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The Effect of 2-propanol on The Shifting Band Gap of ZSM-5-TiO_2 Composite Prepared Via Sol-Gel Method

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Abstract

ZSM-5 is a material that has a pore of 0.53 nm and high acidity that can be used as an adsorbent in the waste treatment process. The modification of ZSM-5 with the addition of metal oxide (TiO_2) will give the catalyst alloy properties i.e. photocatalysis by TiO_2, supported by ZSM-5 properties, i.e. large external surface, large pore volume and mesoporous volume. A mixed precursor containing Titanium(IV) isopropoxide and ZSM-5 was used to prepare ZSM-5-TiO_2 composite through sol-gel method. The effect solvent on material structure was studied. The results revealed that the materials have crystal structure of anatase TiO_2. Furthermore, 2-propanol as solvent has little effect on shifting band gap 0.05 eV. The materials can be considered as a perspective material in catalyst and its material can be a subject of further investigations.

INTRODUCTION

Titanium dioxide (TiO_2) mediated based photodegradation have advantages in the complete removal of organic pollutants from wastewater, such as good optical-electronic properties, low-cost, chemical stability, and nontoxicity [1]. Despite its advantages, the energy bandgap of TiO_2 in 3,2 eV makes its only active in UV light region [2]. Beside that, TiO_2 easy recombination of electron pairs and holes [3] thus limiting its usage and efficency in its application in real life (sunlight lumination) [2].

The modification of TiO_2 for improving absorption in visible light region has become one of the actively researched topics in the field of photocatalysis. One approach is to use either anion or cation dopants (main group elements, transition metals, or rare earth metals) into the TiO_2 structure. However, these doped systems are thermally unstable [4] and enhanced the rate of recombination of the photo-produced electrons and holes [5]. Therefore, TiO_2 photocatalyst can be enhanced performance with adding substrate. Substrates that have been commonly used include CNTs [3], MOF [6], zeolite [7,8], TUD-C [9] with various applications.

Zeolite is a material having surface area with high active side, has photochemical stability and can work on UV-Vis radiation. Zeolites have the cavity range of 3-15Å, uniform micropore networks in molecular dimensions can selectively accommodate molecules, the shape of zeolites and the effect of molecular sieve selectivity play an important role in catalyst applications [10].Based on these advantages, zeolite is an alternative material as a support of TiO_2 photocatalyst [3]. ZSM-5 has pore (5.3Å), particle size (hundreds of nano to micro size), and it is easily synthesized using the natural resources such as kaolin bangka as silica source so can reduce the costs of synthesis and the calcined ones [11, 12]. When ZSM-5 is coupled with TiO_2 (3nm), TiO_2 dispersed unevenly on the surface of ZSM-5 so that it will only affect the surface area external, mesoporous pore volumes and volumes become larger [13], but are randomly assigned and not well organized and uncontrolled. Getting TiO_2 coated on ZSM-5 with high regularity and evenly it should use different techniques with the above techniques. The hypothesis of this technique

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is carried out by adding a precursor TiO_2 compound such as alkoxy titania which can be evenly distributed in the ZSM-5, so that when the precursor is converted to TiO_2 by heating it will be obtained a well-balanced composite ZSM-5-TiO_2 and cause external pore which is more regular with meso size. The properties of the ZSM-5-TiO_2 composite that the presence of TiO_2 to the ZSM-5 surface will increase the conductivity of water molecules so that the ZSM-5-TiO_2 composite has high hydrophilic properties [14].

The amount of TiO_2 on ZSM-5-TiO_2 composite can be controlled by addition 2-propanol as solvent. In this work, the role of 2-propanol was evaluated on crystal growth and the shifting band gap of ZSM-5-TiO_2 composite.

EXPERIMENTAL

Material

The materials used in this study were titanium dioxide (TiO_2) (98%, Acros Organic) as reference, titanium(IV) isopropoxide (TiIP) (97%, Aldrich) as precursors TiO_2, aluminum oxide (Sigma-Aldrich), ZSM-5 with Si/Al = 50 (Acros Organic), 2-propanol (97%, Merck).

Preparation of ZSM-5-TiO_2 Composite Via Sol-Gel Method

A mixed precursor containing Titanium(IV) isopropoxide (TiIP) and ZSM-5 was used to prepare ZSM-5-TiO_2 composite (TPZ) through sol-gel method. TiIP added dropwise to 2-propanol in a vapor plate on hot plate equipped with a magnetic stirrer. The solution then stirred 60 rpm for 5 minutes at room temperature. The next step was the addition of ZSM-5 followed by stirring 60 rpm at room temperature until gel formed. The gel then aged for several minutes until white powder formed. The resulted powder was then calcined in 550°C for 3 hours.

