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Research Article

Structural and Photocatalytic Properties of TiO_2/Zeolite Synthesized using Sol-Gel Method

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ABSTRACT

Titanium dioxide (TiO_2) is supported into natural zeolite to enhance its photocatalytic activity. TiO_2/zeolite is synthesized using sol-gel method at composition ratio of 5:95; 10:90; 20:80 and 30:70%. Structural properties are measured by X-ray diffraction showed TiO_2/zeolite in various composition has characteristic of anatase and modernite phase. The energy dispersive spectroscopy characterization shows TiO_2/zeolite containing Ti element which indicates that TiO_2 is successfully supported into natural zeolite. Vibration mode of Infrared and Raman spectra tend shifted to higher wavenumber as increasing of TiO_2 content indicating the higher energy vibration due to molecular interaction between TiO_2 and zeolite. Photocatalytic activity test toward methylene blue degradation shows that TiO_2/zeolite has higher activity than TiO_2 and zeolite itself.

Keywords: Photocatalyst, titanium dioxide, zeolite

1. Introduction

Anatase phase of titanium dioxide is well-known photocatalyst with superior activity and stability toward organic pollutant degradation. However, this photocatalyst needs to be modified due to its low adsorption capability [1], low surface area [2], agglomeration tendency and resulted in difficulty in recycling process [3]. For practical application, anatase can be supported on porous material such as silica [4], activated carbon [5], kaolinite [6], montmorillonite [7], natural zeolite [8] and synthesized zeolite [9] to overcome those limitations. Photocatalytic activity of support TiO_2 on Y-zeolite was reported to increase methyl orange degradation until 92% compared to unsupported TiO_2 (52%) [10]. The rate of reaction TiO_2/zeolite toward methyl orange degradation is faster than unsupported TiO_2 [11]. Furthermore, supporting TiO_2 on zeolite provides a stable adsorption capacity after five-time degradation process [12].

Zeolite material is one of Indonesian natural resources which exist abundantly. Supporting anatase into Indonesian natural zeolite supposed to increase its photocatalytic activity at lower cost production. Since some impurities content in natural zeolite, this material should be activated to diminish or at least to reduce the impurities content. Yulianis et al. [13] reported acid activated zeolite has higher surface area (12.238 m^2/g) than inactivated zeolite (10.469 m^2/g) so it can provide larger surface area for active component. A high content of anatase on zeolite material is known to provide a high active component during photocatalytic process. However, it would reduce the surface area of photocatalyst and tend to lessen the adsorption capacity of zeolite. Therefore, the active component ratio over supporting material has an important role in optimizing the photocatalytic process.

Photocatalytic properties of supported anatase on zeolite clearly depend on preparation method. Preparation method affected active component bounded into support material. Sol-gel technique has been applied as preparation method in this work. Sol gel provides a homogenous mixture between zeolite and titanium precursor in liquid phase. In situ reaction through sol gel process in liquid Ti precursor is applied to optimize the supporting process of anatase on zeolite surface, pore or channel. Immersing zeolite in liquid Ti precursor is supposed to increase Ti distribution on zeolite and the interfacial forces between anatase and zeolite. In this research, supported photocatalyst was synthesized at various composition of anatase TiO_2 (5-30% w/w) on zeolite to reveal the effect of anatase content on structural and photocatalytic properties of anatase/zeolite photocatalyst. Photocatalytic activity of all synthesized materials was tested in methylene blue degradation which was commonly used as dyes for coloring in textile industry.

2. Materials and Methods

2.1. Materials

Natural zeolit was supplied from Indonesia and the chemicals used were HCl 37% (Merck), titanium isopropoxide (TTIP) (Merck), isopropanol >95% (Merck), acetic acid > 90% (Merck), methylen blue (Merck), and distilled water.

2.2. Preparation of Zeolite Material

Indonesian natural zeolite was activated with HCl 6 M. Zeolite immersed in HCl solution for 24 h, then filtered, washed and neutralized with distilled water. Neutral zeolite (pH 7) dried at 80˚C (12 h) then calcined at 550˚C for 4 h and resulted in activated zeolite.

