio of TZS and its concentration in solution, and initial RhB concentration. They reported that the presence of the zeolites enhanced the photo efficiency of the titanium dioxide due to synergistic effects of the improved adsorption of RhB with efficient delocalization of photogenerated electrons and TiO<sub>2</sub> photocatalysis. However, they did not show how the photogenerated electrons are dispersed and they operate at higher pH (10), which is not advisable for treatment of water [80].

Kuwahara *et al.*, (2012)[68] prepared highly hydrophobic/organophilic FAU by predealumination treatment using concentrated mineral acids and subsequent calcination treatments. They estimated the hydrophobic/organophilic character of the zeolite by detailed adsorption measurements using water and toluene molecules as adsorbates and they reported the formation of hydrophobic zeolite FAU. From their TG, FT-IR, and  $^{29}\text{Si}$  MAS NMR analyses they claimed that the enhancement in hydrophobicity originates from the formation of a refined silica surface with fewer adsorption sites. Finally they tested the photocatalytic activity of the 10 wt% loaded the as synthesized zeolite in the degradation of 2- propanol under the illumination of UV light and they obtained higher photocatalytic degradation owing to its high crystallinity, structural and thermal stability, and hydrophobicity than the pristine  $\text{TiO}_2$  that is, the hydrophobic zeolite surface with fewer adsorption sites provides organic molecules with high diffusibility within the micropore channels and high accessibility to the  $\text{TiO}_2$  active sites. They reported that a distinct correlation was found between the hydrophobicity of zeolites and photocatalytic activity of the supported  $\text{TiO}_2$ .

Kamegawa *et al.*, (2013) prepared  $\text{TiO}_2$ /FAU composite material using the conventional impregnation method from Y-zeolite with different  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio and two kinds of  $\text{TiO}_2$  precursors (titanium ammonium oxalate and ammonium hexafluorotitanate) followed by calcination in range of temperature (400-700  $^\circ\text{C}$ ) for 5 h. They tested the photocatalytic activity of the composite for the degradation of 2-propanol diluted in water. They reported 30% conversion of 2-propanol in 1 h on the photocatalyst material calcined at 700  $^\circ\text{C}$  obtained from ammonium hexafluorotitanate titanium source and

Zeolite Y with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 810. They found that  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of Y-zeolite and  $\text{TiO}_2$  precursors strongly affect the photocatalytic performances of composites in the degradation of 2-propanol in water due to the different adsorption properties of organics and crystallinity of  $\text{TiO}_2$  [81]. Important parameters which affect the photocatalytic activity such as the particle size of the  $\text{TiO}_2$ , the crystalline phase of  $\text{TiO}_2$  in the composite have not been reported. In addition, the reusability and leaching of the  $\text{TiO}_2$  was not reported.

Jansson *et al.*, (2015) [82] assessed the photocatalytic properties of a series of zeolite/ $\text{TiO}_2$  composites for the degradation of pollutants in the gas phase. They prepared the composites by incipient wet impregnation method using an acidic  $\text{TiO}_2$  sol precursor and five different zeolites (CBV 600, CBV 780, CBV 2314, CBV 8014, CBV 2814) followed by calcination at 500 °C in air for 3 h. The authors studied the influence of the content of  $\text{TiO}_2$ , the zeolite structure (Zeolite Y and ZSM-5) and the Si/Al ratio in the textural properties, adsorption capacity and the photodegradation activity of the zeolite/ $\text{TiO}_2$  composites. They used formaldehyde ( $\text{HCHO}$ ) and chlorinated hydrocarbons, trichloroethylene ( $\text{C}_2\text{HCl}_3$ ) as model volatile organic compounds (VOCs). They reported that the nature of the pollutant and the physicochemical characteristic of the zeolites have a strong influence on the adsorption ability and in the photocatalytic performance of the composites. They concluded that Zeolite/ $\text{TiO}_2$  hybrid composites (at high  $\text{SiO}_2/\text{Al}_2\text{O}_3$ ) exhibit excellent photocatalytic performances for the degradation of both, formaldehyde and trichloroethylene in the gas phase, mainly due to the hydrophobic nature of the zeolites. However, the authors did not report important factors that affect

photocatalytic activity of a material i.e. the effect of zeolites on the band gap and crystallite phase of  $\text{TiO}_2$  in the composite materials they prepared. Besides, they did not show if the material is reusable or not.

Kanakaraju *et al.*, (2015) [83] prepared acidic integrated photocatalytic adsorbent (IPA) from acid-alkaline pre-treated natural zeolite and Titanium (IV) tetrakisopropoxide as a source of Ti followed by calcination at 300 and 450 °C for 2 h. They tested the IPA material for photocatalytic degradation of amoxicillin (AMX) and found that the IPA was superior to the pure  $\text{TiO}_2$  attributed to the adsorption capability of zeolite, the acidic nature of zeolite, effectively converting AMX, at least in part, by hydrolysis and the photocatalytic activity of  $\text{TiO}_2$ , consecutively degrading AMX and its hydrolysis products. The authors tested the reusability of the IPA and found that the photocatalytic activity of the system decreased to 69% in the third cycle while it was 88% in the first cycle. The authors claimed that this decrement is due to accumulation of AMX and its degradation products on the surface and within the pores of the zeolite, blocking the available active sites for adsorption and consequently passivating the  $\text{TiO}_2$  photocatalyst. However, no experimental evidence was provided for their claim. Leaching of the  $\text{TiO}_2$  can also be the reason behind for the poor reusability but the leaching experiment was not done. Generally the authors provided much attention for the photocatalytic reactions and less emphasis was given to the characterization of the photocatalytic material. Thus, important parameters such as optical property (band gap) of the IPA, the particle size and crystalline phase of  $\text{TiO}_2$  in the IPA and its pure form are missing.

TiO<sub>2</sub> supported on zeolitic matrices (HBETA, HY and HZSM-5) were synthesized by Gomez *et al.*, (2015) [84] for photocatalytic degradation of dichlorvos (DDVP). The authors synthesized their samples by means of the hydrothermal crystallization method using tetrapropylammonium hydroxide (TPAOH) for the ZSM-5 structure and tetraethylammonium hydroxide (TEAOH) for the BETA structure as directing agents followed by thermal treatment under nitrogen flow for 8 h at 500 °C and then calcinations in air at 500 °C for 10 h. The authors reported that the TiO<sub>2</sub>/HBETA presented more photocatalytic activity than TiO<sub>2</sub>/HY and TiO<sub>2</sub>/HZSM-5 of the same TiO<sub>2</sub> loading due to higher adsorption of DDVP on it. The authors further studied the reusability of the system. They choose TiO<sub>2</sub>/HBETA because it was the catalyst with better performance in their study and reported that no noticeable photocatalytic degradation was observed until the 8<sup>th</sup> cycle. They calculated the particle size of TiO<sub>2</sub> using the Scherrer equation, though they did not show whether the particles size of TiO<sub>2</sub> is homogeneously distributed.

From the above mentioned selected reports, it is possible to conclude that the photocatalytic efficiency has improved over the years using zeolites as supports; however, there is still room for in-depth systematic studies leading to better understanding of the structural, textural and optical properties responsible of the improved efficiency.

### **1.5. Motivation of the study**

The textile industry uses different dyes and other chemicals in its dyeing, bleaching and finishing steps. It consumes large quantities of water and produces large volumes of wastewater, which contains a mixture of different dyes and other chemicals from the different processes. Globally, through textile waste effluents, around one thousand tons of non-biodegradable textile dyes are discharged into natural streams and water bodies every year [35]. Wastewater with such composition is carcinogenic (or at least pro-carcinogenic) and exhibit high level of toxicity and/or mutagenicity for several living organisms either directly or through some of their metabolites [85]. For the treatment of the wastewater with such pollutants, most studies have focused on the bio-degradation processes[86], chemical oxidation [87] and adsorption methods [88-90]. These methods have the disadvantage that they are either not cost-effective or are unable to convert the pollutants into non-toxic product/s. For example, treatment methods such as adsorption by activated carbon merely concentrate the chemicals present by transferring them to the adsorbent and do not convert them into non-toxic wastes. Thus, cost effective methods, which could completely degrade textile pollutants into harmless products must be requested.

Due to several investment incentive packages, large numbers of international and local investors are participating in the Ethiopian textile industries, whereby large wastewater is being disposed to the environment. According to the Ethiopian Textile Industry Development Institute (ETIDI) data, Ethiopian textile processing units consumed about 15, 000 tons of various types of dyes and chemicals in 2011 of which upto 40 % of

these chemicals are disposed without/ or below standard treatment. The Ethiopian government established the Environmental Protection Authority (EEPA) as an environmental regulatory and monitoring body (Proclamation Number 295/2002) and set laws on environmental pollution control (Proclamation Number 300/2002). Thus, there is an urgent need for wastewater treatment to meet the requirements set by the government. Therefore, understanding, developing and planting effective industrial wastewater treatment technology is environmentally and economically important. This is the first motivation why this PhD research has focused on the textile wastewater treatment technology.

From the literature survey [76-80, 91, 92], zeolites play a crucial role in enhancing the photocatalytic activity of  $\text{TiO}_2$  photocatalyst. Among the Ethiopian natural zeolites identified previously, some of them are tested for different applications such as a catalyst [93] and fluoride removal for drinking water [94]. Some of these identified natural zeolites also possess interesting chemical compositions with high Titanium (Ti) and Iron (Fe) content. This high content of Titanium (Ti) and Iron (Fe) may produce *in-situ* photocatalyst material self-supported on the natural zeolite.

In the previous studies of  $\text{TiO}_2$  supported on zeolites; the photocatalytic enhancement of the hydride systems was mainly attributed to high adsorption capacity of zeolites [35, 81, 91, 95-97]. However, there is no study devoted to analyze the role of zeolites in modifying the electronic property of  $\text{TiO}_2$  supported on zeolites besides enhancing the adsorption. In this PhD research, the role of zeolites in modifying the electronic

properties of supported  $\text{TiO}_2$  will be studied in addition to their known adsorption role for the photocatalytic enhancement of supported  $\text{TiO}_2$ . Moreover, chemical modifications of zeolites will also be considered to further enhance the properties of the supports and thus the photocatalytic activity of the hybrid system. Furthermore, in previous studies, supporting of  $\text{TiO}_2$  on zeolites was accompanied by calcination of the hybrid system at higher temperature for long period of time [76-80, 91, 92] because it is considered in the literature that crystalline  $\text{TiO}_2$  is the best photocatalytic material [98, 99]. In this PhD research, the photocatalytic activity of semi amorphous  $\text{TiO}_2$  supported on zeolites without calcination will be studied.

Although photocatalytic enhancement has been reported in the literature upon supporting  $\text{TiO}_2$  on zeolites, all those systems function in the UV light range. In the literature, it has been also reported that the  $\text{TiO}_2$  band gap can be narrowed by metal and/or nonmetal doping. However, to the best of our knowledge such efforts on zeolite supported  $\text{TiO}_2$  are rare. Therefore, the electronic and photocatalytic activity effects of Ce/N co-doped on zeolite supported  $\text{TiO}_2$  will also be studied in this PhD research.

Finally, the leaching of  $\text{TiO}_2$  both on the pristine  $\text{TiO}_2$  nanoparticles and zeolite supported  $\text{TiO}_2$  nanoparticles will be evaluated since it is important to consider the leaching extent in photocatalytic applications considering the toxicity of the  $\text{TiO}_2$  nanoparticles [64-67]. Thus studies on leaching of pristine and zeolite supported  $\text{TiO}_2$  nanoparticles will be conducted.

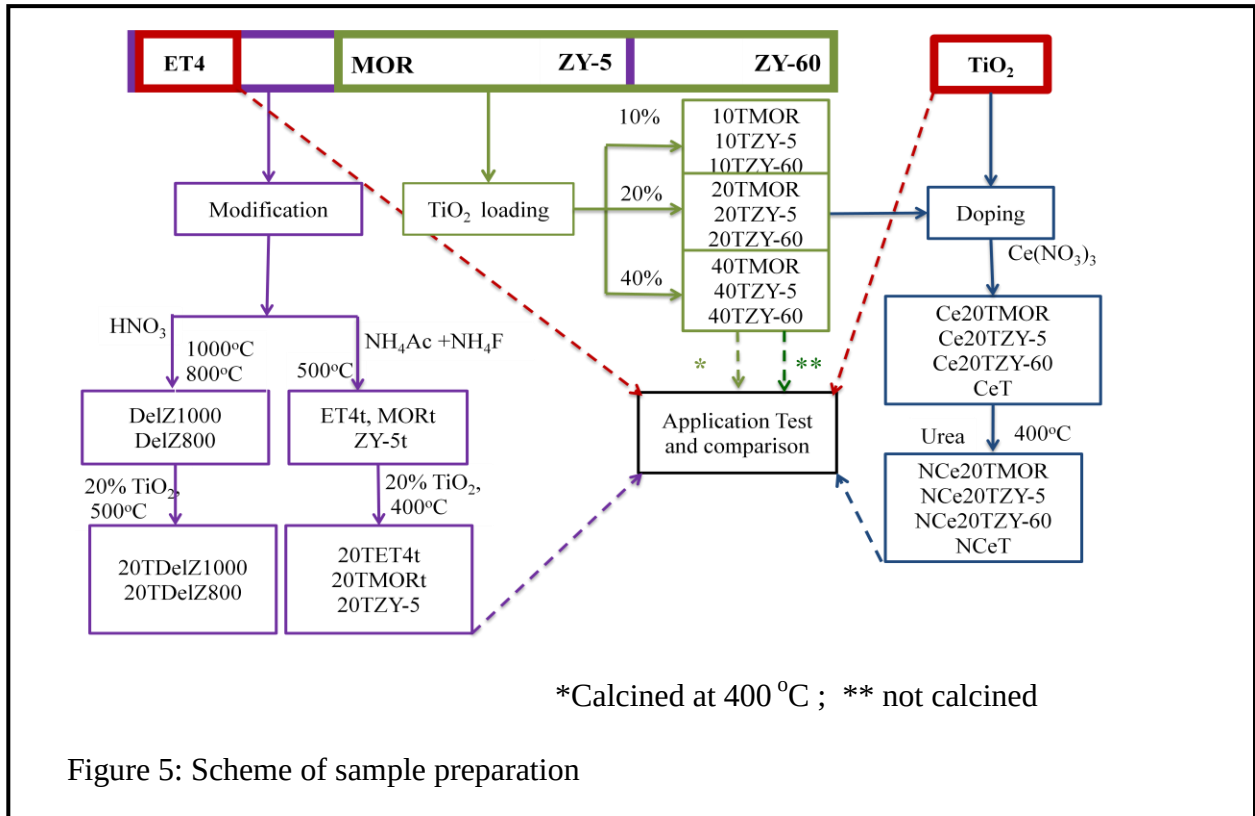
## **1.6. Objectives**

The general objective of this PhD research is focused on preparation, characterization and photocatalytic activity of  $\text{TiO}_2$  supported on zeolites for treatment of textile wastewater.

The specific objectives of this PhD research are:

1. Characterization and photocatalytic application of Ethiopian natural zeolites;
2. Preparation, characterization and photocatalytic application of  $\text{TiO}_2$  supported on synthetic zeolites;
3. Preparation, characterization and photocatalytic application of  $\text{TiO}_2$  supported on modified synthetic zeolites;
4. Preparation, characterization and photocatalytic application of semi amorphous  $\text{TiO}_2$  supported on synthetic zeolites;
5. Preparation, characterization and photocatalytic application of Ce/N co-doped  $\text{TiO}_2$  supported on synthetic zeolites

To achieve these objectives, the thesis is organized in 5 chapters. Chapter One deals with the introductory part of the thesis. In this chapter, the current state of photocatalysis research, motivation and objectives of this PhD research has already been described. In Chapter Two, characterization techniques and photocatalytic experimental procedures will be presented. The potential of Ethiopian natural zeolites for photocatalysis will be presented in Chapter Three. Chapter Four will mainly focus on photocatalytic activity of  $\text{TiO}_2$  supported on synthetic zeolites. Different modification methodologies and preparation tools will be tested in order to enhance the photocatalytic activity. Figure 5 summarizes the different approaches employed for the preparation of zeolite supported  $\text{TiO}_2$  photocatalyst



## **2. Characterization and Photocatalytic Tests**

Different zeolite based photocatalysts have been prepared and sample preparation methods are described in the respective sections with their brief introductions. The characterization techniques used and the photocatalytic test procedures are described hereunder.

### **2.1. Characterization Techniques**

Photocatalytic activity is determined by the interplay of the surface and electronic properties of the photocatalyst material. A combination of tools is necessary to give a balanced description of the photocatalytic systems. In this work, diffraction, microscopic and spectroscopic techniques have been used for the structural, surface and electronic characterization of the zeolite supported TiO<sub>2</sub> photocatalysts.

#### **2.1.1. X ray diffraction (XRD)**

XRD involves focusing beams of X-rays (generated as in Figure 6 [100]), which scatter in a constructive manner from lattices in the sample forming diffraction patterns. At certain angles, scattered X-rays are combined constructively and are measured as a function of diffraction angle,  $2\theta$  [101]. The structural information can be obtained using the Bragg equation ( $n\lambda = 2d\sin\theta$ ). The diffraction patterns formed can be used as a “fingerprint” for the crystal lattices found in the material. This allows for the determination of the crystalline phase, quantitative composition of multi-component systems, lattice parameters, crystal size etc. As any crystalline materials, zeolites and

TiO<sub>2</sub> have their own XRD “fingerprint”. Therefore, to study the effect of different treatment conditions such as loading of TiO<sub>2</sub>, calcination and dealumination on the zeolite framework structure, XRD patterns were collected with a X’Pert Pro PANalytical diffractometer (CuK<sub>α</sub> radiation = 0.15406 nm with Ni filter). The measurements were made at room temperature with the accelerating voltage of 45 kV and applied current of 40 mA. It was operated in continuous scan mode, in the range 4.00037308° – 89.99188826° and the obtained peaks were analyzed using version = "2.1E" XPERT-PRO software.

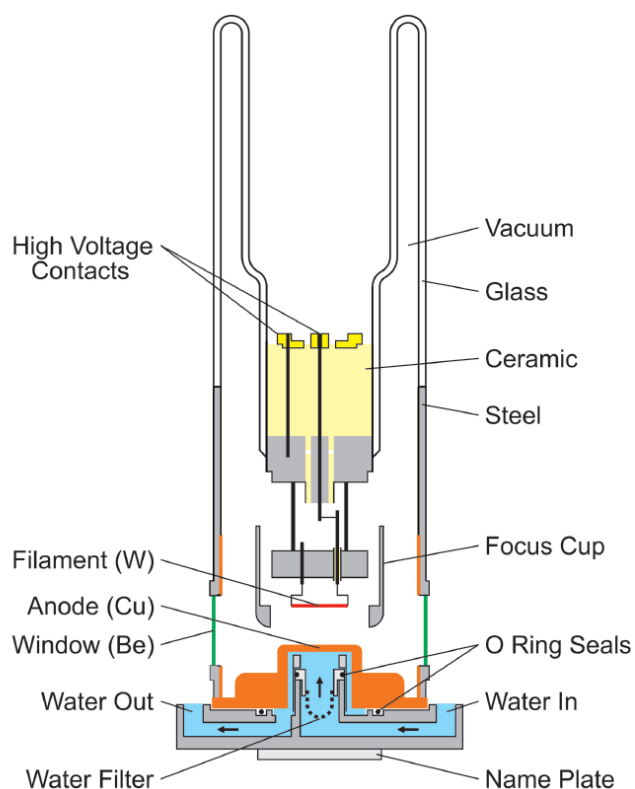


Figure 6: Schematic diagram of X-ray tube with key components

### 2.1.2. Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)

The bulk chemical composition of the samples were determined by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) using a Perkin-Elmer Optima 3300 DV equipment. Digestion of the samples was performed by alkaline fusion.

### 2.1.3. N<sub>2</sub> Adsorption/Desorption Isotherms

According to IUPAC recommendation in 1985 [102] and updated very recently in 2015, [103] porous materials can be classified as micro-, meso- and macroporous materials depending the pore size of the porous material. Gas adsorption measurements are used to determine the surface area and pore size of the different solid materials [102, 103]. When gases such as nitrogen are adsorbed on solid materials, different isotherm types are obtained as shown in Figure 7.

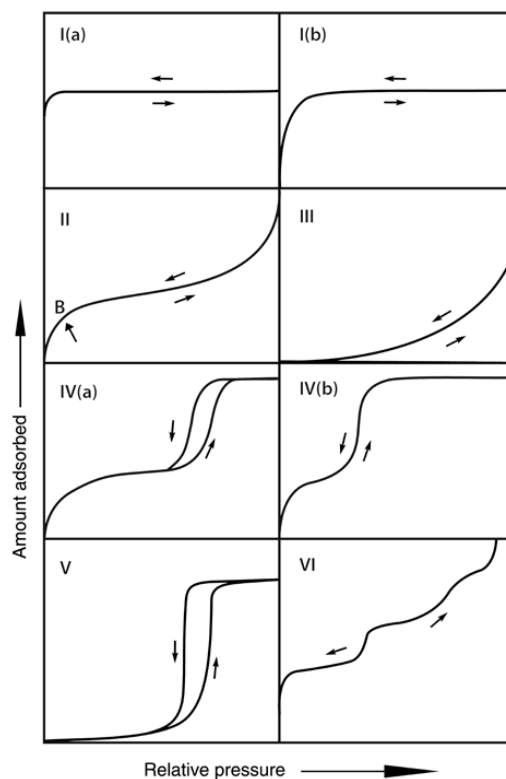


Figure 7: Types of physisorption isotherms

In this work, we used nitrogen adsorption/desorption isotherms to study the effect of TiO<sub>2</sub> loading, calcination, mild treatment conditions on the surface area, nature and type of porosity of the zeolites. The isotherms were measured based on the IUPAC 1985 recommendations [102] in a Micromeritics ASAP 2420 physisorption analyzer and the samples were degassed at 350 °C for 16 h prior to data collection except for the semiamorphous samples which were degassed at 150 °C for 16 h.

#### **2.1.4. Scanning Electron Microscopy/ Energy Dispersive X ray Spectroscopy (SEM/EDS)**

Scanning Electron Microscopy provides morphological images of a material. SEM is carried out by scanning a narrow electron beam over the surface of the sample. Electron beam interaction with the specimen in SEM can generate multiple signals, as has been shown in Figure 8. Secondary and backscatter electrons, transmitted electrons (if the specimen is sufficiently thin), Auger electrons, characteristic X-rays, and photons can be detected depending on the detector configuration [104]. Backscatter electron imaging provides information about the atomic number (Z) of the specimen. For determining specimen chemistry inside the SEM, EDS is the technique of choice. It involves ionization of the sample. The X-ray emissions from this ionization event are then analyzed with a solid-state energy dispersive detector. Each element gives out a unique pattern of X-ray lines from the K, L, and M shells which allows for straightforward analysis. Therefore, SEM can also provide elemental analysis when coupled with Energy Dispersive X ray Spectroscopy (EDS).

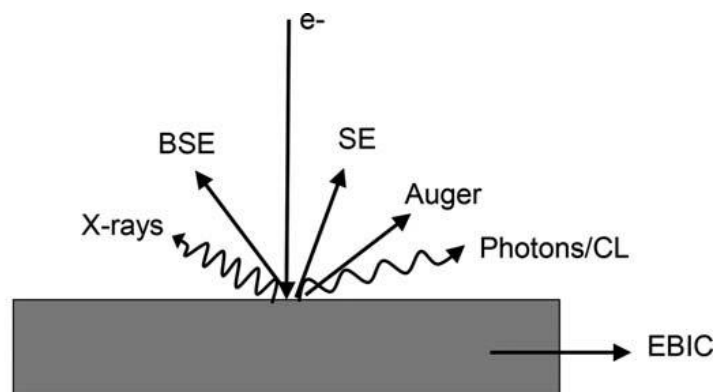


Figure 8: Different signals generated when electron beam interacts with specimen

In this work, two different scanning electron microscopes were used: Hitachi TM-100 and a FEI NOVA NANO SEM 230, both with backscattered electrons detector and EDS detector. We use this methodology for morphology analysis, phase identification and elemental mapping of Ethiopian natural zeolites.

#### 2.1.5. Scanning Transmission Electron Microscopy (STEM)/Electron Energy Loss Spectroscopy (EELS)

Transmission Electron Microscopy (TEM) working on Scanning Transmission Electron Microscopy (STEM) mode, combined with Electron Energy Loss Spectroscopy (EELS) allows high resolution imaging and at the same time atomic chemical information [105]. TEM functions by generating a primary electron beam of high energy and high intensity that passes through a condenser to produce parallel beams that irradiate the sample. Magnified images of the sample are formed by combining the transmitted electrons using an electromagnetic objective lens. TEM is primarily used to give information on topography, morphology and crystal structure at atomic resolution [106]. It can also be used for bulk composition when coupled with EELS and/or EDS [107]. STEM combines

both scanning and transmission modes and utilizes scanning coils to illuminate a small area of the sample from which bright or dark field images are obtained. STEM can be combined with the high-angle annular dark field (HAADF) detector to provide Z-contrast images which can distinguish atoms of different atomic number[108](Figure 9). The image brightness is dependent on the square of the atomic number ( $Z^2$ ) of the atoms present. Elemental composition of a sample can also be determined by combining EDS and EELS analysis with STEM images. In EELS analysis, the ionization event that occurs in the sample leads to a characteristic loss in energy of the transmitted electrons that can also be detected. These techniques are also useful for constructing elemental maps to characterize the microstructural composition and elemental distribution of multicomponent catalysts on the nanometer scale.

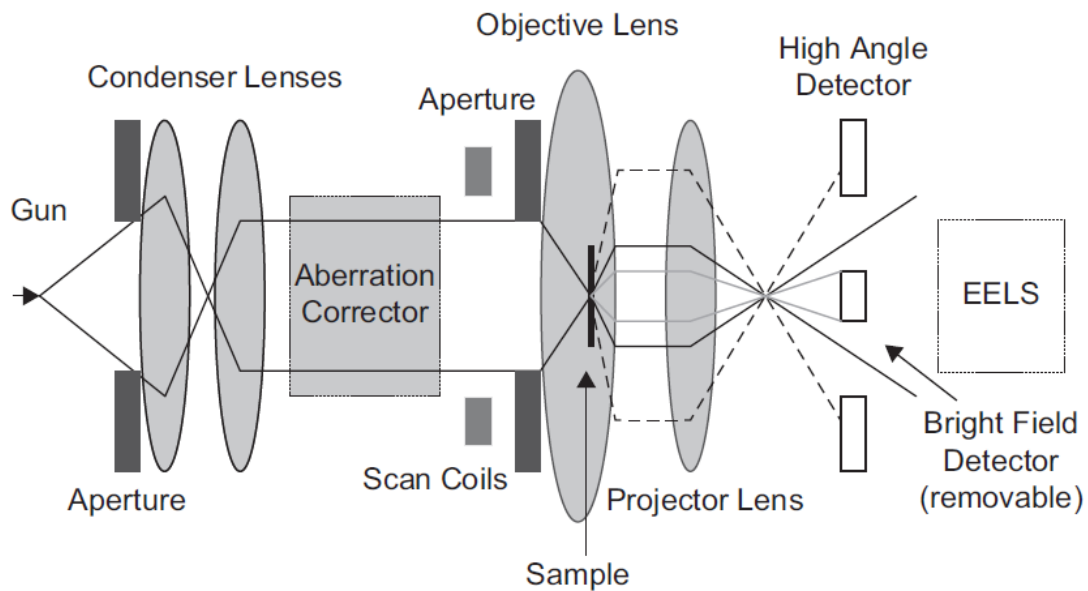


Figure 9: Schematic of an aberration-corrected STEM

In Figure 9 electron trajectories at the edge of the apertures are indicated with solid lines. High-angle scattering used to form the Z-contrast image is indicated with dashed lines

and low-angle scattering used to form the bright-field image is indicated with gray lines [108].

In this particular work, STEM/HAADF was performed in a spherical aberration corrected FEI Titan XFEG, which was operated at 300 kV equipped with a corrector for the electron probe allowing a maximum resolution of 0.8 Å; the microscope was also equipped with an EDS detector and a Gatan Tridiem energy filter (for EELS measurements). Prior to observations, the samples were crushed, dispersed in ethanol and placed onto a holey carbon copper microgrid.

#### **2.1.6. UV-Vis Diffuse Reflectance Spectroscopy (DRS)**

UV-Vis diffuse reflectance spectroscopy is a characterization technique used to obtain information about the electronic structure of the photocatalyst system based on the absorptive and light scattering properties of the sample under light excitation from the 200–800 nm range. The sample absorbance is then referenced against a standard and the Kubelka - Munk function can be calculated for the sample that allows determination of the optical band gap for photocatalyst materials [109]. The optical band gap determines how much photon energy is required to generate excited electron/hole pairs in the bulk of the photocatalyst material. In our particular characterization, 50 mg of each sample was used to determine the electronic properties (band gap energy) of the prepared samples. UV-Vis Diffuse Reflectance Spectroscopy (UV-Vis DRS) measurements were done using a Varian Cary 5000 double-beam UV-Vis-NIR spectrophotometer. Collected spectra were converted to Kubelka–Munk function,  $F(R)$  and plotted against wavelength.

For concentration determination of the photocatalytic reaction results, PerkinElmer Lambda 950 UV-Vis spectrophotometer was used.

#### **2.1.7. Photoluminescence Spectra (PL)**

Photoluminescence spectroscopy (PL) is a complimentary technique to UV-vis DRS. UV-vis DRS gives information on the transition from the valence band to the conduction and PL spectroscopy gives information on the fate of these excited systems. This process is relevant to the study of photocatalyst systems since fluorescence occurs when electrons in the conduction band recombine with holes in the valence band. This characterization technique can thus give information on electron transfer phenomena during the photocatalytic process. In our particular case, the photoluminescence spectra were recorded using a Perkin Elmer LS 50B Luminescence Spectrometer equipped with a Xe lamp source. The measurement was done at room temperature with excitation wavelength at 310 nm and the same sample size was taken in all measurements.

#### **2.1.8. X ray Photoelectron Spectroscopy (XPS)**

The surface analysis of solids is fundamental to the study of the mechanical, physical and chemical properties. X-ray photoelectron spectroscopy is based on the study of the energy of the electrons emitted by the solid when irradiated with X-ray photons such techniques allow the identification of elements and provide detailed information about the state of chemical bonds and the concentration of surface atoms. In this particular work, the surface chemical composition was analyzed by X-ray photoelectron spectroscopy (XPS) using a SPECS instrument with UHV system (pressure of about  $10^{-10}$

mbar), equipped with a PHOIBOS 150 9MCD energy analyzer. A non-monochromatic Mg X-ray source was used working at 200 W and 12 kV. The powder samples were pressed into self-supporting wafers and stuck on the sample holder with double-sided adhesive conductive carbon tape. Spectra were referenced against the C 1s emission line of adventitious carbon (binding energy set to 285.0 eV) to correct for charging effect. Relative atom ratios were calculated from the sum area of the two 2p level components of Ti, Si and Al, using the relative sensitivity factors provided by CasaXPS software.

#### **2.1.9. Thermogravimetric Analysis (TGA)**

Thermogravimetric analysis (TGA) is performed on samples to determine changes in weight as a function of temperature. TGA was used to determine the thermal stability of the photocatalyst by monitoring the weight loss that occurs as the photocatalyst was heated. The analysis of the samples was done on Perkin-Elmer TGA7 in the range 25-900 °C with 20 °C/min heating rate in a flowing atmospheric air.

### **2.2. Photocatalytic Degradation Test**

In order to test the photocatalytic activities of the prepared photocatalytic materials, Methyl Orange (Mol. Formula:  $C_{14}H_{14}N_3O_3S$ ; Mol. Wt: 327.33) (Figure 10) was used as a model pollutant. It is a stable azo dye, which is used in many textile factories. It has been used as a model pollutant in many photocatalytic tests [110-120]. Figure 10 shows its molecular structure and UV-Vis spectrum (dissolved in deionized water).

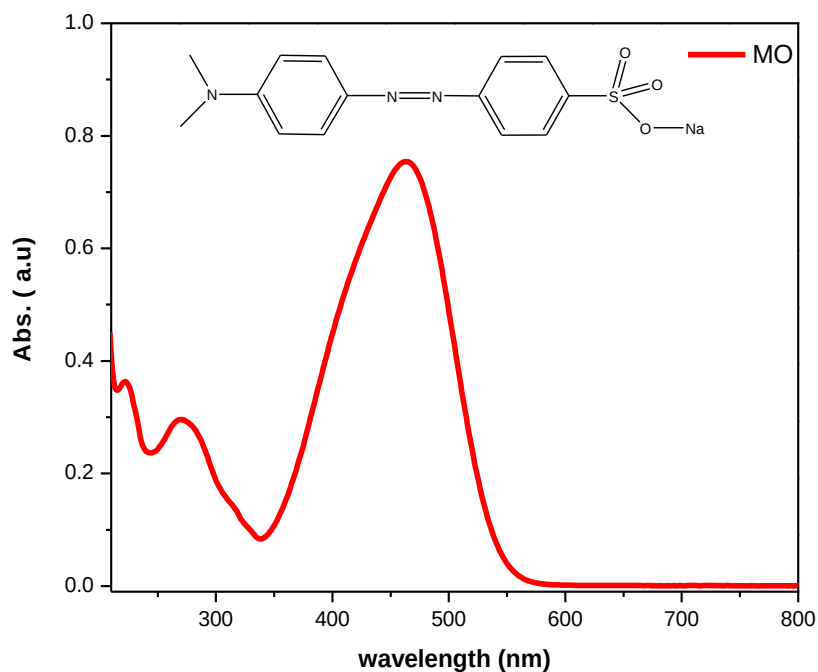


Figure 10: Methyl Orange (MO)

For a particular photocatalytic degradation of MO, 0.5 g of sample was suspended in a 750 mL of 10 ppm aqueous solution of MO in a quartz glass reactor equipped with quartz glass cooling pipe and ports for sample withdrawing and oxygen purging. The mixture was stirred for 30 minutes under continuous purging of Oxygen to maintain adsorption-desorption equilibrium of MO with the powder photocatalyst material. The suspension was then irradiated with a 150 W UV lamp (Heraeus medium pressure mercury lamp, Figure 11).



Figure 11: Heraeus medium pressure mercury lamp, photocatalytic reactor

Samples were withdrawn in time intervals for analysis after filtering out the photocatalyst. The withdrawn samples were analyzed using PerkinElmer Lambda 950 UV-Vis spectrophotometer. The spectra were recorded from 200- 800 nm and the absorbance ( $A$ ) at  $\lambda_{\max}$  (wavelength at maximum absorbance) was taken for percentage degradation calculation. The percentage degradation was calculated using the following equation: Photocatalytic degradation (%) =  $(A_0/A_t) \times 100$ ; where  $A_0$  is the absorbance at  $\lambda_{\max}$  of the solution before any photocatalyst is immersed and  $A_t$  is the absorbance after time  $t$  in the same  $\lambda_{\max}$ . The photocatalytic degradation of real textile wastewater was done under similar conditions and the Chemical Oxygen Demand (COD), Total Organic Carbon (TOC), and Total Nitrogen (TN) of the real wastewater was measured.

Reusability of the selected photocatalyst was done as follows: At the end of the first photocatalytic cycle, the photocatalyst was separated from the resulting suspension by filtering, washed, oven-dried at 110 °C, and then reused without any calcination treatment. The same procedure was employed after the second and all the cycles of use.

