Chemical Fluid Deposition of Ru/MCM-41 as Catalyst

for Hydrogenation in Green Environments

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ABSTRACT

In this work, the Ru/MCM-41 catalyst prepared by chemical fluid deposition technique by using supercritical CO_2 as solvent exhibited high catalytic activity for aromatic hydrogenation of bisphenol A and benzyl alcohol. Supercritical CO_2 could provide the mobility for the Ru metal precursors to disperse and penetrate throughout the mesoporous silica support MCM-41. The characterizations of Ru/MCM-41 were performed by transmission electron microscopy (TEM), X-ray diffraction (XRD) and energy dispersive X-ray spectroscopy (EDS). On the other hand, water was found to be a suitable and green solvent for aromatic hydrogenation. Moreover, the addition of acid (CO_2 and acetic acid) and base (sodium hydroxide) in water could significantly enhance the reaction rate of benzyl alcohol and BPA, respectively.

Keywords: Supercritical CO_2, Ru/MCM-41, Hydrogenation, Bisphenol A, Benzyl alcohol, Water

1 INTRODUCTION

Supercritical CO_2 ($SCCO_2$), which means CO_2 at a temperature and pressure above its critical point (304 K and 7.38 MPa), has been widely used for producing nano-catalysts in recent years. Chemical fluid deposition (CFD) is a technique that dissolves organometallic precursors in $SCCO_2$ followed by reduction or thermal decomposition of the precursors, metal nanoparticles or films can then be deposited inside or on the surface of a support. In our group, several monometallic (Ru, Rh and Pd) and bimetallic (Ru-Rh, Ru-Pd and Rh-Pd) nanoparticles supported on mesoporous silica (MCM-41) were prepared using CFD technique [1]. The Ru/MCM-41 catalyst prepared by CFD exhibited the highest catalytic activity for hydrogenation of p-xylene which was nearly 8 times of that of a conventionally prepared Ru/MCM-41 catalyst. This result may be attributed to the addition of $SCCO_2$ causing a better dispersion of metal nanoparticles throughout the support. Nowadays, the use and disposal of organic solvents have been serious discussed due to the environmental impact. Therefore, it is necessary to find out the alternative "green" solvents which could eliminate the shortcomings of traditional organic solvents. Recently, using green solvents such as $SCCO_2$, CO_2-expanded liquids (CXLs), water and compressed CO_2/water as reaction media has become a popular research field.

CXLs, which means an organic solvent containing dissolved CO_2, have been widely used in precipitation and chemical reaction processes. The physicochemical properties such as density, viscosity, and solvating power of CXLs can be varied with the dissolved CO_2 amount through adjustment of temperature and pressure [2-6]. The use of CXLs as the solvent in tetralin and p-chloronitrobenzene (p-CNB) hydrogenation have been reported in our group to enhance the product selectivity and the reactant conversion respectively [2-3]. The enhancement can be explained by the increases in hydrogen solubility and mass transfer rate. The chromatographic peak broadening technique was also applied to measure the diffusion coefficients of p-CNB in CO_2-expanded methanol in order to verify the statement [4]. The measured diffusion coefficients of p-CNB in the CO_2-expanded methanol were observed to be higher than those in pure methanol, and to be increased with increasing CO_2 mole fractions in methanol, indicating the benefit of CO_2 dissolution in methanol for diffusion. This observation can partially explain a favorable operation in a CXL for hydrogenation reactions.

On the other hand, using water as the solvent in hydrogenation reactions is also a popular and favorable application nowadays. An ideal green reaction can be approached by using water as the solvent. If the products are less soluble in water, which is common for many organic compounds, they could be easily separated out of the water phase by precipitation or filtration. It was also found out that water provides a suitable environment for the silica based catalyst (Ru/MCM-41). From our experiments, the hydrogenation of low water solubility compounds, bisphenol A (BPA) and bisphenol F (BPF) proceeded most rapidly in water than in other organic solvents when using Ru/MCM-41 catalyst [7]. The catalytic activity and the durability of the Ru/MCM-41 catalyst were also tested to be superior to a commercial carbon supported catalyst (Ru/C). The hydrophilic property of the silica support causes the entire catalyst to have a better dispersion in the water phase than the hydrophobic type carbon supported catalyst. Accordingly, the hydroxyl groups from the surface of silica may exhibit a strong interaction, such as hydrogen bonding, with the reactants. More contacts between the reactant and the catalyst would occur with the assistance of the strong interaction thus increasing reaction rate.

Until now, there is still a lack of information of using green solvents for the aromatic hydrogenation reactions. Thus, to discover more extended examples of using green solvents for hydrogenation reactions remains our primary goal.

