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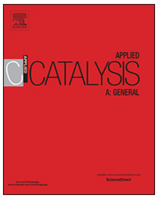

# Influence of silica sources on structural property and activity of Pd-supported on mesoporous MCM-41 synthesized with an aid of microwave heating for partial hydrogenation of soybean methyl esters

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## ABSTRACT

MCM-41 has been hydrothermally synthesized using fumed silica ($SiO_2$) and silatrane [$Si(TEA)_2$] as silica sources. Pd nanoparticles were successfully impregnated to the mesoporous MCM-41 supports. Soybean oil methyl ester was partially hydrogenated by the Pd/MCM-41-$SiO_2$ and Pd/MCM-41-silatrane catalysts under a mild condition (low temperature and pressure). Both catalysts could rapidly and selectively convert the polyunsaturated fatty acid methyl esters (C18:3 and C18:2) to monounsaturated fatty acid methyl esters (C18:1) at 100 °C and 0.4 MPa $H_2$ within 4 h. The results verified that the Pd/MCM-41-silatrane catalyst with the greater surface of Pd active sites had higher catalytic activity, representing in term of turnover frequency (TOF), in partial hydrogenation than Pd/MCM-41-$SiO_2$ under both C18:2 conversions of 40% and 60%. Even if the lower selectivity toward *cis*-C18:1 was obtained for the former. In addition to the better stable structure of MCM-41-silatrane support as compared to MCM-41-$SiO_2$ support, silatrane precursor is more favorable to diminish the extent of complete hydrogenation than fumed silica as it provided the lower index. Even though, this silica precursor sues for more synthetic step. Due to the higher oxidative stability of Pd/MCM-41-$SiO_2$, MCM-41-$SiO_2$ support was further studied for the later research. When varying the Pd loadings in 0.5–2 wt.% on MCM-41-$SiO_2$ support, the Pd(2)/MCM-41-$SiO_2$ catalyst gave the highest performance (TOF) whether the complete hydrogenation was concurrently accompanied. Results signify that the nature of the silica source and the Pd concentration modified the surface active sites and size distribution of metallic particles, which determine the catalytic reactivity and selectivity.

## 1. Introduction

Biodiesel, so-called Fatty Acid Methyl Esters (FAMEs), is considered as one of possible substitutes for conventional diesel fuels. It is industrially synthesized by renewable biological sources, such as various vegetable oils (soybean, rapeseed, palm…etc.), animal fats and waste cooking oils [1,2] through transesterification in the presence of short-chain alcohols, such as methanol. The advantages of biodiesel are biodegradability, renewability, non-toxic, and low emission profiles compared to conventional diesel fuels [3,4]. However, the unsaturated FAME components in biodiesel have strong influences on the quality of biodiesel, especially for oxidative stability and cold flow property [2,5]. A higher degree of unsaturation exhibits lower oxidative stability [1]. On the other hand, the higher the saturated fatty acid composition, the worse the cold flow property is [4]. Further disadvantages of the FAME are the following; higher kinematic viscosity, hydrolytic property of the ester bond, lower energy content, phosphorous- and alkali metal content [6]. Since the monounsaturated FAMEs, such as methyl oleate (18:1) and methyl palmitoleate (16:1), are the ideal components of biodiesel, the selective hydrogenation of polyunsaturated FAMEs to monounsaturated FAMEs has been regarded as one of the most promising solutions to increase the oxidation stability of biodiesel whilst

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maintaining a good cold flow property [7].

Palladium catalysts are considered as outstanding catalysts for hydrogenation of unsaturated hydrocarbons and many other applications, such as environmental catalysts, compared to other catalysts [8–10]. The activity of the Pd catalysts in partial hydrogenation can be theoretically increased by increasing the Pd dispersion. Various porous materials have been used as supports, such as carbon, silica, alumina, and zeolite, which increase the Pd dispersion as well as the selectivity of isomerization [5]. Although the selectivity in isomerization of *trans/cis* products is similar, they demonstrated that the Pd/$SiO_2$ catalyst showed a higher activity in partial hydrogenation of sunflower oil than others with similar loadings and particle sizes.

From our previous study [11], we found that both Pd/$SiO_2$ and Pd/MCM-41 catalysts presented higher catalytic activity than Pd/ZSM-5. This can be explained that Pd supported on micropores give lower hydrogenation rate than other materials due to the mass transfer limitation. This implies that some optimal pore structure is required for this reaction. The application of mesoporous materials with large pore sizes, allowing the bulky molecules to penetrate the porous structures was reported during the catalytic applications and sorption [12]. Among the mesoporous materials, MCM-41 with a 2D hexagonal *p6mm* pore structure is widely applicable because of its well-controlled pore structure and high surface area [13]. Moreover, the area of silica-based materials has been largely developed because of real industrial applications and their varied potentials [14]. The large pore Pd/MCM-41 catalyst showed a higher activity in liquid-phase hydrogenation of 1-hexene at 25 °C and hydrogen pressure of 1 atm than small pore Pd/MCM-41 and random pore Pd/$SiO_2$ catalysts [15]. There are many parameters which influence the formation of mesostructure; nature and the relative concentration of the surfactant, chemical characteristics of the precursor and its concentration, as well as temperature and pH [16]. The production of mesoporous systems with different pore sizes, pore volumes, and wall thicknesses can be obtained by changing the silica source. This change will also affect the thermal, hydrothermal, and mechanical stabilities of the materials. Silica, tetraethoxysilane (TEOS) and related commercial alkoxides or sodium silicate have been usually selected as silica precursors for the silica MCM-41 synthesis [14]. However, the main problem found related to these silica precursors is the high hydrolytic activity which can create problems in chemical processing. A solution to overcome this difficulty is based on the use of atrane complexes. Silatrane complexes are good candidates for a silica source due to the fact that these materials are hydrolytically stable in air for periods of up to several weeks. In addition, the final ordered mesoporous materials are thermally stable and show unimodal porosity, as well as homogeneous microstructure and texture [14–18].