Characterization methods

X-Ray Diffraction (XRD)

XRD was used for phase identification of a crystalline material (ZSM-5-TiO_2 composite). Solids were placed on a sample holder and fed into the diffraction XRD equipment at 2ϴ 5-50°. The XRD parameter was used Cu Kα radiation (λ = 1.5406 Å), with a voltage of 40 kV and a current of 30 mA.

Fourier transform infrared (FTIR) Spectroscopy

FTIR was used to analyze the function group in TiO_2, ZSM-5, and ZSM-5-TiO_2 composite. The FTIR spectra were recorded on 8400 Shimadzu from KBr pellets at room temperature. All FTIR spectra were measured over a wave number range 4000 – 500 cm^{-1} in transmittance mode.

Diffuse Reflectance UV-Vis (DR-UV)

DR-UV was carried out on Perkin-Elmer spectrometer (wavelength 19) equipped with an integrated spherical embossment. DR-UV was used to characterize optical properties, such as band gap value.

RESULT AND DISCUSSION

XRD analysis

The XRD patterns of ZSM-5 and different TiO_2 content supported in ZSM-5 are shown in Fig 1. ZSM-5 zeolite shows the characteristic peaks of MFI structure in the range 7-10° and 22-35°. TiO_2 shows typical diffraction patterns attributes to the (101) phase at around 25.3°; (113), (004), (112) phase at around 37.5° and (200) phase at around 47° of an anatase structure. As observed, all the incorporation of TiO_2 on ZSM-5 exhibit diffraction peaks of ZSM-5 and TiO_2 (at 25.3), also no crystalline pattern was observed, which might be because of the fine distribution of in the lattice. It appeared that incorporation of TiO_2 had little effect on the crystalline structure of the host zeolite. The peak at 25.3 (anatase) of TiO_2 was almost concident with 25.2 of ZSM-5, and the peak width broadening as TiO_2 loading increased, which attributed to the process of two-phase mixing. On the other hand, the gradual increase in the intensity of TiO_2 peaks and the corresponding decrease in the intensity of ZSM-5 peaks clearly indicating the increase in TiO_2 loading on the surface of the zeolite framework. At the lower coverage (2.5-5%), the diffraction patterns for the ZSM-5 zeolite is sharper than TiO_2, showing the largely grown zeolite crystals. While at the high coverage of titanium (10%), the anatase peaks approach the line narrowness characteristic of the well-formed crystals.

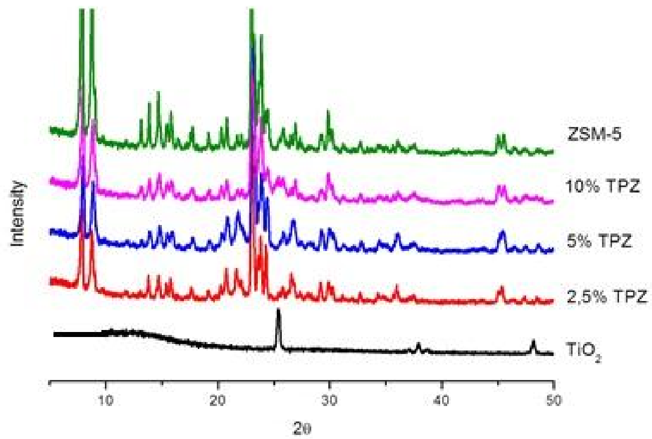
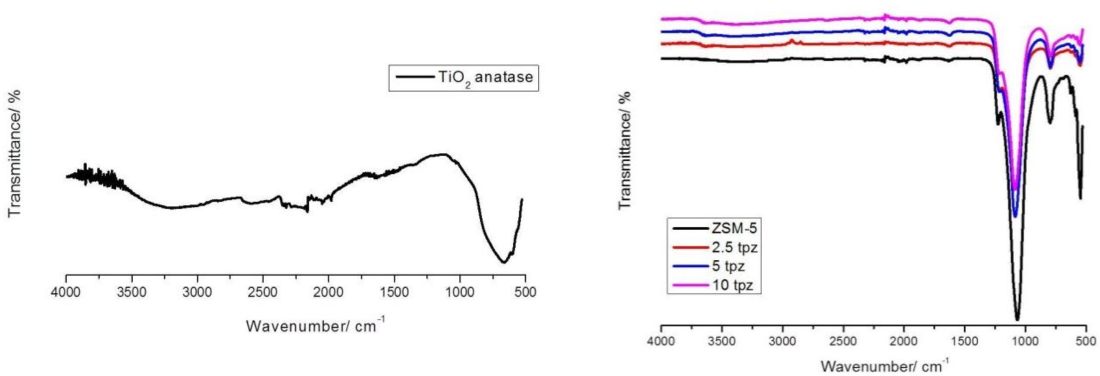


