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THE EFFECT OF DIFFERENT TYPES OF SOLVENTS ON MORPHOLOGY OF CARBON-MODIFIED TiO_2/H-ZSM-5 COMPOSITE

Djoko Hartanto[1,✉], A.K. Indrawan[1], Ani Iryani[2], Afifah Rosyidah[1], A.I. Rozafia[1] and A.R. Widyanto[1]
[1]Department of Chemistry, Faculty of Science and Data Analytics, Institut Teknologi Sepuluh Nopember, Sukolilo, Surabaya 60111, Indonesia
[2]Department of Chemistry, Faculty of mathematics and natural Science, University of Pakuan Bogor
✉Corresponding Author: djokohar@its.ac.id

ABSTRACT

This study aims to investigate the effects of different solvents (isopropanol, benzene, and toluene) on the synthesis of carbon-modified TiO_2/H-ZSM-5 composites. Carbon-modified TiO_2/H-ZSM-5 composites were characterized by FTIR, XRD, and SEM. XRD analysis revealed that the TiO_2 peaks at 2 = 25.3, 37.8, and 48.2° had distinct characteristics. FTIR analysis revealed that I-ZTC, B-ZTC, and T-ZTC had comparable absorption bands to ZSM-5 at 3464, 1639, 1222, 1097, and 545 cm^{-1}, respectively. Additionally, the FTIR data revealed that I-ZTC, B-ZTC, and T-ZTC all display absorption bands around the wavenumber 450 cm^{-1}, indicating the Ti-O bond's stretching vibration. Additionally, SEM-EDX analysis revealed that Ti was more evenly distributed on the surface of T-ZTC than on the surfaces of B-ZTC and I-ZTC. It was shown that the solvent's polarity has an effect on TiO_2 dispersion. A less polar solvent disperses TiO_2 more effectively. In terms of TiO_2 dispersion, toluene was the preferable solvent for the production of carbon-modified TiO_2/H-ZSM-5.

Keywords: Morphology, Composite, ZSM-5, TiO_2, Dispersion.
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INTRODUCTION

Zeolite was a hydrated aluminosilicate crystal comprised of group IA and IIA elements, mainly Ca and Na. Zeolites have complex structures, notably tetrahedral polymers of AlO_4 and SiO_4 that are extended to infinity, thereby generating a large cavity. Zeolite has a uniform framework, a large pore volume, excellent thermal stability, and high porosity with an average pore size of around 1-10.[1,2] Zeolite Socony Mobil-5 (ZSM-5), a zeolite, has a 5 Å pore width channel with a moderate Si/Al ratio (5/1). ZSM-5 is utilized as a catalyst in the oil refining and petrochemical sectors. In the area of catalysts, ZSM-5 is considered to be a heterogeneous catalyst as it possesses both Bronsted and Lewis sites. ZSM-5 is a multifunctional catalyst that could be employed in a range of processes, including alkylation, isomerization, catalytic cracking, and hydrolysis.[3] Another use of ZSM-5 could be employed as membrane filler.[4] ZSM-5 has outstanding properties such as chemical and thermal stability, non-toxicity, a wide surface area, and cations that may undergo exchange. Hence, these properties can be used as ion exchangers and adsorbents.[5,6] On the other hand, surface area affects the adsorption capabilities of ZSM-5 since the surface area is directly related to adsorption capacity. Modified H-ZSM-5 could enhance the surface area by the introduction of a secondary pore in ZSM-5. Lima *et al.*[7] reports that the hierarchization process by desilication improves the specific surface area of ZSM-5 from 418 to 450 $m^2 g^{-1}$. It is a hierarchical zeolite with mesopores (up to 2 nm) that has several advantages over unmodified zeolite, including increased outer surface area, an abundance of active sites, a shorter diffusion route, and excellent hydrothermal durability.[8–10] One simple method is post-treatment by alkaline methods, which reduce the silica content with a base solution.[11] In addition, this is widely regarded as one of the most practical and cost-effective procedures for creating intra-crystalline and/or inter-crystalline secondary porosity.[12] While the ZSM-5 hierarchy shows promise in color adsorption, it has limitations since it takes extra steps to clean adsorbents polluted with dyes. To address

