The effect of synthesis TiO$_2$/SiO$_2$ methods for epoxidation of methyl oleate
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Abstract:
Nowadays the shortage of petroleum tends to be more serious. The largest share of renewable resource is biodiesel or fatty acid methyl ester (FAMEs). The major compositions derived from palm oil is methyl oleate. Unsatuated fatty acid methyl esters such as methyl oleate can be used to synthesize high-value products such as epoxides. The methyl oleate epoxide can be used as plasticizers and stabilizers in polymers, additives in lubricants, cosmetics, and pharmaceuticals. In this present study, three methods of synthesis TiO$_2$ on SiO$_2$ supported (grafting, wet impregnation, and incipient wetness impregnation) were tested as heterogeneous catalysts for epoxidation of methyl oleate. All methods use 0.89 cm$^3$ of titanium (IV) isopropoxide (TIP) onto 5 g of fumed-SiO$_2$ support. The three catalyzes were characterized by X-ray diffraction, N$_2$ adsorption-desorption, UV-Vis and SEM. The different synthesis had an effect on their catalytic properties when used as catalysts for epoxidation of methyl oleate with hydrogen peroxide in acetonitrile at 50 °C for 5 hours.

1. Introduction
Nowadays the shortage of petroleum and CO$_2$ emission from fossil fuels tend to be a serious problem. Thus, the development of renewable raw materials is likely to be an important issue.$^{1-5}$ The largest share of renewables in the industry is fatty acid methyl ester (FAMEs) or biodiesel. Vegetable oils and their FAMEs are large scale, biodegradable, eco-friendly, low toxicity and inexpensive. Therefore, the synthesis of high-value products from biodiesel such as hydrogenation, ozone cleavage, and epoxidation is of interest. The largest scale of vegetable FAMEs is from palm oil and the major composition derived from palm oil is methyl oleate, so epoxidation reaction is the most interesting.$^{5,6}$ According to Figure 1, an epoxidation reaction converts the unsaturated double bonds in the fatty acid methyl ester to oxirane ring or epoxide. Epoxidized fatty acid derivatives are used in large-scale applications such as plasticizers, stabilizers, intermediates, components for lubricants, cosmetics, and pharmaceuticals.$^{1,7-12}$

Figure 1. Epoxidation of methyl oleate.

In industrial scale, the epoxidation reaction is obtained by a homogeneous reaction called Prileschajew reaction. Prileschajew reaction is widely used in PVC plasticizer and intermediates. This reaction uses soluble mineral acids such as H$_3$PO$_4$, HCl or H$_2$SO$_4$ as catalysts. Percaboxylic acid such as peracetic or performic with hydrogen peroxide is used as oxidant. Hydrogen peroxide promotes the formation of peracetic acid. The peracetic acid will attack the double bonds, then form the oxirane ring.$^{3,2,7,13-15}$ Furthermore, there are problems regarding this reaction such as toxicity, corrosion, separation and low selectivity. The side reactions of epoxidation are ring opening, oxidative cleavage, and rearrangement. The
most considerable side reaction is the oxirane ring opening.

Heterogeneous catalysts are easy to separate, reuse and give high selectivity. Over the past decade, a heterogeneous catalyst such as metal oxide catalyst has been widely developed within the structure of microporous and mesoporous materials according to the broad modification such as calcination temperature, metal loading, and support material of heterogeneous catalysts. Metal ions used as catalysts have been reported such as rhenium, molybdenum, titanium, vanadium, chromium, and tungsten. Titanium-silica catalysts have been widely studied due to high conversion, selectivity, and recoverability. This study focuses on heterogeneously catalyzed epoxidation of methyl oleate with hydrogen peroxide as oxidant, acetonitrile as solvent at constant temperature and pressure. This study interests in catalytic activity, the selectivity of different synthesis of TiO2 with fumed SiO2 supported.

2. Materials and Methods
2.1 Catalyst synthesis
2.1.1 TiO2/SiO2 catalyst using incipient wetness impregnation method

5 g of fumed-silica (powder, 0.007 μm, Aldrich) was dried at 110°C overnight. Then 0.3 mmol (0.89 cm3) of titanium isopropoxide (TIP, 97%, Aldrich) was added in 3 mL absolute ethanol (100%, Merck). The titanium isopropoxide solution was dropped to fumed-silica at room temperature until it became slurry. The product was dried at room temperature for 1 h and at 110 °C overnight. The solid was crushed into fine powder, followed by calcination at 550 °C under air for 5 h to obtain TiO2/SiO2.

