Effect of thermal treatment on the photocatalytic behavior of TiO₂ supported on zeolites

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Abstract: Photocatalysts based on TiO₂ supported on two different synthetic zeolites (Faujasite CBV 760: SiO₂/Al₂O₃ = 60 and Mordenite CBV 21A, SiO₂/Al₂O₃ = 20), containing 10 wt % and 40 wt % TiO₂ loading, have been synthesized using a sol-gel method without any further calcination. The structural, textural and optical properties of the samples have been characterized using X-ray diffraction (XRD), elemental analysis (ICP-OES), N₂ adsorption-desorption isotherms, aberration corrected Scanning Transmission Electron Microscopy with High Angular Annular Dark Field detector combined with Electron Energy Loss Spectroscopy (STEM/HAADF/EELS), and UV-Vis Diffuse Reflectance Spectroscopy (UV-Vis DRS). Characterization data evidenced that an amorphous layer containing polycrystalline anatase TiO₂ was formed efficiently on the surface of the zeolites, showing 2-4 nm crystalline domains. The photocatalytic activity of the different samples was tested for the photocatalytic degradation of methyl orange showing increasing adsorption of the dye molecule, and faster degradation reaction than the calcined counterparts. Interestingly, although the supported TiO₂ catalysts were not calcined, the best catalysts, 10TZY60nc and 40TZY60nc, showed negligible Ti⁺⁴ leaching and reusability was verified for three cycles without noticeable photocatalytic activity decrement.

Keywords: small crystalline domains TiO₂, Methyl Orange, photocatalysis, STEM/HAADF/EELS

Introduction

Titanium dioxide (TiO_2) is the photocatalyst most widely used for environmental applications. Previous studies have shown that the photocatalytic activity of this semiconductor is significantly influenced by its intrinsic properties, among others the crystalline phases and degree of crystallinity.¹⁻⁹ Ohtani *et al.* (1997) compared the photocatalytic activity of amorphous TiO_2 powders and crystalline anatase TiO_2 powders in photocatalytic degradation of 2-propanol and concluded that the photocatalytic activity of amorphous TiO_2 was negligible, increasing almost linearly as a function of anatase content, and further improving by calcination of completely crystallized powder.⁸ They attributed the negligible photocatalytic activity of amorphous TiO_2 to the recombination of photo excited electrons and positive holes at defects located on the surface and in the bulk of particles. Li *et al.* (2007) highlighted the importance of the thermal treatment of TiO_2 for improving its photocatalytic efficiency.¹⁰ They reported that thermally treated TiO_2 has an increasing light absorption, a greater number of surface defects, a higher efficiency of charge separation, and thus a higher intrinsic activity for phenol degradation. Some authors have shown that amorphous TiO_2 films can have a substantial photocatalytic activity, which can be explained by the presence of very small crystalline domains not detectable in their XRD patterns.¹¹

Supporting TiO_2 on zeolites has been widely surveyed in an attempt to increase its versatility. Kuwahara *et al.* prepared TiO_2 loaded on zeolites from an aqueous ammonium titanyl oxalate solution, which was stirred at room temperature for 6 h followed by evaporation of water under vacuum and calcination at 600 °C for 6 h.⁶ Kamegawa *et al.* impregnated Y zeolite with $(\text{NH}_4)_2[\text{TiO}(\text{C}_2\text{O}_4)_2]$ or $(\text{NH}_4)_2[\text{TiF}_6]$ followed by calcination up to 700 °C for 5 h in air.⁷ Similarly, Gomez *et al.* synthesized titania supported on zeolitic matrices (HBeta, HY and HZSM-5) by *in situ* generation of TiO_2 from titanium(IV) isopropoxide followed by calcination of the system to 450 °C.¹² In addition, Sun *et al.* prepared TiO_2 nanoparticles supported on a natural zeolite via a simple hydrolysis of TiCl_4 and then calcined at various temperatures (300, 400, 500, 600 and 700 °C).⁹ They tested the photocatalytic activity of these samples in photocatalytic reduction of Cr(VI) and found that the sample calcined at 500 °C showed the

highest photocatalytic activity, which was attributed to its high crystallinity. Similar works have been also reported by different groups.¹³⁻²⁰

In our work, we tried to study the effect of the formation of TiO₂ loaded on zeolites without calcination as part of our investigations to obtain photocatalysts with high activity.²¹ Thus, we report here the photocatalytic activity of the small crystalline domains of TiO₂ supported on the synthetic zeolites Y (SiO₂/Al₂O₃ = 60) and Mordenite (SiO₂/Al₂O₃ = 20) without any calcination treatment.