Leaching of TiO<sub>2</sub> nanoparticles was measured using ICP-MS for Ti isotopes in the treated water was analyzed using ICP-MS equipment. The analysis was done with NexION 300X ICP-MS equipped with collision gas technology (Perkin Elmer) with RF power 1500 watts; Auxiliary gas (H<sub>2</sub>) flow 1.2 L/min; Nebulizer (Ar) gas flow 0.90 L/min and plasma gas (Ar) coolant flow 18.0 L/min. External calibration graph was constructed using a series of aqueous titanium standards at concentrations 0.0, 0.5, 1.0, 5.0, 10 and 20 ppb. Titanium isotopes (<sup>47</sup>Ti and <sup>49</sup>Ti) were monitored in sample solutions that were diluted to 10-fold using 1% nitric acid solution before measurement. Concentrations evaluated at both isotopes of Ti agreed well showing absence of polyatomic interference in the results of analysis.

### **3. Preparation, Characterization and Photocatalytic Activity of Ethiopian Natural Zeolites Based Photocatalyst**

#### **3.1. Introduction**

In his book “demand/supply survey of the Ethiopian industrial mineral subsector” Morgan highlighted that extensive deposits of zeolite (Mordenite and Clinoptilolite) are present in the Rift Valley sediments near Nazret and Bora, west of Nazret and in the vicinity of Lake Tanna. The author further recommended that more field and laboratory integrated studies should be conducted to determine the extent, quality and possible applications of the Ethiopian natural zeolites [121]. In the past few years, attempts to locate zeolite deposits in Ethiopia have shown that several other natural zeolites exist in different parts of the country [94]. Among them, a natural zeolite (Mordenite) containing more than 5 wt% of titanium has been found in Hashenge, Tigray region. This sample, called ET4, contains other non-zeolitic phases like celadonite and ilmenite, which may add potential application of this high Ti-containing sample for photocatalysis.

Several research reports have used commercial natural zeolites as a support for  $\text{TiO}_2$  nanoparticles to enhance its photocatalytic activity [59, 76, 96, 122, 123]. In this work, first the Ethiopian natural zeolites will be tested for photocatalysis since the natural zeolites obtained has photoactive material ( $\text{FeTiO}_3$ ) composites. Further works will be attempted to enhance the photocatalytic activity by loading  $\text{TiO}_2$  and/or purifying the natural zeolites.

### 3.2. Sample Preparation

In order to obtain a photocatalytically active natural zeolite, different approaches were tested:

- A. Simple calcination of raw zeolite ET4 sample with the aim of obtaining the oxide phases required: 1 g of natural zeolite (ET4) was calcined in air for 3 h at 300, 400, 500 and 600 °C at a rate of 3 °C/min. The resulting samples were labeled as ET4-300, ET4-400, ET4-500 and ET4-600, respectively.
- B. Loading of raw zeolite ET4 sample with 20% TiO<sub>2</sub> followed by calcination at 500 °C, labeled 20TET4-500: 1.6 g of ET4 is suspended in a solution of 2.01 mL of titanium butoxide (Ti(OBut)<sub>4</sub>) dissolved in a mixture of 2-propanol (CH<sub>3</sub>CHOHCH<sub>3</sub>) and water (H<sub>2</sub>O) with volume ratio of 1:10:2 (Ti(OBut)<sub>4</sub>: CH<sub>3</sub>CHOHCH<sub>3</sub>: H<sub>2</sub>O). The suspension was stirred at room temperature for 24 h. The solvent was removed by rotary evaporator and dried at 110 °C. The sample was then calcined in a furnace at 500 °C for 3 h at 3 °C/min.
- C. Modification of the natural zeolite using acidic treatment aiming to remove impurities, followed by TiO<sub>2</sub> loading: A 9.0 g of ET4 was immersed in 270 mL of 2.0N aqueous nitric acid solution and refluxed for 12 h with stirring. After 12 h of reflux, the samples were filtered and washed several times with deionized water until complete elimination of the acid is achieved, and then samples were dried at 110 °C overnight. The resulting material was calcined for 6 h in air at 550 °C and 1000 °C. The obtained samples were denoted as deAlET4 500 and deAlET41000. These samples were then loaded with 20% TiO<sub>2</sub> as described in

part (B) of this section and the samples were denoted as 20TdeAlET4 500 and 20TdeAlET4 1000.

- D. Modification of the natural zeolite using mild treatments followed by  $\text{TiO}_2$  loading: 2 g of ET4 was stirred in 26 mL of 3 M  $\text{CH}_3\text{COONH}_4$  ( $\text{NH}_4\text{Ac}$ ) at room temperature for 30 min. Then a 12 mL of aqueous solution of 2.4 M  $\text{NH}_4\text{F}$  was added drop wise at 80 °C under magnetic stirring. The suspension was stirred for 30 min. The sample was then filtered and washed with distilled water and dried at 100 °C for 12 h. After this it was calcined at 550 °C for 6 h at rate of 3 °C/min and then loaded with 20%  $\text{TiO}_2$  as in part (B) of this section followed by calcination at 500 °C and the sample was labeled as 20TET4t.
- E. In another attempt to remove impurities from the natural zeolite sample, mechanical separation processes were surveyed followed by  $\text{TiO}_2$  loading: 3g of ET4 were suspended in two 60 mL distilled water and stirred by magnetic stirrer. At every 20 minutes the magnetic stirrer was withdrawn from the solution and the magnetic solid was collected. Finally the samples were labeled as MET4 and deMET4 referring to “magnetic iron compound” separated from ET4 and “demagnetized” ET4, respectively. These samples were calcined at 500 °C and labeled as MET4 -500 and deMET4-500. Part of the samples were loaded with  $\text{TiO}_2$  following the procedure in part (B) of this section, 20%  $\text{TiO}_2$  was loaded to these samples and the samples were labeled as 20TMET4 and 20TdeMET4. Another part of the samples were further chemically treated following the procedure in part (D) of this section and then loaded with 20 %  $\text{TiO}_2$  following

the procedure in part (B) of this section and the samples were labeled as 20TMET4t and 20TdeMET4t.

### 3.3. Results and Discussion

Figure 12 shows a photograph of the sample collected from Hashenge, Ethiopia. The XRD and ICP analysis results are shown in Figure 13 and table 1, respectively.



Figure 12: Photograph of the natural zeolite collected from Hashenge, Tigrai

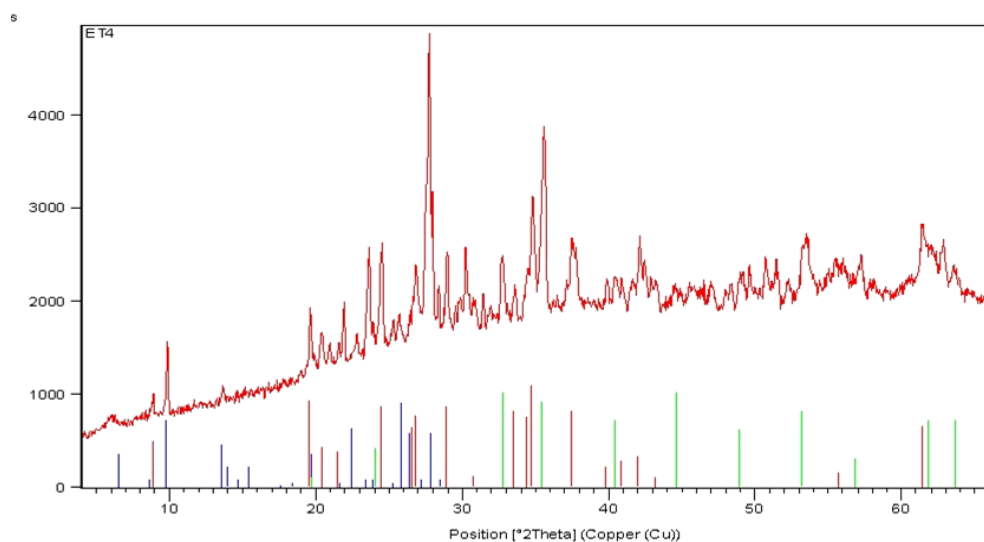


Figure 13: XRD profile of natural zeolite from Ethiopia, ET4

In Figure 13, the sample is identified as a mixture of Celadonite in red (00-017-0521), Mordenite in blue (00-038-0318) and Ilmenite in green

Table 1: ICP elemental analysis results of Ethiopian natural zeolite ET4

| Sample | Al<br>(wt %) | Si<br>(wt %) | Na<br>(wt %) | K<br>(wt %) | Ca<br>(wt %) | Mg<br>(wt %) | Fe<br>(wt %) | Ti<br>(wt %) |
|--------|--------------|--------------|--------------|-------------|--------------|--------------|--------------|--------------|
| ET4    | 3.6          | 22.9         | 1.3          | 3.6         | 1.8          | 1.1          | 10.2         | 3.5          |

The elemental composition reported in Table 1 yields a Si/Al molar ratio of 6.11, a bit higher than that of natural mordenite, which varies between 4 and 6 ( $\text{Na}_{1.1}\text{Ca}_{0.5}\text{K}_{0.1}\text{Al}_{2.2}\text{Si}_{9.8}\text{O}_{24} \cdot 5.9 \text{H}_2\text{O}$ ) [124]. This difference must be due to a significant contribution of silicon provided by Celadonite ( $\text{KMg}_{0.8}\text{Fe}^{2+}_{0.2}\text{Fe}^{3+}_{0.9}\text{Al}_{0.1}\text{Si}_4\text{O}_{10}(\text{OH})_2$ ), which is also responsible of larger amounts of K, Mg and Fe. Finally, the surprisingly high content on Ti is expected to be related to the Ilmenite phase ( $\text{FeTiO}_3$ ), although the coexistence of Ti in the zeolitic Mordenite phase should not be discarded.

In order to corroborate this distribution of elemental composition, ET4 sample was studied by scanning electron microscopy coupled with energy dispersive X ray spectroscopy (SEM-EDS). Figure 14 collects representative SEM micrographs of ET4 where the nice hexagonally shaped crystals of Mordenite could be observed (Figure 14A) along with larger shapeless particles identified as Celadonite (Figure 14B), and brighter particles (due to the higher atomic number) identified as Ilmenite (Figure 14C).

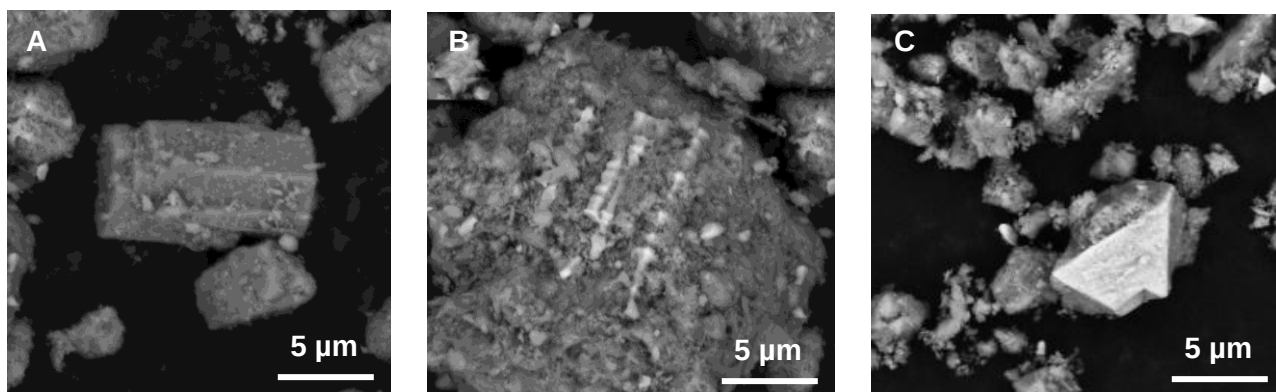


Figure 14: SEM micrographs of sample ET4

There seems to be higher ratio of Celadonite than the rest of the phases, and more Ilmenite than in other zeolites samples collected in the same region. Nevertheless, what makes this sample interesting is that the phases with Ti also seem to be associated to some Si. The exhaustive SEM study coupled with EDS mapping (Figure 15) shows that the particles with a higher amount of Na found by EDS could be richer in MOR and those with Mg could be richer in Celadonite. On the other hand, there are clearly Ilmenite particles always showing brighter contrast due to the higher atomic number with  $\text{Fe/Ti} = 1$  by EDS, although the presence of Ti is also observed in Si-related particles as mentioned before.

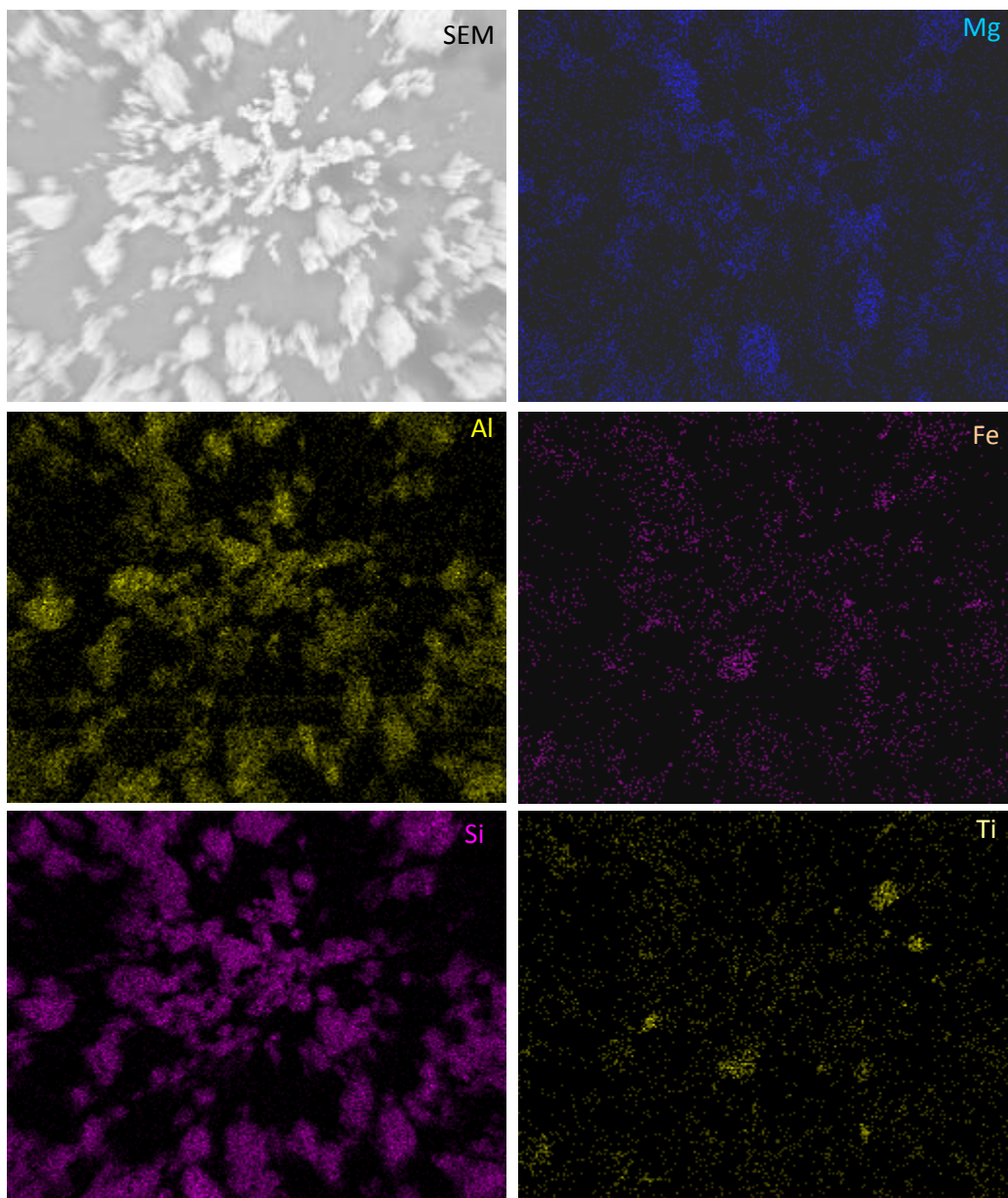


Figure 15: SEM/EDS mapping of sample ET4.

Range of calcination temperatures were tested to obtain the desired phases. The XRD patterns confirm that the zeolite structure remains stable after calcination up to 600 °C showing no diffraction peaks of either rutile or anatase phases (Figure 16). The SEM analysis of sample ET4 500 shows no presence of segregated phases of  $\text{TiO}_2$ , while the three main phases of parent ET4 could be clearly observed concluding that the

calcination process has not inferred any morphological change to the natural zeolites (Figure 17). However, there is some intensity changes at the lower 2theta diffraction angles. Particularly, the diffraction peak of MOR at around  $6^\circ$  (110) and at  $9.89^\circ$  (200) are more clearly observable in the raw zeolite. However, this diffraction angles disappear in the calcined samples, probably due to the closure of the entire pores or pore mouths of the mordenite zeolite. This is may be due to the crystal growth of the mineral composites. Since the diffraction peak at 2theta  $22.5^\circ$  is clearly observed we can conclude that the MOR is not collapsed. Furthermore, SEM micrograph indicates the presence of Moredenite after calcinations to  $500^\circ\text{C}$ . This may happen due to crystal growth of the celadonite as a result of calcination which can be confirmed by the intensity enhancement at the diffraction peak of  $8.9^\circ$ .

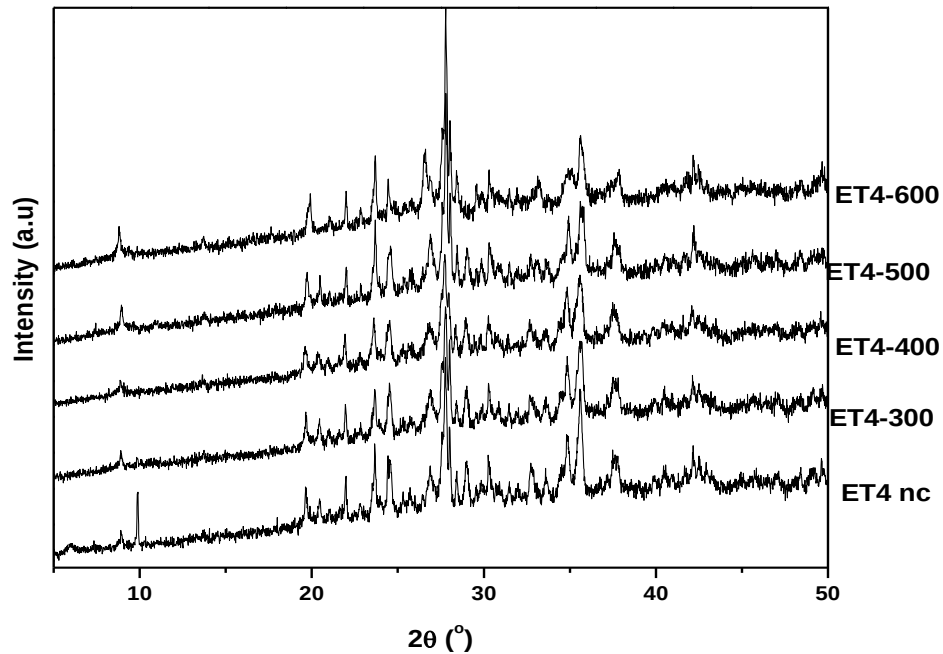


Figure 16: XRD patterns of ET4 calcined at different temperatures

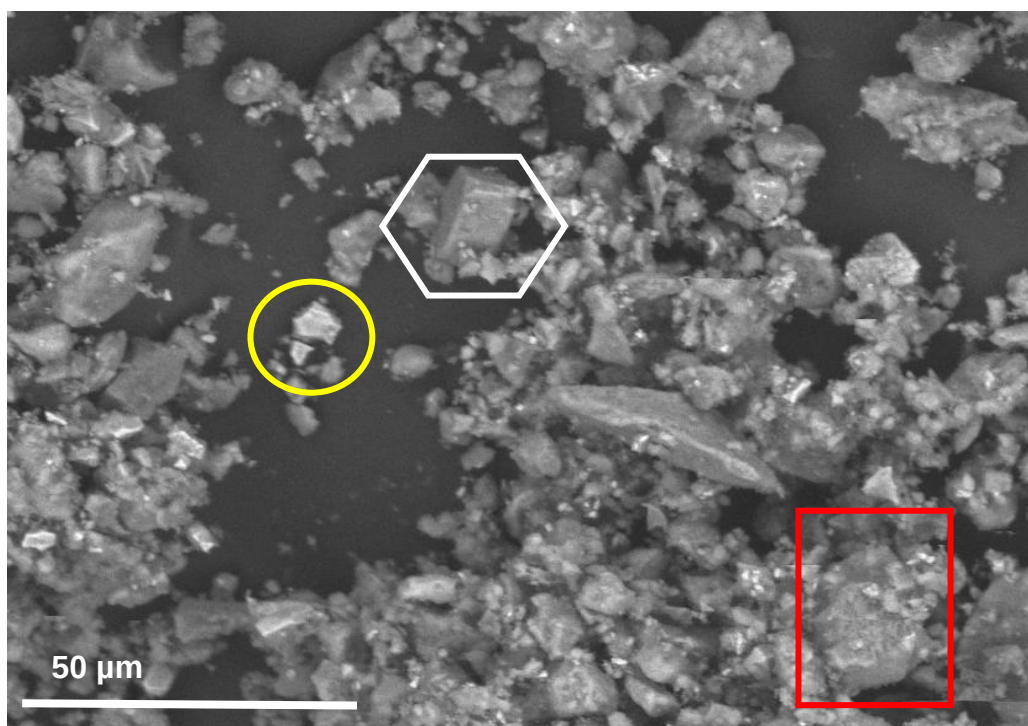


Figure 17: SEM micrograph of sample ET4 500

Figure 17 shows crystals of Mordenite (hexagon), Celadonite (rectangle) and Ilmenite (circle) phases, identified by their shape and EDS in sample calcined at 500 °C

As can be seen from the diffuse reflectance spectra of the samples calcined at different temperatures (Figure 18), the absorption edge has been extended to wider wavelength with increasing calcination temperature. The absorption edge of ET4nc and ET4-300 were around 450 nm. Upon further calcination the absorption edge for ET4-400 and ET4-500 is shifted to 521 nm and 560 nm, respectively. However, further calcination to 600 °C does not bring a change in the absorption edge. Thus the shift of absorption edge from ET4nc to ET4-500 may be indicating that calcination within this temperature range provokes electronic modification on the samples. The band gap energy of these samples

is estimated using Tauc plot by plotting the root square of the product of the Kubelka–Munk function ( $F(R)$ ) and photon energy ( $h\nu$ ) of diffuse-reflectance of each sample against energy. Accordingly, it was found that the band gap energy of the ET4nc, ET4-300, ET4-400, ET4-500 and ET4-600 become 2.63eV, 2.63eV, 2.21eV, 1.52eV, and 1.52eV, respectively.

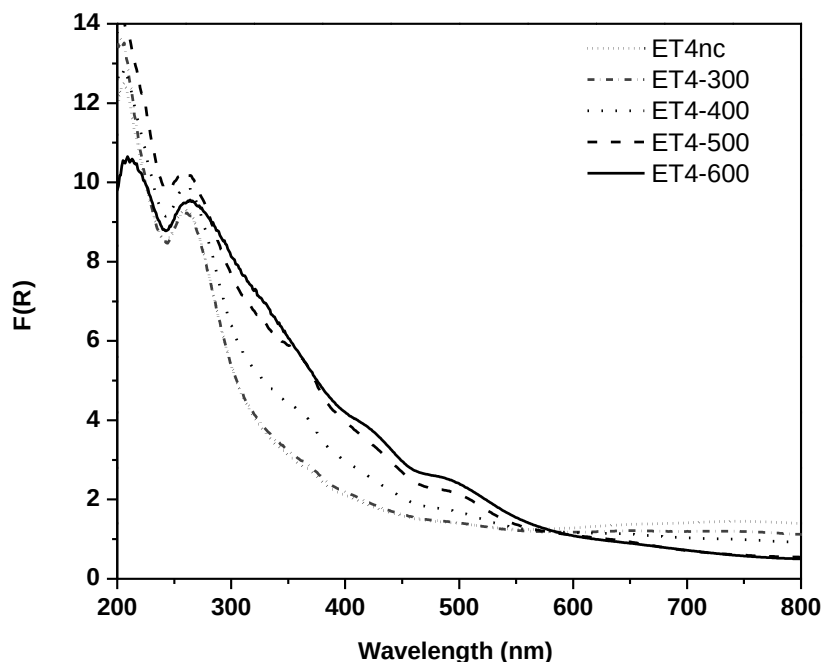


Figure 18: Diffuse reflectance spectra of ET4nc, and calcined at different temperatures.

From the diffuse reflectance spectra, this particular natural zeolite could be a promising photocatalyst. The photocatalytic activity of the samples was tested for the degradation of 10 ppm MO. However, no photocatalytic activity was found both on the ET4nc and ET4-500. Further attempt (section 3.2 B) was carried out in order to enhance the photocatalytic potential of the sample. Extra loading of 20 %  $\text{TiO}_2$  was included to ET4 yielding a material that contains Ti species potentially active for photocatalysis. The sample was then fully characterized by XRD, ICP-OES and UV-Vis DRS. According the

XRD profile (Figure 19), the crystal phases of the raw zeolite do not change up on loading 20 wt % of  $\text{TiO}_2$  and calcinations except intensity decreament especially in the low angle diffraction peaks. Due to the overlap of the XRD peaks, it is difficult to identify the presence of the  $\text{TiO}_2$  crystalline phases.

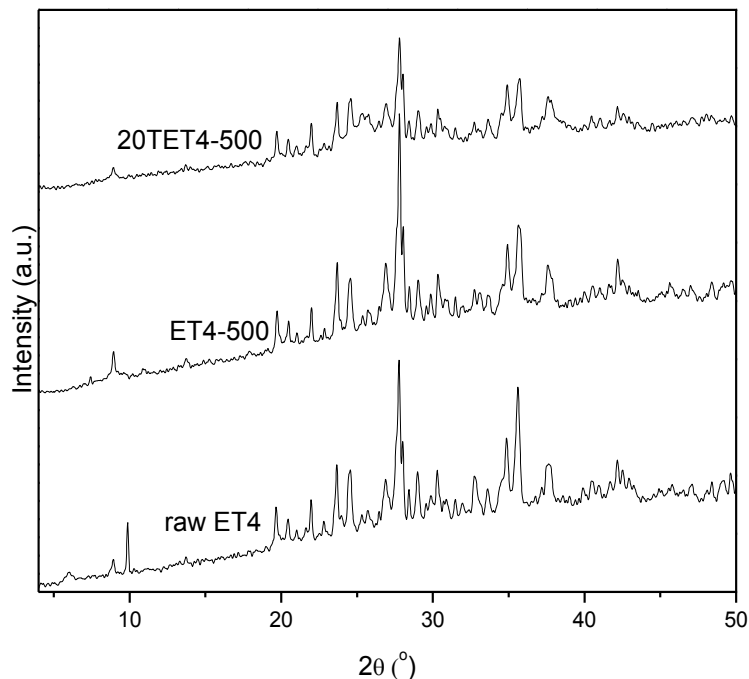


Figure 19: XRD profile of raw ET4, ET4 500, and 20TET4 500

However, the elemental analysis (ICP-OES) (Table 2) confirmed the loading of the Ti species. From the ICP analysis it is clear that the  $\text{TiO}_2$  loading procedure has led to a remarkable decrease in the content of Si in sample 20TET4-500 with a final Si/Al ratio of 3.48, (Table 2) which was 6.11 in the raw ET4 (Table 1). This Si/Al ratio decrement is may be due to some of the Si atoms in the celadonite mineral has dissolved and removed by the solvents used in  $\text{TiO}_2$  loading.

Table 2: Elemental Analysis (ICP-OES)

| Sample      | Al<br>(% wt) | Si<br>(% wt) | Na<br>(%wt) | K<br>(% wt) | Ca<br>(%wt) | Mg<br>(% wt) | Fe<br>(%wt) | Ti<br>(%wt) |
|-------------|--------------|--------------|-------------|-------------|-------------|--------------|-------------|-------------|
| ET4t        | 8.22         | 20.90        | 1.40        | 3.78        | 2.99        | 1.67         | 9.84        | -           |
| 20TET4-500  | -            | -            | -           | -           | -           | -            | -           | 17.50       |
| 20TET4t-500 | -            | -            | -           | -           | -           | -            | -           | 17.00       |

The UV-Vis diffuse reflectance spectra of these samples are plotted in (Figure 20). It is evident that, incorporation of  $\text{TiO}_2$  led to an increase of the area of absorption band for 20TET4-500.

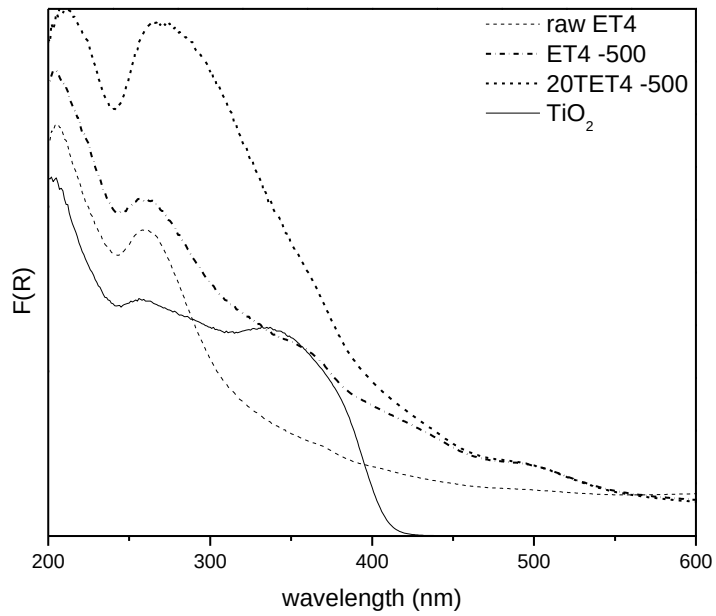


Figure 20: UV-Vis DRS of raw ET4, ET4 500, and 20TE4 500 and  $\text{TiO}_2$

Similar to the ET4nc and ET4-500, the 20TET4-500 does not show any photocatalytic activity in the degradation of 10 ppm MO. We presume that the reason behind this low activity is the presence of impurities in the extra framework of the zeolite that could deplete the path of the photogenerated electron-hole pairs of the system, required for photocatalysis. The raw ET4 was further subjected to different treatments to remove the impurities. First the raw ET4 was treated in drastic condition followed by calcination at 550 °C, 800 °C and 1000 °C and 20% of TiO<sub>2</sub> was loaded to each sample calcined at different temperatures (Section 3.2 C). However, as shown in Figure 21 the structure of the zeolite collapsed and amorphous powders were obtained. This may be is due to the acidity of the 2N nitric acid followed by the high calcination temperature (Section 3.2 C).

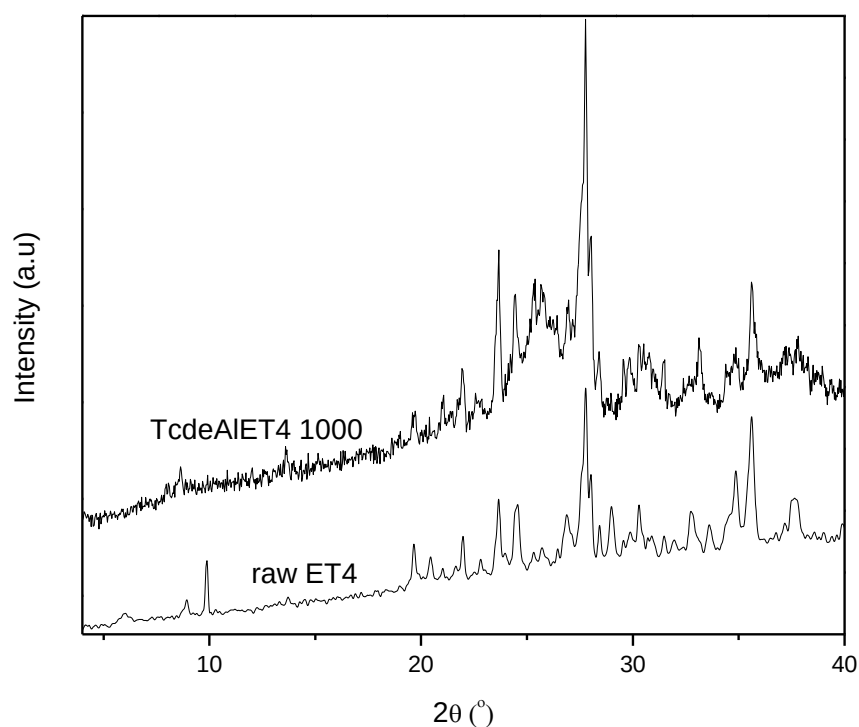


Figure 21: XRD profile of raw ET4 and treated ET4

The samples were then treated using milder conditions; with ammonium acetate solution at pH 6 followed by ammonium fluoride (Section 3.2 D). The XRD profile of the 20TET4t is presented in Figure 22. It can be observed that the crystalline phases of the raw ET4 is maintained after this treatment and loading of 20%  $\text{TiO}_2$ . Similar to XRD profile in Figure 19,  $\text{TiO}_2$  crystalline phases were not identified, but the elemental analysis (Table 2) confirms the presence of Ti species. Furthermore, the ICP results indicate that the treatment of ET4 sample with  $\text{NH}_4\text{Ac} + \text{NH}_4\text{F}$  yields further decrease in the Si content yielding a Si/Al ratio of 2.54.

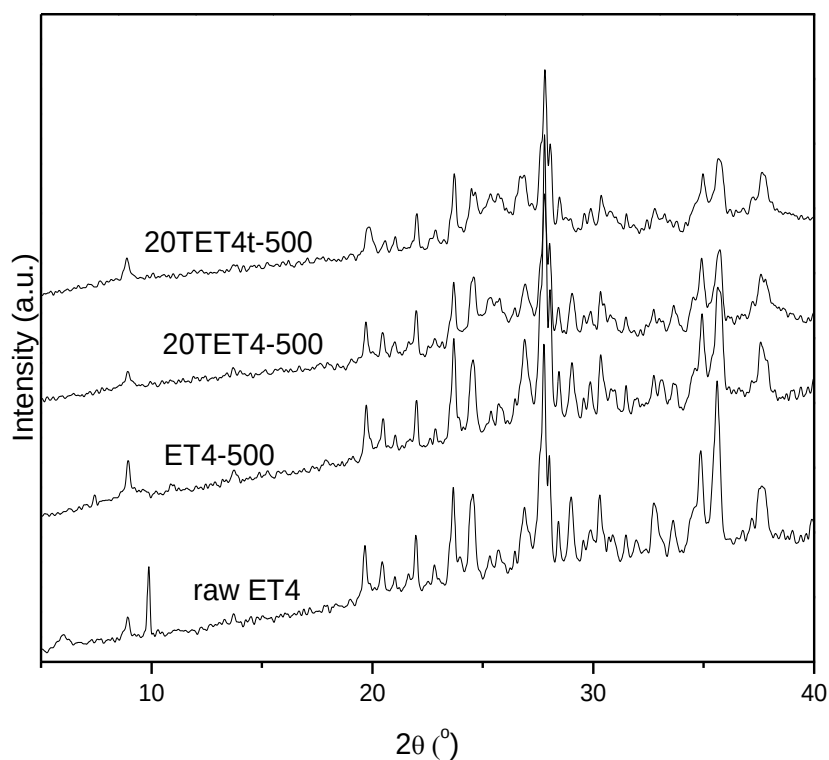


Figure 22: XRD profile of raw ET4, ET4-500, 20TET4-500 and 20TET4t-500

The UV-Vis diffuse reflectance spectra (DRS) of these samples are plotted in Figure 23.