Our previous study successfully synthesized MCM-41 with a high surface area and uniform crystallization from commercial silica by microwave radiation-assisted hydrothermal synthesis in a short synthesis period [11]. In this study, the influences of silica sources and Pd loading on the catalytic activities of the Pd/MCM-41 catalysts in partial hydrogenation of polyunsaturated FAMEs derived from soybean oil were investigated. To investigate these two effects on the catalytic activity, we synthesized Pd/MCM-41 through an incipient wetness impregnation method. The parameters in partial hydrogenation of soybean biodiesel into hydrogenated FAME were studied over the supported Pd catalysts and fuel properties, with oxidative stability and cold flow properties, of the obtained products tested and compared to EN 14214.

## 2. Materials and methods

### 2.1. Materials

Soybean oil, which was obtained from Thai Vegetable Oil Public Company Limited, was used as a feedstock for biodiesel production. The $Pd(NH_3)_4Cl_2 \times H_2O$, (Pd:40.16%) N.E. Chemcat Corporation, Japan, was used as a Pd precursor. The following materials were employed during synthesis of silatrane [$Si(TEA)_2$]: triethanolamine (TEA, $N(CH_2CH_2OH)_3$), ethylene glycol ($HOCH_2CH_2OH$), acetonitrile ($CH_3CN$), which were all supplied by Labscan, and fumed silica ($SiO_2$), which was received from Aldrich Chemical Co. The additional chemicals used for MCM-41 synthesis were: hexadecyltrimethyl ammonium bromide ($C_{16}$TAB, Sigma Chemical Co.), and sodium hydroxide (NaOH, Sigma Chemical Co.).

### 2.2. Transesterification of soybean oil with methanol

Soybean methyl ester was produced via the transesterification of soybean oil in a batch reactor. Firstly, 50 g of soybean oil was added to a batch reactor and heated up to 60 °C. After that, 16.9 g methanol (9:1 methanol to oil molar ratio) and KOH (1 wt.% based on the total amount of oil) were completely mixed under stirring. This mixture was added to the heated soybean when the temperature reached 60 °C and then stirred at 300 rpm for 1 h. After the reaction, the transesterification product was allowed to settle in a separating funnel for glycerol separation. The lower of phase glycerine was removed, while the upper phase of biodiesel was washed until the pH values of the final batch of biodiesel and the final wash were nearly neutral (pH = 7).

FAME composition in the feed biodiesel was identified using a Hewlett-Packard gas chromatograph (GC) 5890 series II equipped with a flame ionization detector (FID). A 30 m × 0.25 mm DB-WAX fused-silica capillary column, coated with a 0.1 μm film, was applied. In addition, a Thermo Nicolet Fourier Transform Infrared spectrometer (FTIR) Nexus 670 model was used to identify the chemical functional group of the feed biodiesel.

### 2.3. Synthesis of MCM-41

The following formulation of Si: 0.3 $C_{16}$TAB: 0.25 NaOH: 90 $H_2O$ was used to prepare the gel of MCM-41 [19]. In this synthesis, 970 μL of 2 M NaOH solution was added to 12.571 g of water. After that, 0.848 g of $C_{16}$TAB was added and stirred with slightly heating (50 °C) until the clear solution was obtained. Then, fumed silica of 0.466 g was added to the above solution under vigorously stirring for an hour. In order to reduce the temperature gradient and time period for the MCM-41 synthesis, the gel mixtures was treated under microwave irradiation 500 W at 70 °C for 5 h. The white precipitate was filtered, washed thoroughly with DI water several times for neutralization, and then dried at 60 °C overnight. Calcination was carried out at 500 °C for 6 h with a heating rate of 0.5 °C/min in air. As a result, the MCM-41-$SiO_2$ support was obtained [19]. Silatrane [$Si(TEA)_2$] precursor was prepared according to the procedures as reported by Thanabodeekij et al. [19]. Silatrane was formed by mixing 0.1 mol fumed silica with 0.125 mol triethanolamine in ethylene glycol (EG) as solvent. The reaction temperature was set at 200 °C (the distillation point of EG) to remove water as a by-product and EG from the system. The reaction was run for 10 h and the residual EG was removed under vacuum (1.6 Pa) after reaction. In similar, the MCM-41-silatrane support was synthesized with the aid of microwave irradiation as mentioned above.

### 2.4. Preparation of Pd-supported MCM-41 catalysts

The 1 wt.% Pd on MCM-41 with different silica precursors and various Pd loadings on MCM-41-$SiO_2$ (0.5, 1, and 2 wt.%) were prepared by an incipient wetness impregnation method using a $Pd(NH_3)_4Cl_2$ precursor which was obtained from N.E. Chemcat Corparation. The catalysts with several Pd loadings are denoted as Pd(0.5)/MCM-41-$SiO_2$, Pd(1)/MCM-41-$SiO_2$, and Pd(2)/MCM-41-$SiO_2$, respectively. The supports were impregnated with a solution of Pd precursor for 24 h. After that, the catalysts were dried for 6 h, and then calcined under an oxygen stream at 400 °C with a heating rate of 0.5 °C/min for 2 h. Prior to activity test in the partial hydrogenation reaction,

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