Experimental

Sample Preparation

Commercially available synthetic zeolite Y, CBV 760 (SiO₂/Al₂O₃ = 60), and mordenite, CBV 21A (SiO₂/Al₂O₃ = 20), were purchased from Zeolyst. Hereafter, the zeolites will be called ZY-60 and MOR, respectively. In a typical synthesis of 10 wt% TiO₂ loaded on mordenite zeolite (10TMOR) 18 g of MOR were suspended in a solution of 10.15 mL of titanium(IV) butoxide (Ti(OBut)₄) dissolved in 101.5 mL of 2-propanol (CH₃CHOHCH₃) and 20.3 mL of deionised water under magnetic stirring. The stirring was maintained at room temperature for 24 h. The solvent was removed by rotary evaporator and the resulting composite dried at 110 °C. Similarly, 10 and 40 wt% of TiO₂ were prepared by suspending each zeolite (ZY-60 and MOR) in a solution of titanium butoxide dissolved in a mixture of 2-propanol and water with volume ratio of 1:10:2 (Ti(OBut)₄: CH₃CHOHCH₃: H₂O). For comparison purposes, bulk TiO₂ was synthesized using the same recipe and conditions without adding zeolite. The samples were labeled “10T” and “40T” referring to the theoretical wt % TiO₂ loading, followed by the zeolite code (ZY-60 and MOR) and “nc” to indicate that the samples are “not calcined”. Thus, the sample codes will be 10TZY-60nc, 40TZY-60nc, 10TMORnc, 40TMORnc and TiO₂nc. The calcined counterparts are used for comparison, labeled as 10TZY-60, 40TZY-60, 10TMOR, 40TMOR, and TiO₂. These samples were obtained by calcination in air at 400 °C for 3 h with 3 °C min⁻¹ heating ramp.²¹

Characterization

X-ray diffraction (XRD) patterns were collected with an X'Pert Pro PANalytical diffractometer (CuKα radiation, λ=0.15406 nm). Nitrogen adsorption-desorption isotherms were measured in a

Micromeritics ASAP 2420 physisorption analyzer and all the samples were degassed at 150 °C for 16 h prior to data collection. Micropore volume and non-microporous (mesopore and external) surface area were determined by the t-plot method. Chemical composition was determined by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) using a Perkin-Elmer Optima 3300 DV equipment. Digestion of the samples was obtained by alkaline fusion. UV-Vis Diffuse Reflectance Spectroscopy (DRS) measurements were done using a Varian Cary 5000 double-beam UV-Vis-NIR spectrophotometer. Collected spectra were converted to Kubelka–Munk function, $F(R)$ versus wavelength. Scanning Transmission Electron Microscopy (STEM) 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 GatanTridiem energy filter (EELS). Prior observations, the samples were crushed, dispersed in ethanol and placed onto a holey carbon copper microgrid.

Photocatalytic degradation test

For a particular photocatalytic test, 0.5 g of sample was suspended in 750 mL of a 10 ppm aqueous solution of methyl orange (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 in continuous purging of oxygen to maintain adsorption-desorption equilibrium of MO with the powder photocatalyst material. Then, the suspension was irradiated with a 150W UV lamp (Heraeus medium pressure mercury lamp) and samples were withdrawn at time intervals for analysis after filtering out the photocatalyst with a 0.22µm nylon filter. The samples were analyzed in a PerkinElmer Lambda 950 UV-Vis spectrophotometer. The spectra of the sample were recorded from 800 to 200 nm and the absorbance at 462 (maximum absorbance) of methyl Orange (MO) was taken for concentration calculation. $(\text{Degradation } (\%) = (A_t/A_o) \times 100$ where A_t is absorbance at 462 nm at time t and A_o is the initial absorbance of MO before it is mixed with the photocatalyst material. For the reusability test, the photocatalyst was recovered after the degradation reaction was completed, then washed and dried at 110 °C.