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these issues, various investigations have been conducted using ZSM-5 composites with photocatalyst materials to degrade the adsorbed color component without the need for extra treatment procedures. TiO_2 is a common photocatalyst ingredient used in ZSM-5 composites. TiO_2 is highly photocatalytic, non-toxic, and cheap.[14,15] Furthermore, employing 2-propanol as a solvent to synthesize H-ZSM-5-TiO2 composites has been demonstrated to lower band-gap energy, but not significantly.[16] Zhang *et al.*[17] suggest that doping TiO_2 may be used to reduce the band-gap energy of TiO_2. Metal dopants are regarded as less eco-friendly due to secondary pollution, thus non-metallic dopants including carbon, nitrogen, and boron are suitable alternatives.[18] Furthermore, carbon doping involves adding external carbon sources or changing the technique, which takes place under a nitrogen atmosphere in order to obtain a source of carbon from the precursors of alkoxide.[19,20] Thus, in this study, observations were made on the effect of the use of solvent types on the unification of H-ZSM-5 with TiO_2 in the synthesis of composites TiO_2/H-ZSM-5 hierarchy of modified carbon.

EXPERIMENTAL

Material

Sodium hydroxide, ZSM-5 (Pingxiang Naike Chemical, Jiangxi, China with a Si/Al ratio of 50), aqua DI, Whatman filter paper number 40, nitrogen gas (N_2), titanium (IV) isopropoxide (Sigma-Aldrich, 97%), isopropanol (Sigma-Aldrich), toluene (Sigma-Aldrich), and benzene (Sigma-Aldrich) were utilized in the investigation.

Synthesis of H-ZSM-5

ZSM-5 pore modification is done through post-synthesis methods by reacting ZSM-5 and NaOH. The First 100 mL NaOH 0.25 M in a polypropylene bottle is heated at 65 °C for 10 minutes with an oil handler. Then added 3 grams of ZSM-5 pretreatment resulted into a solution of NaOH that has been warm. For 30 minutes, the mixture is agitated using a magnetic stirrer. After the stirring is finished, the reaction is halted by immersing a polypropylene bottle holding a solution of ZSM-5 and NaOH in an ice handler until the solution reaches ambient temperature. After the mixture has cooled enough, it is filtered. The remainder of the residue is then rinsed with aqua DI to neutralize the pH. The neutralized residue is evaporated for 12 hours at a temperature of 105 °C in an oven. After the solids have dried, the materials are dissolved with CH_3COOH 1M that has been preheated to 65 °C for 10 minutes. For 30 minutes, the mixture is agitated using a magnetic stirrer. After the mixing stage is finished, the reaction is terminated by immersing a polypropylene bottle holding a solution of ZSM-5 desilication and CH_3COOH in a nice handler until the solution reaches room temperature. After the mixture has cooled enough, it is filtered. The remainder of the residue is then rinsed with aqua DI to neutralize the pH. The neutral residue is then dried for 12 h at 105 °C. The resultant solid is denoted Na-ZSM-5. After that, Na-ZSM-5 is reacted with CH_3COONH_4 at 60 °C to initiate the cation exchange reaction. Under closed circumstances, 3 grams of Na-ZSM-5 hierarchy is reacted with 60 mL CH_3COONH_4 1M using a succession of reflux devices. The reaction is allowed to run for three hours before being halted and filtered. After obtaining the residue, it is rinsed with aqua DI. The washed residue is then heated for 12 hours at 105 °C. The resultant solid is designated NH_4-ZSM-5. The NH_4-ZSM-5 hierarchy is converted to the H-ZSM-5 hierarchy by a 6-hour calcination procedure at 550 °C.