2.3. Synthesize of TiO_2/Zeolite Material

Solution of titanium isopropoxide (TTIP) in a 30 mL isopropanol was added into 5.17 mL of acetic acid. Obtained solution was stirred until gel formed and it was mixed with activated zeolite in 100 mL of water. Stirring process was continued for 4 h, then aged for 24 h at room temperature. Aging product subsequently filtered, dried (100˚C, 3 h), and calcined at 550˚C for 4 h. This supported photocatalyst was synthesized at various w/w ratio (TiO_2/zeolite) of 0/100, 5/95, 10/90, 20/80, 30/70 and 100/0.

2.4. Characterization of TiO_2/Zeolite Material

The structural properties of TiO_2, TiO_2/zeolite, and zeolite were characterized by Powder X-Ray Diffraction (XRD). Data were collected by XPert MPD Diffractometer using Cu-Kα radiation at 2θ 5-90˚. Obtained data were compared to ICSD (Inorganic Crystal Structure Database) standard for TiO_2 phase and IZA structure for zeolite phase. XRD data were subsequently analyzed by Le Bail Refinement method using Rietica program to obtain its the crystallographic data. The typical vibrational mode of structure was studied with Infrared Spectroscopy (FT 1000 Varian) at 450-4000 cm^{-1}. The vibrational mode of local structure was determined by Raman Spectroscopy (Bruker Senterra) at 30-1560 cm^{-1} with resolution ~3-5 cm^{-1} using green laser (532 nm) as the source of excitation. Photocatalytic activity was tested in methylene blue degradation under ultraviolet radiation at 0-120 min of time reaction.

2.5. Photocatalytic Activity Test of TiO_2/Zeolite Material

Sample 0.1 mg was immersed in 100 mL of methylene blue solution and irradiated with ultraviolet radiation at 0-120 min, interval 15 min. Photocatalytic activity was tested for 3 times of repetition. Methylene blue concentration was determined by UV-Vis instrumentation and was measured based on its standard calibration curve.

3. Result and Discussion

XRD pattern from all synthesized material is shown in **Figure 1**. Unsupported TiO_2 crystallized is in anatase phase while supported photocatalyst (TiO_2/zeolite) crystallized is in anatase phase and zeolite phase structure. Anatase phase is more clearly observed as increasing weight compared to zeolite content. There is no alteration on peaks caused by interaction between TiO_2 and zeolite. Further analysis on XRD data by Le Bail refinement methods resulted in that activated Indonesian natural zeolite crystallized in modernite phase with orthorombic lattice. Mordenite Crystal has *Ccmc* space group and asymmetric unit (Z) 1. Refinement result on zeolite, TiO_2 and TiO_2/zeolite samples is shown in **Figure 2** and is listed on **Table 1**. TiO_2/Zeolite refined using 2 phase standards of anathase phase and mordenite phase. Anatase phase crystallized is in tetragonal lattice, $I4_1amd$ space group and asymmetric unit (Z) 4 while mordenite phase crystallized is in same characteristic with zeolite itself.