Results and Discussion

X-ray diffraction profiles of non-calcined TiO_2 (TiO_2 nc) and TiO_2 calcined at 400 °C (TiO_2) are shown in Figure 1. Bulk TiO_2 calcined at 400°C shows sharp diffraction peaks at $2\Theta = 25.7^\circ$

(101), 38.2° (004) and 48.2° (200) assigned to anatase crystalline phase and diffraction peaks at $2\theta = 27.6^\circ$ (110), 36.1° (101) and 41.3° (111) indexed to rutile phase, marked as “A” and “R”, respectively in Figure 1. The diffraction observed at 31° is characteristic of brookite. In the XRD profile of the same TiO_2 but without calcination (TiO_2 nc), the diffraction peaks of rutile decrease notably. Besides, the diffraction peaks of anatase appeared broadened and less intense, indicating either small crystal size in anatase domains or the presence of amorphous material and organic leftovers. This broadening is even more pronounced when the TiO_2 nc is supported on zeolites.

Figure 1: XRD profile of TiO_2nc (non calcined) and TiO_2 (calcined)

Figure 2: XRD profile of ZY-6, 40TZY-60 (calcined) and 40TZY-60nc (non calcined). Anatase peaks are labeled with “A”.

Figure 2 shows the XRD profile of 40TZY-60 nc (40 wt% TiO_2 loaded ZY-60 non calcined), 40TZY-60 (40 wt% TiO_2 loaded ZY-60 calcined at 400°C) and the pure zeolite (for clarity the intensity is divided by factor of 2). From Figure 2 the diffraction peak at 25.4° ascribed to anatase, proves the presence of TiO_2 upon loading. There is clear difference in the profile of the anatase phase upon calcination. The diffraction peaks of anatase at 25.4° , 37.8° , 48° , 54.5° and 62.5° increase in intensity when the composite is calcined (40TZY-60). These diffraction peaks in the non-calcined sample, 40TZY-60nc, are very broad and lower in intensity confirming that in the zeolite composite there is also either very small domains of anatase, or amorphous residue. Similar trends were observed by decreasing the loading of TiO_2 to 10%, or upon changing the zeolite to Mordenite at different loadings.

As shown in Table 1, the actual loading of TiO_2 from ICP-OES analysis of the samples is slightly lower than the expected yield of TiO_2 . The 10 wt% loaded samples, 10TZY-60nc and 10TMORnc yielded 91 and 96% of the expected loading, respectively. Similarly, the yield for 40TZY-60nc and 40TMORnc was 75 and 78% of the expected loading, respectively. In general, the yield decreases upon increasing the loading although the procedure seems reproducible

obtaining systematically the same trends regardless of the weight % loading and type of zeolite used.

N₂ adsorption/desorption isotherms of TiO₂nc, 10TZY-60nc and 40TZY-60nc, are shown in Figure 3 and the textural properties are compared in Table 1 with the calcined counterparts.

Table 1: Chemical and textural properties of prepared samples and amount of Ti leached in photocatalytic tests.

Sample	TiO ₂ (% wt)	BET surface area (m ² g ⁻¹)	Mesopore + external surface area (m ² g ⁻¹)	Micropore volume (cm ³ g ⁻¹)	Leaching Test TiO ₂ (μg/l)
ZY60		746	198	0.27	
10TZY60nc	9.1	593	209	0.21	<5
10TZY60	8.5	704	134	0.26	0.89
40TZY60nc	30.1	439	197	0.15	38
40TZY60	30.1	467	213	0.16	
MOR		549	47	0.20	
10TMORnc	9.6	487	58	0.18	
10TMOR	7.8	501	56	0.18	
40TMORnc	31.5	393	161	0.14	
40TMOR	31.5	365	113	0.13	
TiO ₂ nc		209	210	0.00	6009
TiO ₂		86	84	0.00	28.48

Figure 3: N₂ adsorption/desorption isotherms of 10TZY-60 nc, 40TZY-60 nc and TiO₂ nc