2 EXPERIMENTAL

2.1 Catalyst Prepartaion

The metal precursor bis(2,2,6,6-tetramethyl-3,5-heptanedionato)(1,5-cyclooctadiene)ruthenium [Ru(cod)(thmd)$_2$, Strem] and the silica support MCM-41 (SiO$_2$, Sigma-Aldrich) were all used as received. In a typical trial, 285 mg of MCM-41 and ca. 87 mg of Ru(cod)(thmd)$_2$ were added together into a high pressure cell leading to a maximum metal ratio of 5% by weight. At 423 K, 10 MPa of H$_2$ and 10 MPa of CO$_2$ were premixed in a gas reservoir and injected into the cell for a reaction of 2 hr. After the reaction, the cell was depressurized and flushed with CO$_2$ for a few times to eliminate the unreacted metal precursors. The remaining powder sample was then collected for further analysis and catalytic testing.

2.2 Hydrogenation Reactions

The experiments for the hydrogenation of aromatic compounds were implemented in a semi-batch autoclave. Benzyl alcohol [99%, Sigma-Aldrich], Bisphenol A [4,4'-isopropylidenediphenol, 99+%, Sigma-Aldrich], acetic acid [100%, Merck] were all used as received. In a typical trial, a mixture of 50 mg of the catalyst, 1 g of the benzyl alcohol and 50 g of deionized water were loaded into the high pressure autoclave. A CO$_2$ pressure of 3 MPa was first introduced into the cell and then followed by a H$_2$ pressure of 6 MPa. The reaction was set at a temperature of 323 K for a reaction time of 5 hr. After the reaction, the system was cooled in an ice bath and the samples were extracted with diethyl ether. The products were then analyzed by a gas chromatography-mass spectrometry (GC-MS; HP5890II/HP5972). A dimethylpolysiloxane based GC capillary column (Agilent HP-5MS) was used. The injector and the detector temperatures were set at 523 K and 533 K, respectively. A temperature program was employed for analysis starting at 323 K (hold for 5 minutes), followed by a 25 K/min program rate to 473 K (hold for 5 minutes). The products, 4,4'-isopropylidenedicyclohexanol [HBPA, 97%, Sigma-Aldrich], toluene [HPLC-grade 99.9%, Echo], methylcyclohexane [HPLC-grade 99.9%, Echo], cyclohexanemethanol [99%, Sigma-Aldrich] were used as the standard in the analysis.

3 RESULTS AND DISCUSSTIONS

3.1 Catalyst Characterization

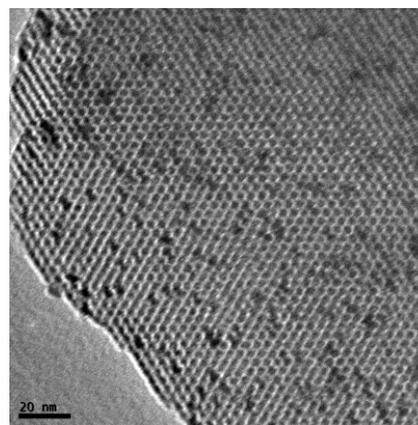The image of transmission electron microscopy (TEM)
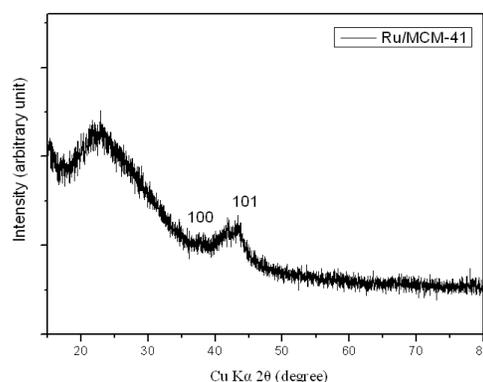

Figure 1: TEM image of Ru/MCM-41.

Figure 2: Powder XRD (Rigaku Ultima IV) patterns of Ru/MCM-41 wide angle from 10 to 80 degree.

was taken by Joel JEM-2100, which is shown in Fig. 1. The synthesized catalyst powder was diluted with ethanol and ultrasonicated for 5 minutes. Droplets of the prepared solution were put on a copper grid and dried in a vacuum oven of 100 °C overnight. The statistics calculations of the particle size distribution were made by using an interactive imaging software OPTIMAS5. At least 100 particles were recorded in order to obtain the average particle size and standard deviation. The average particle size was calculated as 2.6 nm, and the particles could be observed that the smaller ruthenium nanoparticles were grown inside the pores of MCM-41 while the bigger clusters were only attached to the outer part of the support.

From energy dispersive X-ray spectroscopy (EDS) analysis, the Ru metal loading was found to be 3.7% by weight. The overall yield of the chemical fluid deposition process could also be calculated and an efficient 75% yield (from maximum metal loading 5%) was obtained. Reproducibility of the catalyst was also examined and the overall yield was within a ± 5% range.

