Mesostructured Titanosilicates Catalyst for Synthesis of Vitamin K3

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Abstract

Titanium silicalite-1 (TS-1) is the outstanding catalyst for selective oxidation of various organic compounds with aqueous H\textsubscript{2}O\textsubscript{2}. However, one disadvantage of TS-1 is that their pore size are too small for access by bulky reactants. In this paper, we report the synthesis of mesoporous TS-1 using cetyltrimethylammonium bromide as a mesoporous template. The mesoporous TS-1 are being expected to overcome the limited accessibility of bulky molecule. Various techniques including X-Ray Diffraction, Fourier Transform Infrared, N\textsubscript{2} adsorption-desorption, pyridine adsorption-FTIR, and Scanning Electron Micrographs were employed for material characterization. The catalytic activity of the prepared materials was tested in the synthesis of vitamin through oxidation reaction of 2-methyl naphthalene using aqueous H\textsubscript{2}O\textsubscript{2} as oxidant and acetonitrile as a solvent.

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Introduction

TS-1 is the excellent catalytic oxidation under mild conditions using H\textsubscript{2}O\textsubscript{2} as oxidant. However, the limited accessibility of the TS-1 due to their microporous nature (pore diameter < 2 nm) disables them to process large molecules (Stevens et al., 2007). In order to overcome this problem, many research have been developed the titanium containing mesoporous material. Incorporation of titanium into the framework mesoporous material (MCM-41, MCM-48, HMS, MSU, and SBA-15) have been done. Because of their large pores, they accommodate bulky substrates which cannot enter into the microporous zeolite. Unfortunately, compared with TS-1, the titanium containing mesoporous materials, particularly Ti-MCM-41 have relatively low oxidation and hydrothermal stability (Eimer et al., 2009). Therefore, novel mesoporous TS-1, which are capable of exhibiting high stability as well as high catalytic oxidation activity, are being expected to overcome the limited accessibility of bulky molecule such as vitamin K3.

Vitamin K3 is a synthetic vitamin K which has antihemorrhagic and antitumor activity (Zhou et al., 2008). In a well-known process, vitamin K3 is synthesized by oxidation of 2-methyl naphthalene using catalyst H\textsubscript{2}SO\textsubscript{4}, HClO\textsubscript{4}, carboxylate acid, acid anhydride, Ti-MMM-2 (Kholdeeva et al., 2007), Ti-MCM-41 (Anunziata et al., 2004) and metal complexes (Zalomaeva et al., 2007). Oxidation of 2-methyl naphthalene using Ti-MCM-41 was studied: the conversion of 2-methyl naphthalene was 60% and the selectivity of vitamin K3 even reached 90% (Anunziata et al., 2004), using CrO\textsubscript{3} as oxidant and H\textsubscript{2}SO\textsubscript{4} catalyst give the vitamin in 40 to 50% (Kholdeeva et al., 2007). This process have some disadvantages like chrome toxicity, waste, and high cost. As a green chemistry of oxidant, H\textsubscript{2}O\textsubscript{2} is can be an alternative oxidant because of high oxygen active, and only produce water as a byproduct.

In this paper, we reported the activity of mesoporous TS-1 to oxidize 2-methyl naphthalene using H\textsubscript{2}O\textsubscript{2}. Mesoporous TS-1 is a potential catalyst because it has similar structure with Ti-MCM-41 and better hydrothermal stability than the other mesoporous material (Cheneviere et al., 2010).

Methodology

Catalyst preparation

TS-1 was prepared by using tetraethylorthosilicate (TEOS, Merck 99%) as a silicon source, tetraethylorthotitanate (TBOT, Merck 99%) as a titanium source, tetrapropylammoniumhydroxide (TPAOH, Merck 40%) as a framework template, and cetyltrimethylammoniumbromide (CTABr, Applichem 99%) as a meso template. The synthesis procedure used in this work is similar to that presented by Eimer et al (2008). In addition, TS-1 was synthesized using hydrothermal time for 4 day at 80 °C.

Catalyst characterization

The solid structure was characterized by powder XRD for the crystallinity and phase content of the solid materials using JEOL JDX-3530 with the Cu Ka (λ = 1.5405 Å) radiation as the diffracted monochromatic beam at 40 kV and 30 mA. The sample was scanned in the 2θ range between 1.5 and 40° with step scan...
previous step of mesoporous material forming using surfactant as template is the forming of CTABr micelle surfactant. When the surfactant concentration is increased, the spherical micelles begin to pack together to form a cubic phase. If concentration is further increased, the micelles change from spherical to rod shaped. These rod shaped micelles tend to arrange themselves into a hexagonal phase. As concentration is still further increased, these rod micelles change again and become flat bi-layer sheets. This arrangement is known as the lamellar phase. The next step is the removal of CTABr template by calcination so that forms a porous material because loss of its template from structure (Campbell, 2006).