The loaded zeolites exhibited combined type I and IV isotherms, characteristic of micro- and mesoporosity with H4 hysteresis loop. Similar trends were recorded for the parent zeolites and 10TMORnc and 40TMORnc samples. Textural data calculated from these isotherms (Table 1) show that the parent zeolite ZY60 possesses significantly higher BET surface area than MOR, which can be attributed partly to its higher micropore volume. Nevertheless, the high surface area of sample ZY60 is mainly due to the important contribution of mesopores, which originate from the dealumination treatment required to prepare this zeolite from its parent, high aluminium content faujasite, and add a large non-microporous surface area to that of the external surface of zeolite crystals. As shown in Table 1, deposition of TiO₂ on the surface of both zeolites leads to a partial loss of surface area, mainly in the micropore region, together with a decrease of micropore volume. This loss of microporosity, which increases with TiO₂ loading, indicates that some of the micropores of the zeolite are either blocked or populated with TiO₂ particles and/or organic residue from the Ti precursor and 2-propanol. The calcination of TiO₂-loaded zeolites leads to a partial recovery of the micropore surface area and volume, which can be attributed to an increased accessibility of micropores due to the release of the organic residues as well as to a

certain degree of sintering of the TiO_2 phase. In the case of bulk TiO_2 , a sharp decrease of surface area is found upon calcination, evidencing the agglomeration and growth of the crystals. In order to identify the nature of the broadened diffraction peaks and to locate the TiO_2 particles, 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 4 shows the images corresponding to the 10 wt% loading of TiO_2 nc in ZY-60 zeolite (10TZY-60 nc).

Figure 4: C_s -corrected STEM/HAADF of 10TZY-60nc: a) Low magnification image. b) A closer look at the TiO_2 nanoparticles; the small domains can be identified. c) Ultra-high resolution image of the zeolite framework. d) Area selected for chemical analysis from the red 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).

Figure 4a exhibits the low-magnified image, where the higher number of TiO_2 particles can be observed with bright contrast in the peripheral edge and central part of the zeolite crystal. Figure 4b is a high magnification STEM/HAADF image showing that the zeolite surface is covered by a matrix containing a polycrystalline material in which very small domains of crystalline TiO_2 are

formed without calcination. The size of these domains is consistently of 2-4 nm and observed in other areas of the sample. The C_s -corrected STEM-HAADF high resolution image of the zeolitic structure reveals that after deposition of TiO_2 the framework remains intact, although no Ti atoms could be visualized inside the zeolite cavities (Figure 4c). The EDS elemental images (Figure 4e) taken from the rectangular area selected in Figure 4d allows identifying in red color the Ti atoms and in blue the Si atoms. It is clear from the image in Figure 4e that the semi amorphous section in Figure 4b is a titanium containing compound and Figure 4f reveals that this Ti compound is TiO_2 from the EELS analysis. Interestingly, this crystallinity was also envisaged in the bulk TiO_2 sample prepared without the zeolite support, although the lack of support led to an inefficient agglomeration of these small domains, which is later on reflected in a lower photocatalytic activity. Figure 5 depicts the high-resolution spherical aberration (C_s -corrected) STEM-HAADF image of several nanoparticles agglomerated.

Figure 5: C_s -corrected STEM/HAADF image (a) and EELS (b) of TiO_2 non-calcined

As it can be seen, pointed by white arrows, some of these nanoparticles observed present a well-defined crystal structure, while others, pointed by red arrows, exhibit an amorphous nature. The d-spacing measured for the crystalline nanoparticles was around $d \approx 0.35$ nm which would be in agreement with the (101) plane of anatase. With the intention of gaining information of the TiO_2 phase, EEL spectra analysis was performed on the as-synthesized material. The Ti- $L_{2,3}$ spectrum signal after background subtraction is presented in Figure 5b. There can clearly be identified the two edges corresponding to Ti- L_3 at 456 eV and Ti- L_2 at 462 eV. From the Ti-L edges we cannot

assign the spectrum to a specific TiO_2 phase, although the shape of the Ti-L_3 edge suggests that it adopts the anatase phase.^{22,23}