FIGURE 1. XRD patterns of ZSM-5 and different TiO_2 content supported in ZSM-5

FTIR analysis

Figure 2 shows FTIR ZSM-5 spectra with four peaks of wave numbers around 545, 792, 1090 and 1222 cm^{-1}. The absorption bands that appear around 1200-1000 cm^{-1} show the internal bond tetrahedral vibration of the asymmetric strain of Si-O-T where T is Si or Al. The external asymmetry stretching vibration is indicated by the absorption band at 1200 cm^{-1} while the internal asymmetry stretch vibration is indicated by the 1100 cm^{-1} absorption band. The absorption band of about 788 cm^{-1} shows internal vibration. The five ring in the zeolite structure of ZSM-5 can be shown from the absorption band at about 546 cm^{-1}. The existence of ZSM-5 can be determined by the appearance of peaks in these areas. On the FTIR spectrum of ZSM-5-TiO_2 composites (TPZ) have the same peak on ZSM-5 and absorption peak between 600cm^{-1} indicates TiO_2. The ZSM-TiO_2 composite (TPZ) have an absorption peak at a wave number of about 1600cm^{-1} indicating the presence of C=C. This suggests that 2-propanol contributes a small amount of carbon in the ZSM-5-TiO_2 composite.



(a) (b)

FIGURE 2. Spectra IR of (a) TiO_2 and (b) different TiO_2 content supported in ZSM-5

Diffuse Reflectance UV-Vis (DR-UV) Spectra

The UV-Visible absorption spectra of the prepared samples were measured to study the optical properties of ZSM-5-TiO_2 composites (TPZ) shown in Figure 3. All the absorbance intensity of the samples has different values and it is clearly shown that the absorbance intensity does not influence the value of the absorption edge. This can be resolved by extrapolating the linear drop of the spectra towards the horizontal axis. As it can be seen, ZSM-5-TiO_2 composites (TPZ) exhibit a significant shift of the absorption edge toward the visible region compared with a reference, which is slightly lower. This shifting is called red shift, where there is an increase of wavelength. It can be deduced that the role of 2-propanol on the shifting band gap of ZSM-5-TiO_2 composite so effect the band gap value and its potential application as a visible light active photocatalyst.

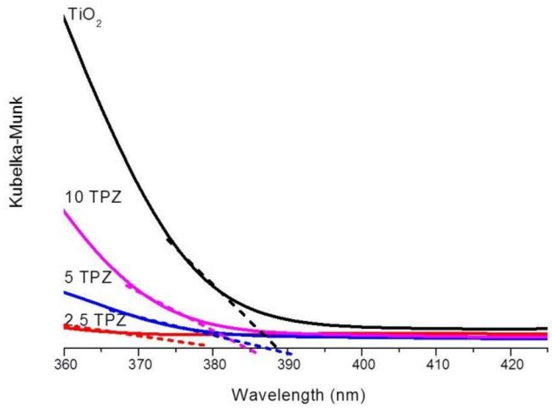


FIGURE 3. UV-Vis diffuse reflectance spectra of TiO_2 and different TiO_2 content supported in ZSM-5

The values of the indirect energy gap (Eg) for all the ZSM-5-TiO_2 composites (TPZ) samples with the reference were accordingly determined by the linear extrapolation of the high slope of the corresponding curve (Figure 3) and are presented in Table 1.

TABLE 1. Energy Gap of Samples as Calculated from UVDR Spectra

Samples	Wavelength (nm)	Eg (eV)
TiO_2	388	3.20
2.5% TPZ	380	3.26
5% TPZ	390	3.18
10% TPZ	385	3.22

The more 2-propanol is added, the more TiO_2 is contained in the ZSM-5-TiO_2 composite, but does not affect the bandgap value. The shifting ZSM-5-TiO_2 composites (TPZ) band gap value 0.05 eV, briefly. Band gap value for 5% TPZ is the optimum value so its potential application as a visible light active photocatalyst..

CONCLUSION

A mixed precursor containing Titanium(IV) isopropoxide and ZSM-5 was used to prepare ZSM-5-TiO_2 composite through sol-gel method. The effect solvent on material structure was studied. The results revealed that the materials have crystal structure of anatase TiO_2. Furthermore, 2-propanol as solvent has little effect on shifting band gap 0.05 eV. The materials can be considered as a perspective material in catalyst and its material can be a subject of further investigations.

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