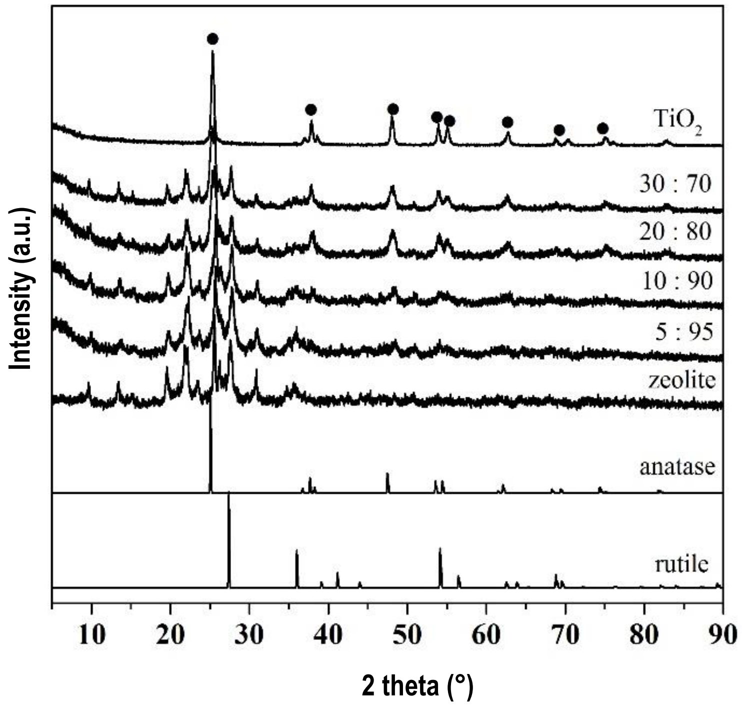

Figure 1. XRD pattern of activated zeolite, TiO_2 and TiO_2/zeolite.

Table 1. Crystallographic Data of Activated Zeolite, TiO_2 and TiO_2/Zeolite

Parameter	Sample									
	TiO_2	5 : 95		10 : 90		20 : 80		30 : 70		Zeolite
		TiO_2	Zeolite	TiO_2	Zeolite	TiO_2	Zeolite	TiO_2	Zeolite	
a (Å)	3.785	3.709	18.255	3.722	18.255	3.785	18.255	3.785	18.255	17.969
b (Å)	3.785	3.709	20.533	3.722	20.533	3.785	20.533	3.785	20.533	20.534
c (Å)	9.519	9.514	7.542	9.514	7.542	9.514	7.542	9.514	7.542	7.498
Z	4	4	1	4	1	4	1	4	1	1
V (Å^3)	136.371	130.891	2827.259	131.863	2827.259	136.299	2827.259	136.299	2827.259	2766.656
R_p	12.73	9.56		10.72		10.64		10.67		10.72
R_{wp}	10.26	12.00		12.84		11.06		12.64		15.02
GoF	0.1677	0.3223		0.3675		0.1816		0.3626		0.2357

Vibrational structure of TiO_2/Zeolite is observed by Fourier Transform Infrared (FTIR) Spectroscopy. FTIR spectra of mordenite zeolite and TiO_2/Zeolite are shown in **Figure 3**. All spectra are observed band at 1641 and 3459 cm^{-1} which are associated with bending vibration and stretching vibration of OH group. Anatase phase is shown charasteristic peaks at 1370 cm^{-1} band which is attributed to Ti-O-Ti structural network or lattice vibration and at 667 cm^{-1} which is related to symmetrical strechting Ti-O-Ti. Zeolite phase is shown characteristics vibration peak at 460, 690-795 and 1070 cm^{-1}. Band at 460 cm^{-1} is associated with bending vibration of O-Al-O and O-Si-O in AlO_4 or SiO_4 tetrahedron system. Bands at 690-795 cm^{-1} are related to symmetrical stretching vibration of T -O-T (690 cm^{-1}: Si-O-Al and 795 cm^{-1}: Si-O-Si/O-Si-O), and band at 1070 cm^{-1} is related to asymmetrical stretching of T-O-T (T: Si/Al) in external linkage. In zeolite spectra, shoulder band at 1257 cm^{-1} is detected as asymmetrical stretching of internal tetrahedron. For all TiO_2/zeolite samples, both caharacteristic spectra for TiO_2 and mordenite zeolite are also observed. It can be concluded that TiO_2 in zeolite system form composite system or physical interaction between intermolecular forces. No new peak is detected for such chemical interaction or chemical bonding formed between TiO_2 and zeolite such Ti-O-Si bonding. Band at 1070 cm^{-1} tends to be shifted as increasing of TiO_2 content. It indicates that asymmetrical stretching of external linkage increases due to strengthened bond of Ti-O-Ti bond caused by stronger intermolecular interaction between TiO_2 and zeolite.

