

Research Article

The Photocatalytic Activity of TiO₂-Zeolite Composite for Degradation of Dye Using Synthetic UV and Jeddah Sunlight

Laila M. Al-Harbi,¹ Samia A. Kosa,¹ Islam H. Abd El Maksod,^{1,2} and Eman Z. Hegazy^{1,2}

¹Chemistry Department, King Abdulaziz University, P.O. Box 42805, Jeddah 21551, Saudi Arabia

²Physical Chemistry Department, National Research Centre, Cairo, Egypt

Correspondence should be addressed to Eman Z. Hegazy; ehgazy77@yahoo.com

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In this research different composites of impregnated TiO₂ with LTA or FAU zeolites were used as different weight% ratio for photodegradation of organic dye. Normal laboratory UV-lamps were used as a source of UV irradiation. In addition a setup of system of mirrors was used to collect real Jeddah sunlight. A comparison of UV and real sunlight photodegradation activity showed that the real sunlight enhances new centers of active sites exhibiting higher catalytic activity than that of UV irradiated samples.

1. Introduction

Decomposition of organic pollutants photocatalytically in the presence of TiO₂ appears as a sustainable decontamination process of common application, as gas or liquid [1, 2]. The ultraviolet (UV) energy/excitation source becomes the most practical applications due to the fact that the absorption edge of anatase TiO₂ is about 380 nm. The most solar radiation intensity reaching the earth surface is in the visible range. Systems with visible-light as an active radiation have become a priority for developing the upcoming generation of photocatalytic materials.

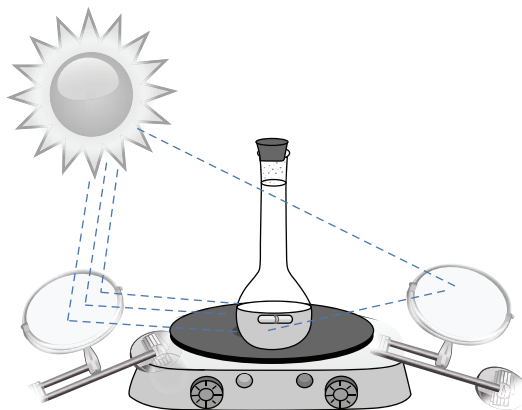
The composite of TiO₂ fine particles with other supports such as active carbon has been proved to exhibit efficient photocatalytic reactivity [3–5]. However, black active carbon inhibits the incident UV-vis radiation to excite semiconductor photocatalysts. In comparison, TiO₂ supported on transparent constituents in UV-vis regions, such as porous materials [6–10] or clays [11], has also been conveyed to show greater photocatalytic reactivity than sole TiO₂. Moreover, TiO₂ particles loaded on ZSM-5 zeolite [12] as well as TiO₂ powders mechanically grinded with MOR zeolite [13] were proved for efficient removal of highly volatile acetaldehyde.

In addition, TiO₂/Y-zeolite hybrid photocatalysts [14] were used efficiently for removal of toluene or benzene molecules.

The above behavior could be explained by the fact that the zeolitic material adsorbs the organic compounds and easily supplies them onto the TiO₂ photocatalyst surface. Another advantage of zeolite-TiO₂ composite is that the adsorption capacity of the pure TiO₂ sample rapidly deteriorated, while the TiO₂/zeolite hybrid system maintained a high adsorption efficiency to remove such aromatic compounds for a long period [14]. In this research, we will study the effect of different composites of TiO₂-zeolite, namely, LTA and FAU materials, on the photocatalytic decomposing of organic dye using UV irradiation. In addition a developing system using direct sunlight was also used as a future system for photocatalytic decomposition of such systems.

2. Experimental

2.1. Materials Used. Materials used were titanium isopropoxide (Merck), LTA, FAU zeolites (synthesized from kaolin by hydrothermal treatment with NaOH), LTA zeolite chemical structure being Na₁₂Al₁₂Si₁₂O₄₈·37H₂O with pore size of 4.5 Å, FAU chemical structure being



SCHEME 1: The direct sunlight reactor.

$\text{Na}_{86}\text{Al}_{86}\text{Si}_{94.6}\text{O}_{361}\cdot 228\cdot 5\text{H}_2\text{O}$ with pore size diameter of 7.5 Å, and methyl orange (Merck).

2.2. Synthesis. Titanium isopropoxide was loaded by different wt% composition on LTA or FAU, namely, 20, 50, and 70 wt%, after which calcination at 550°C was performed.

2.3. Characterization Techniques

2.3.1. Photocatalytic Decomposition. A 100 mL of 500 ppm solution of methyl orange was mixed with 0.5 g of composite using a horizontal cylinder annular batch reactor. A xenon lamp (300 W), covered by a UV filter, was used for irradiation of the photocatalyst. The photocatalytic reaction was carried out at room temperature.