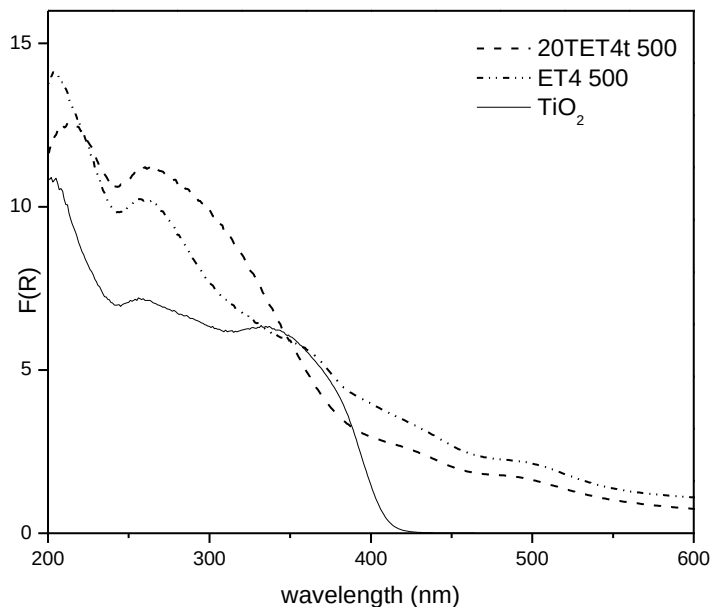


Figure 23: UV-Vis DRS of ET4 500, 20TET4t 500 and TiO<sub>2</sub>

The photocatalytic activity of 20TET4t-500, 20TET4-500 and ET4-500 materials is presented in Figure 24. The sample that has been treated before TiO<sub>2</sub> loading (20TET4t-500) shows higher activity than 20TET4-500 and ET4-500 although it is still very low compared with that reported for pure TiO<sub>2</sub> using the same experimental device as in the present work [125]. Despite the small improvement given by the treatment, there are still a number of factors that hinder the photocatalytic efficiency of the tested natural zeolites, most likely related to specific impurities.

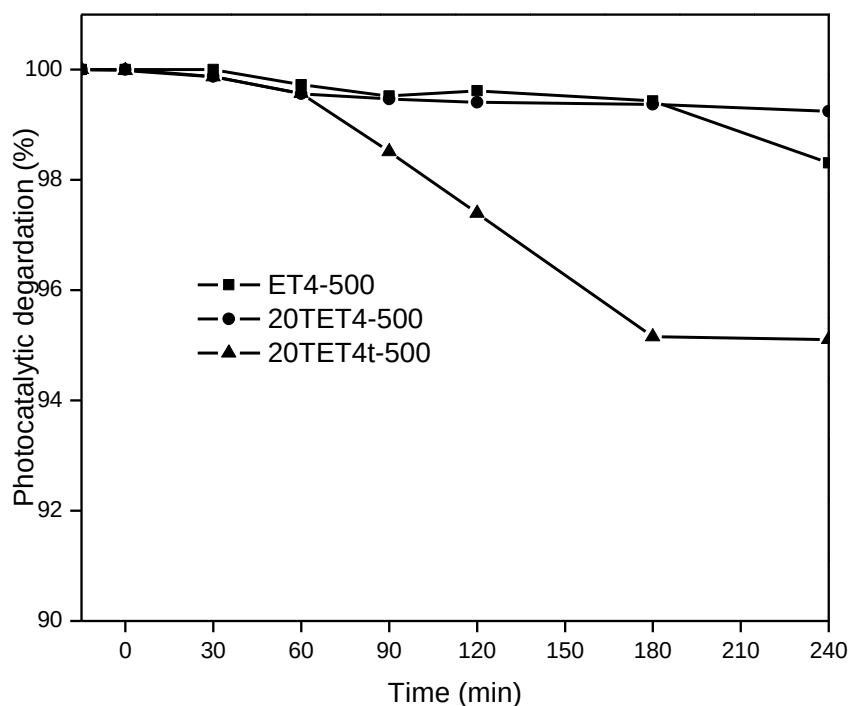


Figure 24: Photocatalytic degradation of 10 ppm MO on ET4 500, 20TET4 500 and 20TET4t 500

Further mechanical processes were tested in order to remove impurities which have magnetic properties (section 3.2 E). The XRD profiles of mechanically purified ET4 samples are shown in Figure 25. From the profiles, it is shown that the “demagnetized” sample, deMET4 consists on the diffraction peaks mainly for MOR and celadonite. The sample which contains much of the magnetic part, MET4 contains mainly Ilmenite diffraction peaks with few peaks of Celadonite. The sample has been successfully separated in terms of magnetic properties.

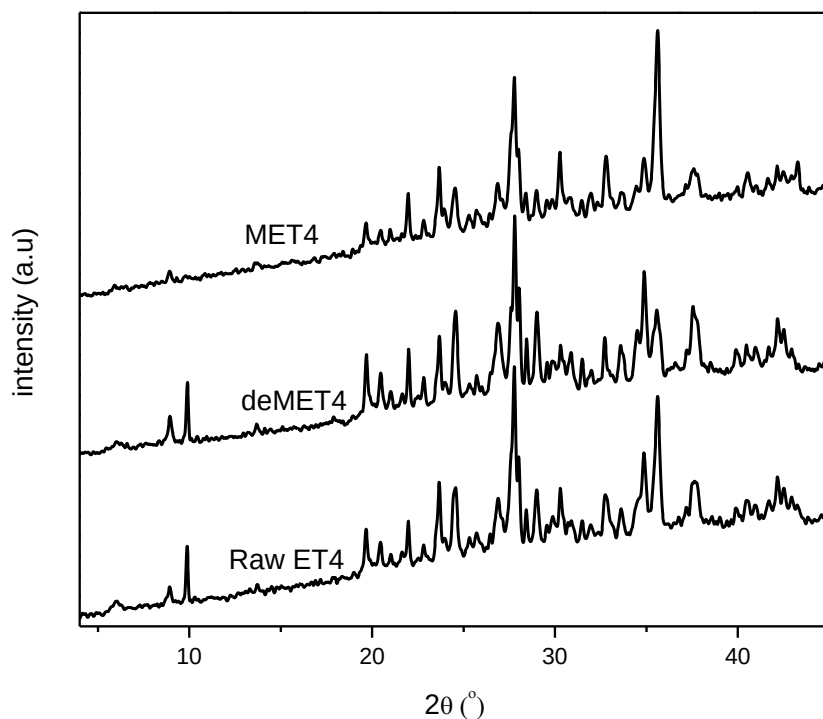


Figure 25: XRD profile of raw ET4, deMET4 and MET4

These samples were tested in the degradation of MO showing no photocatalytic activity. Thus, the samples were loaded with 20%  $\text{TiO}_2$ , though this also showed no improvement in photocatalytic activity either.

### 3.4. Conclusion

The Ethiopian natural zeolite sample (ET4) can be potentially used for photocatalytic applications. This sample contains other non-zeolitic phases like celadonite and ilmenite, which may synergize the potential application of this high Ti-content sample for photocatalysis. However, since it has large number of cations with appreciable amounts, complete removal of these cations is required to customize it to a photocatalyst. Mechanical purification of natural zeolite does not show any beneficial improvement,

thus the chemical modification is the main solution. Among the chemical treatments, those with harsh conditions may lead to a purification of the sample, although sacrificing the properties of the zeolite. Mild treatments can be applied showing improvement in the surface modification of the zeolite.

## **4. Photocatalytic Activity of TiO<sub>2</sub> Supported on Synthetic Zeolites**

### **4.1. Preparation, Characterization and Photocatalytic activity of TiO<sub>2</sub>**

#### **Supported on Synthetic Zeolites**

##### **4.1.1. Introduction**

From the experience with natural zeolites we conclude that the presence of impurities and a variety of cations probably halted the movement of photogenerated electron hole pairs and thus the photocatalytic activity gets hindered [126]. Therefore, the next chosen step is to evaluate the photocatalytic activity of TiO<sub>2</sub> supported on equivalent synthetic zeolites with the same structure where there are no impurities except the charge balance cation, H<sup>+</sup>. As it has been indicated in the introductory part of this thesis, different authors reported enhanced photocatalytic activities of TiO<sub>2</sub> supported on zeolites. In those reports, the discussions on the role of the zeolitic supports have been mainly limited to enhancing adsorption capacity due to their high specific surface area and/or hydrophobicity. However, there is still an unresolved issue in the literature which refers to the role of zeolites in lowering the electron/hole recombination rate of the supported TiO<sub>2</sub> nanoparticles. In this work, we have loaded different TiO<sub>2</sub> amounts on three different zeolites with different SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio and different zeolite framework type. Mordenite (CBV 21A, SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 20), Zeolite Y in its pristine form (CBV400, SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 5.1) which is also compared with a dealuminated form (CBV 760) with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 60 that includes mesopores. Furthermore, we present a full characterization study aiming to understand not only the adsorption properties of the zeolite but the role of zeolites in lowering the electron/hole recombination rate of the final photocatalysts.

#### 4.1.2. Sample Preparation

Two commercially available HY zeolites: CBV 400  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 5.1$  and CBV 760  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 60$ , and one Mordenite (H-form): CBV 21A with  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 20$ , were purchased from Zeolyst. Hereafter, the samples will be called ZY-5, ZY-60 and MOR, respectively.  $\text{TiO}_2$  was loaded on the zeolites in 10, 20 and 40 wt% of. In a typical synthesis of 10% loaded mordenite zeolite (10TMOR) 18 gram of MOR was suspended in a solution of 10.15mL of titanium butoxide ( $\text{Ti}(\text{OBut})_4$ ) dissolved in 101.5 mL of 2-Propanol ( $\text{CH}_3\text{CHOHCH}_3$ ) and 20.3 mL of water ( $\text{H}_2\text{O}$ ) under magnetic stirrer. The stirring was maintained at room temperature for 24 hours. The solvent was removed by rotary evaporator and dried at 110 °C. Similarly, 10, 20 and 40 wt% of  $\text{TiO}_2$  was prepared by suspending each zeolite (ZY-5, ZY-60 and MOR) in a solution of titanium (IV) butoxide ( $\text{Ti}(\text{OBut})_4$ ) dissolved in a mixture of 2-Propanol ( $\text{CH}_3\text{CHOHCH}_3$ ) and water ( $\text{H}_2\text{O}$ ) with volume ratio of 1:10:2 ( $\text{Ti}(\text{OBut})_4$ :  $\text{CH}_3\text{CHOHCH}_3$ :  $\text{H}_2\text{O}$ ). The samples were then calcined in air at 400 °C for 3 hours at 3 °C  $\text{min}^{-1}$ . Pure  $\text{TiO}_2$  was also synthesized in a similar method without adding zeolites for comparison. The samples were labeled 10T, 20T and 40T referring to the theoretical wt% $\text{TiO}_2$  loading, followed by the zeolite code (ZY-5, ZY-60 and MOR).

#### 4.1.3. Results and Discussion

X-ray diffraction profiles of parent zeolites ZY-60,  $\text{TiO}_2$ -loaded ZY-60 and pure  $\text{TiO}_2$  are shown in Figure 26. According to the diffraction patterns, the crystalline framework of the zeolites have been maintained after loading different ratios of  $\text{TiO}_2$  and calcined to 400 °C. However, the intensities decreased as the loading increases.

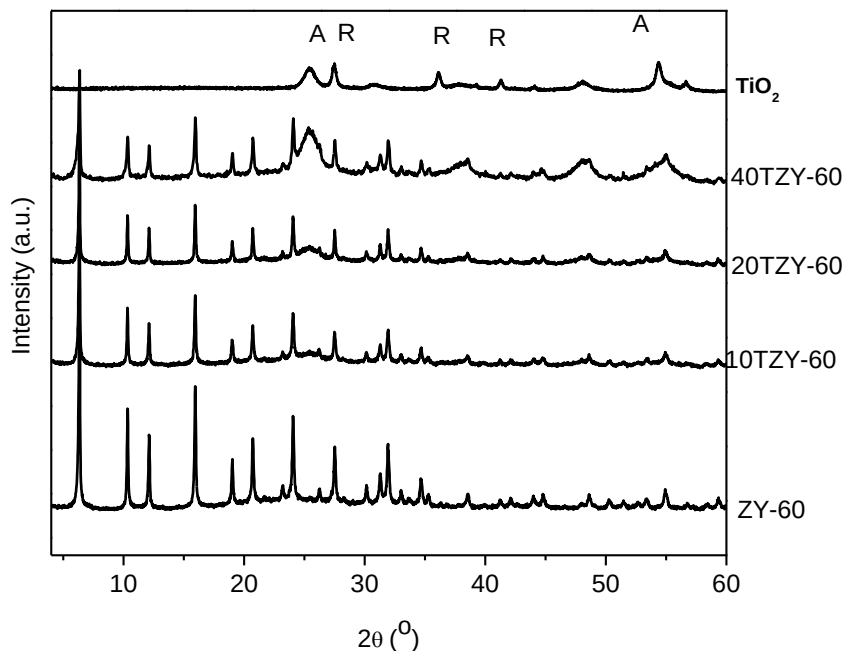


Figure 26: XRD profile of  $\text{TiO}_2$ , ZY-60, 10TZY-60, 20TZY-60 and 40TY-60.

For pure  $\text{TiO}_2$  calcined at 400 °C, the diffraction peaks at  $2\theta = 25.4^\circ$  (101),  $37.8^\circ$  (004),  $48.0^\circ$  (200), and  $54.5^\circ$  (105) can be assigned to anatase crystalline phase of  $\text{TiO}_2$  and diffraction peaks at  $2\theta = 27.6^\circ$  (110),  $36.1^\circ$  (101),  $41.3^\circ$ , and  $56.7^\circ$ , are assigned to rutile phase of  $\text{TiO}_2$ , marked as “A” and “R”, respectively in Figure 26. However, in the supported  $\text{TiO}_2$  under the same experimental conditions, no intensities for rutile phase of  $\text{TiO}_2$  could be observed, indicating that somehow the presence of microporous zeolites increase the phase transition temperature of anatase to the most stable phase of  $\text{TiO}_2$ , rutile or anatase particles are favorably stabilized on the surface of the zeolite matrix [84]. Though different from synthesis method to synthesis method, usually rutile crystalline phase of  $\text{TiO}_2$  appears after calcination of 350 °C. Though, the intensities at  $25.4^\circ$  and  $27.6^\circ$  of  $\text{TiO}_2$  diffraction peaks overlap with the diffraction patterns of the zeolite, there is clear indication of the presence of anatase since the diffraction  $25.4^\circ$  is broadened after

TiO<sub>2</sub> loading, more pronounced in 40% TiO<sub>2</sub> loaded zeolites. In addition, 36.1° (101) was used to confirm the absence of rutile and at 54.5° (105) to confirm the presence of anatase (Figure 26).

As expected, the XRD profile of pure ZY-5 and loaded ZY-5 show similar trends with ZY-60 (Figure 27). However, unlike in the 10% and 20% loaded ZY-60, the anatase diffraction patterns were not detected in the 10% and 20% loaded ZY-5. Anatase was only detected in the 40 % loaded ZY-5 at 25.4° (101) and 54.5° (105).

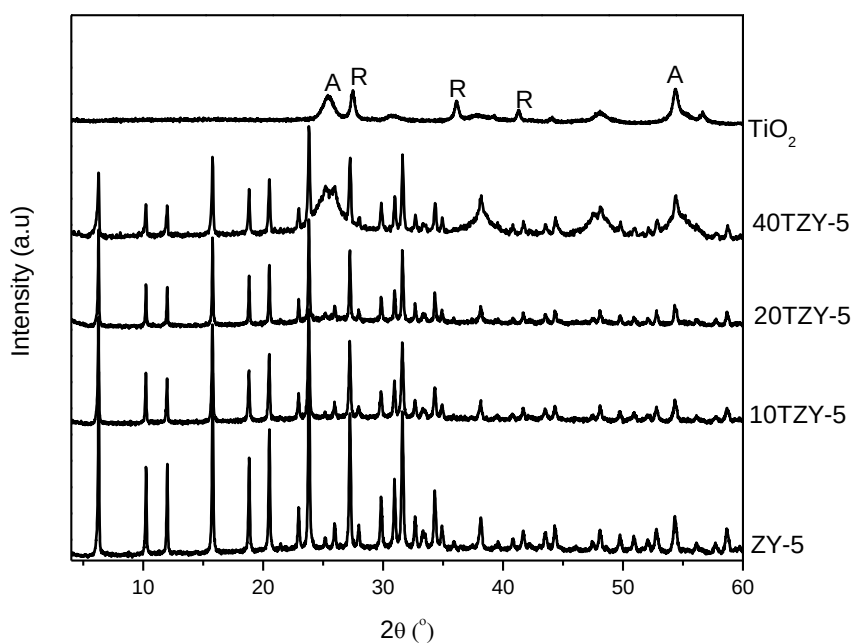


Figure 27: XRD profile of TiO<sub>2</sub>, ZY-5, 10TZY-5, 20TZY-5 and 40TZY-5

The XRD profile of pure MOR, loaded MOR and pristine TiO<sub>2</sub> is shown in Figure 28. Similar to ZY-60 and ZY-5, although the crystalline framework is maintained after loading different ratio of TiO<sub>2</sub> and calcination to 400 °C, there is a general decrement of

intensity of the diffraction peaks when loading increased. As in ZY-60 and ZY-5 case, the presence of anatase phase of  $\text{TiO}_2$  was confirmed from the diffraction peaks at  $25.4^\circ$  (101) and  $54.5^\circ$  (105) (Figure 28).

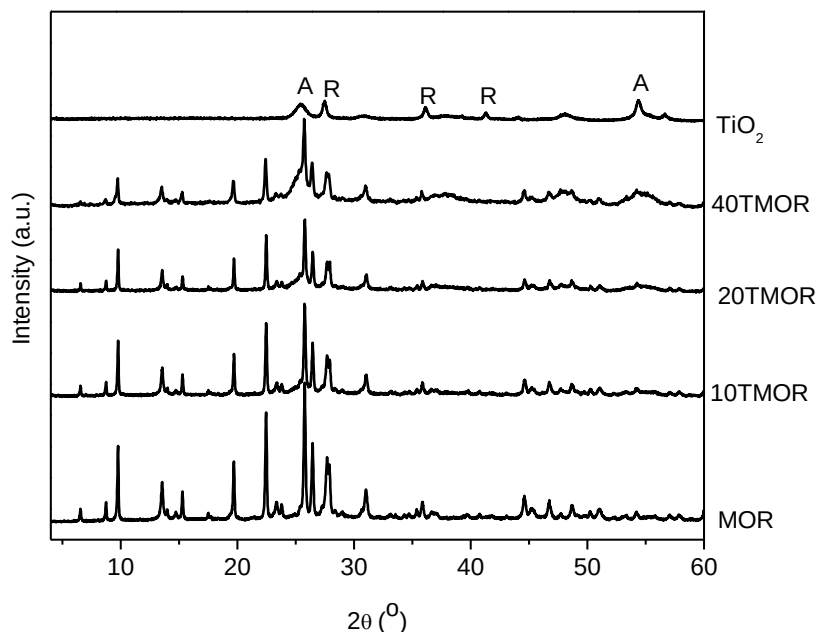


Figure 28: XRD profile of  $\text{TiO}_2$ , MOR, 10TMOR, 20TMOR and 40TMOR

Table 3 collects the ICP analysis results and textural properties of the samples. As shown in Table 3, the actual loading of  $\text{TiO}_2$  from ICP analysis of the samples is below the expected yield of  $\text{TiO}_2$ . For example, in the 10TZY-60, 10TZY-5 and 10TMOR 10 wt%  $\text{TiO}_2$  was expected. However, the actual  $\text{TiO}_2$  obtained from the ICP-OES analysis is 8.5, 7.49 and 7.85 wt% respectively. The same is true for the 20 and 40 wt%  $\text{TiO}_2$  loaded samples; the loading procedure seems reproducible since the yield obtained is higher than 75% in all the zeolites with small difference regardless of the zeolite structure or the amount loaded. The  $\text{TiO}_2$  loading has produced a decrease in the BET surface area ( $S_{\text{BET}}$ ) as can be seen from the data collected in Table 3. This indicates that some of the pores of

the zeolite are either blocked and/or populated with TiO<sub>2</sub> particles. The decrement of S<sub>BET</sub> is more pronounced in the 40 wt% TiO<sub>2</sub> loaded samples mainly due to large amount of extra TiO<sub>2</sub> particles blocking the pores. Figure 29 shows the trend of S<sub>BET</sub> decreament versus wt% TiO<sub>2</sub> loading. Similar observations were also reported in the literature [84, 127, 128] in loaded TiO<sub>2</sub> over zeolitic supports.

Table 3: Chemical and textural properties samples

| Sample           | TiO <sub>2</sub><br>( wt %) <sup>a</sup> | S <sub>BET</sub><br>(m <sup>2</sup> g <sup>-1</sup> ) | t-plot<br>micropore<br>area (m <sup>2</sup> g <sup>-1</sup> ) | t-plot<br>external<br>surface<br>area (m <sup>2</sup> g <sup>-1</sup> ) | Micropore<br>V <sub>p</sub> (cm <sup>3</sup> g <sup>-1</sup> ) |
|------------------|------------------------------------------|-------------------------------------------------------|---------------------------------------------------------------|-------------------------------------------------------------------------|----------------------------------------------------------------|
| ZY60             |                                          | 720                                                   | -                                                             | -                                                                       | -                                                              |
| 10TZY60          | 8.5                                      | 542                                                   | 423                                                           | 135                                                                     | 0.218                                                          |
| 20TZY60          | 16.78                                    | 503                                                   | 273                                                           | 231                                                                     | 0.140                                                          |
| 40TZY60          | 30.14                                    | 415                                                   | 196                                                           | 219                                                                     | 0.101                                                          |
| ZY5              |                                          | 730                                                   | -                                                             | -                                                                       | -                                                              |
| 10TZY5           | 7.49                                     | 558                                                   | 316                                                           | 226                                                                     | 1.63                                                           |
| 20TZY5           | 16.52                                    | 603                                                   | 338                                                           | 264                                                                     | 0.174                                                          |
| 40TZY5           | 29.95                                    | 471                                                   | 257                                                           | 214                                                                     | 0.132                                                          |
| MOR              |                                          | 500                                                   | -                                                             | -                                                                       | -                                                              |
| 10TMOR           | 7.851                                    | 385                                                   | 320                                                           | 65                                                                      | 0.165                                                          |
| 20TMOR           | 16.55                                    | 355                                                   | 271                                                           | 84                                                                      | 0.140                                                          |
| 40TMOR           | 31.49                                    | 304                                                   | 192                                                           | 112                                                                     | 0.099                                                          |
| TiO <sub>2</sub> | 100                                      | 96                                                    | -                                                             | -                                                                       | -                                                              |

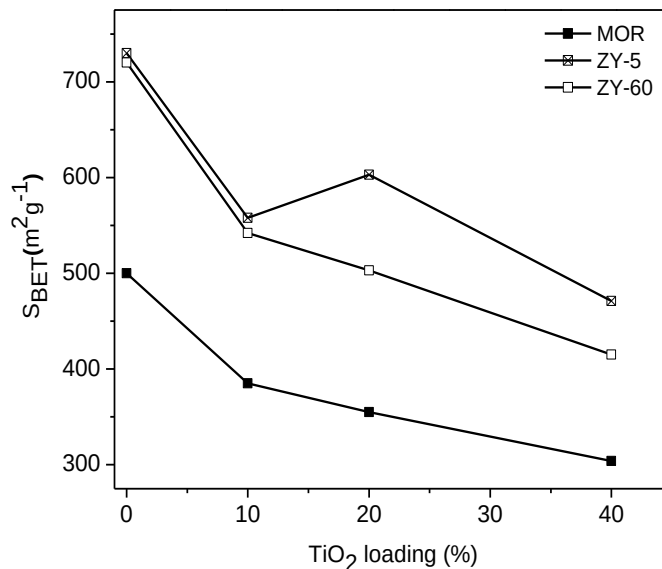


Figure 29:  $S_{BET}$  trend when loading (wt %) increased

As shown in Table 3 the t-plot micro pore area decreases along with  $S_{BET}$  up on increasing wt%  $TiO_2$  loading and the t-plot external surface area increases with increasing the wt%  $TiO_2$  loading Figure 30 shows the ratio of t-polot micropore area to  $S_{BET}$ .

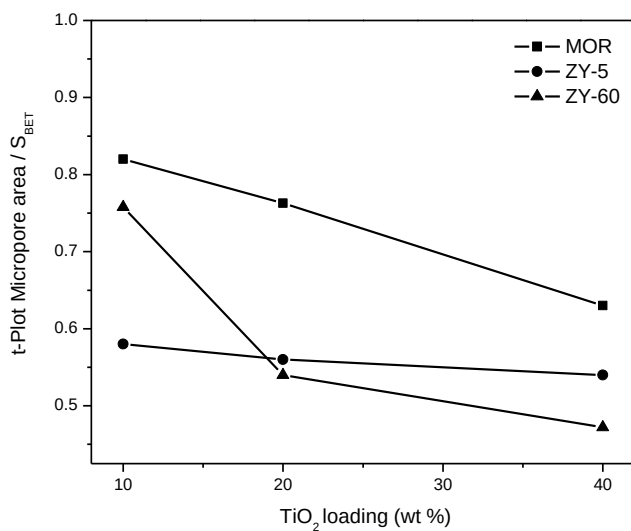


Figure 30: Ratio of t-Plot micropore area to  $S_{BET}$  at various  $TiO_2$  loading

N<sub>2</sub> adsorption/desorption isotherms of pristine TiO<sub>2</sub>, loaded ZY-60, loaded ZY-5 and loaded MOR are shown in Figures, 31 32 and 33. TiO<sub>2</sub> exhibited type IV isotherm, which is related to the mesoporous structure with H2 hysteresis loop, indicative of the presence of cylindrical and spherical pores, which are mainly textural porosity. On the other hand, the loaded zeolites exhibited combined type I and IV isotherms, characteristic of micro- and mesoporosity with H4 hysteresis loop.

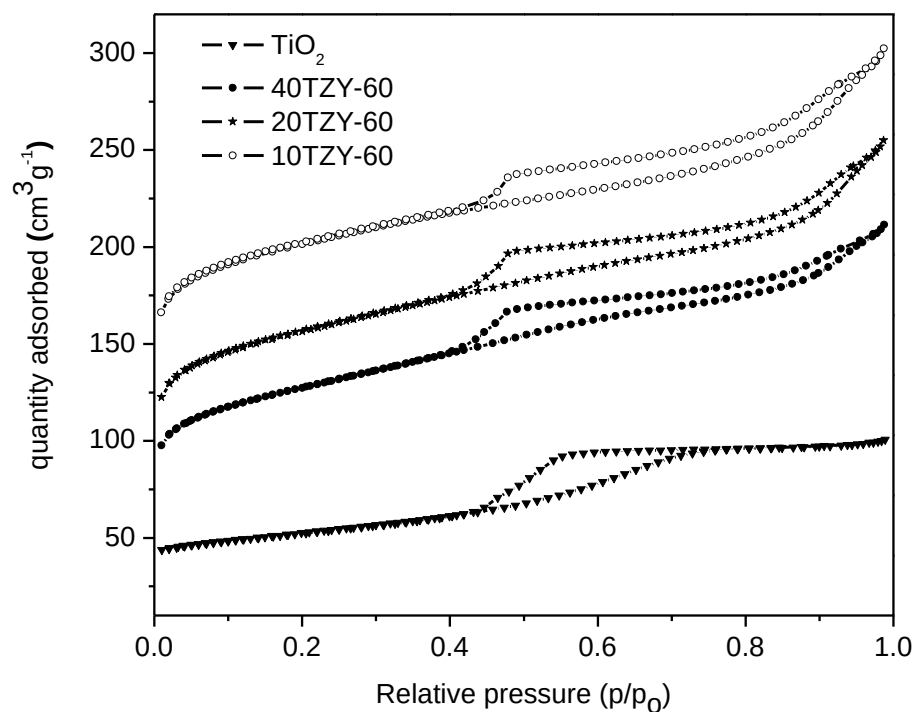


Figure 31: N<sub>2</sub> isotherms of TiO<sub>2</sub>, 10TZY-60, 20TZY-60 and 40TZY-60

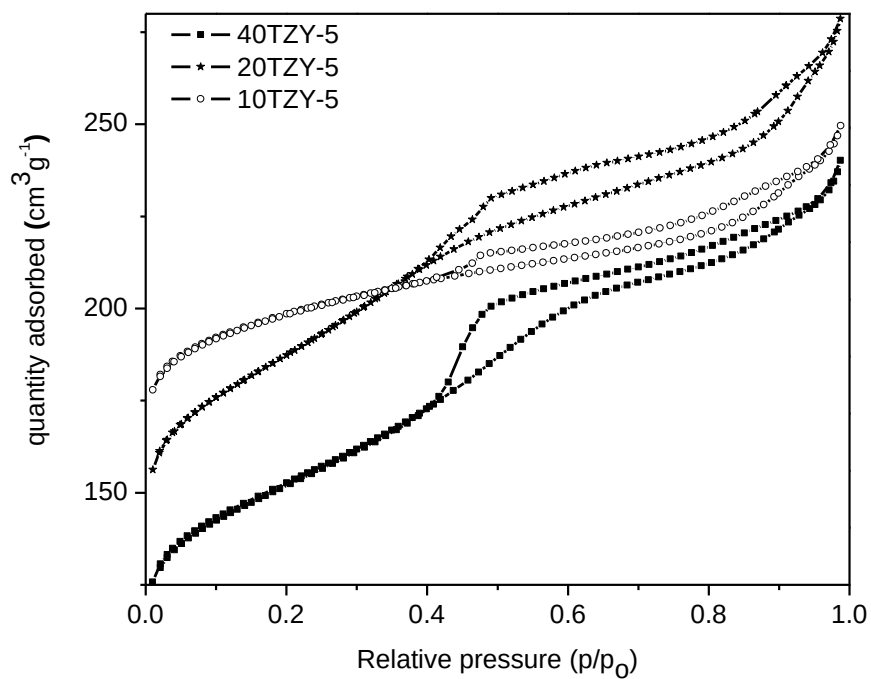


Figure 32: N<sub>2</sub> isotherms of 10TZY-5, 20TZY-5 and 40TZY-5

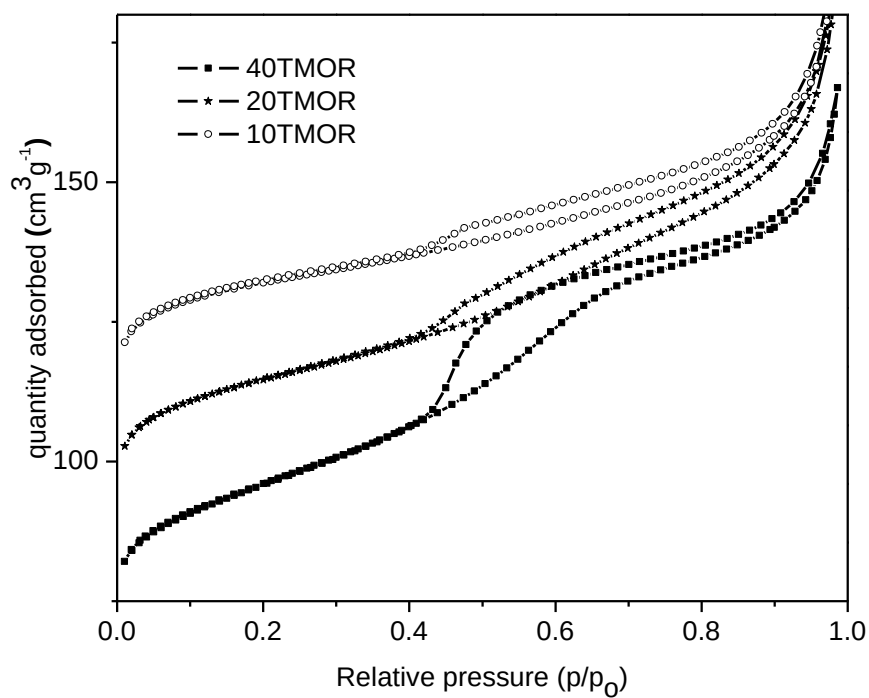


Figure 33: N<sub>2</sub> isotherms of 10TMOR, 20TMOR and 40TMOR

In order to locate the  $\text{TiO}_2$  nanoparticles and estimate their particle size, spherical aberration corrected ( $C_s$ -corrected) Scanning Transmission Electron Microscopy (STEM) mode was chosen, coupled with High Angular Annular Dark Field detector (STEM-HAADF). This kind of observations, using a  $C_s$  corrected microscope for the condenser system, has allowed in the past to locate Ti atoms in the titanosilicate ETS-10 microporous solid [129, 130]. In this study, the extreme loadings were chosen for observations. Figure 34 shows the images corresponding to the 40% and 10% loading of  $\text{TiO}_2$  in ZY-60 zeolite. The low-magnification images of both materials clearly reveal the high difference in  $\text{TiO}_2$  loading level. Both FFT diffractograms, shown in the inset, can be indexed assuming  $Fd-3m$  corresponding to the FAU framework. A closer look at the  $\text{TiO}_2$  phase proves that for 40%  $\text{TiO}_2$  not only the amount covering the zeolite crystallites is much higher presenting large agglomerates, but they also exhibit good crystallinity (Figure 34b). In the case of 10TZY-60, one can clearly see more  $\text{TiO}_2$ -free zeolite surfaces with less crystalline  $\text{TiO}_2$  (Figure 34e). The microporous structure of the zeolite remains unaltered and in good condition after the treatment as shown in Figures 34c and 34f.

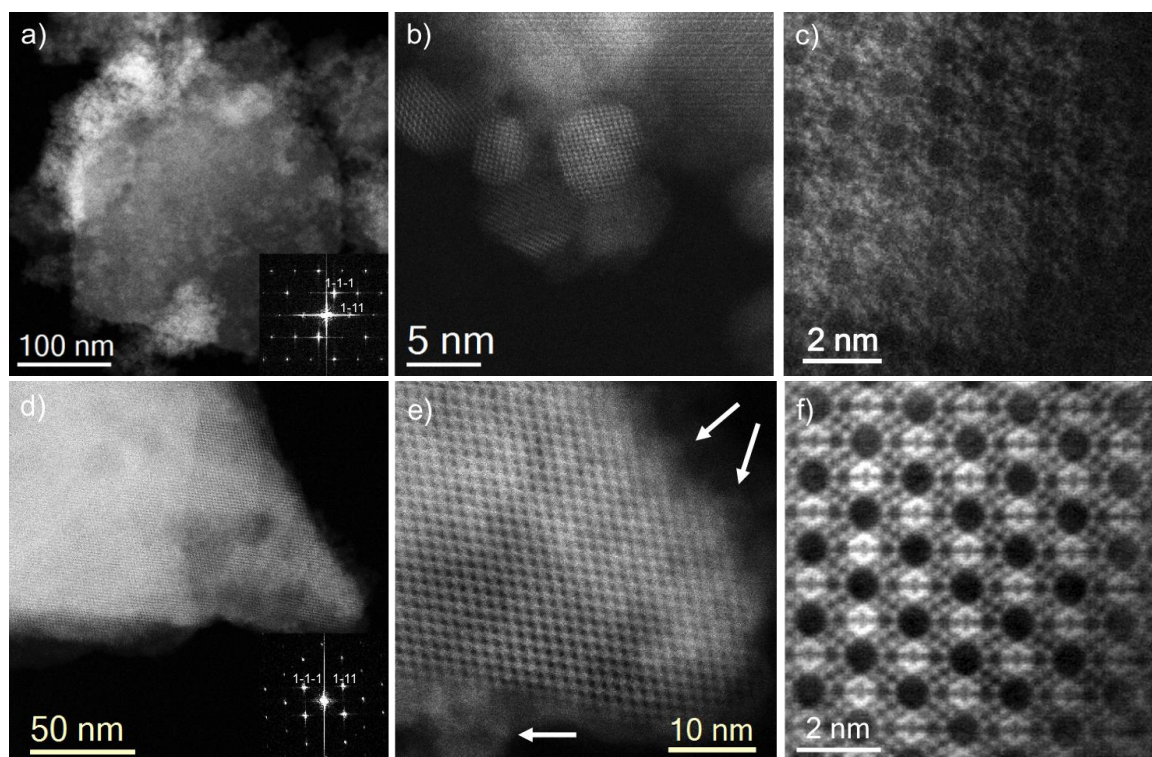


Figure 34:  $C_s$ -corrected STEM-HAADF images of 40TZY-60 and 10TZY-60

- a) Low- magnification image of 40TZY-60. b) A closer look at the  $TiO_2$  nanoparticles, where the structure can be identified. c) Ultra-high resolution image of the zeolite framework. d) Low-magnification image of 10TZY-60. e) A closer look on the zeolite surface where the amorphous  $TiO_2$  is marked by arrows. f) Atomic resolution image of the porous structure

Figure 35 presents the particle size distribution of  $TiO_2$  in 40TZY-60.  $TiO_2$  is found to be 6.44 nm size in 40TZY-60. On the other hand, the particle size of 10TZY-60 can not be determined from the images mainly due to the agglomerated nature of the  $TiO_2$  particles and it is less crystalline nature.