The UV-Vis DRS of 10 wt% and 40 wt% loaded ZY-60nc, and TiO_2nc are presented in Figure 6. No significant differences were observed in comparison with UV-Vis DRS spectra of the calcined counterparts.²¹ 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^{4+} framework with higher 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 $2p(\text{O})$ to $3d(\text{Ti})$. According to the energy band structure of TiO_2 it corresponds to the valence band to the conduction band transition, and appears in the 412 to 240 nm range for the pristine TiO_2 .^{12-14, 16,18,24}

Figure 6: UV-Vis DRS analysis of 10TZY-60nc, 40TZY-60nc and TiO_2nc

The photocatalytic activity of the non-calcined samples was tested in the degradation of 10 ppm methyl orange (MO). Figure 7 shows the photocatalytic degradation using TiO_2nc as compared to the calcined counterpart. The non-calcined sample shows higher adsorption of MO in the dark, since 26% of methyl orange disappeared from the solution before irradiating with the UV-lamp, while the calcined counterpart adsorbed less than 10% under the same conditions. The higher surface area of the TiO_2nc sample in comparison to TiO_2 (Table 1) might account for the higher adsorption observed with the former. In addition, it already indicates that the non calcined sample is probably more hydrophobic, due to the presence of organic residues, favoring the

adsorption of the organic dye. In any case the actual MO photocatalytic degradation is much faster also for the later sample, giving a total degradation of 97.4% in 90 minutes against the 58.4% reached with the calcined sample. Furthermore, its degradation curve shows a steeper slope than that of the calcined sample, indicating a more efficient process most probably due to the small particle size observed in TEM. Although it is a generally accepted phenomenon that TiO_2 has to be crystalline for an optimum photocatalytic activity, this result evidences that smaller crystallite domains together with an efficient dispersion of the nanoparticles may have a remarkable effect, which is possible to achieve without calcination.⁸⁻¹⁰

Figure 7: Photocatalytic degradation profile using TiO_2nc (not calcined) and TiO_2 (calcined).

Figure 8 shows the degradation profile of non-calcined and calcined TiO_2 -containing ZY60 (A) and MOR (B) samples, together with the corresponding parent zeolites for comparison. During the photocatalytic reaction, 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 a certain period of time, the solution became colorless and the photocatalyst powder regained its original appearance. The color variation upon addition of the catalyst to the MO solution was observed systematically in all the experiments carried out with non-calcined samples, whilst it was not observed for the calcined systems [21].²¹

Figure 8: Photocatalytic degradation profile using (A) ZY60- and (B) MOR-based systems.

Despite the small shifting of the maximum of the absorption band observed in the UV-Vis spectra of the MO solutions, the concentration of MO that had disappeared from the solution was systematically estimated and plotted as % MO degradation to compare the evolution of all the non-calcined catalysts with the calcined materials. Like in the case of bulk TiO_2 , the main difference between calcined and non-calcined catalysts is the notable contribution of the

adsorption of MO on the solids before UV irradiation, which is even more noticeable in the ZY60nc catalysts. In the case of 10TZY60nc, 76.85% and for 40TZY60nc, 86.8% of total absorbance disappeared after adsorption in the dark (0 min irradiation time), i.e., as the MO solution was in contact with the catalysts, without UV irradiation, it turns red. Figure 8A shows that the adsorption is not related to the zeolite structure since parent Zeolite Y CBV-760 (ZY60) does not adsorb above 5% of MO at all time range. The contribution of the adsorption in these systems as compared to the parent zeolites, may be related to the use of butoxide as Ti source and propanol as solvent, which may contribute to make the surface of the zeolite more hydrophobic. On the other hand, the larger contribution of the adsorption in the zeolite Y as compared to the mordenite system may be related to the mesoporosity of the parent zeolite used, as the large molecular size of MO suggests that it would hardly diffuse inside the micropore channels and cavities of both zeolites. CBV 760 is a commercial zeolite that has been dealuminated by steaming, which creates mesopore surface area in addition to the external surface of zeolite crystals and, hence, provides a much larger non-microporous surface area compared to mordenite, as well as a more hydrophobic surface framework, favoring the diffusion of the Ti-butoxide further in the mesoporous system and enhancing its adsorption, which may not occur in the mordenite sample (CBV 21A) with more aluminum in the framework and without mesopores.^{21,25} However, adsorption in the dark appears to be mostly influenced by the calcination of titania-loaded zeolites. As in the case of bulk TiO₂, calcination produces a marked decrease of the amount of MO adsorbed in the dark on any given catalyst, which again suggests that the presence of organic residues on non-calcined samples might increase surface hydrophobicity and enhance adsorption of the dye. Interestingly, in the case of non-calcined, Ti-loaded ZY60 catalysts, the degradation or disappearance of MO has in the early stages of the reaction a similar slope as the calcined counterpart despite the larger contribution of the adsorption in the non-calcined catalyst. In particular, the reaction is completed within 10 minutes using 40TZY60nc catalyst implying the effect of the concentration of TiO₂ in the catalytic efficiency in these non-calcined systems. In general terms, the total degradation performance at 30 min is faster in all the non-calcined systems.