2.1.2 TiO2/SiO2 catalyst using wet impregnation method

5 g of fumed-silica (powder, 0.007 μm, Aldrich) was dried at 110°C overnight. Then 0.3 mmol (0.89 cm3) of titanium isopropoxide (TIP, 97%, Aldrich) was added in 5 mL absolute ethanol (100%, Merck). Fumed-silica was added and stir with titanium isopropoxide solution at 50 °C for 5 h. Then dried at 110 °C overnight. The solid was crushed into fine powder, followed by calcination at 550 °C under air for 5 h to obtain TiO2/SiO2.

2.1.3 TiO2/SiO2 catalyst using grafting method

5 g of fumed-silica (powder, 0.007 μm, Aldrich) was dried at 110°C overnight. Then 0.3 mmol (0.89 cm3) of titanium isopropoxide (TIP, 97%, Aldrich) was added in cyclohexanol (99%, Sigma–Aldrich). Fumed-silica was added to titanium isopropoxide solution (C_{TIP} = 0.02 mol/l) under reflux at 160 °C for 2 h. Then dried at 110 °C overnight. The solid was crushed into fine powder, followed by calcination at 550 °C under air for 5 h to obtain TiO2/SiO2.

2.2 Catalyst characterization

The morphology and metal distribution on surface of the catalysts were investigated with SEM-EDX using Link Isis series 300 program SEM (JEOL model JSM-5800LV).

The crystallinity and phases were analyzed by X-ray diffractometer (Bruker D8 Advance) using Cu Kα irradiation at range between 20° to 80° with a scan speed 0.5 sec/step. The lattice parameter and d-spacing were calculated based on Bragg’s law. Crystallite size was calculated by Scherrer equation.

UV-vis analysis was used to obtain information about the coordination geometry of Ti cations and the ligand environment. The absorption range was 200 to 500 nm obtained by Perkin Elmer Lambda 650 spectrophotometer. The step size for the scan was 1 nm.

N2 physisorption were carried out on a micromeritics chemisorb 2750 to determine the specific area at the single point of TiO2/SiO2 by using 30% N2/He after preheat sample at 200°C for 1 h.
2.3 Catalytic Experiments

Catalytic epoxidation tests were carried in a 50 cm³ three necked round-bottom glass reactor with a reflux condenser. The reactor was heated in an oil bath with a reaction temperature at 50°C and a stirring rate at 500 rpm. Methyl oleate (MO, 99%, Aldrich) was used as reactant. Naphthalene (98%, Fluka) was used as internal standard, acetonitrile (99.8%, Aldrich) as solvent and hydrogen peroxide (30% w/w in H₂O, Aldrich) as oxidant. First, 300 mg of catalyst was added in the reactor, followed by addition of substrate solution (1:100:0.6, volume ratio of MO: C₁₀H₈:CH₃CN) and wait until substrate solution became 50°C. Then 70 mg of hydrogen peroxide was added. The epoxidation started at the time hydrogen peroxide added.

0.2 cm³ of samples was taken from the reaction mixture after 1, 2, 3, 4 and 5 h of reaction. The catalyst was removed from the samples by filtration. The reaction mixtures were analyzed by gas chromatography-mass spectroscopy (GC-MS). GC-MS instruments were equipped with a DB-5 column (30 m x 0.25 mm x 0.25 um). The temperature of column increased from 180 °C to 250 °C then held for 10 min, at heating rate 5 °C/min. Temperature of injector and detector was 250 °C.

3. Results & Discussion

3.1 Epoxidation of methyl oleate

Three different catalyst synthesis for the conversion of epoxidation of methyl oleate with hydrogen peroxide and TiO₂/SiO₂ were selected as catalyst. According to Figure 2A, the catalytic activity of those prepared from three different methods was increased with reaction time. The conversion of the reactions using the catalysts prepared from incipient wetness impregnation, wet impregnation and grafting methods at 5 h were 38.23%, 35.21% and 38.52%, respectively. Thus, the three different catalyst synthesis showed similar catalytic activity.

The epoxide selectivity for epoxidation of methyl oleate was showed in Figure 2B. The catalyst that gave highest selectivity was TiO₂/SiO₂ catalyst using wet impregnation method. On the other hand, both TiO₂/SiO₂ catalyst using incipient wetness impregnation and grafting method gave similar selectivity of methyl oleate epoxide.