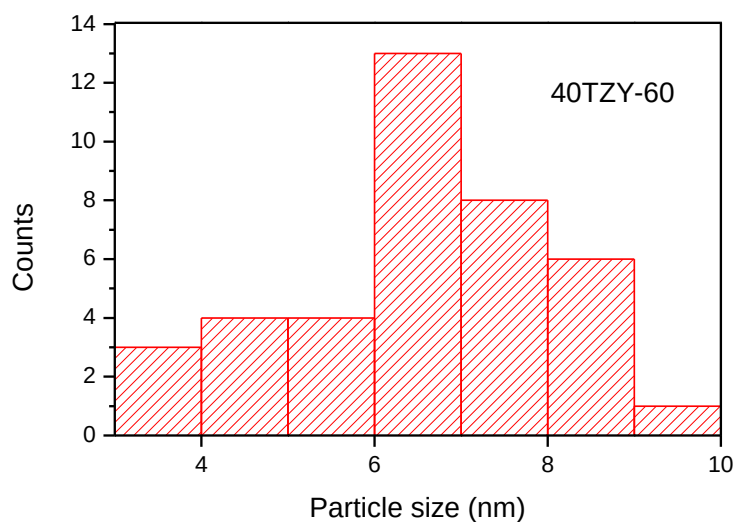


Figure 35: Particle size distribution of 40TZY-60

Although the presence of remaining  $\text{TiO}_2$  or  $\text{Ti}^{4+}$  species could not be imaged inside the pores/cages of zeolites Y, EDS chemical analysis (Figures 36) proves the presence of Ti in an area where external Ti species couldn't be identified both in 40TZY-60 and 10TZY-60. In Figure 36, the EDS analyses of the  $\text{C}_s$ - STEM-HAADF images extracted from the white rectangle are presented in the left side of the image.

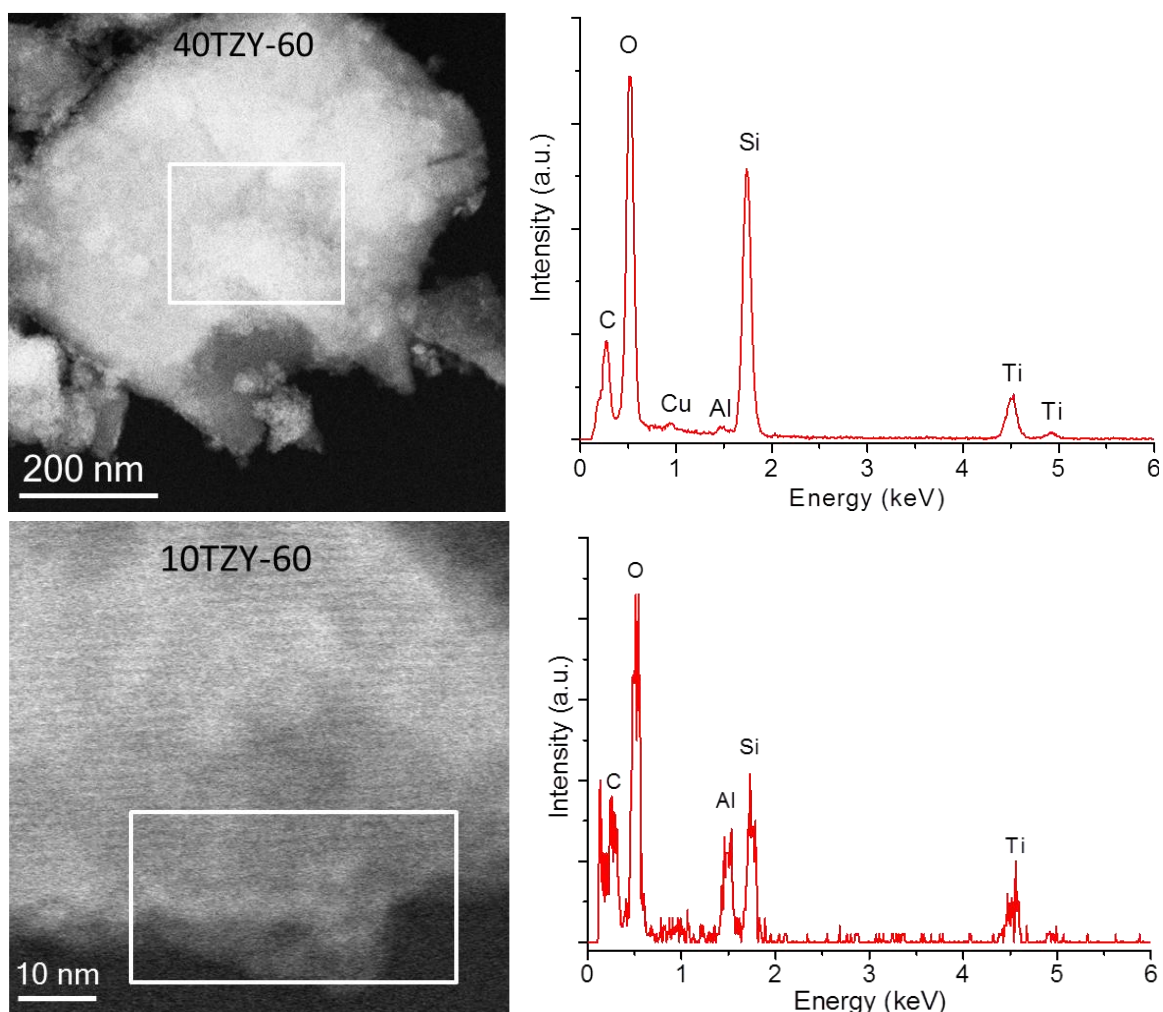


Figure 36:  $C_s$ -corrected STEM-HAADF images of 40TZY-60 and 10TZY-60 and EDS analyses

Figure 37 depicts the same observations obtained for 40TYZ-5 and 10TYZ-5. Figure 37a corresponds to the low-magnification image of 40TYZ-5, where large crystalline  $\text{TiO}_2$  aggregates are easily identified (Figure 37b). In the case of 10TYZ-5, it seems that in this case the surface of the crystals it is still highly covered by  $\text{TiO}_2$ , in contrast with the results observed for 10TZY-60 (Figures 34d and 34e). Both FFT diffractograms, shown in the inset, corroborate the high crystallinity of the zeolite and can be indexed assuming

*Fd-3m* symmetry. A closer observation of the  $\text{TiO}_2$  species is presented in Figures 37b and 37e, which in both cases present a good crystallinity. As for the previous materials, the zeolitic structure remains intact after loading.

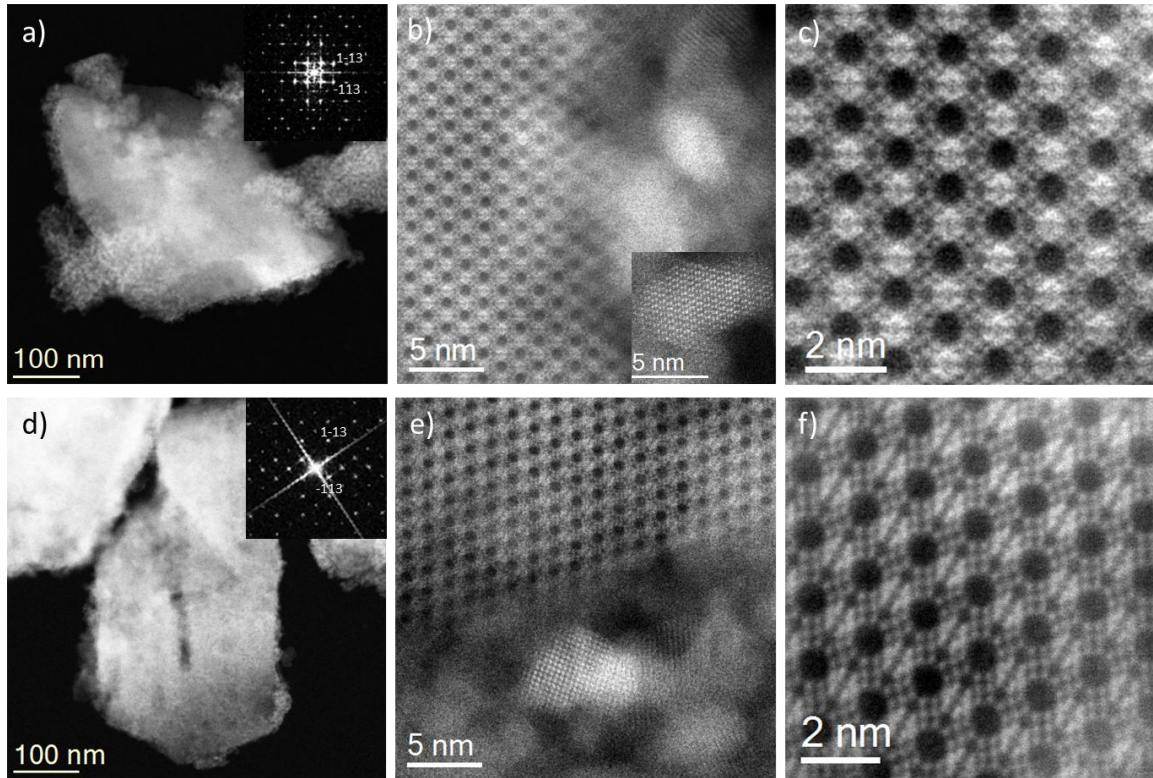


Figure 37:  $C_5$ -corrected STEM-HAADF images of 40TZY-5 and 10TZY-5

- a) Low-magnification image of 40TZY-5
- b) A closer look at the  $\text{TiO}_2$  nanoparticles, where the structure can be identified.
- c) Ultra-high resolution image of the zeolite framework.
- d) Low-magnification image of 10TZY-5.
- e) A closer look on the zeolite surface where the amorphous  $\text{TiO}_2$  is marked by arrows.
- f) Atomic resolution image of the porous structure.

The  $\text{TiO}_2$  particle size distribution is shown in Figure 38 with an average of 6.15 nm in 10TZY-5 and 6.3 nm in the 40TZY-5

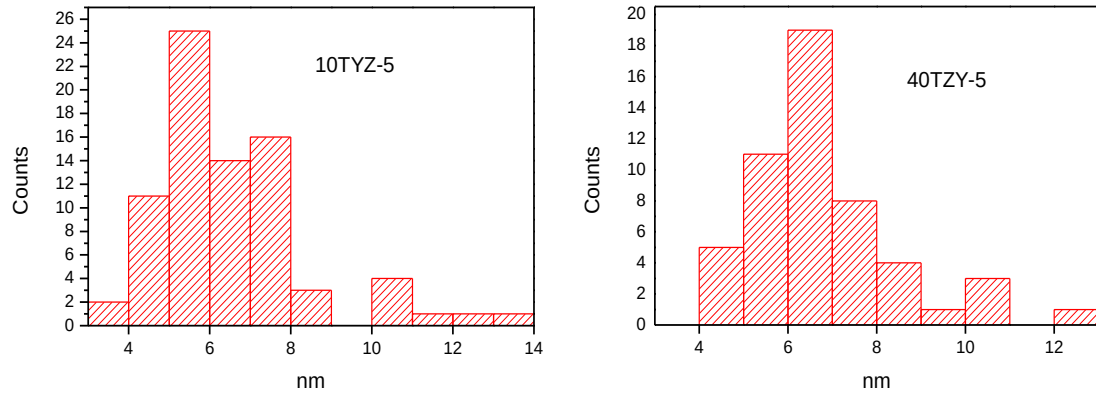


Figure 38: Particle size distribution of  $\text{TiO}_2$  in 40TZY-5 and 10TZY-5

The EDS analyses of 40TZY-5 and 10TZY-5 is shown in Figure 39

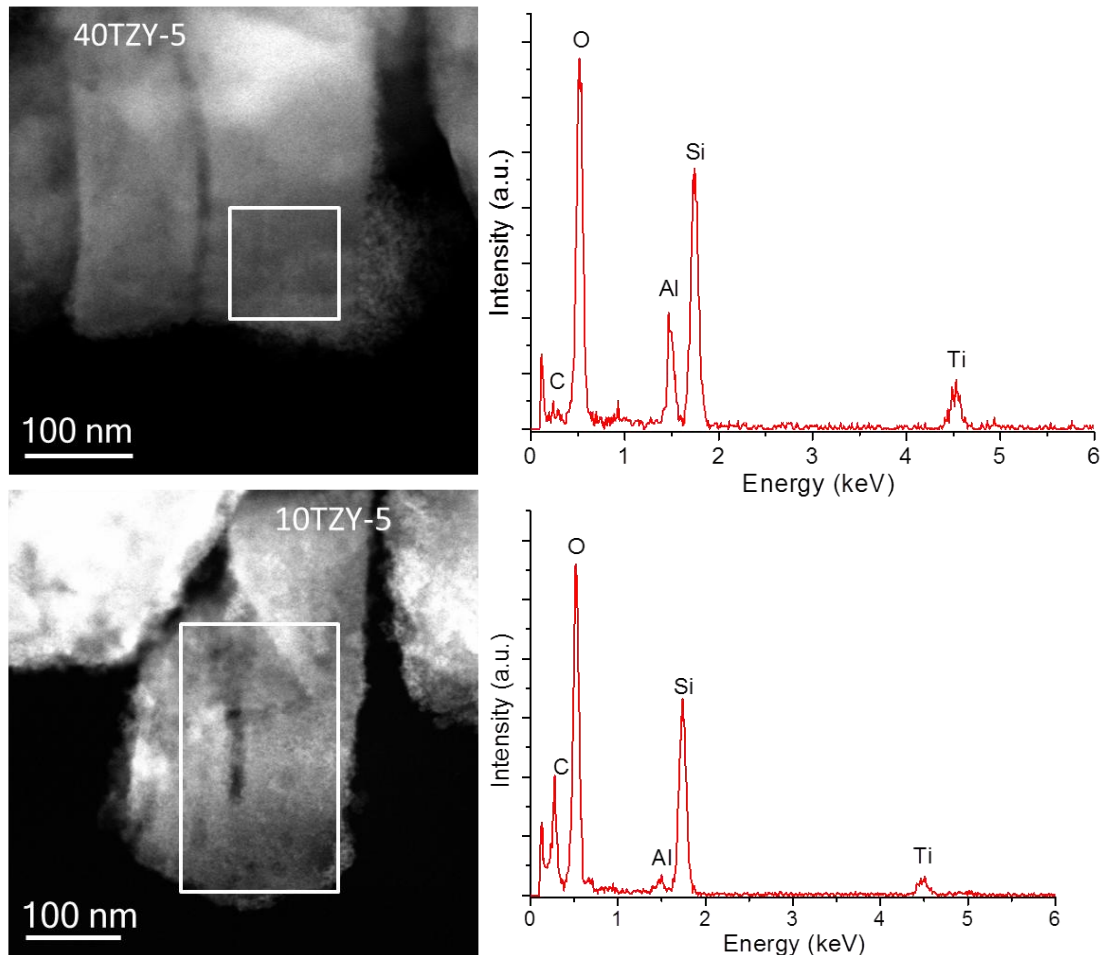


Figure 39:  $C_s$ -corrected STEM-HAADF images of 40TZY-5 and 10TZY-5 and EDS analyses

Similarly, Figure 40 shows the images corresponding to the 40 % and 10% loading of  $TiO_2$  in MOR zeolite. Figures 40a and 40d exhibit the low-magnified images of both materials, respectively, where the higher number of  $TiO_2$  nanoparticles for the 40TMOR can be observed. From the Figure 40,  $TiO_2$  presented good crystallinity (Figures 40b and 40e) in both materials. It is clear from the image in Figure 40 that in 40TMOR; most of the  $TiO_2$  is detected outside as an extra phase, hindering the possible observation of any  $TiO_2$  inside the zeolite structure. The  $C_s$ -corrected STEM-HAADF high resolution

images of the zeolitic structure reveals that after  $\text{TiO}_2$  treatment the framework still remained intact (Figures 40c and 40f). Both images are oriented with the pore system parallel to the electron beam and the FFT (shown in the inset in Figures 40a and 40d) can be indexed assuming  $Cmcm$  symmetry.

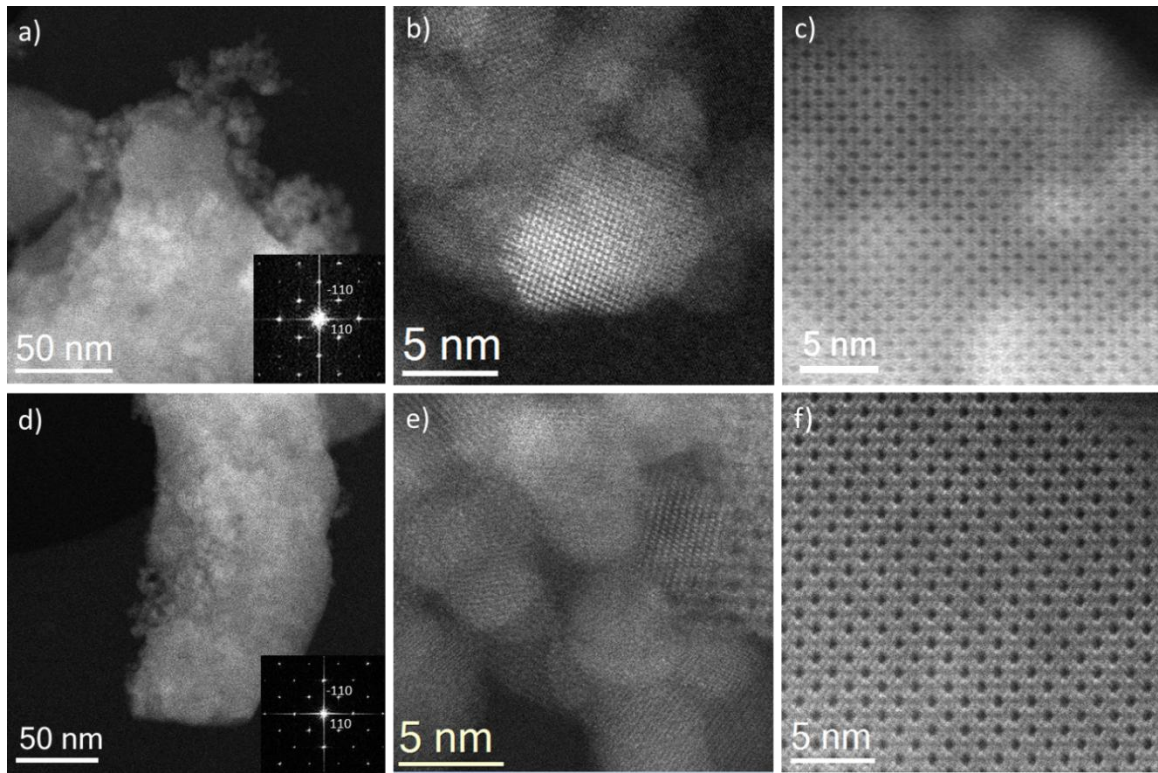


Figure 40:  $C_5$ -corrected STEM HAADF images of 40TMOR and 10TMOR

a) Low-Magnification image of 40TMOR showing the  $\text{TiO}_2$  nanoparticles on the surface with the zeolite FFT shown inset. b) Several of the  $\text{TiO}_2$  nanoparticles. c) High-magnification image showing the porous structure along the  $[001]$  orientation. d) Low-magnification image of 10TMOR with the indexed FFT shown inset. e) Several  $\text{TiO}_2$  nanoparticles. f) Highly magnified image of the zeolite framework along the  $[001]$  orientation.

Figure 41 shows the particle size distribution of  $\text{TiO}_2$  on the 40TMOR and 10TMOR and it was found that 40TMOR and 10TMOR presented average particle size of  $\text{TiO}_2$  of 7.30 and 7.52 nm, respectively

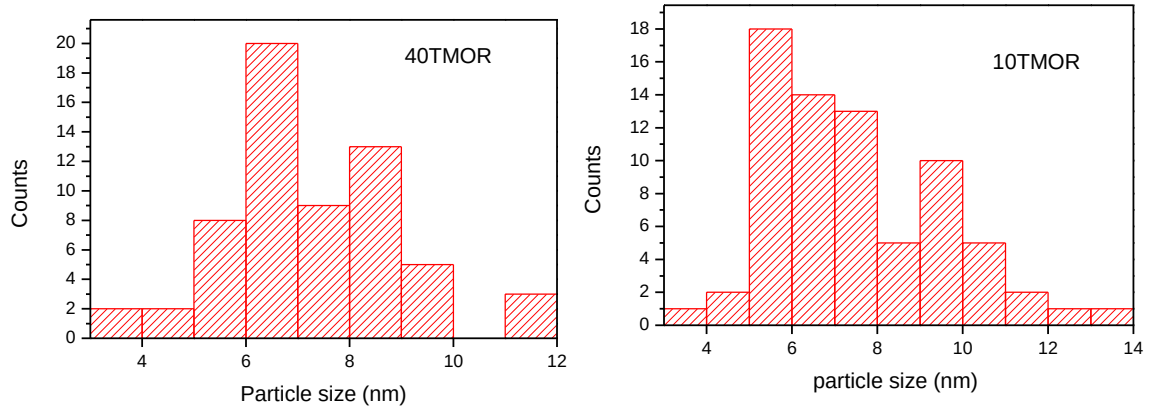


Figure 41: Particle size distribution of  $\text{TiO}_2$  in 40TMOR and 10TMOR

The presence of the remaining  $\text{TiO}_2$  inside the pores of the mordenite structure cannot be unequivocally ascertained, although the EDS statistical screening identifies the presence of Ti in areas where no external particles could be identified Figure 42).

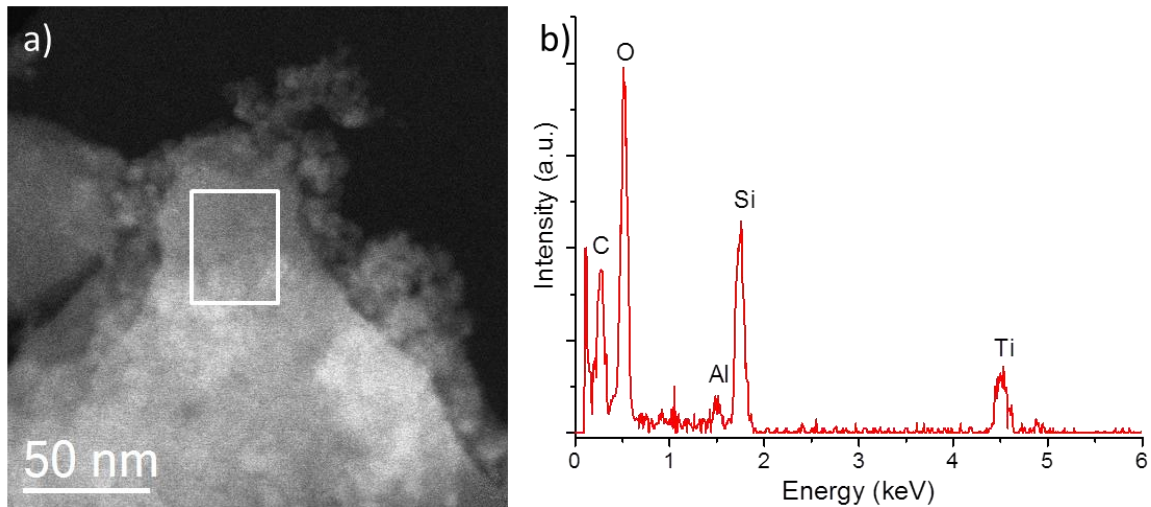


Figure 42:  $C_s$ -corrected STEM/HAADF image of 40TMOR and EDS analysis.

The atomic resolution data of the  $\text{TiO}_2$  nanoparticles (Figure 43) can unambiguously be indexed according to the anatase structure, space group  $I4_1/amd$  with lattice constants  $a = b = 3.71 \text{ \AA}$  and  $c = 9.51 \text{ \AA}$ .

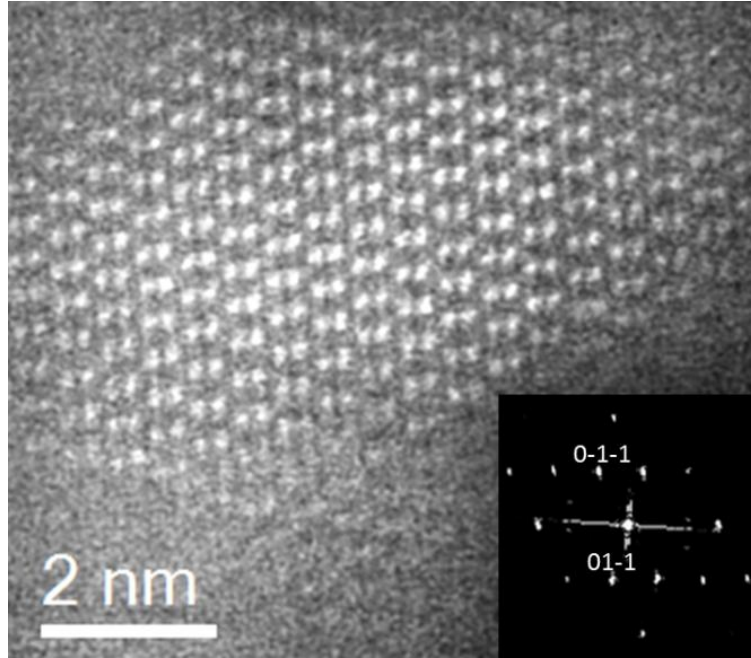


Figure 43:  $C_s$ -corrected STEM-HAADF image and FFT of  $\text{TiO}_2$  along the  $[100]$

Further, chemical analysis was carried out by means of Electron Energy Loss Spectroscopy (EELS), where the chemical compositional maps are depicted and allow a clear location of the Ti present on the zeolite crystallites. Figure 44 shows as an example the  $C_s$ -corrected STEM-HAADF image of 10TZY60 in which the green rectangle indicates the area where spectrum imaging was acquired, and extracted EELS spectrum after background subtraction where the Ti and O edges are clearly identified. The RGB map where Titanium (Ti) appears in green, Oxygen (O) in blue and Silicon (Si) in red clearly shows the correspondence between the nanoparticles observed in the image and

the presence of Ti. Two EELS spectra extracted from two different positions are shown in Figure 44 showing a clear difference in the Ti signal.

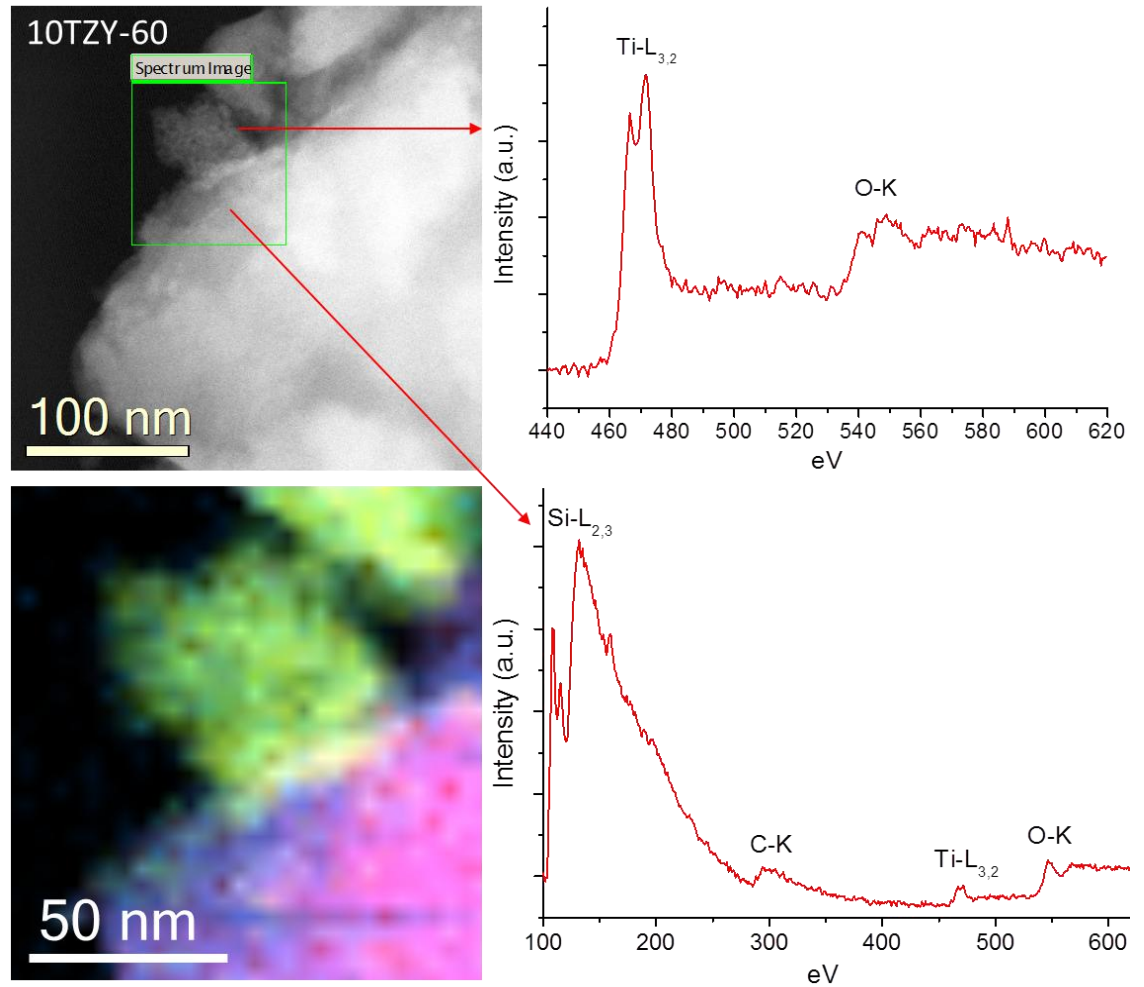


Figure 44:  $C_s$ -corrected STEM/HAADF image of 10TZY-60 and EELS spectra .

Similarly, Figure 45 shows as an example the  $C_s$ -corrected STEM-HAADF image of 10TZY-5 in which the the green rectangle indicates the area from where spectra imaging were acquired. Extracted EELS spectra after background subtraction where the Ti and O edges are clearly identified. The RGB map where Ti appears in green, O in blue and Si in red clearly shows the correspondence between the nanoparticles image and the presence

of Ti from EELS spectra. Both spectra extracted from different positions also exhibit a clear difference in the Ti signal

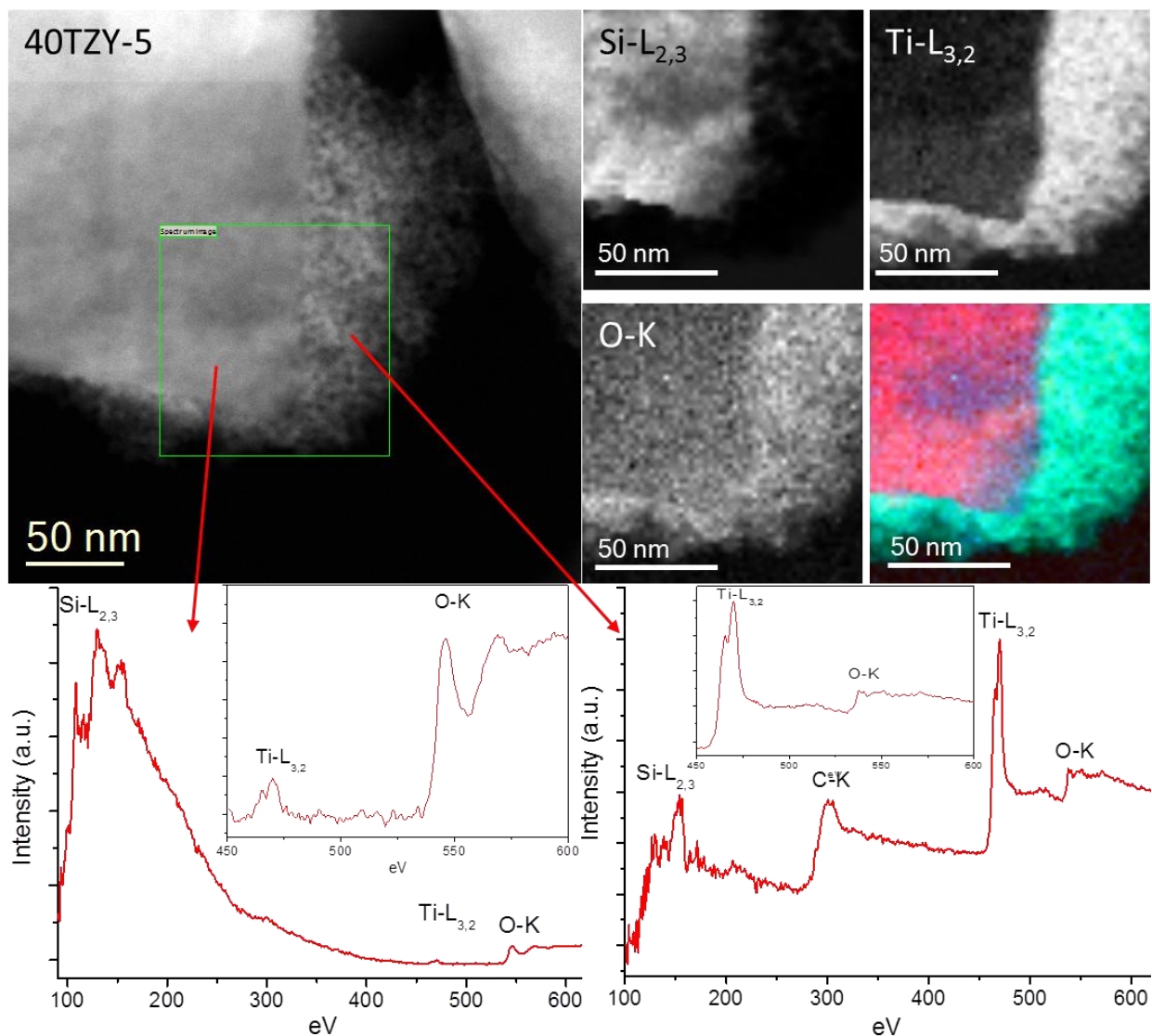


Figure 45: Cs-corrected STEM-HAADF images of 40TZY-5 and EELS spectra

The Ti-L<sub>3,2</sub> edges and O-K edges do not present significant differences between the zeolite 10TZY-60 (Figure 44) and 10TZY-5 (Figure 45) suggesting the formation of anatase as a general TiO<sub>2</sub> phase in agreement with XRD data recorded

Diffuse reflectance UV-Vis spectra of pure zeolites, loaded zeolites and pristine TiO<sub>2</sub> are shown in Figures 46, 47 and 48. The absorption band at around 200–240 nm is due to electron transfer excitation from the ligand-oxygen to an unoccupied orbital of the Ti<sup>4+</sup> with more intensity in the loaded zeolites. The loaded zeolites spectra are also characterized by a large unresolved absorption band ranging from 360 to 240 nm, which is assigned to the electronic transition from 2p(O) to 3d(Ti), corresponding to the valence band to the conduction band transition according to the energy band structure of TiO<sub>2</sub> [84, 96, 127, 128, 131, 132] while it is from 412 to 240 nm for the pristine TiO<sub>2</sub>. From these spectra, it can be seen that the pure zeolites (ZY-60, ZY-5 and MOR) do not show any absorbance above 240 nm wavelength. However, upon loading different amounts of TiO<sub>2</sub>, the absorbance edge of the materials is extended to higher wavelength compared to the pure zeolites. On the other hand, TiO<sub>2</sub>-loaded samples exhibit a blue shift compared with pristine TiO<sub>2</sub>. Cosa *et al.*, (2002) obtained such blue shift when they prepared TiO<sub>2</sub> nanoclusters on series of zeolite Y, Beta, ZSM-5, and mordenite[133]. April *et al.*, (2008) also indicated such blue shift in their review of different zeolites used to support TiO<sub>2</sub>[134]. Further comparison among the different loaded samples shows that there is a red shift in the absorbance edge upon increasing the TiO<sub>2</sub> loading from 10 to 40 wt %. All wt% TiO<sub>2</sub> supported on MOR show high absorption coefficient than the pristine TiO<sub>2</sub>. Similarly, 10TZY-60, 40TZY-60 and 40TZY-5 showed high light absorption coefficient compared to pristine TiO<sub>2</sub>. Figure 49 shows comparison of the light absorption coefficient among the 40 wt %TiO<sub>2</sub> loaded zeolites and pristine TiO<sub>2</sub>.