The direct sunlight reactor shown in schematic diagram 1 was used using the same previous concentration of dye and same amount of the catalyst (Scheme 1).

2.3.2. XRD (X-Ray Diffraction Analysis). X-ray diffractograms of various solids were collected using a Bruker D8 advance instrument with $\text{CuK}\alpha 1$ target with secondly monochromator 40 kV, 40 mA. Crystal lattice and space group analysis were performed using PhilipsX'Pert Plus V. 1.0 23. 04. 1999.

2.3.3. SEM and EDX Analysis. SEM images combined with EDX analysis were taken using instrument and EDX analysis was performed using instrument "JXA-840 A electron probe microanalyzer, Japan".

2.3.4. UV Visible Spectrophotometer. The decomposition of organic dye followed using UV spectrophotometer.

2.3.5. HPLC. Some selected samples were reanalyzed by HPLC system and nearly the same results of UV were obtained. Visible spectrophotometer was attained.

The HPLC system used consisted of an Alliance Waters separations module 2695, waters 2996 photodiode array

detector, and Waters 2475 multi λ fluorescence detector (Milford, MA, USA). HPLC system control and data processing were performed by Empower software (Build 1154, Waters). Screw capped V-shaped vials, 300 μL , with PTFE liners were used (Alltech, GmbH, Unterhaching, Germany). Heating oven (Heraeus, Kendro, Hanau, Germany) was adjusted at 60°C. Calibrated digital microtransfer pipettes, 5–250 μL , Brand, Wertheim, Germany, were used.

3. Results and Discussion

3.1. XRD. The XRD diffraction patterns showed that at high loading of TiO_2 (70%) only anatase phase is showed with no trace of zeolite matrix for both LTA and FAU zeolite. For low loading, in case of FAU, also only anatase phase is observed with very low trace of FAU zeolite. In contrast at low loading (20%) over LTA only zeolite matrix was observed with no trace of anatase phase.

The crystal lattice analysis (Table 1) showed that in case of 20% TiO_2 /LTA the lattice parameters slightly decreased meaning that the disappearance of anatase phase is accompanied by dissolving the TiO_2 into the LTA zeolite substituting the framework [15]. In other words the change in lattice parameters of TiO_2 loaded sample compared with pure LTA zeolite, $a = 12.28$ (pure LTA) to $a = 12.23$ (20% TiO_2 /LTA), gives indication that the TiO_2 was incorporated into the framework of zeolite.

3.2. SEM and EDX. Figures 1 and 2 showed the SEM images of different loaded samples. The images showed that in case of high loaded samples only TiO_2 agglomerate matrix was observed while for low loaded samples small agglomerate of TiO_2 is dispersed over an observable zeolite matrix. The EDX analysis was manipulated in Tables 2 and 3. From this table it is clearly observed that at 20% TiO_2 /LTA zeolite the surface TiO_2 observed by EDX analysis is much lower than those corresponding to 20% TiO_2 /FAU which supports the previous XRD analysis data that the TiO_2 is incorporated inside the framework of LTA zeolite.

TABLE 1: Crystal lattice analysis of different investigated samples.

Sample	Phase name	Degree of crystallization	Crystal system	a (Å)	b (Å)	c (Å)	Alpha (deg)	Beta (deg)	Gamma (deg)	V (Å ³)
20% TiO ₂ /FAU	Anatase	40%	Tetragonal (body centered)	3.775(17)	3.775(17)	9.55(7)	90.000000	90.000000	90.000000	136.1(13)
70% TiO ₂ /FAU	Anatase	100%	Tetragonal (body centered)	3.7787(15)	3.7787(15)	9.504(7)	90.000000	90.000000	90.000000	135.70(12)
20% TiO ₂ /LTA	No anatase crystals just LTA	0		12.2353(4)	12.2353(4)	12.2353(4)	90.000000	90.000000	90.000000	1831.66(10)
LTA		0		12.2800(4)	12.2800(4)	12.2800(4)	90.000000	90.000000	90.000000	1851.809
70% TiO ₂ /LTA	Anatase	100	Tetragonal (body centered)	3.779(5)	3.779(5)	9.486(14)	90.000000	90.000000	90.000000	135.4(3)