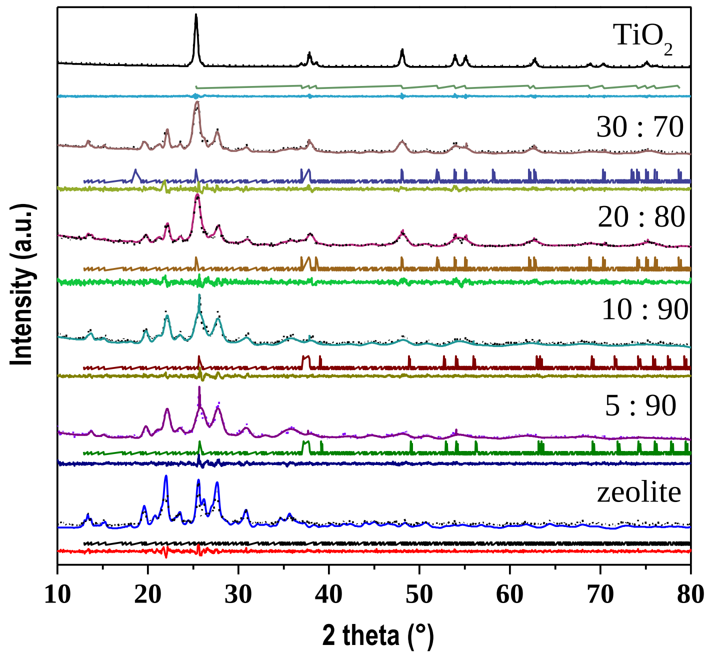

Figure 2. Plot of Le Bail refinement of activated zeolite, TiO_2 and TiO_2/zeolite.

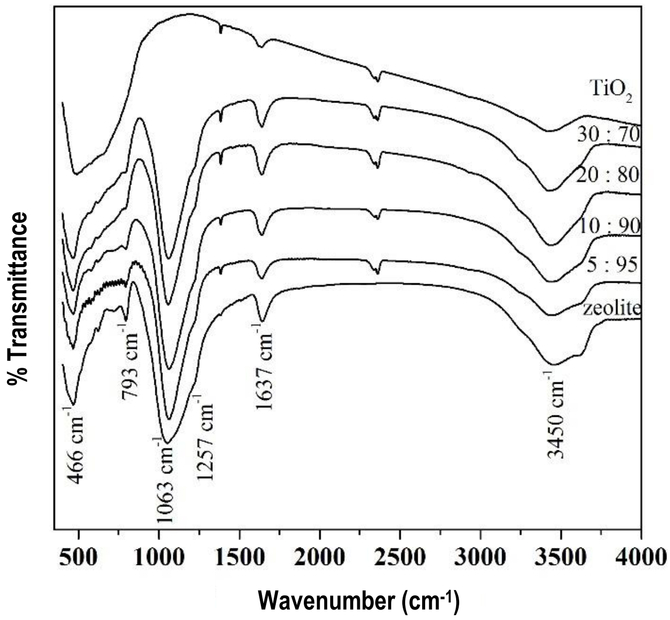

Figure 3. FTIR spectra of mordenite zeolite, TiO_2, TiO_2/zeolite at various composition.

Local vibrational structure of TiO_2/Zeolite is studied by Raman Spectroscopy. Raman spectra of all samples are shown in **Figure 4**. Raman spectra for mordenite zeolite show high fluorescence. It can be caused by various elements which are generally found in natural resources. Typical local vibration mode for TiO_2 is observed as typical mode vibration of anatase phase. The highest intensity peak at ~144 and ~637 cm^{-1} is related to local symmetric stretching vibration of O-Ti-O bond. Symmetrical bending is assigned to band at ~398 cm^{-1} and asymmetrical bending is associated with band at ~516 cm^{-1}. Raman spectra for TiO_2/zeolite at various composition show vibrational mode of anatase phase characteristic. Further insight on the highest peak at ~144 cm^{-1} shows the shifted peak to higher wavenumber as increasing of TiO_2 content compared to unsupported TiO_2. It indicates the higher energy vibration due to molecular interaction between TiO_2 and zeolite became strengthened.