Leaching of Ti⁴⁺ during the photocatalytic reaction was tested for TiO₂nc, 10TZY-60nc and 40TZY-60nc systems using ICP-MS. The results are collected in Table 1 and indicate that in the zeolite supported systems the presence of the zeolite somehow prevents from leaching in these

non-calcined systems as compared with the pure TiO_2nc . The latter shows a leaching of 6 ppm of Ti to the reaction solution while the concentration of Ti in solution falls to the ppb range for the zeolite-supported catalysts. Similarly, the leaching of Ti^{+4} species from calcined TiO_2 and calcined 10TZY-60 were measured and found 28.5 and 0.9 ppb respectively. This effect could support that in the zeolite Y-non calcined systems, the source of Ti diffuses inside the porous systems more efficiently forming small crystalline domains, as those observed by TEM on the surface of the crystals. Upon calcination, the sintering of these domains is commonly produced on the surface of the crystals contributing to the growth of the TiO_2 particles, larger than those observed in the non-calcined systems. In the bulk TiO_2nc there is no efficient trapping of the small crystalline domains and get released to the solution upon washing off of the organic residues during the catalytic reaction. Furthermore, the recycling study was conducted on 10TZY60nc to determine the stability of the non-calcined catalysts over three cycles. At the end of the first photocatalytic cycle, the photocatalyst was separated from the resulting suspension by filtering, washed, and oven dried at 110 °C. Figure 9 plots the degradation profiles of the three cycles. Given that there is no significant leaching of Ti species during reaction, the decrease observed in the amount of MO adsorbed in the dark after the first photocatalytic cycle is probably due to the loss of the organic leftover from the Ti source, basically butoxide and propanol molecules, that might be washed off in the first cycle. Anyhow, the photocatalytic activity remained significantly high after the 3 cycles tested corroborating the trapping effect of the zeolitic framework which has efficiently produced a safe catalytic composite.

Figure 9: Reusability test on 10TZY60nc.

Conclusion

Small crystal domains of TiO_2 supported on two different zeolites, zeolite Y and mordenite, with 10 wt% and 40 wt% TiO_2 have been prepared successfully without any calcination treatment. Polycrystalline TiO_2 was formed efficiently on the surface of the zeolites, showing 2-3 nm crystalline domains. The photocatalytic activity of the different samples was tested for the photocatalytic degradation of 10 ppm MO showing an increased adsorption of the dye molecule and faster degradation reaction than non-calcined materials. The results show that these samples are active photocatalysts and the zeolite efficiently prevents leaching.

Supplementary data: Further characterization of the rest of the catalysts is included: XRD of ZY-60, 10TZY-60, 40TZY-60nc, MOR, 10TMORnc and 40TMORnc; N_2 isotherms of 10TMORnc and 40TMORnc; TEM images of TiO_2 small crystals covering the surface of the zeolite crystals in sample 10TZY60nc that are systematically observed in all the samples. Color variation during the photocatalytic reaction: A) 10 ppm MO, B) 10 ppm MO + 0.5 g 40TZY-60nc, C) 10 ppm MO + 0.5 g 40TZY-60nc + 10 min UV light irradiation. UV-Vis absorbance of

MO using TiO₂nc and 10TZY-60nc at different reaction time and using 10TZY-60nc at different cycles.

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