3.2 Characterization of the catalysts

SEM micrographs of fumed silica support (Figure 3A), TiO₂/SiO₂ by incipient wetness impregnation (Figure 3B), TiO₂/SiO₂ by grafting (Figure 3C) and TiO₂/SiO₂ by wet impregnation (Figure 3D) show similar small sphere particles morphology. Ti wt% measured on the surface of catalyst from SEM-EDX (Table 1) showed that the wet impregnation method gave higher Ti wt% more than both incipient...
wetness impregnation and grafting. Single point surface area of TiO$_2$/SiO$_2$ catalyst (Table 1) showed that the incipient wetness impregnation gave the highest surface area. Therefore, surface area, Ti wt% and surface morphology did not affect to catalytic activity. However, the Ti wt% had an effect on catalyst selectivity. The highest Ti wt% gave highest selectivity.

**Figure 3.** SEM micrographs of A) fumed silica support, B) TiO$_2$/SiO$_2$ by incipient wetness impregnation, C) TiO$_2$/SiO$_2$ by grafting and D) TiO$_2$/SiO$_2$ by wet impregnation.

**Table 1.** Wt% of Ti on TiO$_2$/SiO$_2$ surface from SEM-EDX analysis and surface area from N$_2$ physisorption analysis

<table>
<thead>
<tr>
<th>Method</th>
<th>Ti wt%</th>
<th>Surface area (m$^2$/g)</th>
<th>Conversion (at 5 h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Incipient wetness impregnation</td>
<td>1.78</td>
<td>312</td>
<td>38.23%</td>
</tr>
<tr>
<td>grafting</td>
<td>1.55</td>
<td>273</td>
<td>38.52%</td>
</tr>
<tr>
<td>Wet impregnation</td>
<td>3.41</td>
<td>304</td>
<td>35.21%</td>
</tr>
</tbody>
</table>

The three different TiO$_2$/SiO$_2$ catalyst synthesis in Figure 4 showed strong reflection around 2$\Theta$ = 22, attributing to the amorphous SiO$_2$. No significant intensity was observed for the reflection around 2$\Theta$ = 25.40, which is the characteristic peak of crystalline titanium dioxide (TiO$_2$) in the anatase phase, probably due to low TiO$_2$ loading. In addition, no characteristic peaks either in anatase or rutile phases of TiO$_2$ crystalline were observed at the TiO$_2$ loading range of 1-15 wt%.  

**Figure 4.** X-ray diffraction patterns of TiO$_2$/SiO$_2$ by wet impregnation, incipient wetness impregnation and grafting method.

**Figure 5.** UV-Vis spectra of TiO$_2$/SiO$_2$ by wet impregnation, incipient wetness impregnation and grafting method.

Nature and coordination geometry of Ti were characterized by UV-Vis spectra. The UV-Vis spectra of TiO$_2$/SiO$_2$ of three different catalysts were compared in Figure 5. It is well known that isolated tetrahedral Ti oxide coordination shows a typical band below 250 nm. The peak around 210 nm was assigned to the ligand- to- metal charge-transfer (LMCT) transition of the isolated Ti oxide monomer with tetrahedral coordination. The results show that those three TiO$_2$/SiO$_2$ catalysts had Ti oxide with tetrahedral coordination. No band centered at 260-300 nm and near 330 nm, which
indicated the absence of the hexacoordinated Ti species and anatase phase. TiO$_2$/SiO$_2$ by wet impregnation has higher intensity due to high Ti wt\%.

4. Conclusion

TiO$_2$/SiO$_2$ catalysts gave good catalytic activity and selectivity for epoxidation of methyl oleate. The results from SEM, XRD and N$_2$ physisorption showed that the three TiO$_2$/SiO$_2$ catalysts prepared from different methods gave similar morphology, crystallinity and surface area. However, the distribution of Ti on the catalyst surface and UV-Vis spectra of those three catalysts were different. Specifically, the Ti wt\% in TiO$_2$/SiO$_2$ prepared by wet impregnation method was higher than those prepared by incipient wetness impregnation and grafting method. Therefore, the UV-Vis of TiO$_2$/SiO$_2$ prepared by wet impregnation method gave higher intensity than the other two methods. The catalytic activity of those three TiO$_2$/SiO$_2$ catalysts were similar. However, the selectivity of TiO$_2$/SiO$_2$ prepared by wet impregnation method was higher than those prepared by incipient wetness impregnation and grafting method probably because the TiO$_2$/SiO$_2$ prepared by wet impregnation method had more TiO$_2$ on the silica surface than the other two methods.

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References