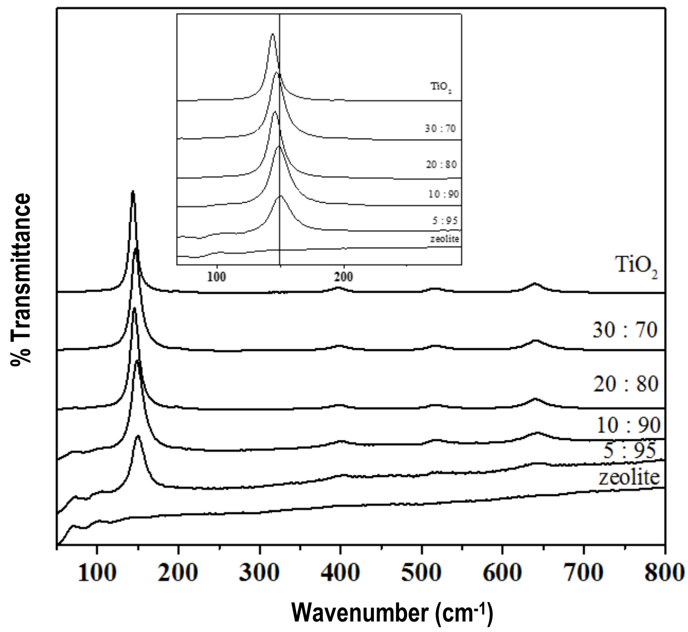

Figure 4. Raman spectra of mordenite zeolite, TiO_2, TiO_2/zeolite at various composition.

Photocatalytic activity of TiO_2/zeolite at various composition is tested in methylene blue degradation (**Figure 5**). The activity test is compared with TiO_2, zeolite and methylene blue solution without lamp and without catalyst as control. Significant degradation is obtained at 15 min reaction of photocatalytic activity and remains constant in 15-120 min of interval time reaction. Among all samples, TiO_2/zeolite (5/95%) shows the highest activity at 90% degradation. Increasing TiO_2 content on zeolite does not resulted in significant acceleration of degradation process. It may be caused by surface area catalysis which usually tend to decrease as supported material increased.

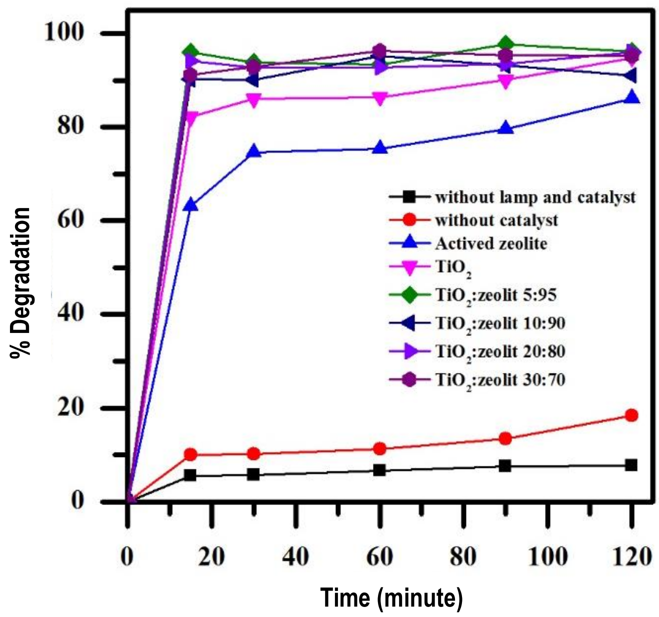

Figure 5. Photocatalytic activity test toward methylene blue degradation.

4. Conclusion

Photocatalyst of TiO_2/zeolite is successfully synthesized by sol gel methods at 5-30% w of TiO_2 ratio over zeolite. All TiO_2/zeolite photocatalysts have characteristic structure of anatase phase and mordenite phase. Vibrational mode of all TiO_2/zeolite photocatalysts are characterized as anatase and mordenite vibrational mode. Vibrational mode of TiO_2/zeolite has higher energy vibration due to the strengthened molecular interaction between TiO_2 and zeolite. Among various composition, TiO_2/zeolite at composition 5/95% weight ratio has the highest activity toward methylene blue degradation.

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