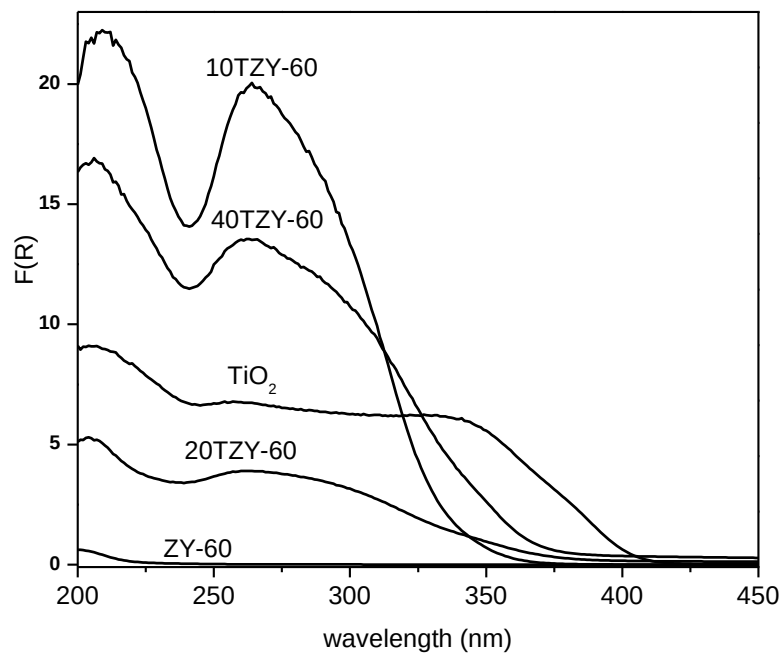


Figure 46: UV-Vis DRS analysis of TiO<sub>2</sub>, ZY-60, 10TZY-60, 20TZY-60 and 40TY-60

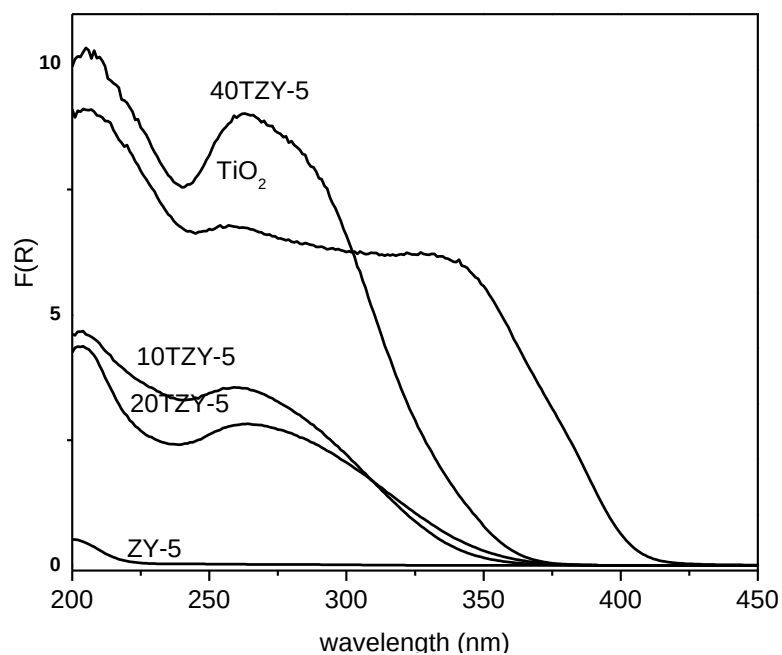


Figure 47: UV-Vis DRS analysis of TiO<sub>2</sub>, ZY-5, 10TZY-5, 20TZY-5 and 40TY-5

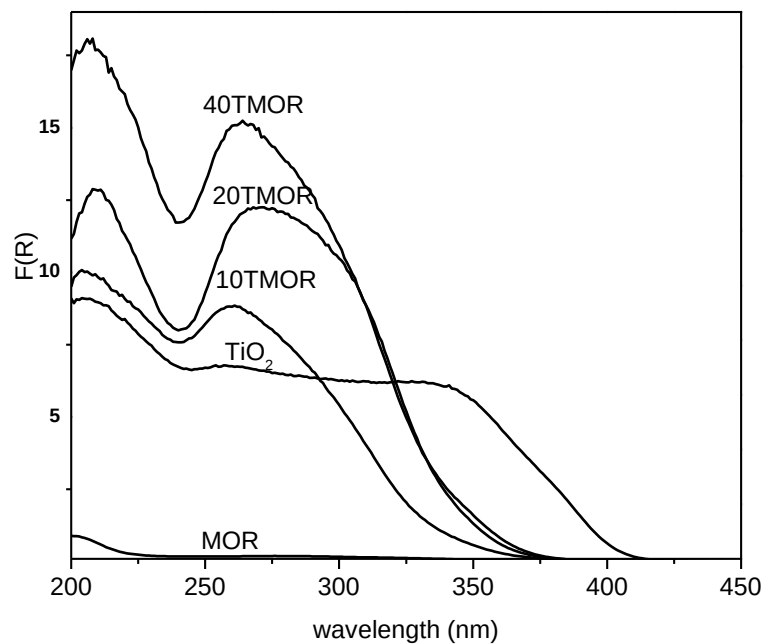


Figure 48: UV-Vis DRS analysis of TiO<sub>2</sub>, MOR, 10TMOR, 20TMOR and 40TMOR

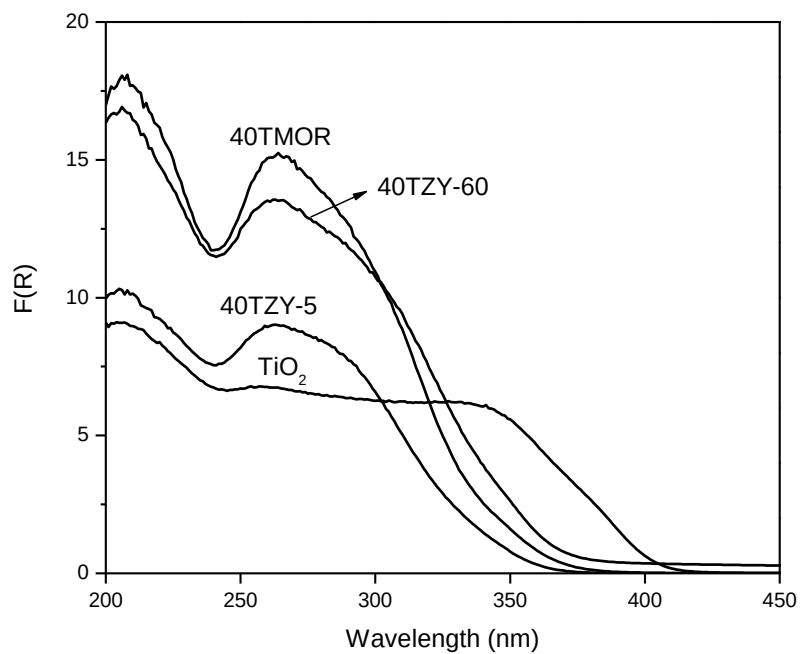


Figure 49: UV-Vis DRS analysis of 40TZY-60, 40TZY-5, 40TMOR and TiO<sub>2</sub>

Photocatalytic degradation of 10 ppm MO on the loaded zeolites and pristine  $\text{TiO}_2$  is plotted versus time in Figures 50, 51 and 52 for ZY-60, ZY-5 and MOR, respectively. As can be seen from the plot in Figure 50, the observed photocatalytic degradation of 10 ppm MO is higher than the photolysis (irradiation of light without photocatalyst) and adsorption of MO (in the presence of a photocatalyst without irradiating with light). This indicates that neither the photolysis nor the adsorption alone play significant role in decreasing the concentration of the 10 ppm of MO, which shows that photocatalytic reaction has taken place.

Moreover, the photocatalytic activity of the 40TZY-60 is higher than the photocatalytic activity of the pristine  $\text{TiO}_2$ . The percentage photocatalytic activity of the 10TZY-60, 20TZY-60 and 40TZY-60 at the 60 minute irradiation are shown in Table 4.

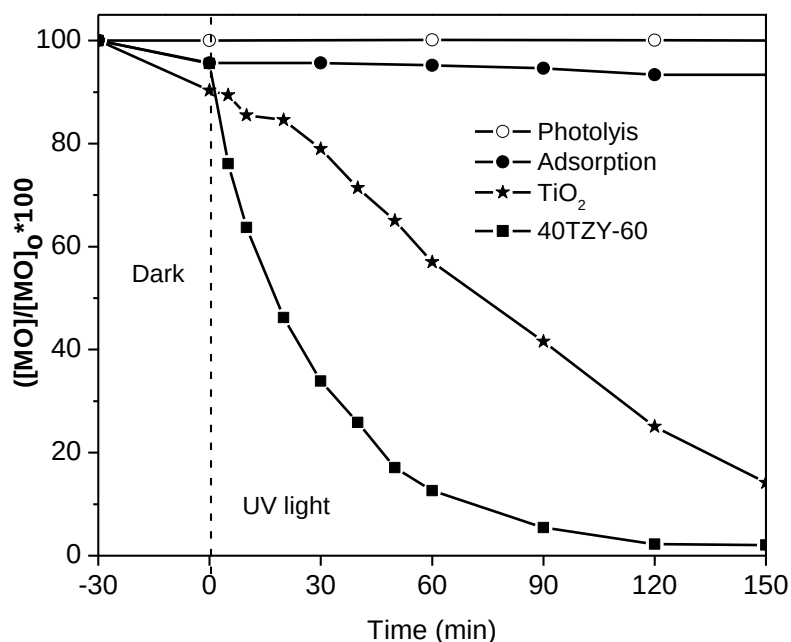


Figure 50: Photolysis, adsorption and Photocatalytic degradation of MO on 40TZY

Similarly, the photocatalytic activities of 40TMOR and pristine  $\text{TiO}_2$  are shown in Figure 51. The photocatalytic activity of the 40TMOR is higher than the pristine  $\text{TiO}_2$ . The percentage photocatalytic activity of the 10TMOR, 20TMOR and 40TMOR at the 60 minutes irradiation are shown in Table 4

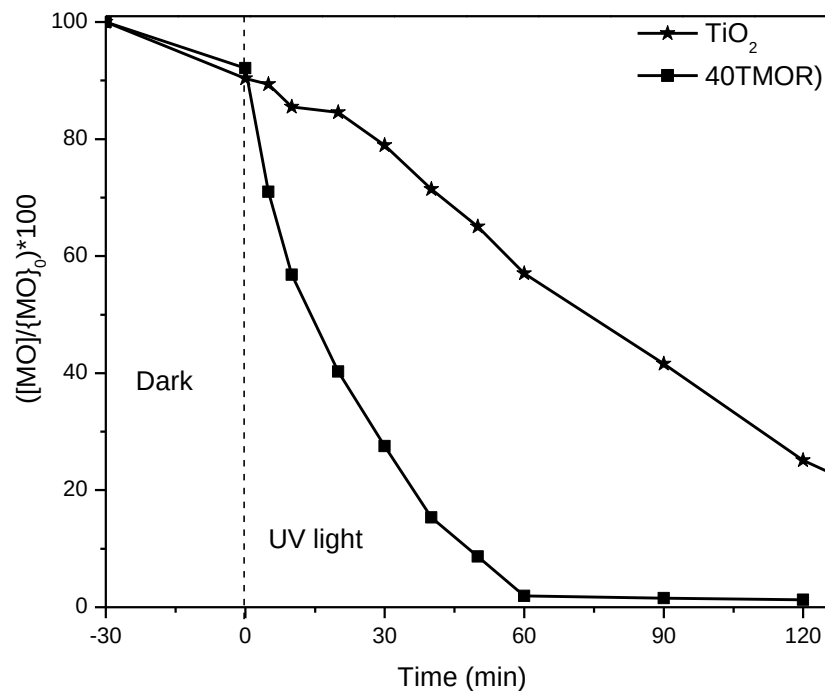


Figure 51: Photocatalytic degradation of MO on 40TMOR and  $\text{TiO}_2$

Table 4: Photocatalytic activity of samples

\*Determined after 60 min UV light irradiation

| Sample  | *MO deg (%) | *TORm<br>( $\mu\text{mol g}^{-1} \text{h}^{-1}$ ) | Sample           | *MO deg (%) | *TORm<br>( $\mu\text{mol g}^{-1} \text{h}^{-1}$ )* |
|---------|-------------|---------------------------------------------------|------------------|-------------|----------------------------------------------------|
| 10TZY60 | 61.18       | 526.03                                            | 10TMOR           | 31.24       | 243.43                                             |
| 20TZY60 | 73.18       | 222.77                                            | 20TMOR           | 58.64       | 216.49                                             |
| 40TZY60 | 87.18       | 177.11                                            | 40TMOR           | 98.05       | 190.24                                             |
| 10TZY5  | 1.5         | 9.38                                              | TiO <sub>2</sub> | 42.98       | 26.25                                              |
| 20TZY5  | 7.5         | 27.11                                             |                  |             |                                                    |
| 40TZY5  | 4.83        | 9.85                                              |                  |             |                                                    |

Regardless of the similarity in wt%  $\text{TiO}_2$  loading, particle size distribution and other textural properties among the  $\text{TiO}_2$  loaded ZY-60, -ZY-5 and MOR zeolites, almost no photocatalytic degradation was observed in 10TZY-5, 20ZY-5 and 40TZY-5 (Figure 52). To explore why the ZY-5 family is not as photocatalytically active as the other samples, adsorption of 10 ppm MO was considered after 30 min stirring without UV irradiation on 40TZY-5, 40TZY-60 and 40TMOR. It was found that 788.18 $\mu\text{g}$  and 448 $\mu\text{g}$  of MO were adsorbed on 0.5g of 40TMOR and 40TZY-60, respectively whereas only 1 $\mu\text{g}$  of MO was adsorbed on 0.5 g of 40TZY-5. Adsorption of the target molecule is the first step in any photocatalytic reactions. Therefore, 40TZY-5 lacks photoactivity probably due to the hindrance of adsorption of the target molecule; MO. Figure 53 presents comparison among the 40TZY-60, 40TZY-5, 40TMOR and  $\text{TiO}_2$

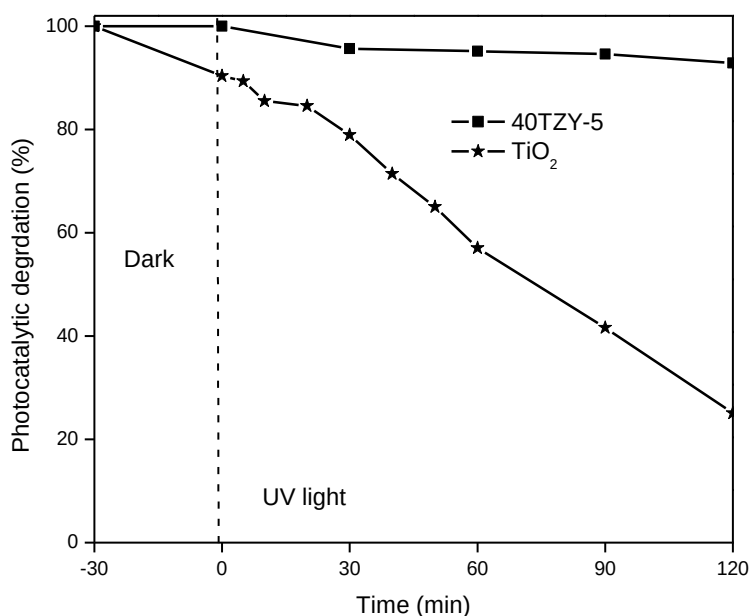


Figure 52: Photocatalytic degradation of 40TZY-5 and  $\text{TiO}_2$

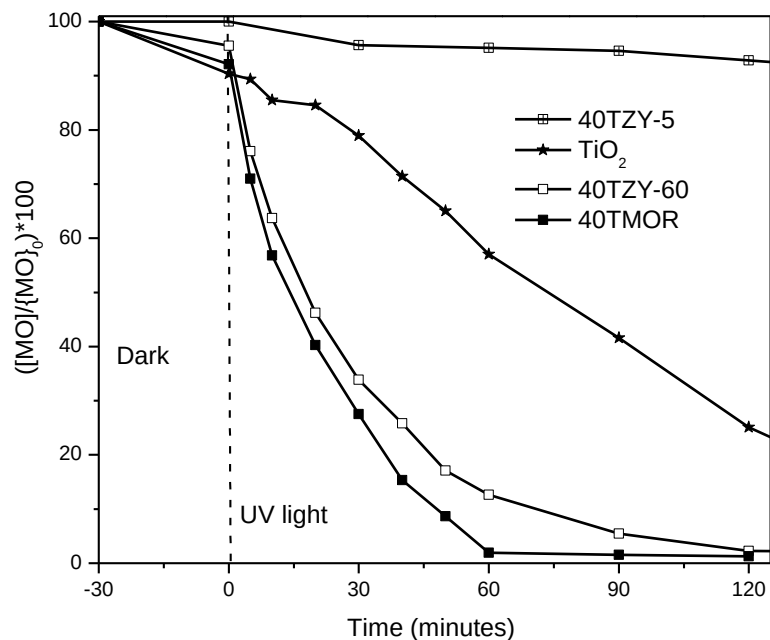


Figure 53: Photocatalytic degradation of 40 wt% loaded zeolites and TiO<sub>2</sub>

The photocatalytic degradation activity of the supported TiO<sub>2</sub> nanoparticles is even more pronounced when we normalized the rate of the photocatalytic degradation by mass of the photoactive material, TiO<sub>2</sub>. Although common understanding is yet to be reached in the literature in calculating turnovers of different photocatalysts, we use mass normalized turnover rate (TOR<sub>m</sub> moles converted of MO per gram of photocatalyst per unit time) [135, 136]. From the data collected in Table 4, it can be found that the TOR<sub>m</sub> of supported TiO<sub>2</sub> is 7-20 times higher than pristine TiO<sub>2</sub>, except for the ZY-5 family (Table 4). Particularly, 10TZY-60 showed highest photocatalytic activity with highest TOR<sub>m</sub> of 526 μmol g<sup>-1</sup> h<sup>-1</sup>. The TOR<sub>m</sub> of TiO<sub>2</sub> supported on ZY-60 and MOR zeolites increase as the loading decreases from 40 to 10 wt% TiO<sub>2</sub>.

To evaluate the reusability of the photocatalysts, 10TZY-60 was chosen since it was the photocatalyst with best  $TOR_m$  in this study. At the end of the first photocatalytic cycle, the photocatalyst was separated from the suspension, filtered, washed, oven dried at 110 °C, and then reused without any calcination treatment for photocatalytic degradation of freshly prepared 10 ppm MO solution. The same procedure was employed after the second and third cycles of use. The Photocatalytic degradation was found 73, 69 and 68 % in the cycle 1, cycle 2 and cycle 3 respectively after UV light irradiation for 60 minutes. The photocatalytic activity did not significantly change giving 5% reduced percentage photocatalytic degradation after the 3 cycles. The small decrease in the degradation percentage is probably due to the accumulation of organic intermediates in the cavities and/or on the surface of the photocatalyst affecting the adsorption of MO, and reducing the photocatalytic activity of the material. These results show that this photocatalytic material can be reused without noticeable photocatalytic activity losses. Similar results have been reported in the literature. For example, Gomez *et al.*, (2015) tested the reusability of situ generated  $TiO_2$  over zeolitic supports for the degradation of dichlorvos pesticides [84] and found that their samples can function for at least eight cycles without noticeable activity decrement. Kanakaraju *et al.*, (2015) also studied the reusability of  $TiO_2$ /zeolite integrated photocatalytic degradation of amoxicillin and found that the photocatalytic degradation was reduced to 69% in the third cycle while it was 88% in the first cycle [83].

The leaching of TiO<sub>2</sub> nanoparticles was measured using ICP-MS for Ti species in the treated water on 10TZY-60. It was found that the leaching from the water treated by pristine TiO<sub>2</sub> is about 29.48 ppb whereas the leaching of Ti species in the water treated water by 10TYZ-60 was found to be about 0.89 ppb. Considering the toxicity of TiO<sub>2</sub> nanoparticles [64-67], this result indicates the additional value to the role of zeolites besides enhancing the photocatalytic activity of the supported TiO<sub>2</sub> nanoparticles. To our best knowledge such reports were not presented in the literature. The amount of TiO<sub>2</sub> used in the loaded zeolites and the structure of the zeolites may contribute for the leaching prevention on the 10TZY-60.

Finally, the photocatalytic degradation of real wastewater from a textile industry of Ethiopia was tested with the Zeolite Y hybrid photocatalysts 40TZY-60 and 10TYZ-60, with the highest TOR<sub>m</sub>, and compared with pristine TiO<sub>2</sub>. Due to the complexity of the wastewater which includes not only mixture of organic dyes but also other chemicals from the bleaching steps (Figure 54), it is rather difficult to calculate concentrations and the turnover number of the degradation reaction. Thus, the quantification of the photocatalytic degradation percentage at specific absorbance band was based on the ratio  $A_t/A_0 \times 100$ ; where  $A_t$  is absorbance at time  $t$  and  $A_0$  is the initial absorbance.

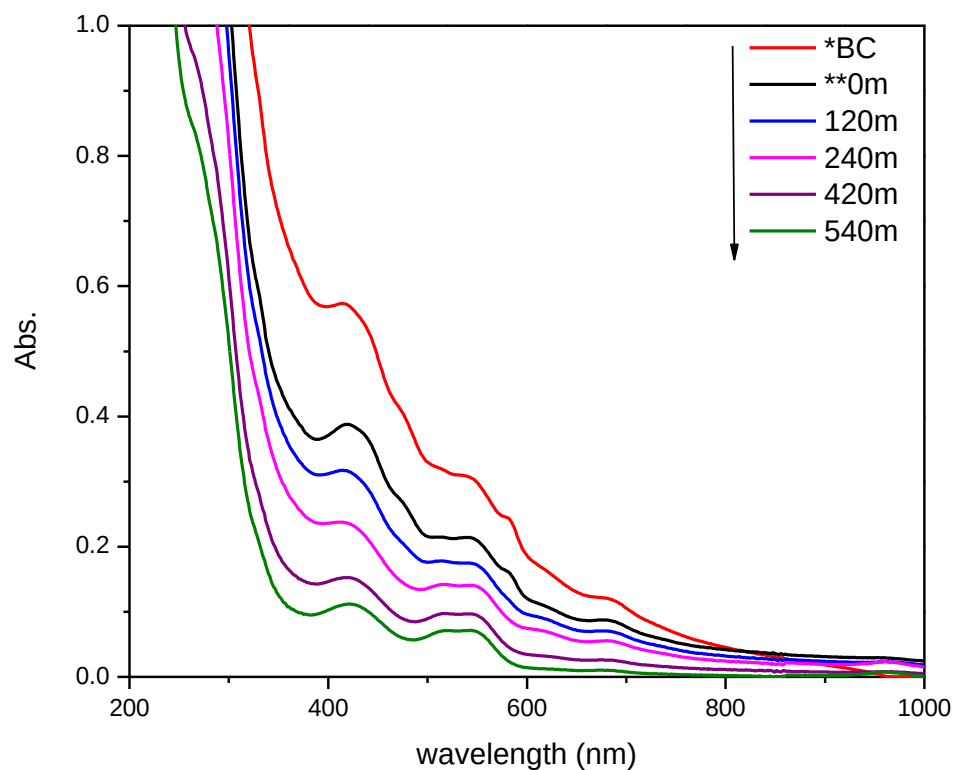


Figure 54: UV-Vis spectra of wastewater at different treatment period on 10TZY-60

Figure 55 shows the evolution of the absorbance (in %) with time at 414 nm. At first glance, Figure 55 indicates that the degradation process in the real wastewater sample takes longer time than in model MO solution, reaching 83% and 87% photocatalytic degradation after 9 hours of reaction time with the 10TZY-60 and 40TZY-60, respectively.

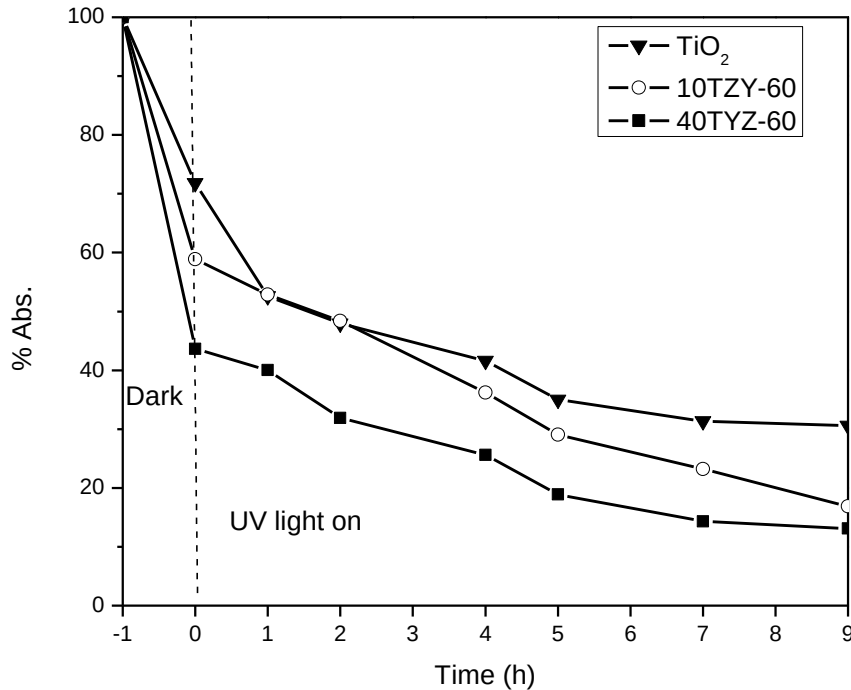


Figure 55: Photocatalytic degradation of real textile wastewater

The hybrid TiO<sub>2</sub>-Zeolite Y photocatalyst performed better than pristine TiO<sub>2</sub> (69%) even though the weight % of TiO<sub>2</sub> in the supported systems is lower. Another remarkable difference in the real system is the notable contribution of the adsorption of pollutants in this case. 41%, 56% and 28% of total absorbance disappears at 0 h, i.e., after putting the real sample in contact with 10TZY-60, 40TZY-60 and TiO<sub>2</sub> catalysts, without UV irradiation. If we take these values as the initial absorbance and account for the total degradation performance at 9h, the actual degradation capacity of 10TZY-60 increases (42%) versus the hybrid photocatalyst 40TZY-60 (30%). Given the difficulty in calculating the turnover in this case, this calculation may tentatively lead to conclude that once again there is a better performance of the hybrid photocatalyst formed by 10% TiO<sub>2</sub> loaded in Zeolite Y. Nevertheless, in this particular case, parameters such as COD, TOC,

TN and pH were analyzed after treatment of the wastewater in order to assess the efficiency of the treatments towards the real application. Table 5 collects the resulting parameters.

Table 5: Wastewater parameters before and after photocatalytic treatment

|                  | COD    | TOC    | TN     | pH   |
|------------------|--------|--------|--------|------|
|                  | (mg/L) | (mg/L) | (mg/L) |      |
| Real Sample *    |        | 34.2   | 15.5   | 7.59 |
| TiO <sub>2</sub> | 263.6  | 17.3   | 10.9   | 8.38 |
| 10TZY-60         | 244.6  | 5.6    | 9.1    | 8.32 |
| 40TZY-60         | 260.27 | 8.21   | 10.91  | 8.38 |

\*COD > 1000 mg/L

With the zeolite treatment, the results shed light to the Ethiopian scenario since the COD resulting value is close to the permitted values (150mg/L COD) and pH between 7 and 9. Further work has to be carried out in this regard, although the scenario may vary from factory to factory depending on the composition of the wastewaters in each case. However, we believe that an optimum catalyst load could be achieved to meet the requirements set by EEPA in each case. The photocatalytic tests conducted above indicate that in both cases, model MO solution and real wastewater sample, the specific photocatalytic activity is enhanced when the TiO<sub>2</sub> loading ratio is 10% on ZY-60 (10TZY-60). This may be due to the presence of smaller and even less crystalline TiO<sub>2</sub> nanoparticles aggregates on the zeolite surface evidenced from the STEM in the 10%

loaded zeolites. In the 40% ZY-60 and MOR, larger  $\text{TiO}_2$  crystals could be identified forming agglomerates, which results in active site covering and/or scattering the incident light. The higher  $S_{\text{BET}}$  of the 10%  $\text{TiO}_2$  loaded zeolites may also be additional reason behind this greater TORM than pristine  $\text{TiO}_2$ .

The photocatalytic activity enhancement of the supported  $\text{TiO}_2$  compared to pristine  $\text{TiO}_2$  can be then explained considering the easier adsorption of the reagent MO, along with the electronic modification of  $\text{TiO}_2$  by the zeolite. First, the moderate hydrophobicity at the outer porous surface of the zeolites and/or the high surface area (4-5 times higher  $S_{\text{BET}}$  than pristine  $\text{TiO}_2$ ) speeds up the adsorption of MO around the photoactive centre of the hybrid material. For effective photocatalytic process, not only the adsorption of the target molecule, but also desorption of the photocatalytic products is very important. If the products of the degradation are not desorbed so soon, adsorption and photoactive sites will be covered and thus further adsorption and photocatalytic degradation will be inhibited. Mesoporosity in ZY-60 (Figure 56) should also improve diffusion, furthermore, the hydrophobic nature of the surface of ZY-60, with very low Al content, may have an impact in the adsorption and desorption of reaction products.

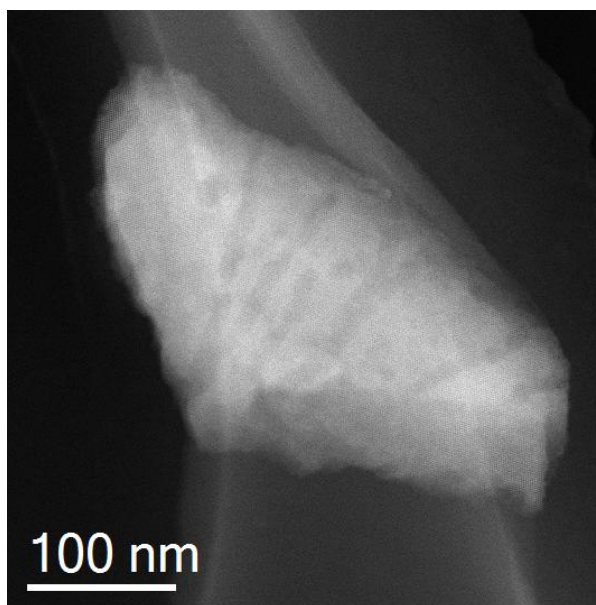


Figure 56:  $C_5$ -corrected STEM-HAADF of 10ZY-60

The porosity of the zeolite somehow controls the growth of the  $\text{TiO}_2$  nanoparticles, which seems to play crucial role on the band gap of the final supported  $\text{TiO}_2$ . As it can be seen in Figures 46, 47, 48 and 49, the UV-Vis absorption band of almost all loaded zeolites possess higher absorption band area than the pristine  $\text{TiO}_2$ . The higher absorption coefficient indicates the absorbance of large number of photons which in turn produce large number of electron/hole pairs which are responsible for photocatalytic degradation reaction directly and/or indirectly. The third possible reason for the enhancement of the photocatalytic activity in the supported  $\text{TiO}_2$  systems could be related to low recombination rate of the photogenerated electron/hole pairs. Photoluminescence (PL) spectra helped us to trace the fates of the photogenerated electron/hole pairs. In the common semiconductor photocatalysts, such as pristine  $\text{TiO}_2$ , the photogenerated electron/hole could follow two paths. One is dissociating and transferring to the adsorbed species and the second path is the recombination and release of the energy absorbed. For

effective photocatalytic reaction the photogenerated electron/hole pair should follow the first path, thus, should not recombine. The PL spectra of 40TZY-5, 40TZY-60, 40TMOR, and pure  $\text{TiO}_2$  are shown in Figure 57. There are emission bands of the samples at around 374, 422, 447, 459, 484 and 529 nm. The PL emission intensity of 40TZY-5 is higher than the others in all of the emission wavelengths (Figure 57) indicating there is a higher rate of recombination of electron/hole pairs though its light absorption coefficient is lower than the other 40 wt% loaded zeolites (Figure 49). This could also be additional reason of its low photocatalytic activity. The PL emission intensity of the pure  $\text{TiO}_2$  is also higher than the PL intensity of 40TZY-60 and 40TMOR as expected from its lower photocatalytic activity when compared with these samples. PL emission intensity is the result of the recombination of photogenerated electron/hole pairs; the lower PL emission intensity indicates a decrease in the recombination rate and the higher photocatalytic activity it provides.

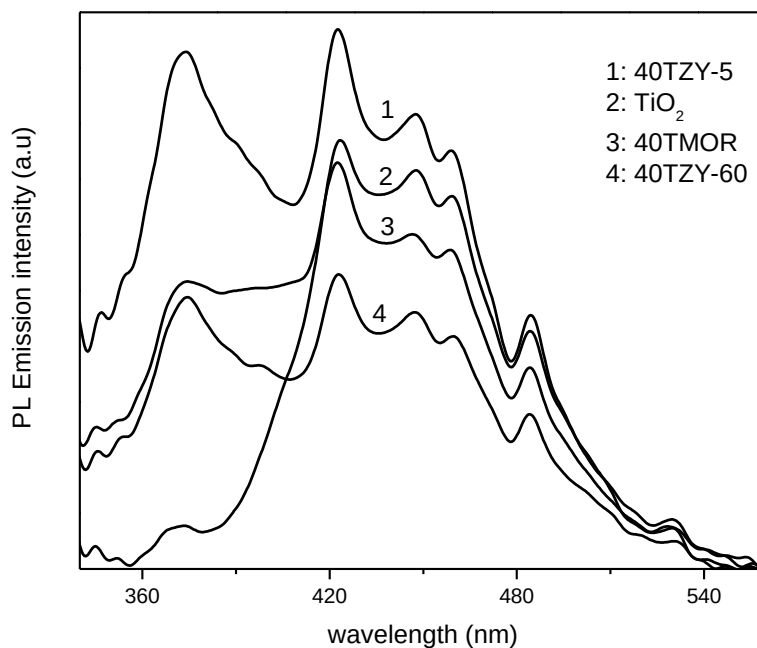


Figure 57: Photoluminescence emissions of 40TZY-60, 40TMOR, 40TZY-5 and  $\text{TiO}_2$

In summary, supported  $\text{TiO}_2$  nanoparticles have been prepared which are effective in photocatalytic degradation of both the model pollutant and real textile wastewater. On top of the role of the zeolites in enhancing the adsorption capacity that has been reported in the literature, in this work we showed that zeolites do have triple role on the supported  $\text{TiO}_2$  that is increasing adsorption capacity; modifying the electronic properties of supported  $\text{TiO}_2$  to delay photogenerated electron/hole pair recombination and preventing leaching of  $\text{TiO}_2$  nanoparticles during the photocatalytic reactions. From the photocatalytic activity of the 40TYZ-60 and 40TMOR, the electronic modification of supported  $\text{TiO}_2$  is even more pronounced than its higher adsorption role. The adsorption capacity of the 40TZY-60, 40TMOR and  $\text{TiO}_2$  is almost similar but the photocatalytic activity of the 40TYZ-60 and 40TMOR is by far higher than non porous bulk  $\text{TiO}_2$  (Figure 53).