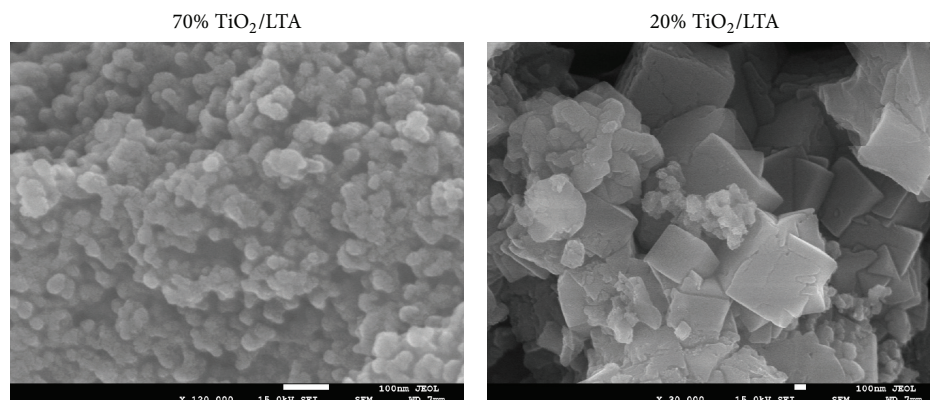
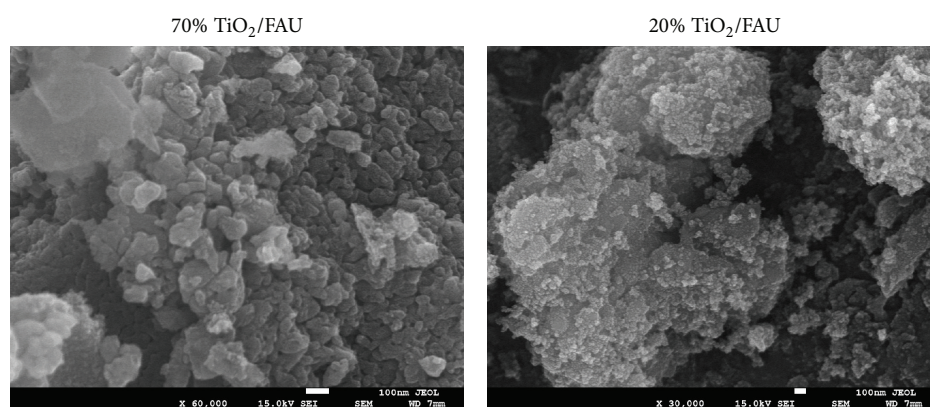
FIGURE 1: SEM of 20 and 70% loaded TiO_2 on LTA zeolite.FIGURE 2: SEM of 20 and 70% loaded TiO_2 on LTA zeolite.

TABLE 2: Elemental EDX analysis of different catalyst samples.

Sample	20% TiO_2/X	70% TiO_2/X	20% TiO_2/A	70% TiO_2/A
	wt%			
O	47.49	47.17	42.93	46.86
Na	4.59	1.60	11.51	0.86
Al	9.35	1.09	18.75	1.12
Si	18.11	2.14	25.41	3.91
Ti	20.45	48.00	1.40	47.25

TABLE 3: Oxide % EDX analysis of different catalyst samples.

Sample	20% TiO_2/X	70% TiO_2/X	20% TiO_2/A	70% TiO_2/A
	Theoretical EDX % of oxide			
Na_2O	8.75	3.04	20.17	1.62
Al_2O_3	17.81	2.07	32.86	2.11
SiO_2	34.50	4.04	44.52	7.36
TiO_2	38.95	90.85	2.45	88.92

3.3. *Photocatalytic Activity.* The photocatalytic activity kinetic curves of all samples (UV irradiated and sunlight irradiated) are presented in Figure 3. From this figure it could be observed that the two zeolites LTA and FAU showed

two different behaviors. Thus, for UV irradiation sample loaded on FAU, the catalytic decomposition activity of 20, 50% TiO_2 loaded samples showed nearly no catalytic activity while only 70% showed about 80% decomposition after nearly 50 min. This could be explained that at this critical composite ratio the adsorbed dye is easily submitted to the surface of TiO_2 while other ratios of loading the adsorbed dye are not transferred easily, which may be due to high adsorption power of FAU.

With sunlight irradiation, a dramatic change occurs that all catalytic activity increased meaning that there are new active sites activated only by sunlight (visible range); these active sites may be due to either some impurities in zeolite matrix or due to partial substitution of Ti into the framework of zeolite.

In contrast to FAU zeolite, LTA loaded with TiO_2 showed another amazing behavior. Thus, regarding the UV irradiation, a dramatic increase of 20% TiO_2/LTA up to 80% decomposition comparing with only 45% decomposition for both 50 and 70% TiO_2/LTA could be explained in the light of previous XRD and SEM and EDX data that explained for this composite ratio most of TiO_2 incorporated into the matrix of zeolite generating new active site to whole matrix accompanied by absence of any anatase phase of TiO_2 . It appeared that the catalytic activity of these new active sites is