Synthesis Carbon Modified TiO_2/H-ZSM-5

Carbon-modified H-ZSM-5-TiO_2 composites were synthesized in this work using the gel sol technique without the addition of water while using a variety of organic solvents (isopropanol, benzene, and toluene). A total of 4.9 mL of Titanium (IV) isopropoxide as a precursor to TiO_2 is dissolved in each kind of organic solvent with a ratio of TTIP volume: isopropanol is 1:14. Then, the TTIP mixture is stirred with a magnetic stirrer for 20 min. The TTIP mixture is added 2 grams of H-ZSM-5 and stirred back with a magnetic stirrer for 2 h. After 36 hours of aging at ambient temperature, the soles are placed in the oven according to their boiling temperatures.

Furthermore, calcination is carried out using a furnace (10°C/min heating rate) at a temperature of 500ºC under nitrogen gas flow (gas flow rate of 1 L/min) for 3 h. The resulting materials of carbon-modified TiO_2/H-ZSM-5 were notation by I-ZTC for isopropanol solvent, B-ZTC for benzene solvent, and T-ZTC for toluene solvent. In addition, an overview of the scheme this study illustrates in Fig.-1.

Materials Characterization

The carbon-modified TiO_2/H-ZSM-5 composites were characterized by XRD (X'Perd MPD (PANalytical)), FTIR (Fourier Transform Infra-Red 8400S (Shimadzu)), and SEM-EDX (Scanning Electron Microscopy EVO® MA 10 - Quantax Energy Dispersive X-Ray (Bruker)). XRD was used to obtain the crystallinity and crystal structure of the composite formed. X-rays that are fired are the result of radiation from Cu Kα (λ = 1.5406), using a 40 kV accelerating voltage and a 40-mA current. The analysis was performed at an angle of 2θ from 5-60° with a scanning interval of 0.017°. FTIR was employed to characterize the carbon-modified TiO_2/H-ZSM-5 composite's functional groups and bonds. The composite sample was ground with KBr powder at a ratio of 1:9 in a mortar until homogenous. In addition, SEM-EDX was utilized to observe the morphology, size, shape, and composition of the synthesized elements. Sample preparation was coated with Au-Pd (Gold-Palladium).