#### **4.1.4. Conclusion**

The presence of zeolite ZY-60 (CBV 760) and MOR enhanced the photocatalytic activity of supported  $\text{TiO}_2$ . The  $\text{TOR}_m$  of supported  $\text{TiO}_2$  systems is 7 to 20 times higher than pristine  $\text{TiO}_2$ , except for the ZY-5 family (CBV 400). The  $\text{TOR}_m$  of  $\text{TiO}_2$  supported on ZY-60 and MOR zeolites increase as the loading decreases from 40 to 10%. This indicates that the specific photocatalytic activity is enhanced when loading ratio decreased. From the STEM/HAADF observations the presence of remaining  $\text{TiO}_2$  inside the pores cannot be unequivocally ascertained, although the EDS statistical screening identifies the presence of Ti in areas where no external particles could be identified. The UV-Vis light absorption coefficient of almost all supported  $\text{TiO}_2$  on zeolites is high

compared to pristine  $\text{TiO}_2$ . More interestingly, 40TZY-60 and 40TMOR (those which showed higher UV-Vis light absorption coefficient) show the lowest photoluminescence emission intensities which confirms lower electron/hole recombination rate. Although it takes relatively longer time, the photocatalytic treatment results of the real wastewater from an Ethiopian textile factory showed similar pattern, yielding excellent performance of both 10 and 40% loaded ZY-60, superior than pristine  $\text{TiO}_2$ . The enhanced photocatalytic activity is again shown in particular for the 10TZY-60 which reduces the Total Organic Carbon of the real water up to 84%. Furthermore, , the reusability and preventing leaching of  $\text{TiO}_2$  nanoparticles is added values to the role of zeolites in enhancing photocatalytic activities.

## **4.2. Preparation, Characterization and Photocatalytic Activity of TiO<sub>2</sub> Supported on Modified Synthetic Zeolite**

### **4.2.1. Introduction**

From the photocatalytic activity of TiO<sub>2</sub> loaded zeolites in section 4.1, we learned that loaded ZY-5 showed very poor photocatalytic activity (almost inactive) unlike the loaded MOR and ZY-60, though it has the same framework topology as ZY-60. Besides, the zeolitic structure, the TiO<sub>2</sub> nanopartcles produced in both systems are very similar, thus the difference observed in the photocatalytic activity could be related to the adsorption capacity towards MO and electron-hole recombination rate [137]. ZY-60 is a commercially available treated (dealuminated) zeolite with some mesoporosity. In the literature, different top-down treatment strategies such as acid, steam, and base treatment are applied at industrial scale to tune the chemistry of zeolites for pre-designed applications [73, 74]. However, in such treatments the amorphization of the framework is frequently high. In our attempt to have hydrophobic zeolite Y, we initially treated zeolite Y with strong acid conditions: 9.0 g of HY (5.8) zeolite was immersed in 270 ml of 2N aqueous nitric acid solution and was refluxed for 12 h with stirring. After 12 h of reflux, the sample was filtered and washed several times with deionized water until complete elimination of the acid is achieved, and then dried at 110 °C overnight. The resulting materials were calcined for 6 h in air at 1000 °C. The obtained sample was denoted as, deAl HY1000. TiO<sub>2</sub> was loaded to this sample and calcined again to 500 °C. This strong treatment led to the complete collapse of the zeolite frame work structure (Figure 58). From the XRD profile in Figure 58, no diffraction peaks of zeolite were detected.

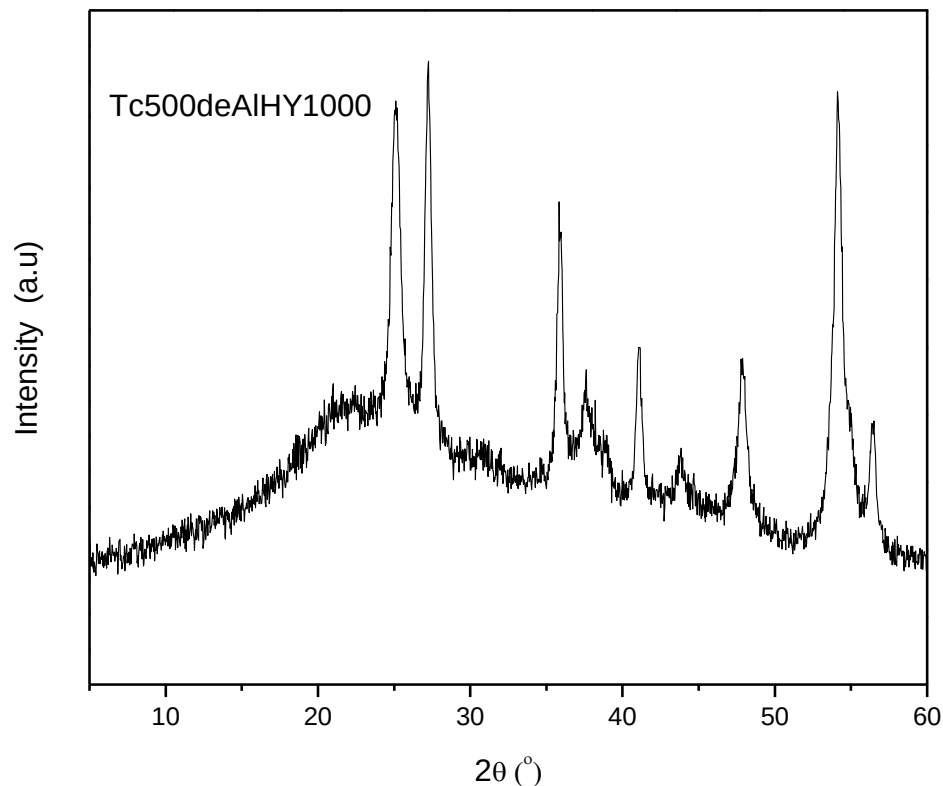


Figure 58: XRD profile of Tc500deAlHY1000

Therefore, mild treatment conditions should be pursued to tune the surface chemistry of zeolite Y without severely affecting the zeolite framework structure. Previously, Mamo *et al.* (2015) [93] tested mild treatments on mordenite zeolite. These treatments were based on the commonly employed cation exchange procedures, which eventually upon calcination generate certain degree of mesoporosity. Though insignificant, due to other determinant factors, we have also observed some enhancement of photocatalytic activity with the treated Ethiopian natural zeolites as mentioned in Chapter 3 of this study [126]. Herein mild condition treatment of Zeolite HY (CBV 400, Si/Al = 2.6, labeled as ZY-5 hereafter) using ammonium acetate ( $\text{NH}_4\text{Ac}$ ) followed by ammonium fluoride ( $\text{NH}_4\text{F}$ ) is reported. The choice of  $\text{NH}_4\text{Ac}$  solutions is based on its mild pH (6) and the chelating

effect of acetate. The moderate acidity together with the presence of chelating agents are expected to dealuminate selectively surface Al atoms [73]. The aim of the following treatment by  $\text{NH}_4\text{F}$  solution is to dissolve the extra framework Si and Al species.  $\text{TiO}_2$  nanoparticles will then be supported on both the treated and parent zeolite followed by characterization and photocatalytic test for photocatalytic degradation of model textile azo dye, MO. Reusability of the photocatalyst and leaching out of  $\text{TiO}_2$  during the photocatalytic reaction will also be analyzed.

#### **4.2.2. Sample Preparation**

Commercially available zeolite CBV 400  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 5.2$  was purchased from Zeolyst. Hereafter, the samples are referred to ZY-5. Parent zeolite ZY-5 was treated as follows [93]: 8g of CBV400 was stirred in 104 mL of 3M  $\text{CH}_3\text{COONH}_4$  ( $\text{NH}_4\text{Ac}$ ) solution at room temperature for 30 min. Then 48 mL of 2.4 M  $\text{NH}_4\text{F}$  solution was added drop wise under stirring. The suspension was stirred for 30 min at 80 °C. The sample was then filtered and washed with distilled water, dried at 100 °C for 12 h and calcined at 550 °C for 6 h. The sample was labeled ZY-5t. For the loading of  $\text{TiO}_2$  on ZY-5, 4.48 grams of ZY-5 was added to a solution of 5.68 mL of titanium (IV) butoxide ( $\text{Ti}(\text{OC}_4\text{H}_9)_4$ ) in 11.2 mL of deionized water and 56.8 mL of 2-propanol. The mixture was left for 24 h under stirring at room temperature. The solvent was removed by rotary evaporator. It was then dried at 110 °C and calcined in air at 400 °C for 3 h. A similar procedure was followed for  $\text{TiO}_2$  loading on ZY-5t. For comparison, pure  $\text{TiO}_2$  was also synthesized in a similar method without adding zeolite. The samples were then labeled 20TZY-5, 20TZY-5t and

TiO<sub>2</sub> for the 20 wt% TiO<sub>2</sub> loaded parent zeolite, 20 wt% loaded treated zeolite and pristine TiO<sub>2</sub>, respectively.

#### 4.2.3. Results and Discussion

X-ray diffraction profiles of ZY-5, ZY-5t, 20TZY-5, 20TZY-5t as well as pure TiO<sub>2</sub> are shown in Figure 59. According to the diffraction patterns, the crystalline framework of the zeolite has been maintained and the crystallinity has increased after the treatment. The zeolite crystalline framework of both the ZY-5 and ZY-5t zeolite is also maintained after the 20 wt% TiO<sub>2</sub> loading. However, the intensities of the diffraction peaks decreased. For pristine TiO<sub>2</sub> calcined at 400 °C, the diffraction peaks at  $2\theta = 25.4^\circ$  (101),  $37.8^\circ$  (004),  $48.0^\circ$  (200), and  $54.5^\circ$  (105) can be assigned to anatase crystalline phase of TiO<sub>2</sub> and diffraction peaks at  $2\theta = 27.6^\circ$  (110),  $36.1^\circ$  (101),  $41.3^\circ$ , and  $56.7^\circ$ , are assigned to rutile phase of TiO<sub>2</sub>. The most intense peaks of the anatase phase ( $25.4^\circ$ ,  $48.0^\circ$  and  $54.5^\circ$ ) can also be identified in the pattern of sample 20TZY-5t, overlapping with the zeolite reflections. However, no detectable intensities for rutile phase of TiO<sub>2</sub> can be observed, indicating that somehow the presence of zeolite delays the phase transition of anatase to the most stable phase of TiO<sub>2</sub>, rutile. Though different from synthesis method to synthesis method, usually rutile crystalline phase of TiO<sub>2</sub> appears after calcination of 350 °C. Since the intensities at  $27.6^\circ$  overlapped with the diffraction patterns of the zeolite, the intensity at  $36.1^\circ$  (101) was used to ascertain if there is detectable rutile phase of TiO<sub>2</sub>. In the case of sample 20TZY-5, peaks corresponding to any TiO<sub>2</sub> can hardly be observed in the XRD pattern. This suggests that this sample possesses nanocrystalline TiO<sub>2</sub> with a particle size below the detection limit of the technique, which indicates a

much higher dispersion of the  $\text{TiO}_2$  phase on the parent zeolite compared to the dealuminated one.

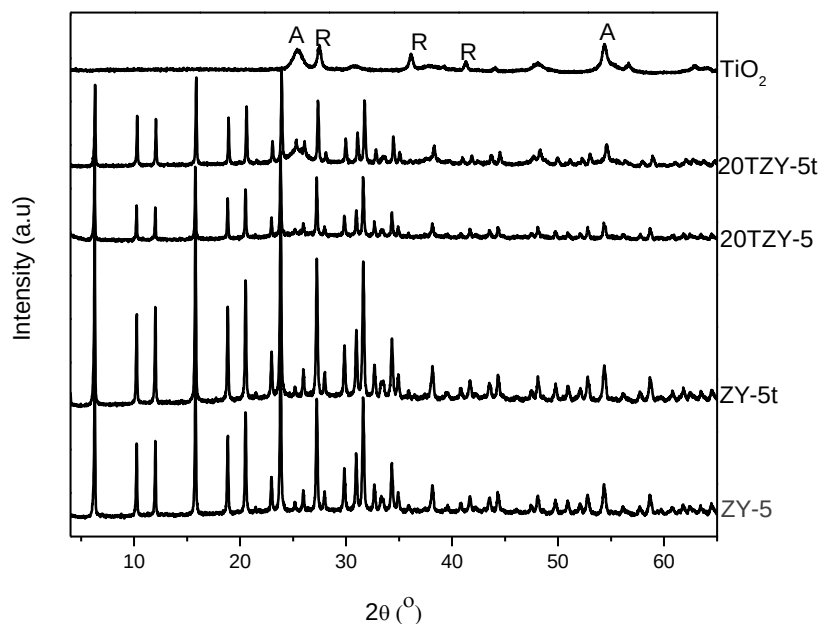


Figure 59: XRD profiles of ZY-5, ZY-5t, 20TZY-5, 20TZY-5t and  $\text{TiO}_2$

The  $\text{N}_2$  isotherms of ZY-5, ZY-5t, 20TZY-5 and 20TZY-5t are plotted in Figure 60. The treatment has not inferred noticeable changes in the textural properties of the Zeolite Y, only small variation in the shape of the isotherms can be observed at high relative pressure probably due to external modifications. Table 6 collects the surface area values which reflect that only the external surface varies upon treatment.  $\text{TiO}_2$  exhibited type IV isotherm, which is related to the textural porosity mainly between  $\text{TiO}_2$  particles. The loaded zeolites exhibited a mixture of type I and IV isotherms proving that the microporosity of the zeolitic structure was retained even after the loading.  $\text{TiO}_2$  loading produces a decrease of the surface area ( $S_{\text{BET}}$ ) as can be seen from the data collected in

Table 6 This indicates that some of the pores of the zeolite are either blocked and/or populated with TiO<sub>2</sub> particles.

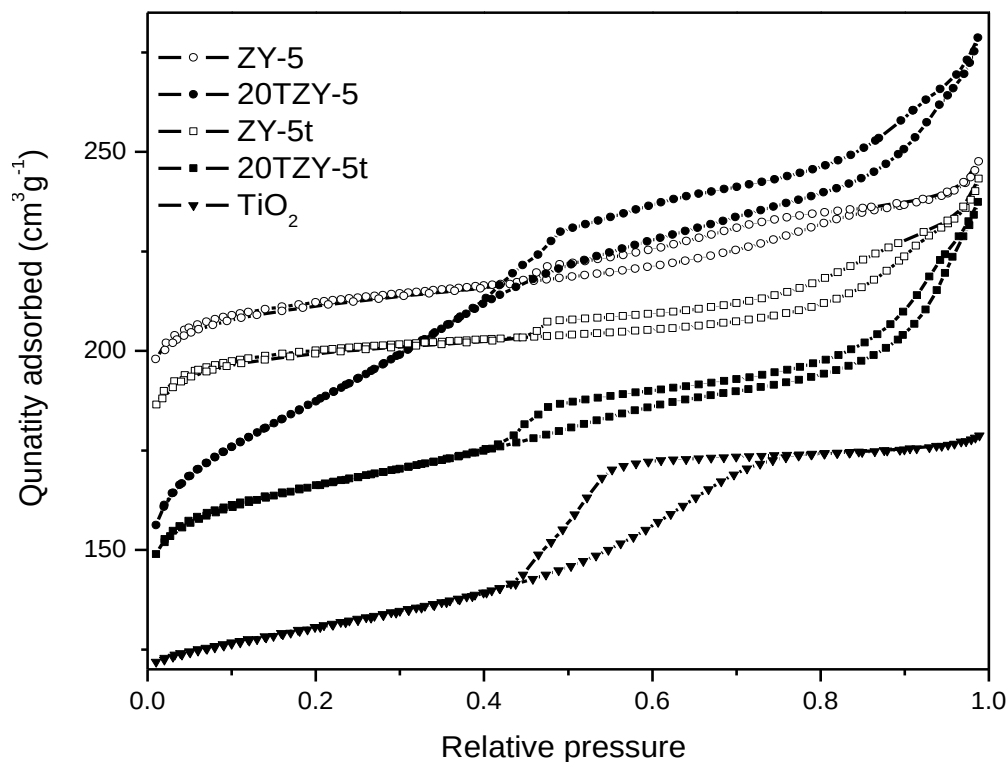


Figure 60: N<sub>2</sub> isotherms of loaded ZY-5, ZY-5t, 20TZY-5 and 20TZY-5t

Table 6: Textural properties of the samples

| Sample           | Surface area (m <sup>2</sup> /g) |                       |                              |
|------------------|----------------------------------|-----------------------|------------------------------|
|                  | S <sub>BET</sub>                 | t-plot micropore.area | t-plot external surface area |
| ZY-5             | 709                              | 666                   | 43                           |
| ZY-5t            | 698                              | 674                   | 24                           |
| 20TZY-5          | 603                              | 339                   | 264                          |
| 20TZY-5t         | 514                              | 406                   | 107                          |
| TiO <sub>2</sub> | 91                               | -                     | 91                           |

From the ICP analysis collected in Table 7, it can be deduced the Si/Al ratio of ZY-5 has increased upon the treatment. The Si/Al ratio of ZY-5 was 2.56 before treatment and increased to 4.77 in ZY-5t.

Table 7: ICP and XPS Analysis

| Sample   | ICP-OES Bulk analysis |       |            | XPS surface analysis |            |
|----------|-----------------------|-------|------------|----------------------|------------|
|          | Ti                    | Si/Al | Ti/(Si+Al) | Si/Al                | Ti/(Si+Al) |
|          | wt%                   | ratio | ratio      | ratio                | ratio      |
| 20TZY-5  | 9.92                  | 2.56  | 0.38       | 2.94                 | 0.08       |
| 20TZY-5t | 10.48                 | 4.77  | 0.43       | 5.77                 | 0.14       |

In order to assess whether the surface dealumination was achieved, XPS spectra of 20TZY-5 and 20TZY-5t were collected (Figure 61). Original and fitted spectra in the regions corresponding to Ti 2p, Si 2p and Al 2p levels are shown in Figure 61. Since Si and Al 2p<sub>1/2</sub> and 2p<sub>3/2</sub> cannot be resolved due to strong overlapping, these spectra have been simulated using a single peak. The binding energy (BE) values obtained are typical of Ti (IV), Si (IV) and Al (III) oxides. For both samples, the BE determined for Si 2p and Al 2p are the same within the experimental error. However, a slight difference is obtained for Ti 2p (0.5 eV) which might indicate some difference in the TiO<sub>2</sub> phase that might be attributed to the difference in chemical composition of the zeolite crystals surface (may be causing different TiO<sub>2</sub> dispersion or different chemical interaction with the zeolite surface). Quantitative surface chemical analysis is presented in Table 7. The surface Si/Al ratio calculated for the loaded parent zeolite (2.9) is very close to the bulk composition

(2.6). Treatment of zeolite, ZY-5 with ammonium acetate removes Al from the surface, increasing the surface Si/Al ratio to 5.8 (this means that 50% of the Al on the outer part of the zeolite crystals is removed). The higher Si/Al ratio determined by XPS compared to the bulk Si/Al ratio confirms that dealumination occurs preferentially in the outer region of the zeolite crystals. XPS analysis also shows that there is also a difference in the concentration of Ti on the surface of both zeolites. Although the same amount of  $\text{TiO}_2$  (ca. 20 wt %) was loaded on both the parent and treated zeolites, the XPS results indicate that higher amount of  $\text{TiO}_2$  is present on the outer region of the particles of the treated zeolite compared to the parent zeolite. This conclusion is in agreement with XRD data that suggest a higher dispersion of the  $\text{TiO}_2$  phase on the parent zeolite.

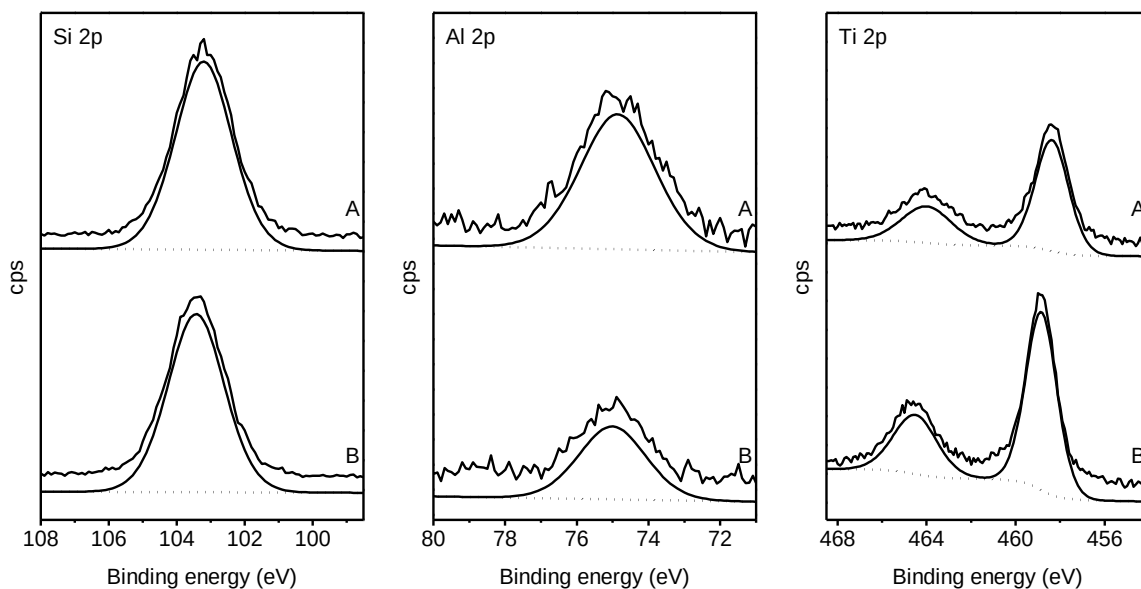


Figure 61: XPS spectra of 20TZY-5(A) and 20TZY-5t (B) for Ti 2p, Si 2p and Al 2p

Diffuse reflectance UV-Vis spectra of pure zeolites, loaded zeolites and pristine  $\text{TiO}_2$  are shown in Figure 62. From these spectra, it can be seen that the pure zeolites do not show any absorbance above 240 nm wavelength. Upon loading 20% of  $\text{TiO}_2$  to both parent and treated zeolites, the absorbance edge of the materials is extended. The absorbance edge of the loaded zeolites shows blue shift as compared with the absorbance of pure  $\text{TiO}_2$  [97, 134]. In Figure 62, the absorption band at around 200–240 nm is due to electron transfer excitation from the ligand-oxygen to an unoccupied orbital of the  $\text{Ti}^{4+}$  framework. The loaded zeolites spectra are also characterized by a large unresolved absorption band ranging from 375 to 240 nm, which is assigned to the electronic transition from 2p(O) to 3d (Ti), corresponding to the valence band to the conduction band transition according to the energy band structure of  $\text{TiO}_2$  [84, 96, 127, 128, 131, 132] while it is from 412 to 240 nm for the pristine  $\text{TiO}_2$ .

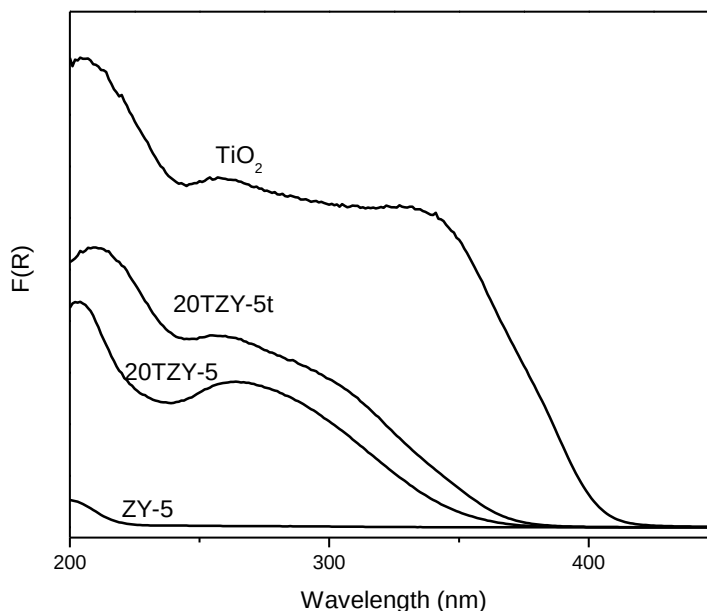


Figure 62: UV-Vis DRS Analysis of ZY-5, ZY-5t, 20TZY-5, 20TZY-5t and  $\text{TiO}_2$

Photocatalytic degradation of 10 ppm MO on the loaded zeolites (both before and after treatment) and pure  $\text{TiO}_2$  is plotted versus time in Figure 63. As can be seen from the plot, the photocatalytic degradation of 10 ppm MO on 20TZY-5 (7.6%) is way below the photocatalytic activity of pristine  $\text{TiO}_2$  which is about 58 % degradation in 90 minutes under UV light irradiation. In contrast, 20TZY-5t reaches 92% degradation of MO in 90 minutes. The photocatalytic degradation activity of the  $\text{TiO}_2$ /treated-zeolite system when compared to pristine  $\text{TiO}_2$  is even more pronounced when we normalized the rate of the photocatalytic degradation by mass of the photoactive material,  $\text{TiO}_2$ . From the data collected in Table 8 It can be observed that the  $\text{TORM}$  of 20TZY-5t is about 12 times higher than its counterpart 20TZY-5 and 9.5 times higher than the pristine  $\text{TiO}_2$ .

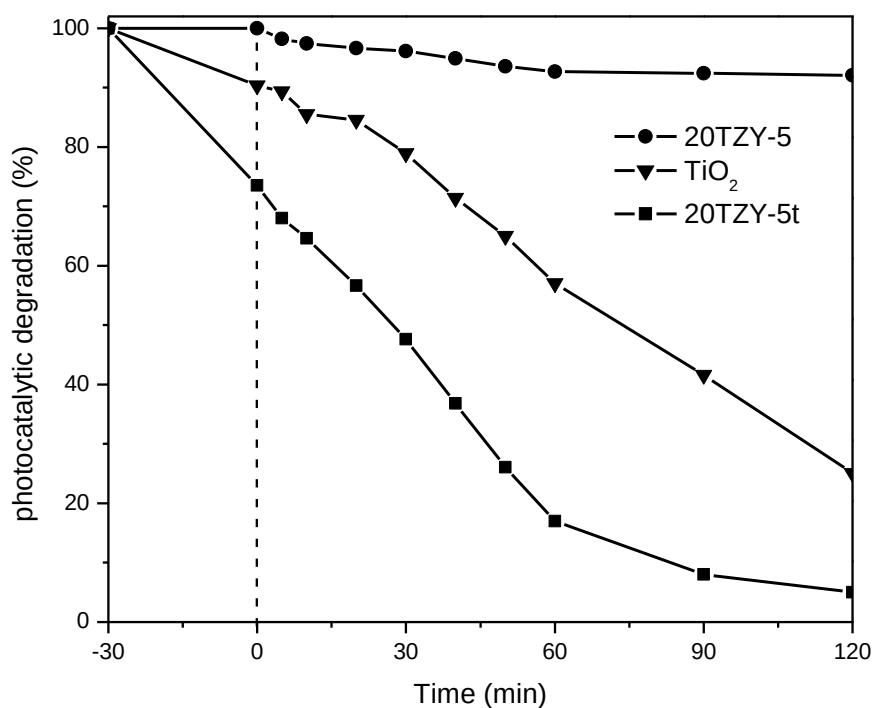


Figure 63: Photocatalytic degradation of MO on 20TZY-5, 20TZY-5t and  $\text{TiO}_2$

Table 8: Photocatalytic activities determined after 90 min UV light irradiation

| Photocatalytic activity | 20TZY-5 | 20TZY-5t | TiO <sub>2</sub> |
|-------------------------|---------|----------|------------------|
| Degradation (%)         | 7.6     | 92       | 58.43            |
| TOR <sub>m</sub>        | 18.70   | 226.43   | 23.63            |

A photocatalyst recycling study was conducted to determine the stability of the synthesized material over three cycles. At the end of the first photocatalytic cycle, the photocatalyst was separated from the resulting suspension by filtering, washed, oven dried at 110 °C, and then reused without any calcination treatment. The same procedure was employed after the second cycle. The Photocatalytic degradation was found 92, 77 and 71% in the cycle 1, cycle 2 and cycle 3 respectively after UV light irradiation for 90 minutes. The decrease in the degradation percentage is probably due to the accumulation of organic intermediates in the cavities and/or on the surface of the photocatalyst affecting the adsorption of MO, and reducing the photocatalytic activity of the material. These results show that these photocatalytic materials can be reused without noticeable photocatalytic activity loss.

In addition to enhanced photocatalytic activity of the 20TZY-5t, it also significantly decreases the leaching extent of Ti species during the photocatalytic reaction. It was found that the leaching from the water treated by pristine TiO<sub>2</sub> is about 29.48 ppb whereas the leaching of Ti species in the water treated by 20TZY-5t was found to be about 0.89 ppb which is very important considering the toxicity of TiO<sub>2</sub> nanoparticles.

In this particular work, the adsorption capacity of the modified zeolite, 20TZY-5t, was found to be higher than 20TZY-5. It was found that after 30 minutes stirring in the dark, 20TZY-5t adsorbed about 26.5% of 10 ppm MO, whereas only 0.01% of 10 ppm MO was adsorbed on 20TZY-5. Thus, 20TZY-5 shows no photoactivity due to its lack of MO adsorption. The higher adsorption capacity in 20TZY-5t may be due to the higher hydrophobicity of the zeolite surface since 50% Al is removed from its surface after the mild treatment. Moreover, this hydrophobicity might also be the reason behind the different Ti content on the surface. From the ICP and XPS data, the Ti/(Si+Al) ratio on the surface of 20TZY-5 is much lower, almost by half than that of 20TZY-5t though both have similar Ti/(Si+ Al) ratio in the bulk. This efficient adsorption of active species is reflected in the electronic properties. As can be observed in Figure 62, UV-vis absorption band area of the 20TZY-5t is higher than that of 20TZY-5, Furthermore, a possible reason for the enhancement of the photocatalytic activity in 20TZY-5t could also be related to low recombination rate of the photogenerated electron/hole pairs. Photoluminescence spectra helped us to trace the fates of the photogenerated electron/hole pairs (Figure 64). For effective photocatalytic reaction the photogenerated electron/hole pair should not recombine. The photoluminescence (PL) spectra could be taken as comparison parameter since the same amount of sample was taken and measured in the same condition. From Figure 64 There are emission bands of the samples at around 371-373.5 nm. These emission bands are mainly due to band to band recombination (conduction band to valence band recombination emissions) [138, 139]. From the PL spectrum in Figure 64, the PL emission intensity of 20TZY-5t is lower than that of 20TZY-5 indicating that there is a lower rate of band to band recombination of

photogenerated electron/hole pairs, which could also be a reason for the higher photocatalytic activity of 20TZY-5t. These combined factors made 20TZY-5t is a better photocatalyst than its counterpart 20TZY-5.

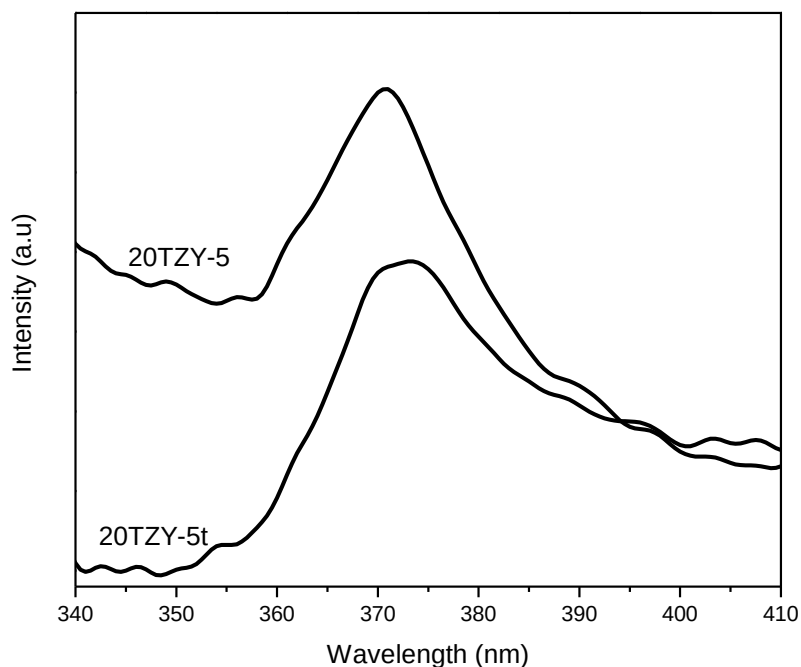


Figure 64: Photoluminescence emissions of 20TZY-5 and 20TZY-5t

#### 4.2.4. Conclusion

ZY-5 is successfully treated using the  $\text{NH}_4\text{Ac}$  and  $\text{NH}_4\text{F}$ , where 50 % of the surface Al is removed without affecting the zeolite's framework structure as confirmed from the ICP-OES, XPS analysis and XRD profiles. The photocatalytic degradation of MO was enhanced 12 times after treatment of the parent zeolite which can be attributed to both its higher adsorption capacity and lower band to band photogenerated electron hole recombination rate as confirmed from the adsorption and photoluminescence analysis

results. Besides its role in enhancing the photocatalytic activity, 20TZY-5t prevented leaching of Ti species into the reaction media and the reusability of the photocatalyst system is maintained for the three cycles measured.

### 4.3. Preparation, Characterization and Photocatalytic Activity of Semi-amorphous TiO<sub>2</sub> Supported on Synthetic Zeolites

#### 4.3.1. Introduction

Many authors have reported that the photocatalytic activity of TiO<sub>2</sub> supported on zeolites has been significantly enhanced [76-80, 91, 92]. However, the loading of zeolites has been done at high calcination temperature for longer period of time because it is considered in the literature that crystalline TiO<sub>2</sub> is the best photocatalytic material [98, 99]. For example, Ohtani *et al.*, (1997) [98] compared the photocatalytic activity of amorphous TiO<sub>2</sub> powders and anatase crystalline TiO<sub>2</sub> powders in photocatalytic degradation of 2-propanol. They reported that the photocatalytic activity of amorphous TiO<sub>2</sub> was negligible, increased almost linearly as a function of anatase, and further improved by calcination of completely crystallized powder. They attributed the negligible activity of amorphous TiO<sub>2</sub> to recombination of photoexcited electron and positive hole at defects located on the surface and in the bulk of particles. Furthermore, Li *et al.*, (2013) [140] recently reported that the thermally treated TiO<sub>2</sub> has a stronger light absorption, a greater number of surface defects, a higher efficiency of charge separation, and thus a higher intrinsic activity for phenol degradation. They further highlighted the importance of the thermal treatment of metal oxide for improving the efficiency of TiO<sub>2</sub> photocatalysis. With regard to TiO<sub>2</sub> supported on zeolites, Kuwahara *et al.*, (2012) [91] prepared TiO<sub>2</sub> loading on zeolites from aqueous ammonium titanyl oxalate solution and they stirred it at room temperature for 6 h followed by evaporation of water under vacuum and calcination at 600 °C for 6 h with a heating rate of 1.5 °C/min in air. Kamegawa *et al.*, (2013) [92] impregnated TiO<sub>2</sub> on Zeolite Y from (NH<sub>4</sub>)<sub>2</sub>[TiO(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>] or (NH<sub>4</sub>)<sub>2</sub>[TiF<sub>6</sub>] followed by calcination up to at 700 °C for 5 h in air. Similarly, Gomez et

al (2015) [84] synthesized Titania supported on zeolitic matrices (HBETA, HY and HZSM-5) by in situ generation of TiO<sub>2</sub> from Titanium (IV) isopropoxide followed by calcination of the system to 450 °C. Very recently, Sun *et al.*, (2015) [99] prepared TiO<sub>2</sub> nanoparticles supported on natural zeolite via a simple hydrolysis of TiCl<sub>4</sub> and then calcined at various temperatures (300 , 400, 500, 600 and 700 °C). They tested the photocatalytic activity of these samples in photocatalytic removal of Cr (IV) and found that the sample calcined at 500 °C showed highest photocatalytic activity attributed to its high crystallinity. Table 9 collects a list of research reports that has been done at high calcination temperature for long period of time.