Results and Discussion

The synthesis procedure used in this work is similar to that reported by Eimer et al. (2008). TS-1 is a sequence of Si-O-Ti which forms MFI structure. In this work, the TBOT and TEOS were used as source of titanium and silicon, respectively. TPAOH acts as the structure directing agent and provides the alkalinity in the synthesis of TS-1, while CTABr surfactant was used a mesophasic template. At the synthesis process, before TEOS mixed with TBOT, TBOT must be dissolved at isopropanol. This step is important to avoid hydrolyseateion of TBOT. When TBOT is hydrolysed, titanium will arrange its structure become TiO₂ that has stable structure. It is disadvantages structure because to build TS-1 frame, titanium has to arrange a sequence with Si. Besides that, TiO₂ can decompose H₂O₂ that used in oxidation reaction. After TBOT in isopropanol, TBOT, and TPAOH was mixed, the mixture was aged to hold crystallization hydrothermal for 4 days. The frame of TS-1 was built in this time that showed with the change of colour mixture become white. After that, CTABr was added in the mixture, filtered, washed, dried and calcinated. At the first hours, N₂ flow was used to make a perfect condition to removal of mesophasic template so that wasn’t destroyed TS-1 structure.

Unlike microporous TS-1 which has limitation in diffusion molecule to the catalyst pore, mesoporous TS-1 is more accessible to contact between molecule and active site in the pore (Schmidt et al., 2003). Surfactant is one of template that commonly used. In this case, mesoporous material was obtained by silica forming using micelle template, followed template removal by calcination (Vinu et al., 2006). In the

0.02/s. FTIR spectra of the samples were collected on a Shimadzu Instrument Spectrum One 8400S. The framework spectra were recorded in the region 1400-400 cm⁻¹. The specific surface area, pore size distribution and total pore volume of TS-1 were determined from N₂-adsorption-desorption isotherms obtained at -196 °C on a Quantachrome instruments. The surface area was determined by BET method and the mesoporous size was calculated by the BJH method. The samples were evacuated under N₂ atmosphere at 120 °C over night before measurement. The acidity of catalyst was observed using pyridine adsorption at 110 °C and was characterized using FTIR.

Catalytic activity

The oxidation of 2-methyl naphthalene using H₂O₂ as oxidant was carried out using 0.5 g 2-methyl naphthalene in 5 mL acetonitrile, 100 mg mesoporous TS-1, 5 mL H₂O₂ (30% in water). The reaction was stirred and conducted at 120 °C. The products were analysed on HP 5890 series II gas chromatography equipped with HP-5 column.

Figure 1. Diffractogram of mesoporous TS-1

XRD patterns of the sample prepared are shown in Figure 1. Diffraction peaks of TS-1 occur at 2θ 7.95; 8.94; 23.2°; 23.7°; 24.1°; dan 24.9° (Treacy and Higgins, 2001). Meanwhile, Peak about 23 – 24° show that there is a change of crystal symmetry from monoclinic symmetry (silicalite structure) become orthorhombic symmetry (TS-1 structure) (Li et al., 2002). In figure 2, FTIR spectra of the sample prepared show the characteristic spectra at about 1230, 1100, 960, 800, 550 dan 450 cm⁻¹. That’s spectra are vibration mode which associated with internal bond in SiO₂ or AlO₃ tetrahedral (Flanigen et al., 1973). Adsorption band at 1230 and 550 cm⁻¹ are specific bands for tetrahedral structure at MFI zeolite frame. Asymmetric and symmetric vibration Si-O-Si showed at 1100 and 800 cm⁻¹ (Drago et al., 1998). The titanium that has been incorporated into the zeolite framework was identified by a characteristic peak at about 960 cm⁻¹ in FTIR spectra. An absorption band at 960 cm⁻¹ also attributes Si-O-H vibration, as a characteristic of silanol network in mesoporous material (Zhang et al, 2008). N₂ adsorption-desorption was employed to examine the pore size and surface area of mesoporous TS-1. It can be seen that mesoporous TS-1 that was synthesized by CTABr template has mesoporous size, surface area, and pore volume of 3.395 nm, 835.96 m²/g and 0.5408 cc/g, respectively (Figure 3). Surface morphology shows that the mesoporous TS-1 has more heterogeneous pore and amorphous structure (Figure 4). In this work, the acidity of catalyst was studied using pyridine as the probe molecule. The
absorption bands at 1540 cm\(^{-1}\) can be described to pyridine interaction with the Brønsted acid sites. The bands at 1450 cm\(^{-1}\) can be assigned to the pyridine coordinated with Lewis acid sites. Based on Emeis equation, the Lewis and Brønsted acid sites concentration reached 0.3459 mmol/g and 0.0871 mmol/g. The catalytic properties of samples in synthesis of vitamin K3 operated in fixed bed reactor. in Figure 5, the catalytic activity of mesoporous TS-1 zeolites for the synthesis of vitamin K3 in the presence of H\(_2\)O\(_2\) is plotted against the time reaction. 2-methyl naphthalene conversion increased with increasing time reaction. At 6 hours reaction time, the conversion of 2-methyl naphthalene and the selectivity of vitamin K3 were 92.21% and 56.20%, respectively. At the same time, the reacted ion without catalyst show the conversion of reactant only 2.92% and no product was observed.

Figure 2. FTIR spectra of mesoporous TS-1

Figure 3. Pore size distribution of mesoporous TS-1

Figure 4. Scanning electron micrographs of obtaining mesoporous TS-1

Figure 5. Conversion of 2-methyl naphthalene using mesoporous TS-1

Conclusions

Mesoporous TS-1 with pore size of 3.395 nm has been synthesized and characterized. The evidence of the incorporation of titanium into zeolite was obtained by XRD and framework IR spectroscopies. The catalytic activity and selectivity of mesoporous TS-1 zeolites in the synthesis of vitamin K3 with H\(_2\)O\(_2\) are 92.21% and 56.20%, respectively.

Acknowledgments

The author would like to thank Chemistry Department, Airlangga University for their laboratory facilities support.

References