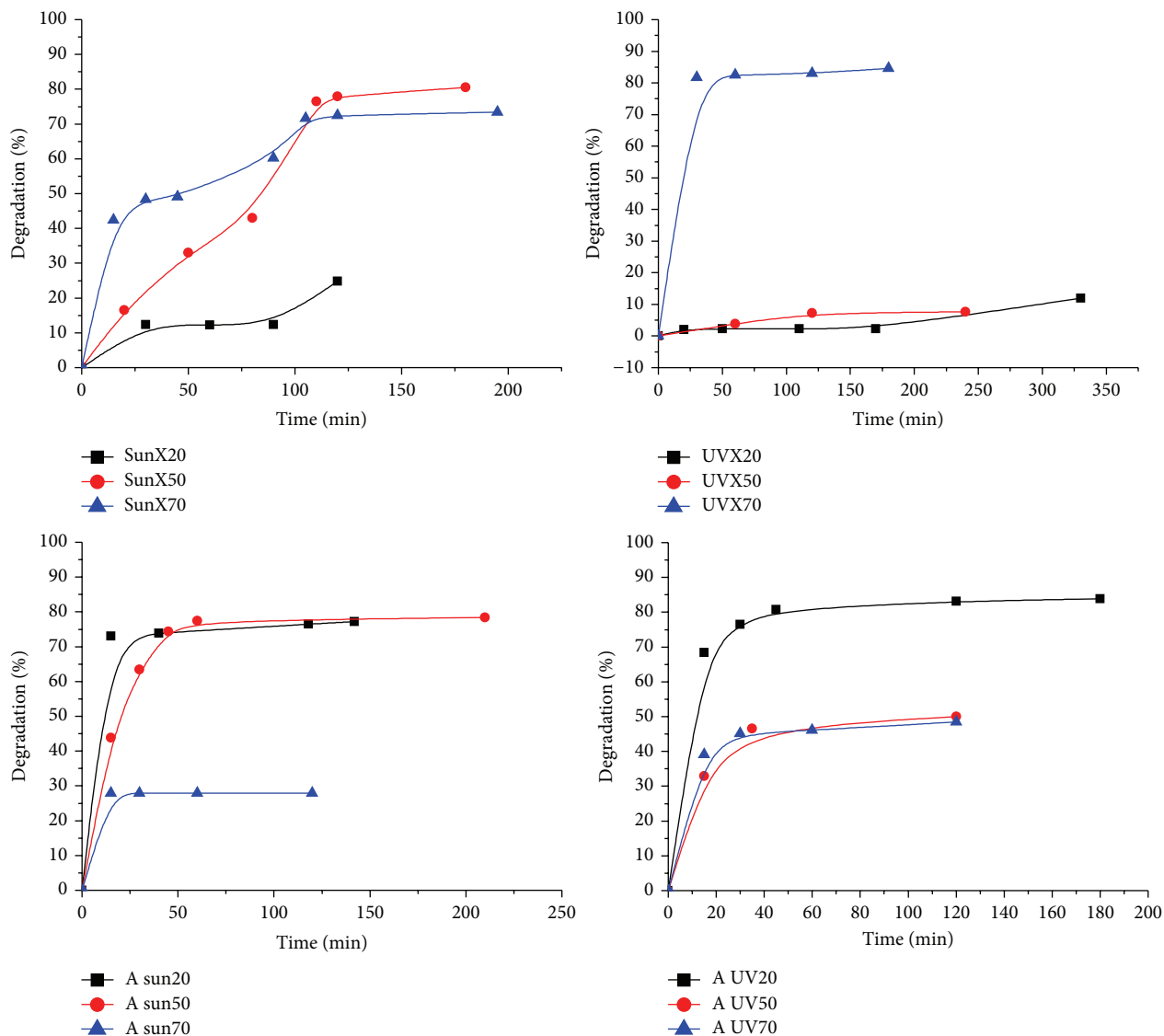


FIGURE 3: Photocatalytic kinetic curves of different samples under UV and direct sun irradiation.

much higher than that of even high loaded TiO_2 with anatase phase detected. Studying the same system under sunlight showed that catalytic activity of 70% TiO_2/LTA decreased than those values obtained by UV irradiation while 50% TiO_2/LTA increased dramatically under sun irradiation to be nearly the same with 20% TiO_2/LTA to be 75% decomposition. This could be explained by that the incorporated Ti into zeolite active sites is active in both sunlight and UV irradiation while at 50% loading both anatase phases with the new incorporated active site seemed to make a synergetic effect increasing dramatically the catalytic activity. However, pure anatase loaded on LTA (70%) is less active in sunlight.

4. Conclusions

The following conclusions could be observed from this research.

- (1) Microporous materials such as LTA and FAU could be effectively used as a good support for TiO_2 photocatalyst.
- (2) Loading TiO_2 on these supports leads to either amorphous dispersed TiO_2 or pure anatase phase of TiO_2 .
- (3) In case of low loading of LTA (20%) some XRD evidences for incorporation of some of titanium into the framework sites of zeolite were found.
- (4) More than one evidence exists of more than one photoactive site for both UV and visible irradiations.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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