Table 9: Publications which used high calcination temperature

| S.No | Loaded sample                                          | Calcination Temperature (°C)   | Ref.  |
|------|--------------------------------------------------------|--------------------------------|-------|
| 1    | 1 % wt TiO <sub>2</sub> on HY, Hb and HZSM-5           | 550 for 6 h                    | [77]  |
| 2    | TiO <sub>2</sub> on USY (Si/Al = 62 and 4.7) zeolites  | 550 for 4 h                    | [131] |
| 3    | Pt modified TiO <sub>2</sub> loaded on natural zeolite | 110, 200, 300, and 500 for 4 h | [96]  |
| 4    | TiO <sub>2</sub> on natural zeolite, Clinoptilolite    | 450 for 5 h                    | [122] |
| 5    | TiO <sub>2</sub> supported on Y zeolite                | 600 for 6 h.                   | [127] |
| 6    | TiO <sub>2</sub> on natural zeolite, Clinoptilolite    | 300–800 h                      | [141] |
| 7    | TiO <sub>2</sub> / NaA-RH                              | 400 for 4h                     | [128] |
| 8    | TiO <sub>2</sub> on natural zeolites                   | 500 for 2 h                    | [80]  |
| 9    | TiO <sub>2</sub> on HBETA, HY and H-ZSM5               | 500 for 10 h                   | [84]  |
| 10   | TiO <sub>2</sub> on ZSM-5 and Zeolite Y                | 500 for 3h                     | [82]  |
| 11   | TiO <sub>2</sub> / natural zeolite                     | 300-450 for 2 h                | [83]  |

However, as it has been described under section 4.1 [137] we found that the sample with semi amorphous  $\text{TiO}_2$  (10TZY-60) showed a higher specific photocatalytic activity compared with the purely crystalline materials tested. Semi amorphous  $\text{TiO}_2$  can be obtained without calcination during the synthesis steps. Preparation of  $\text{TiO}_2$  loading without calcination will therefore be economical since it saves both energy and time. Thus, we are here reporting the photocatalytic activity of the semi amorphous  $\text{TiO}_2$  supported on the same synthetic zeolites (CBV 760:  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 60$  and CBV 400:  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 5.1$ ) and Mordenite (CBV 21A,  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 20$ ) as in section 4.1 using simple sol gel method focusing on the two different loadings (10 and 40 wt %) without any calcination.

#### 4.3.2. Sample Preparation

Two commercially available HY zeolites: CBV 400  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 5.1$  and CBV 760  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 60$ , and one Mordenite (H-form): CBV 21A with  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 20$ , were purchased from Zeolyst. Hereafter, the samples will be called ZY-5, ZY-60 and MOR, respectively. In a typical synthesis of 10 wt%  $\text{TiO}_2$  loaded on mordenite zeolite (10TMOR) 18 g of MOR was suspended in a solution of 10.15 mL of Titaniumbutoxide ( $\text{Ti}(\text{OBut})_4$ ) dissolved in 101.5 mL of 2-Propanol ( $\text{CH}_3\text{CHOHCH}_3$ ) and 20.3 mL of water ( $\text{H}_2\text{O}$ ) using magnetic stirrer. The stirring was maintained at room temperature for 24 hours. The solvent was removed by rotary evaporator and the resulting composite dried at 110 °C. Similarly 10 and 40 wt% of  $\text{TiO}_2$  was prepared by suspending each zeolite (ZY-5, ZY-60 and MOR) in a solution of titanium (IV) butoxide ( $\text{Ti}(\text{OBut})_4$ ) dissolved in a mixture of 2-Propanol ( $\text{CH}_3\text{CHOHCH}_3$ ) and water ( $\text{H}_2\text{O}$ ) with volume ratio of 1:10:2

(Ti(OBut)<sub>4</sub>: CH<sub>3</sub>CHOHCH<sub>3</sub>: H<sub>2</sub>O). The samples were labeled “10T” and “40T” referring to the theoretical wt% TiO<sub>2</sub> loading, followed by the zeolite code (ZY-5, ZY-60 and MOR) and “nc” to indicate that the samples are not calcined.

#### 4.3.3. Results and Discussion

X-ray diffraction profiles of noncalcined TiO<sub>2</sub> (TiO<sub>2</sub> nc) and calcined TiO<sub>2</sub> at 400 °C (TiO<sub>2</sub>) are shown in Figure 65. For pure TiO<sub>2</sub> calcined at 400 °C (Section 4.1), the diffraction peaks at 2theta = 25.4° (101), 37.8° (004), 48.0° (200), and 54.5° (105) can be assigned to anatase crystalline phase of TiO<sub>2</sub> and diffraction peaks at 2theta = 27.6° (110), 36.1° (101), 41.3°, and 56.7°, are assigned to rutile phase of TiO<sub>2</sub>, marked as “A” and “R”, respectively in Figure 65. On the other hand, in the XRD profile of TiO<sub>2</sub> nc, no diffraction pattern of rutile phase of TiO<sub>2</sub> was detected. Besides the absence of rutile diffraction pattern, the diffraction pattern for anatase in the TiO<sub>2</sub> nc is broadened. This may be due to the presence of some amorphous material, organic and small particle size of the TiO<sub>2</sub> residue. In the calcined TiO<sub>2</sub>, the diffraction patterns are more sharp and intense.

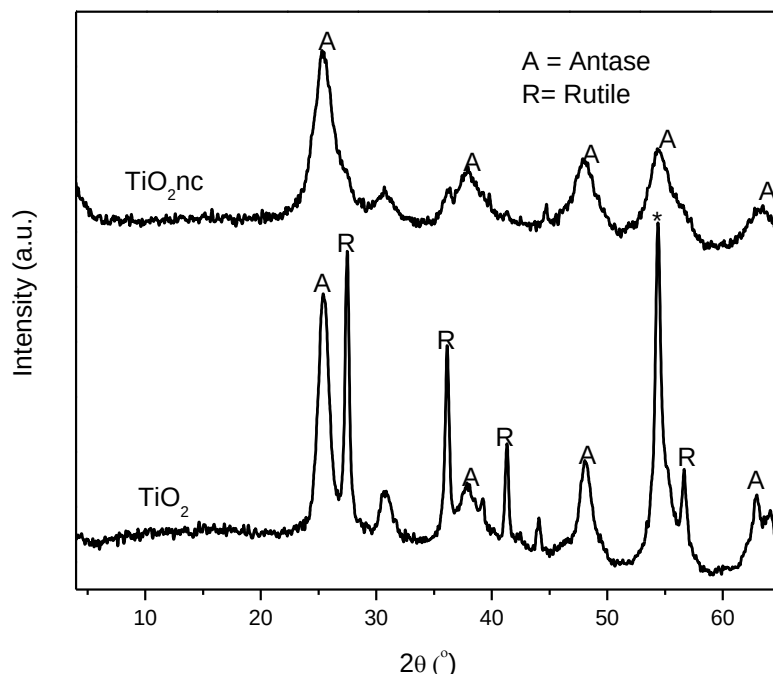


Figure 65: XRD profile of  $\text{TiO}_2\text{nc}$  (not calcined) and  $\text{TiO}_2$  (calcined)

The peak broadening is even more pronounced when the  $\text{TiO}_2\text{nc}$  is supported on zeolites. Figure 66 shows the XRD profile of 40TZY-60 (40 wt%  $\text{TiO}_2$  loaded ZY-60 calcined at 400 °C) and 40TZY-60 nc (40 wt%  $\text{TiO}_2$  loaded ZY-60 not calcined) and the pure zeolite (for clarity the intensity is divided by factor of 2). From Figure 66 it is clearly shown that the diffraction peak at 25.4° is broadened after 40 wt%  $\text{TiO}_2$  loading indicating the presence of anatase phase of  $\text{TiO}_2$ . However, there is clear difference in the diffraction intensity of the 40TZY-60 and 40TZY-60 nc. The diffraction peaks of anatase at 25.4°, 37.8°, 48°, 54.5° and 62.5° in the 40TZY-60 are sharper. However, these diffraction peaks in the 40TZY-60nc are broadened indicating the presence of amorphous residue and/or smaller particle size. Furthermore, the zeolite crystalline frameworks structure is maintained in all cases.

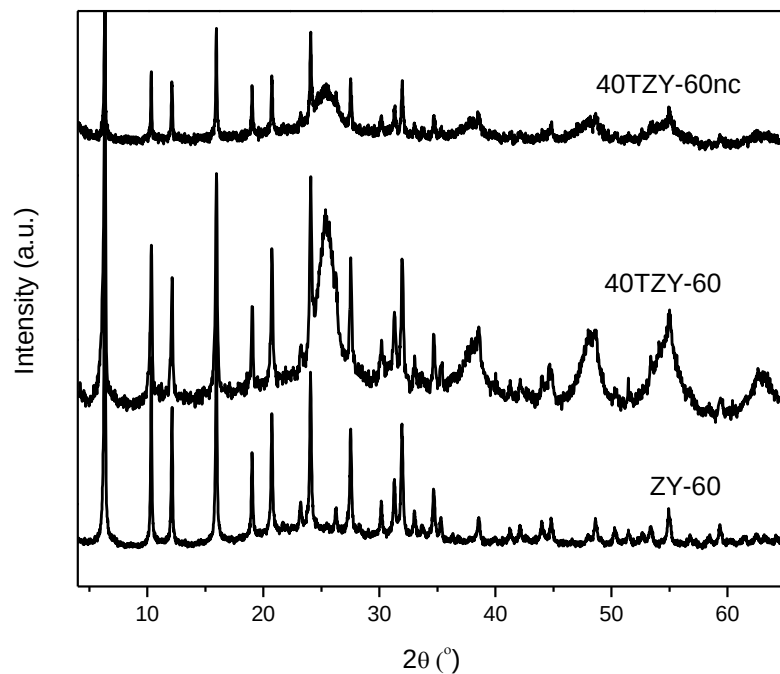


Figure 66: XRD profile of ZY-6, 40TZY-60 (calcined) and 40TZY-60nc

The XRD profiles of 10 wt% and 40 wt% loaded ZY-60, ZY-5 and MOR are shown in Figures 67, 68 and 69. In all cases, the zeolite crystalline frameworks are maintained with decreased intensity upon loading. The intensity decrement is more pronounced in the 40 wt%  $\text{TiO}_2$

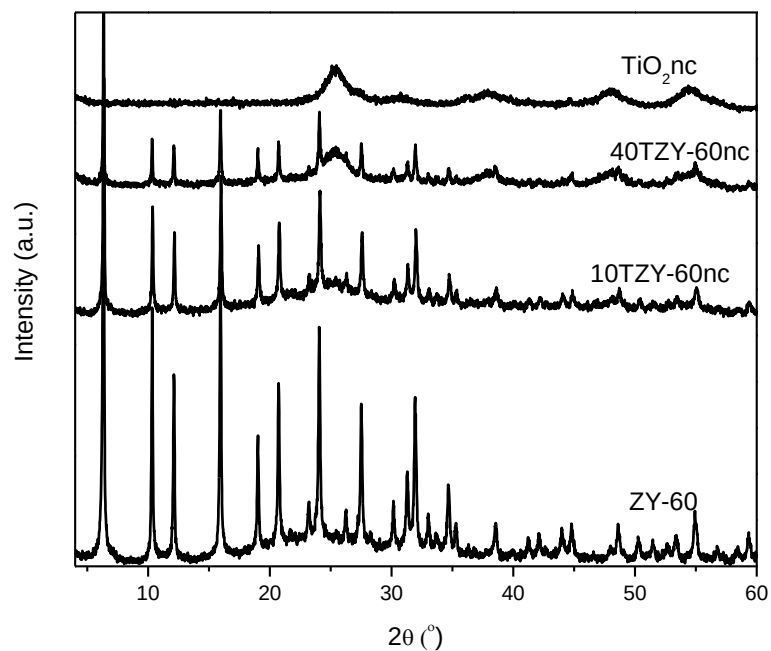


Figure 67: XRD profile of ZY-60, 10TZY-60 nc, 40TZY-60nc and  $\text{TiO}_2$  nc

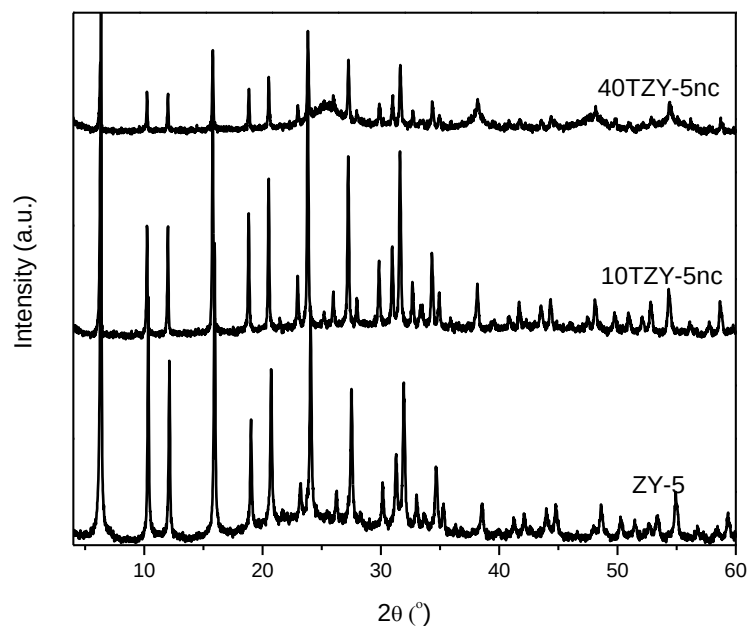


Figure 68: XRD profile of ZY-5, 10ZY-5nc and 40TZY-5 nc

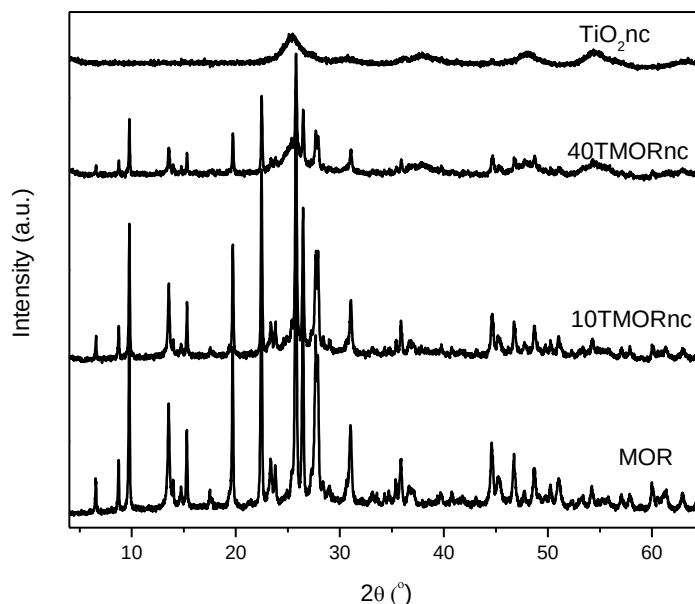


Figure 69: XRD profile of MOR, 10TMORnc, 40TMORnc and TiO<sub>2</sub>nc

In order to try to locate the TiO<sub>2</sub> particles and see their nature of crystallinity, spherical aberration corrected ( $C_s$ -corrected) Scanning Transmission Electron Microscopy (STEM) mode was chosen, coupled with High Angular Annular Dark Field detector (STEM-HAADF). Figure 70 shows the images corresponding to the 10 wt% loading of TiO<sub>2</sub> nc in ZY-60 zeolite (10TZY-60 nc). Figures 70a exhibits the low-magnified images, where the higher number of TiO<sub>2</sub> particles can be observed with bright contrast in the peripheral edge and central part of the material. Figure 70b show high magnification of the STEM/HAADF image showing that the zeolite surface is somewhat covered by semi-amorphous material. The  $C_s$ -corrected STEM-HAADF high resolution images of the zeolitic structure reveals that after TiO<sub>2</sub> treatment the framework still remains intact (Figure 70c). Figure 70e shows the STEM/HAADF/ EDS elemental images taken from the rectangular area selected in Figure 70d. The red color represents Ti atoms and the blue is for Si atoms. It is clear from the image in Figure 70e that the semi amorphous

section in Figure 71b is a titanium containing compound and Figure 71f reveals that this Ti compound is a  $\text{TiO}_2$ .

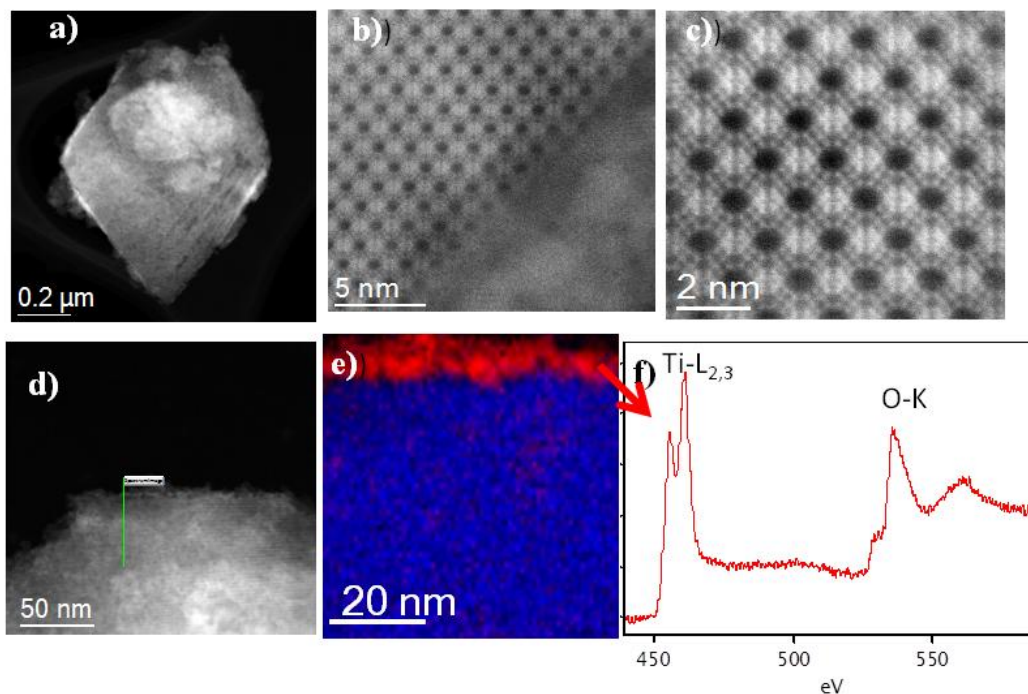


Figure 70:  $C_s$ -corrected STEM/HAADF of 10TZY-60nc

a) Low magnification image of 10TZY-60. b) A closer look at the  $\text{TiO}_2$  nanoparticles, where the semi amorphous can be identified. c) Ultra-high resolution image of the zeolite framework. d) Area selected for chemical analysis from the green rectangular area. e) RB images of the chemical composition with blue for Si and Red for Ti. f) EELS spectrum extracted from the red section of image (e).

$\text{N}_2$  adsorption/desorption isotherms of  $\text{TiO}_2$  nc, 10TZY-60 nc, 40TZY-60 nc, 10TZY-5 nc, 40TZY-5 nc, 10TMOR nc and 40TMOR nc are shown in Figures 71, 72 and 73.  $\text{TiO}_2$  nc exhibited no porosity. On the other hand, the loaded zeolites exhibited combined type

I and IV isotherms, characteristic of micro- and mesoporosity with H4 hysteresis loop. The  $\text{TiO}_2$  loading has produced a decrease in the BET surface area ( $S_{\text{BET}}$ ) as can be seen from Figure 74 and Table 10. This indicates that some of the pores of the zeolite are either blocked and/or populated with  $\text{TiO}_2$  particles and some organic residues from the Ti precursor and 2-propanol solvent.

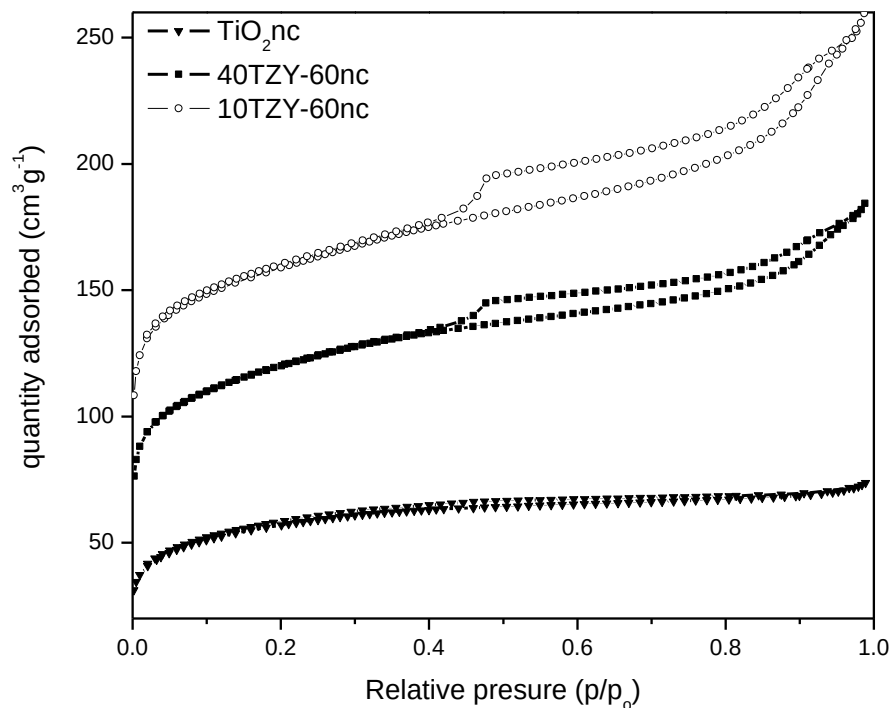


Figure 71:  $\text{N}_2$  isotherms of 10TZY-60 nc, 40TZY-60 nc and  $\text{TiO}_2$  nc

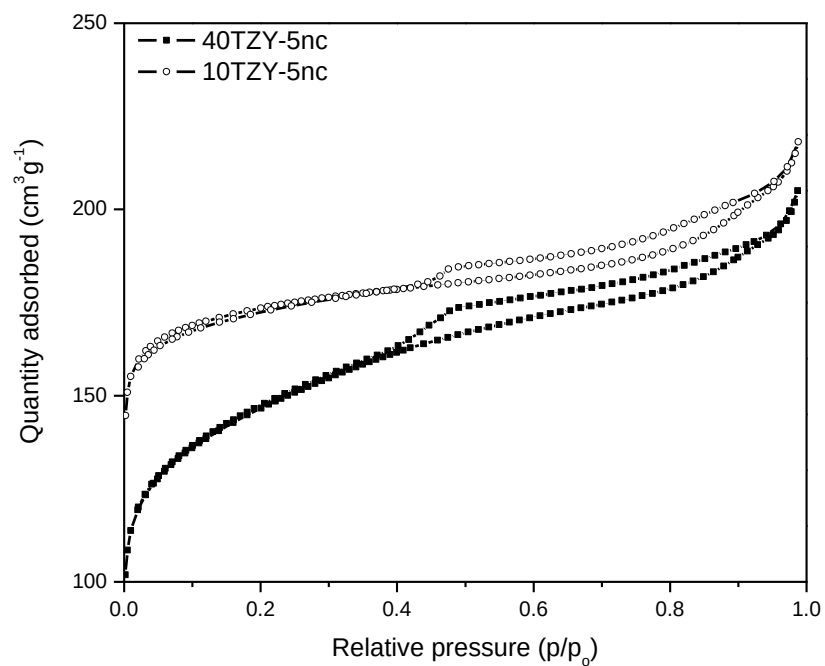


Figure 72:  $N_2$  isotherms of 10TZY-5nc and 40TZY-5nc

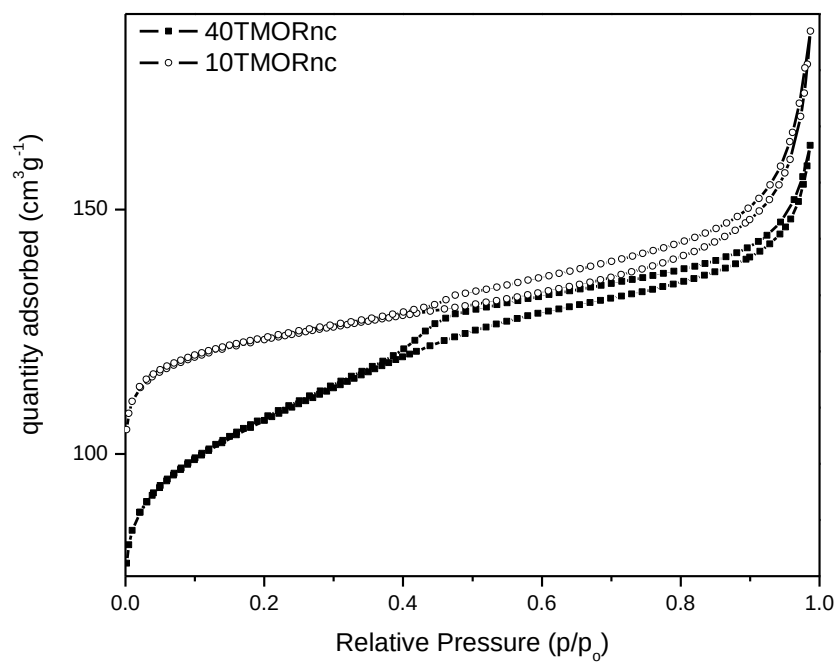


Figure 73:  $N_2$  isotherms of 10TMORnc and 40TMORnc

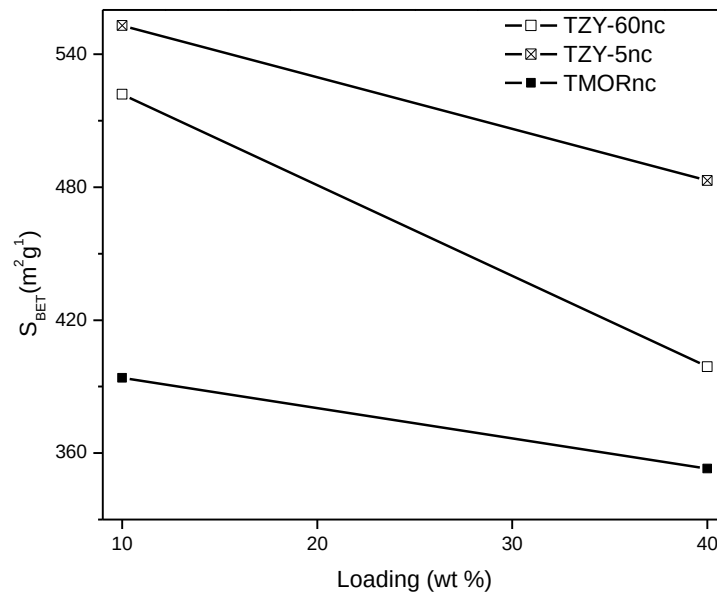


Figure 74: Variation of  $S_{BET}$  with wt % loading

Table 10: Textural properties of prepared samples

| Sample              | $S_{BET}$<br>( $m^2g^{-1}$ ) | t-plot micropor<br>area ( $m^2g^{-1}$ ) | t-plot external<br>surface area ( $m^2g^{-1}$ ) |
|---------------------|------------------------------|-----------------------------------------|-------------------------------------------------|
| 10TZY-60nc          | 522                          | 297                                     | 225                                             |
| 40TZY-60nc          | 399                          | 185                                     | 214                                             |
| 10TZY-5nc           | 553                          | 460                                     | 93                                              |
| 40TZY-5nc           | 483                          | 259                                     | 244                                             |
| 10TMORnc            | 394                          | 314                                     | 74                                              |
| 40TMORnc            | 353                          | 181                                     | 173                                             |
| TiO <sub>2</sub> nc | 191                          | 71                                      | 120                                             |

Figure 75 presents TGA data of  $\text{TiO}_2$ ,  $\text{TiO}_2\text{nc}$ , 40TZY-60 and 40TZY-60nc. The calcined samples ( $\text{TiO}_2$  and 40TZY-60) showed around 4 % weight loss below 100 °C which is attributed to surface adsorbed water. The not calcined samples ( $\text{TiO}_2\text{nc}$ , 40TZY-60nc) however show two weights loses at around 100 °C and 250 °C which are attributed to removal of surface adsorbed solvent and organic compounds from the Ti-precursor respectively.

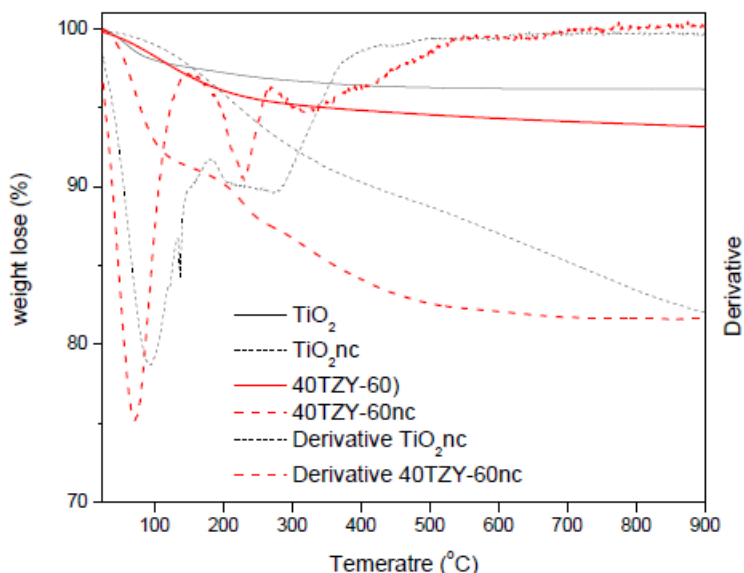


Figure 75: TGA data of  $\text{TiO}_2$ ,  $\text{TiO}_2\text{nc}$ , 40TZY-60 and 40TZY-60nc

The UV-Vis DRS of 10 wt% and 40 wt% loaded ZY-60, ZY-5 and MOR are presented in Figures 76, 77 and 78. There is no fundamental difference with UV-Vis DR spectra of the calcined counterparts (Section 4.1). The absorption band at around 200–240 nm is due to electron transfer excitation from the ligand-oxygen to an unoccupied orbital of the  $\text{Ti}^{4+}$  framework with more intense in the loaded zeolites. The loaded zeolites spectra are also characterized by a large unresolved absorption band ranging from 360 to 240 nm, which is assigned to the electronic transition from 2p(O) to 3d(Ti), corresponding to the valence

band to the conduction band transition according to the energy band structure of  $\text{TiO}_2$  [84, 96, 127, 128, 131, 132] while it is from 412 to 240 nm for the pristine  $\text{TiO}_2$ .

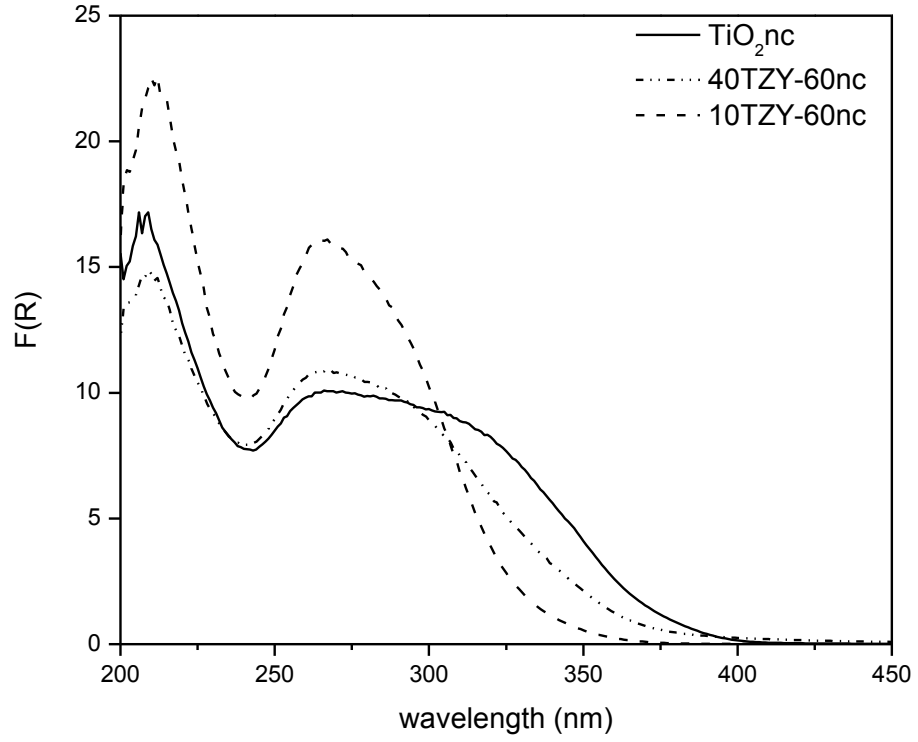


Figure 76: UV-Vis DRS analysis of 10TZY-60nc, 40TZY-60nc and  $\text{TiO}_2$  nc

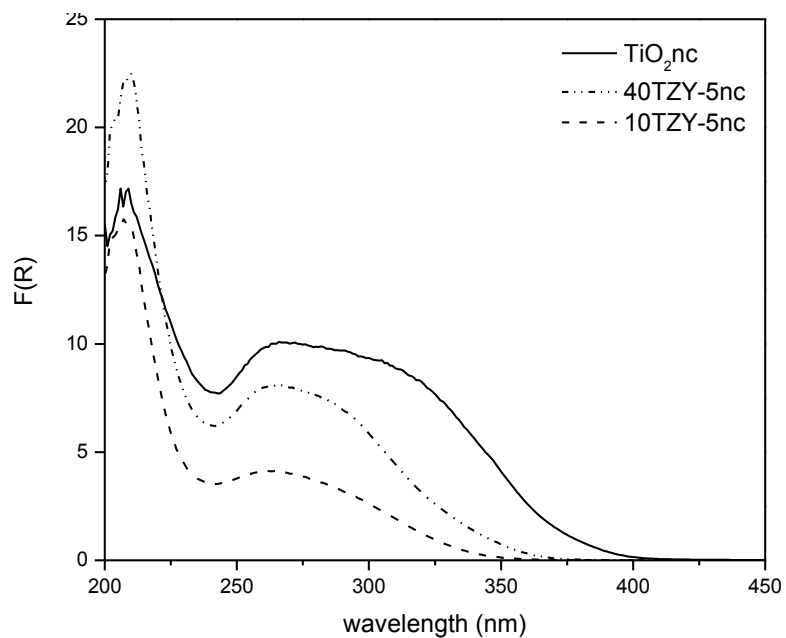


Figure 77: UV-Vis DRS analysis of 10TZY-5nc, 40TZY-5nc and  $\text{TiO}_2\text{nc}$

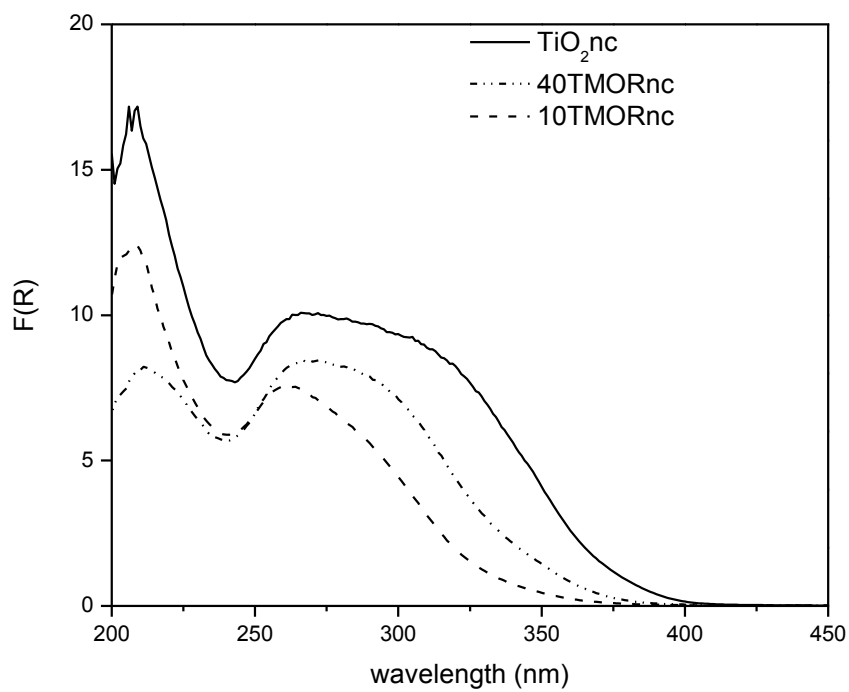


Figure 78: UV-Vis DRS analysis of 10TMORnc, 40TMORnc and  $\text{TiO}_2\text{nc}$

The photocatalytic activities of the prepared samples were tested for the degradation of 10 ppm MO. Unlike in the calcined samples described in 4.1, the absorbance maximum was shifts towards longer wavelength (red shift) and the pH of the MO solution decreases from 4.77 to 2.9 upon adding the catalyst. Thus, it is difficult to convert the absorbance to percentage degradation and the results are presented in the full spectrum of the samples at different irradiation time (Figures 79, 80, 81, 82, 83 and 84). During the photocatalytic reaction process, it was observed that the color of the solution and the photocatalyst changed to red, though the photocatalyst powder was white and the MO solution was orange before the mixture. After UV light irradiation for certain period of time, the solution becomes colorless and the photocatalyst powder regains its original appearance.