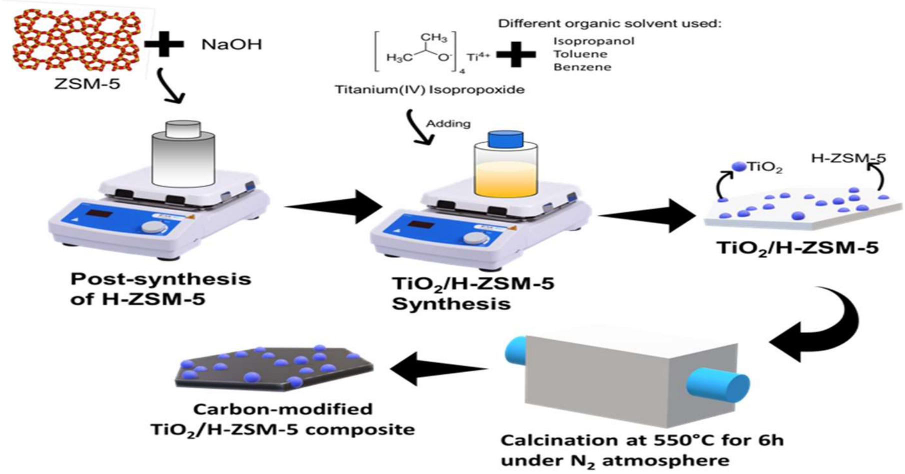

Fig.-1: Schematic illustration of this Study

RESULTS AND DISCUSSION

XRD Characterization

XRD analysis is done to find out the crystal phase of the sample. Figure-2 exhibited a diffractogram of composites. The characteristic peak of ZSM-5 was at about 2θ: 7.87, 8.84, 22.98, 23.29, and 23.89 ° (JCPDS No. 00-049-0657). The characteristic peak of TiO_2 anatase is around 2θ: 25.3, 36.9, 37.8, 38.61, and 48.2 ° (JCPDS No. 96-900-8214). Moreover, it demonstrated that the sample of I-ZTC, B-ZTC, and T-ZTC retained the same structure as ZSM-5, as proven by the existence of the ZSM-5 structure's characteristic peak. Therefore, it suggested that the addition of TiO_2 did not affect the ZSM-5 phase. The typical peaks of TiO_2 anatase were observed at low intensity. The characteristic peak intensity of TiO_2 is seen to be lower than the peak intensity characteristic of ZSM-5 due to the low percentage of TiO_2 use. According to Mohamed and co-workers,[21] TiO_2 intensities were directly proportional to the increasing percentage of use of TiO_2. Furthermore, the characteristic peak of TiO_2 in the T-ZTC sample looks more significant compared to B-ZTC and I-ZTC. It was difficult to observe in a diffractogram but could be observed in intensity comparison in Table-1.

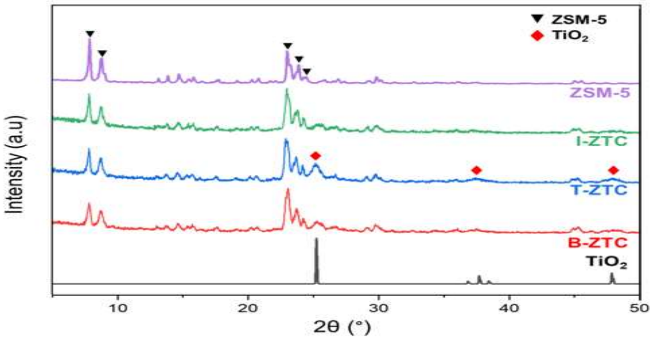

Fig.-2: XRD Diffractogram of Carbon Modified TiO_2/H-ZSM-5 with Different Solvent Use

Table-1: Comparison of Intensity of Each Sample

No.	Angle (°)	Intensity (cps)		
		I-ZTC	T-ZTC	B-ZTC
1	25.31	82.97	264.99	171.07
2	37.6	16.54	51.14	43.15
3	48.2	22.70	60.46	34.95

FTIR Analysis

Characterization with FTIR was done to find out the functional groups contained in the composite (Fig.-3). The characteristic uptake band ZSM-5 was found at wavenumbers 3464, 1639, 1222, 1097, and 545 cm[1].[3,22–24] The absorption band peak at 3464 cm-1 corresponded to the hydroxy group (-OH) vibration, while another absorption band peak at 1639 cm^{-1} corresponded to the bending vibration of the hydroxy group (-OH). The vibration of T-O-T occurred at wavenumbers 1222-1097 cm^{-1}, where T could be either Si or Al.[25] The peak at 545 cm^{-1} corresponds to the five membered ring of the pentasil structure, the zeolite's structural unit with the MFI frame. TiO_2 has a distinctive uptake band between 3500-3000 cm^{-1} and 900-500 cm^{-1}.[26] The absorption spectrum between 3500-3000 cm^{-1} corresponded to the vibration of the hydroxyl group (-OH), while the absorption band between 900-500 cm^{-1} corresponding to the stretching vibration of the Ti-O and Ti-O-Ti groups.[27] The distinctive uptake band TiO_2 has a wavelength of 450 cm^{-1} and corresponds to the stretching vibration of Ti-O.[26]

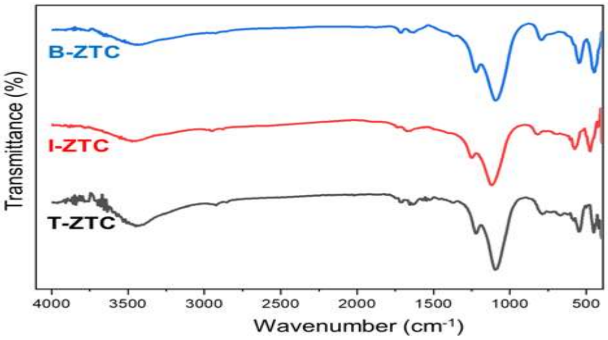

Fig.-3: FTIR of Carbon Modified TiO_2/H-ZSM-5 with Different Solvent Use

Scanning Microscope-Energy Dispersal Spectroscopy (SEM-EDX) Observation

SEM-EDX characterization was done to determine the composite morphology. Figure-4 exhibited the micrographs I-ZTC(a), B-ZTC(b), and T-ZTC (c). The image presented some morphological similarities between the three composites in the form of multilayer hexagonal objects thought to be ZSM-5. The EDX observation of all three composites revealed the presence of C and a variety of Ti, as shown in Table-2. The T-ZTC composite has the highest percentage of Ti mass at 1.82% and the highest C at 14.32%. While the composition of the lowest mass of Ti is owned by the sample of I-ZTC and the composition of the lowest C mass is owned by the B-ZTC sample.

Table-1: Composition of Elements C and Ti in Composites

Materials	Mass%	
	Ti	C
I-ZTC	1.74	8.17
T-ZTC	1.82	14.32
B-ZTC	1.78	7.39

The existence of ZSM-5 is indicated by the element Si which is characterized by bright blue dots while the existence of TiO_2 is indicated by the element Ti which is marked by purple dots. The difference in the distribution of Ti elements in each composite can be seen in Fig.-4. The distribution of Ti on the surface of ZSM-5 on the I-ZTC is less evenly distributed and tends to congregate at only a few points. The distribution of Ti on the T-ZTC on the surface of the ZSM-5 was more diffuse indicated by the purple dots that are a tenuous distance from each other. Since isopropanol is more polar than benzene and toluene, suggesting TTIP hydrolyze faster before TTIP can spread on the surface of ZSM-5 evenly.

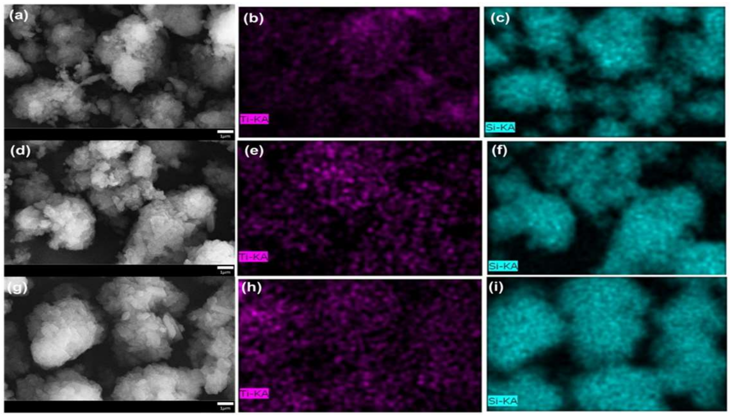

Fig.-4: SEM-EDX Micrographs and Mapping of (a) T-ZTC, (b) Ti, (c) Si Element; (d) I-ZTC, (e) Ti, (f) Si Element; and (g) B-ZTC, (h) Ti, (i) Si Element

CONCLUSION

The sol-gel approach was effectively used to produce the carbon-modified TiO_2/H-ZSM-5 composite. T-ZTC had the greatest intensity of TiO_2 anatase as determined by XRD analysis. The FTIR analysis revealed that there was no structural degradation to ZSM-5 with the addition of TiO_2. The SEM-EDX characterization findings indicate that T-ZTC has the most uniform distribution of Ti elements. It suggests that toluene is a more suitable solvent for the carbon-modified TiO_2/H-ZSM-5 synthesis.

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