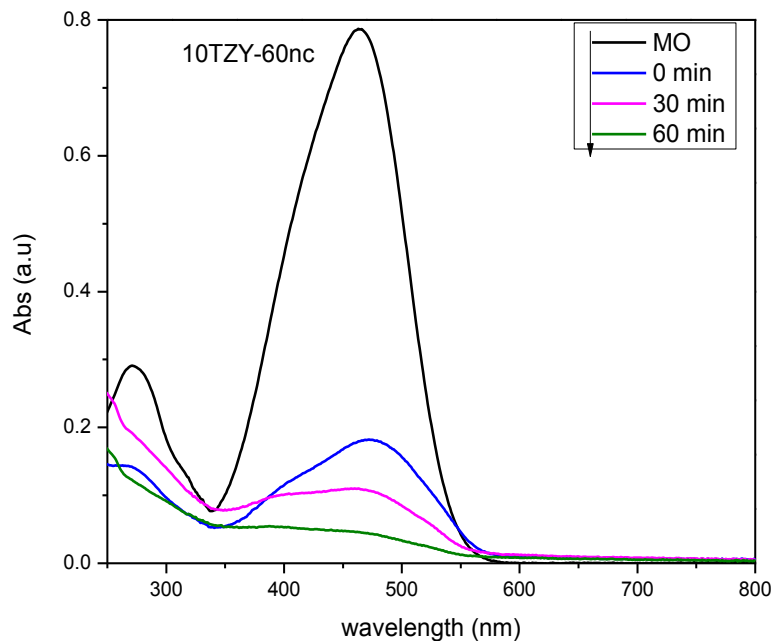


Figure 79: UV-Vis absorbance of MO using 10TZY-60nc at different reaction time

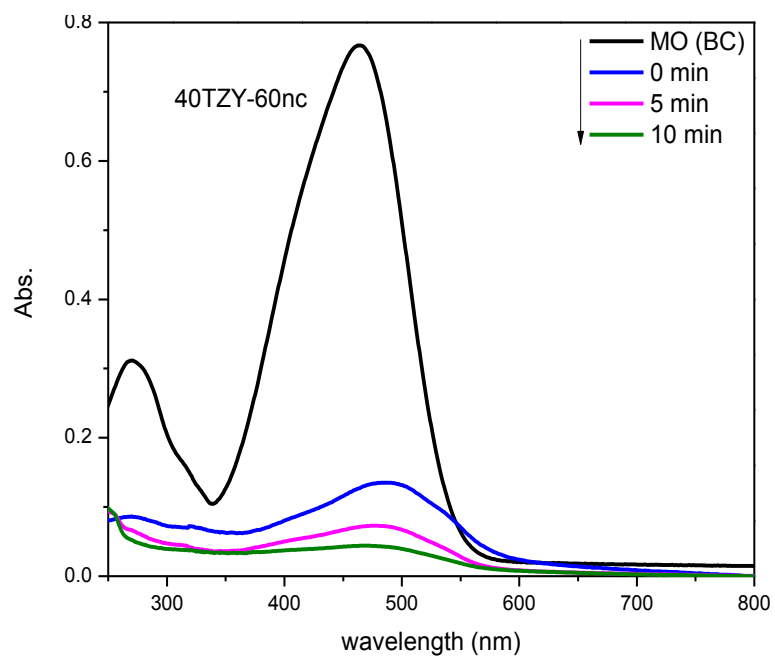


Figure 80: UV-Vis absorbance of MO using 40TZY-60nc at different reaction time

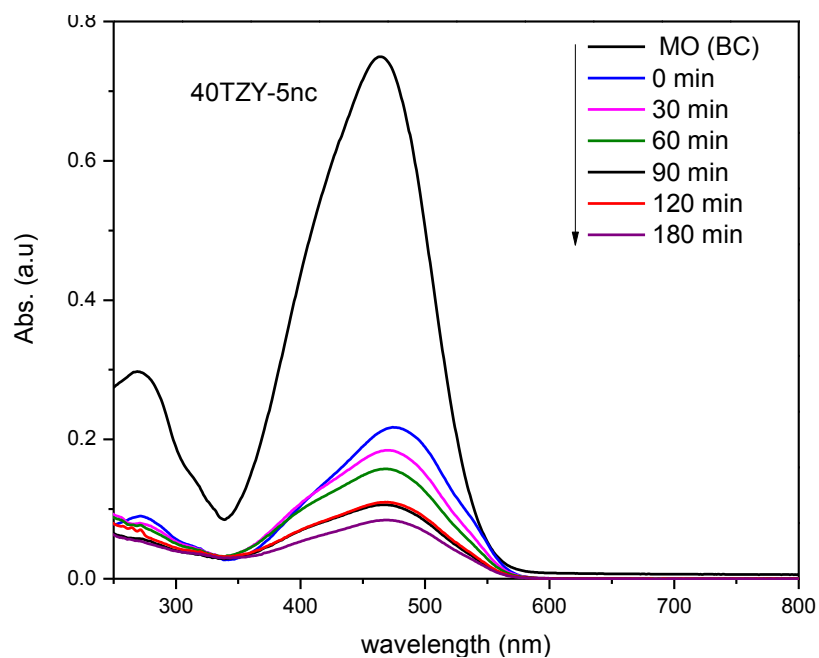


Figure 81: UV-Vis absorbance of MO using 40TZY-5nc at different reaction time

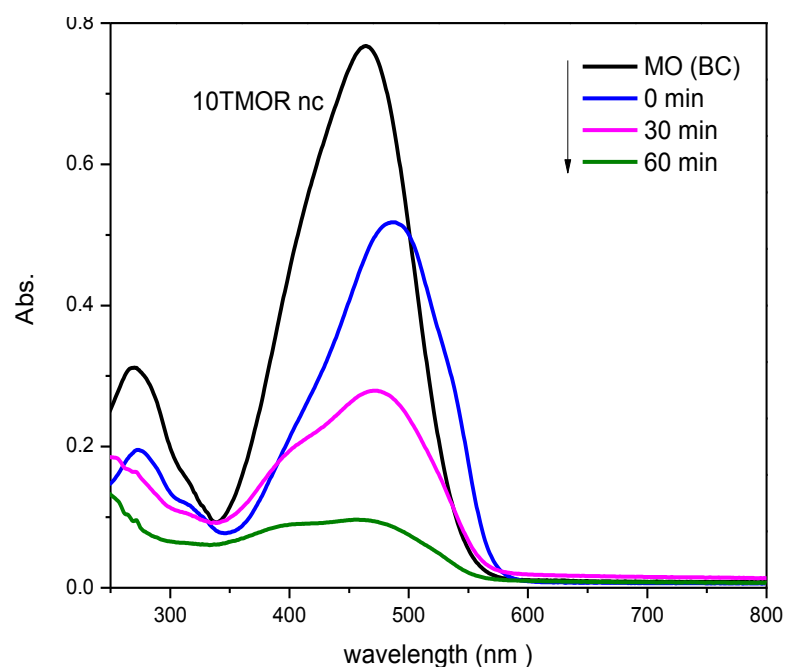


Figure 82: UV-Vis absorbance of MO using 10TMORnc at different reaction time

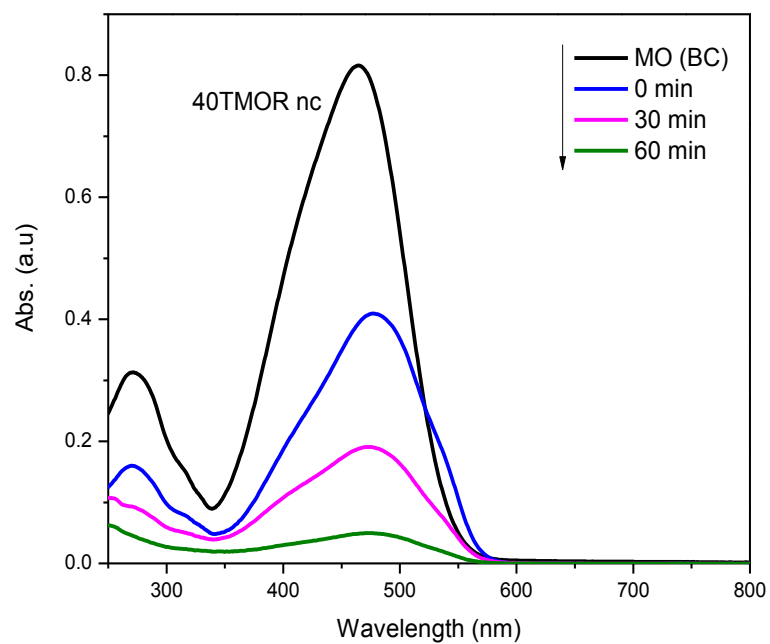


Figure 83: UV-Vis absorbance of MO using 40TMORnc at different reaction time

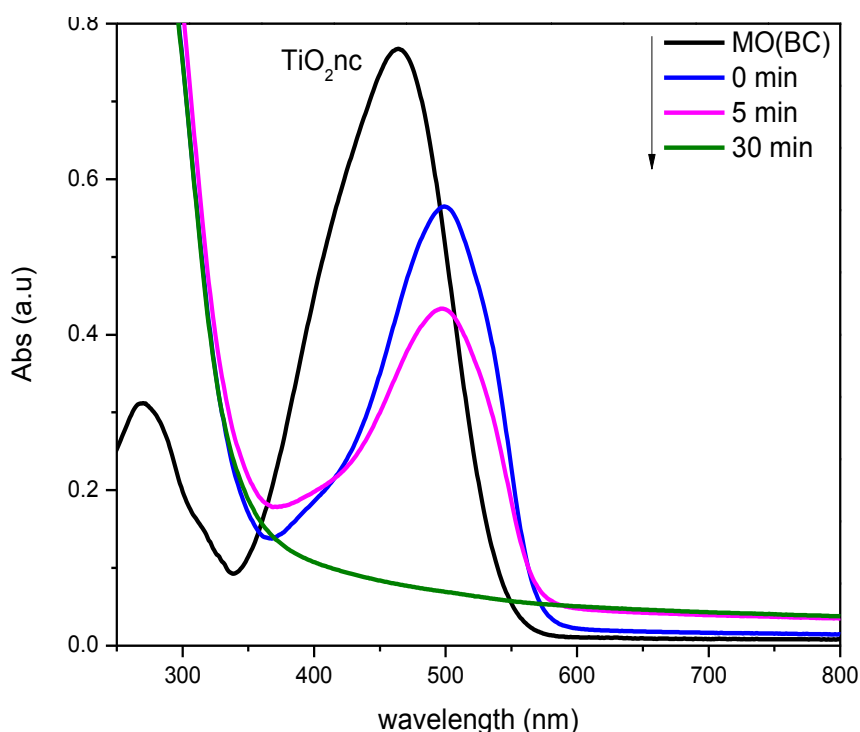


Figure 84: UV-Vis absorbance of MO using  $\text{TiO}_2\text{nc}$  at different reaction time

Although, it is a generally accepted phenomenon that  $\text{TiO}_2$  has to be crystalline for the enhanced photocatalytic activity [98, 99, 140], we found that the semi amorphous  $\text{TiO}_2$  is by far a better photocatalyst than its calcined purely crystalline counterpart in the photocatalytic degradation of 10 ppm MO. In all the samples including the unsupported  $\text{TiO}_2$ , the non-calcined samples took relatively shorter time than their calcined counterparts for degradation of 10 ppm MO. However, we are not in a position to explain the reason behind this better photocatalytic activity of the semi amorphous  $\text{TiO}_2$ . As in the calcined samples, 40TZY-5nc also showed poor photocatalytic activity than other noncalcined samples.

#### **4.3.4. Conclusion**

Semi-amorphous  $\text{TiO}_2$  supported on three different zeolites with 10 wt % and 40 wt %  $\text{TiO}_2$  has been prepared successfully without any calcination. The structural, textural, optical and thermal properties of the samples have been characterized. The photocatalytic activities of the samples have been tested for the photo degradation of 10 ppm MO. The results show that these samples are highly photocatalytically active compared with their calcined and purely crystalline counterparts with some new features which need further investigations.

## 5 Preparation, Characterization and Photocatalytic Activity of Ce/N co-doped TiO<sub>2</sub> Supported on Synthetic Zeolites

### 5.1. Introduction

Although the natural zeolite (Ethiopia) can absorb visible part of the spectrum (Figure 18), its photocatalytic activity is insignificant (Figure 24). The photocatalytic activity of TiO<sub>2</sub> supported on both synthetic zeolite and modified synthetic zeolites (Sections 4.1 and 4.2) showed enhanced photocatalytic activity than the pristine TiO<sub>2</sub> (Figures 50, 51, 53 and 63; tables 4, and 8). However; the enhancement is in the UV light region and the samples show a blue shift on its absorbance as compared to pristine TiO<sub>2</sub> (Figures 46, 47, 48 and 62,). Therefore, the next chosen step was to investigate whether is it possible to modify the band energy of TiO<sub>2</sub>, while maintaining the higher photocatalytic activity of the hybrid system, but extending its absorbance edge to the visible region to harvest the solar light and/or to make the indoor and outdoor photocatalytic experiment simple, safe and sustainable.

So far, many authors have synthesized metals such as Ag, Au, Pt, Pd, Cu, Sr, Sn doped TiO<sub>2</sub>. The photocatalytic activity of the TiO<sub>2</sub> is markedly enhanced by doping of small amounts of the metals described by the easy transfer of electrons which are formed in the TiO<sub>2</sub> by light irradiation to the doped metal particles, simultaneously preventing the electron-hole recombination, which will accelerate the photocatalytic degradation reaction to a greater extent [142]. For example Tong *et al.* (2007)[50] investigated the photocatalytic activity of Ce–TiO<sub>2</sub> for the photocatalytic degradation of Rhodamine B (RB) aqueous solution both under UV and visible irradiation. Doping of Ce<sup>4+</sup> effectively

improves the photocatalytic activity under both UV and visible irradiation with an optimal doping concentration of 0.2 and 0.4%, respectively. They reported that the beneficial effect of  $\text{Ce}^{4+}$  doping under UV irradiation for the efficient separation of photogenerated electrons and holes. According to these authors, for Ce–TiO<sub>2</sub>, the Ce 4f electron configuration plays an important role in interfacial charge transfer and elimination of electron–hole recombination. Lanthanide ions, acting as a Lewis acid, are superior to the oxygen molecule (O<sub>2</sub>) in the capability of trapping CB electrons.  $\text{Ce}^{4+}$  located in the interstitial site could act as an effective electron scavenger to trap the CB electrons of TiO<sub>2</sub> ( $\text{Ce}^{4+} + e^- \rightarrow \text{Ce}^{3+}$ ) which are subsequently transferred to the adsorbed O<sub>2</sub> to form superoxide anion radicals O<sub>2</sub><sup>-</sup> ( $\text{Ce}^{3+} + \text{O}_2 (\text{ads}) \rightarrow \text{O}_2^- (\text{ads}) + \text{Ce}^{4+}$ ). According to these authors, under visible light irradiation, there are two possible pathways contributing to the photodegradation of RB. The first pathway is related to the light absorption of Ce–TiO<sub>2</sub> under visible regions. As mentioned above; the electrons can be excited from the valence band of Ce–TiO<sub>2</sub> into Ce 4f level under visible light irradiation. Subsequently, the photogenerated electrons were transferred to surface adsorbed oxygen to produce superoxide anion radicals, which can further initiate the photocatalytic reaction. The second possible pathway is photosensitization. According to these authors, for the undoped TiO<sub>2</sub> catalyst, the dye molecule excites by absorbing a visible light photon and generates an electron. Subsequently, it will transfer to the conduction band of TiO<sub>2</sub> due to the suitable energy level between the conduction band of TiO<sub>2</sub> and the excited state of the dyes. Then, it will be trapped by adsorbed O<sub>2</sub> to produce superoxide anion radicals, which can further degrade the dye molecule. For the Ce–TiO<sub>2</sub> catalysts, the  $\text{Ce}^{4+}$  ion acts as an electron scavenger to trap the electron of excited dye

molecule. The electron trapped in  $\text{Ce}^{4+}$  sites will subsequently transfer to the adsorbed  $\text{O}_2$  to form oxygen radicals. By this way, Ce doping improves the photodegradation rate of RB. Different attempts were also carried out to dope different nonmetals to  $\text{TiO}_2$  of which nitrogen doping is intensively studied and showed remarkable photoactivity under visible illumination by narrowing the wide band gap of  $\text{TiO}_2$ . Co-doping of metal and nonmetal, two non-metals or two metals has been also a subject of research in  $\text{TiO}_2$  photocatalysis yielding enhanced photocatalytic activities mainly due to the synergy effects of the co doped components.

Although the effect of doping on the photocatalytic activity of pristine  $\text{TiO}_2$  both in the UV and visible region has been extensively studied, research reports in co-doped  $\text{TiO}_2$  supported on synthetic zeolites are rare. Therefore, in this work we are trying the co-doping of N-Ce on  $\text{TiO}_2$  supported on synthetic zeolites, and its impact in the photocatalytic degradation of MO

## **5.2. Sample Preparation**

### **A. Preparation of Ce doped $\text{TiO}_2$ supported on zeolites**

In a typical synthesis, 0.868 g of  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  was dissolved in 56 mL of deionized water. After complete dissolution, a mixture of 284 mL of 2-Propanol and 28.4 mL of Ti (IV) butoxide was added and stirred until complete mixing. To the completely mixed solution, a 22.4 g of zeolite (ZY-60 for this particular case), was added and left for 24 h under stirring at room temperature. The stirring was maintained at room temperature for 24 hours. The solvent was removed by suction filtration and washed by 1L deionized

water. It was then dried at 110 °C. The samples were then calcined in air at 400 °C for 3 hours at 3 °C min<sup>-1</sup>. The sample was labeled as Ce20TZY-60. Using the same procedure, Ce-20TZY-5 and Ce20TMOR were prepared. For comparison purposes, Ce doped TiO<sub>2</sub> (Ce-TiO<sub>2</sub>) was also prepared using similar procedure without adding zeolite.

#### B. Preparation of Ce/N co doped TiO<sub>2</sub> supported on zeolites

Nitrogen was co-doped to the Ce doped samples prepared in (I). In a particular preparation, 3 g of dried Ce(NO<sub>3</sub>)<sub>4</sub> 20TZY-60 before calcination in (A) was mixed with 6 g of urea and calcined in air at 400 °C for 3 hours at 3 °C min<sup>-1</sup> and the sample was labeled as Ce/N-20TZY-60. Ce/N-20TZY-5, Ce/N-20TMOR and Ce/N-TiO<sub>2</sub> were also prepared using the same procedure.

### 5.3. Results and Discussion

The XRD profiles of the co doped samples Ce/N-T and Ce/N-20TZY-60, compared to the pristine ones TiO<sub>2</sub>, and 20TZY60-are shown in Figure 85. Neither crystalline phase of TiO<sub>2</sub> nor the crystalline framework of the zeolites is affected as a result of the co-doping. The effect of TiO<sub>2</sub> loading is observed in similar manner that has been described in Section 4.1 in Figure 26. Furthermore, no traces of CeO<sub>2</sub> diffraction peaks are detected.

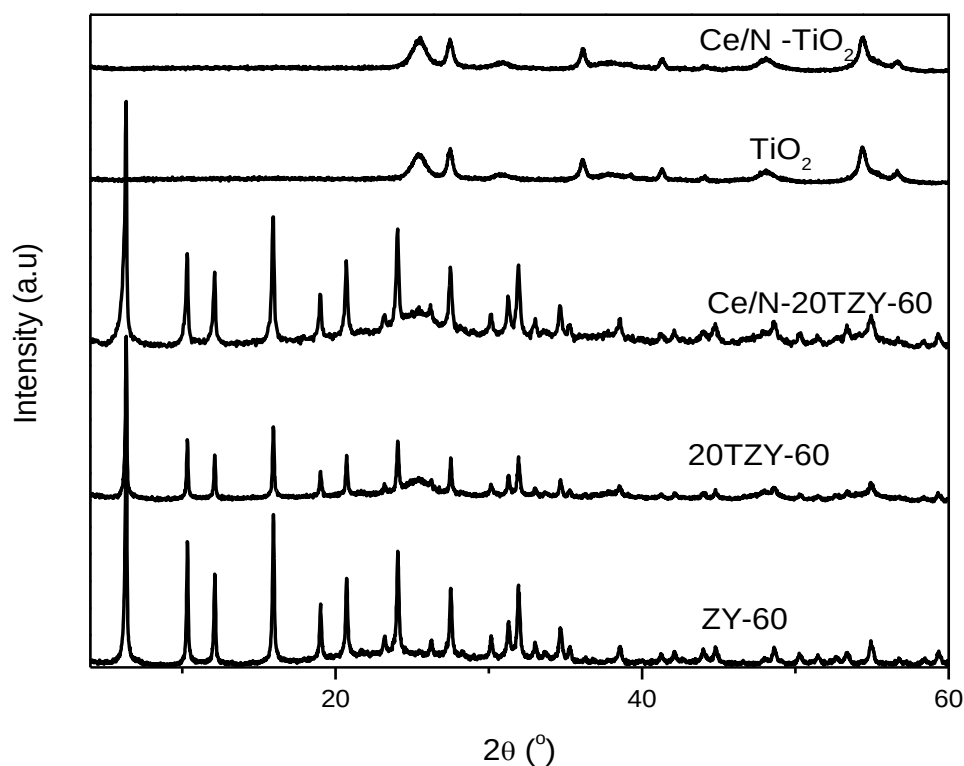


Figure 85: XRD profile of  $\text{TiO}_2$ ,  $\text{Ce/N-TiO}_2$ , 20TZY-60,  $\text{Ce/N-20TZY-60}$  and ZY-60

$\text{N}_2$  adsorption desorption isotherms are presented in Figure 86.  $\text{TiO}_2$  exhibited type IV isotherm (data not shown in the graph), which is related to the mesoporous structure with H2 hysteresis loop, indicative of the presence of cylindrical and spherical pores, which are mainly textural porosity similar to the discussions in section 4.1. The  $\text{Ce/N-TiO}_2$  exhibited the same behaviour showing type IV isotherm, mainly of textural porosity. The loaded zeolites however exhibited combined type I and IV isotherms, characteristic of micro- and mesoporosity with H4 hysteresis loop.

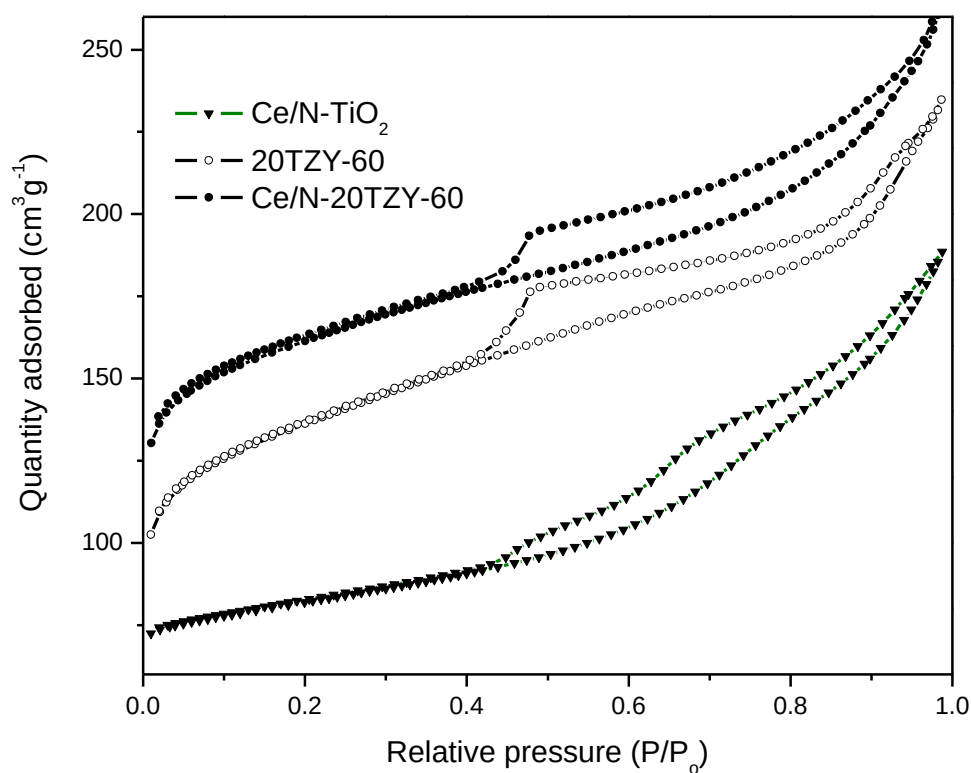


Figure 86: N<sub>2</sub> isotherm Ce/NTiO<sub>2</sub>, Ce/N20TZY -60 and 20TZY-60

The textural properties of the samples are also presented in table 11

Table 11: Textural properties of TiO<sub>2</sub>, Ce/N-TiO<sub>2</sub>, 20TZY-60 and Ce/N-20TZY-60

| Sample                | S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> ) | t-plot micropore<br>(m <sup>2</sup> g <sup>-1</sup> ) | t-plot external<br>(m <sup>2</sup> g <sup>-1</sup> ) |
|-----------------------|----------------------------------------------------|-------------------------------------------------------|------------------------------------------------------|
| TiO <sub>2</sub>      | 86                                                 | -                                                     | 91                                                   |
| Ce/N-TiO <sub>2</sub> | 93                                                 | -                                                     | 96                                                   |
| 20TZY-60              | 503                                                | 272                                                   | 231                                                  |
| Ce/N-20TZY-60         | 514                                                | 306                                                   | 208                                                  |

UV-Vis Diffuse reflectance spectra of Ce/N-TiO<sub>2</sub>, Ce/N-20TZY-60 and pristine TiO<sub>2</sub>, zeolite 20TZY-60, and raw ZY-60 are shown in Figure 87. From the figure it could be seen that pristine TiO<sub>2</sub> has no absorption in the region on (> 412nm), whereas the absorption of Ce/N-TiO<sub>2</sub> is extended to 500 nm with enhanced absorption band area. Similar results were also reported in the literature. However, the co doping does not bring any red shift in the case of TiO<sub>2</sub> loaded zeolites except in enhancing the absorption band area.

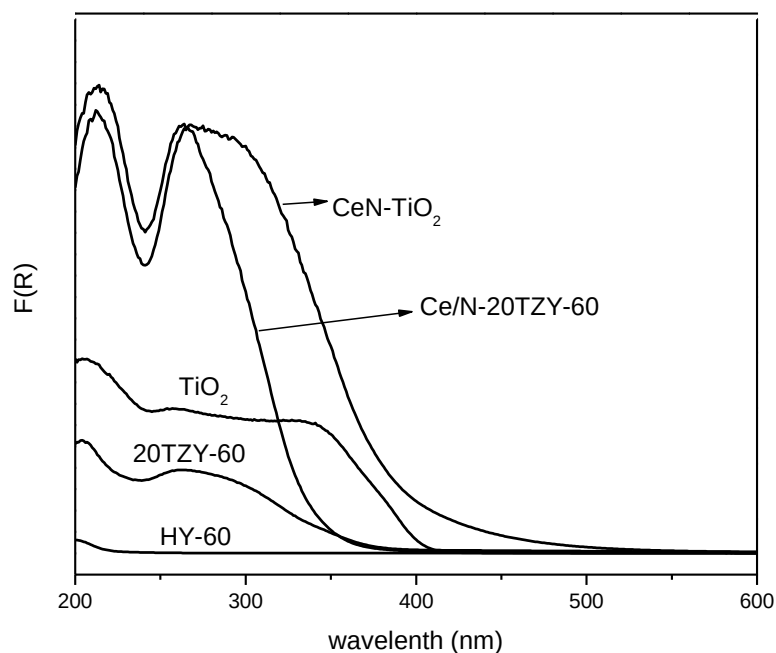


Figure 87: UV-Vis DRS TiO<sub>2</sub>, Ce/N-TiO<sub>2</sub>, 20TZY-60, Ce/N-20TZY-60 and ZY-60

The samples were not subjected for further characterization since the primary objective of the section is (making the loaded zeolite visible light active) not successful. The photocatalytic activity of these samples was tested in photocatalytic degradation of MO using the UV light irradiation (Figure 88). As shown in Figure 88 the photocatalytic activity of Ce/N-TiO<sub>2</sub> is lower than its respective pristine TiO<sub>2</sub>. Similarly, Ce/N-20TZY-

60 showed lower photocatalytic activity than its counterpart with no co doping, 20TZY-60. The samples prepared with MOR and ZY-5 also showed similar trends (data not shown)

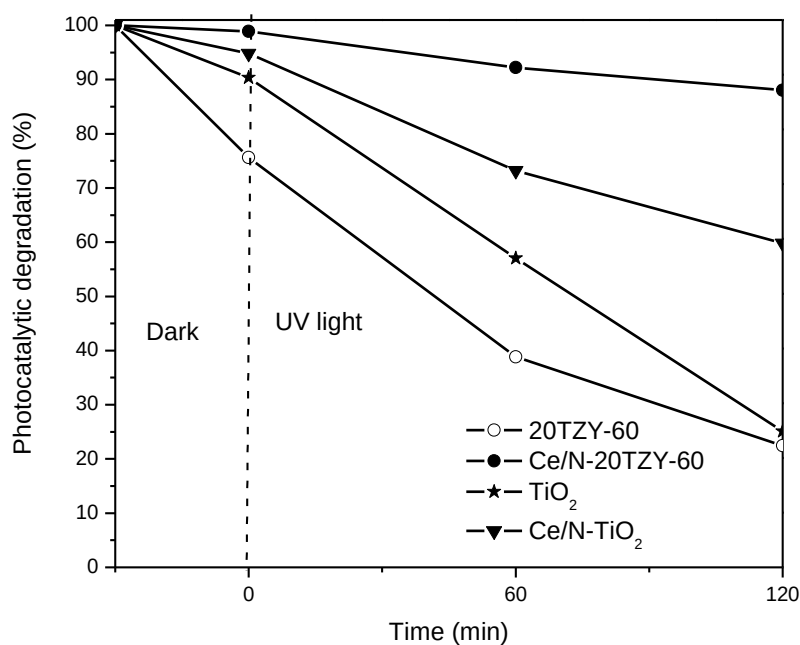


Figure 88: Photocatalytic degradation of 10 ppm MO

#### 5.4. Conclusion

Although, the co-doped samples showed slight visible light sensitivity, the co doping in the supported TiO<sub>2</sub> doesn't bring any change in the absorption edge. The same confinement like in the "undoped" counterpart has been observed. The photocatalytic activity of the co doped is rather low compared to the "undoped" counterparts in the UV light irradiation.

## 6. General Summary and Conclusion

In this study, the Ethiopian natural zeolite was assessed for photocatalysis. Thermal, chemical and mechanical approaches together with loading of 20 wt%  $\text{TiO}_2$  was attempted to customize it for photocatalysis. However, no significant photocatalytic enhancement was obtained

A 10, 20, and 40 wt %  $\text{TiO}_2$  supported on three different zeolites (ZY-60, ZY-5 and MOR) were successfully prepared. Elemental composition, particle size distribution, structural, textural and optical properties were studied using state of the art characterization techniques. The photocatalytic activities of these samples were tested for the photocatalytic degradation of 10 ppm MO. It was found that except for the 10, 20, and 40 wt%  $\text{TiO}_2$  supported on ZY-5, the 10, 20, and 40 wt%  $\text{TiO}_2$  supported on MO and ZY-60 showed higher photocatalytic activity than the pristine  $\text{TiO}_2$ . It was found that the enhanced photocatalytic activity of the supported  $\text{TiO}_2$  on zeolites is attributed to its higher adsorption and reduced recombination rate of the photogenerated electron-hole pairs. Furthermore, the role of the zeolites is also pronounced in reducing the leaching of toxic  $\text{TiO}_2$  nanoparticles. Selected samples were used for the photocatalytic degradation of real textile wastewater from a textile industry in Ethiopia and showed promising results which should be further studied in detail.

ZY-5 (CBV 400) was successfully treated using  $\text{NH}_4\text{Ac}$  and  $\text{NH}_4\text{F}$  sequentially ended up with removing 50% of Al atoms selectively from the external surface without affecting the zeolite framework structure. The  $\text{TiO}_2$  supported on the treated zeolite showed

enhanced photocatalytic activity. Similarly, this enhanced photocatalytic activity is attributed to enhanced adsorption of 10 ppm MO and reduced recombination of photogenerated electron hole pairs.

Semi-amorphous  $\text{TiO}_2$  supported on three different zeolites with 10 wt% and 40 wt%  $\text{TiO}_2$  has been prepared successfully without any calcination and higher photocatalytic activities of each sample than their calcined counterpart have reported. These photocatalytic activities may open new features of  $\text{TiO}_2$  based photocatalysis which needs further studies for better understanding.

Cerium and nitrogen co-doped  $\text{TiO}_2$  supported on ZY-60, ZY-5 and MOR were also prepared to enhance the light absorbance edge of the sample to visible light region keeping the enhanced photocatalytic activity. However, co-doped samples showed lower photocatalytic activity and the absorbance edge was not extended to the visible light region as expected.

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