On the other hand, the Ru/MCM-41 samples were determined by powder X-ray diffraction (XRD), which was conducted by Rigaku Ultima IV. The Cu Kα radiation was 40 kV, 20 mA. The scan rate was 1°/min starting at 10° to

90° (2θ). Fig. 2 shows that the powder XRD analysis of the Ru/MCM-41. The broad peak between 15° to 30° can be assigned to the silica support, MCM-41. Ruthenium has a hexagonal closed-packed (hcp) structure and the major peak (101) is located at 44.0° (2θ). All of the analyses mentioned above could confirm that the Ru nanoparticles were deposited on the mesoporous silica support, MCM-41. Finally, the own-synthesized Ru/MCM-41 was used as catalyst in the following two sections.

3.2 Acid-Catalyzed Hydrogenation of Benzyl Alcohol

In the case of aromatic hydrogenation of benzyl alcohol, the products were methylcyclohexane, toluene, cyclohexenemethanol and cyclohexanemethanol (Scheme 1). Since the structure of benzyl alcohol contains a hydroxyl group, the C-O bond cleavage would also occurred, which is known as hydrogenolysis, during the hydrogenation reaction. In our previous work, it was found that the hydrogenolysis reaction could be avoided and the product selectivity of cyclohexanemethanol could be increased at a reaction temperature of 323 K. Table 1 shows the comparisons of different solvent systems for the hydrogenation of benzyl alcohol using Ru/MCM-41 as the catalyst [8]. The result shown that over 80% of cyclohexanemethanol can be obtained after 20 hr by using water as solvent (entry 1). However, when using compressed CO_2/water system as the solvent (entry 2), the reaction conversion and product selectivity could be significantly enhanced. The preliminary experiment of volume expansion was carried out in a Jerguson gauge. It can be seen that the volume of water could not be expanded by compressed CO_2 (323 K, 3 MPa). According to the literature, the property of compressed CO_2/water can be remained the same with water except for acidity. In this regard, it is believed that CO_2 molecules dissolved in water could form carbonic acid simultaneously and the acid could act as a promoter throughout the reaction. Therefore, a simulated experiment of acid-catalyzed effect by using acetic acid as solvent was designed in entry 3. The pH value of acetic acid (0.01 M) was calculated precisely in order to ensure that the amount of proton was the same with compressed CO_2/water solvent system (pH value is 3.4 at a CO_2 pressure of 3 MPa). From the result in entry 3, it was found that acetic acid also had the ability to elevate the reaction rate. However, the product yield of cyclohexanemethanol was slightly decreased compare to compressed CO_2/water solvent system. Thus, it is believed that the hydrogenation reaction rate of benzyl alcohol could be accelerated by acid-catalyzed effect.

3.3 Base-Catalyzed Hydrogenation of Bisphenol A

Since BPA (4,4'-isopropylidenediphenol) is labeled as
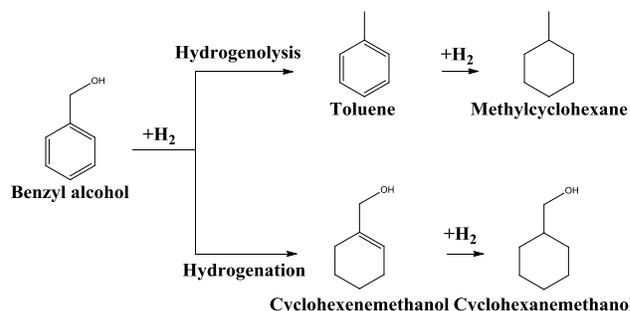
Scheme 1: Reaction pathway of the benzyl alcohol hydrogenation.

Table 1: Acid-catalyzed hydrogenation of benzyl alcohol.

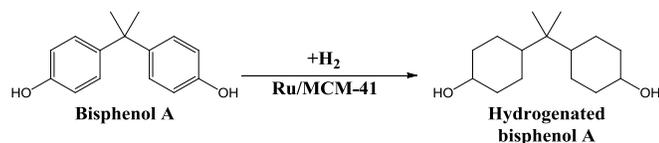| Entry	Solvent	Time (hr)	Conv. (%)	Product yield (%)
1[a]	Water	20	86	82.6
2[b]	Water + CO_2	5	98	90.4
3[c]	Water + acetic acid	5	93	71.4

[a] Benzyl alcohol: 1 g; Catalyst: 3.7 wt% of Ru/MCM-41: 50 mg; solvent: water 50 g; H_2 pressure: 5 MPa; temperature: 323 K; propeller stir: 1000 rpm.
[b] CO_2 pressure: 3 MPa.
[c] Water + acetic acid: 0.01 M, 50 g.

an endocrine disruptor, searching the alternative of using BPA as a raw material in plastic industry has drawn much attention in the recent years. The hydrogenated BPA (HBPA; 4,4'-isopropylidenedicyclohexanol), which is not an endocrine disruptor, could be considered as a substitute to the general usage of BPA. Previously, using Ru/MCM-41 as a catalyst and water as a solvent in the hydrogenation of BPA and BPF has been reported in our group [7]. Therefore, we try to investigate other possibilities to improve the reactivity of BPA in green solvent system. Recently, it was also found out that adding alkali base such as sodium hydroxide could significantly enhance the hydrogenation reaction rate. The results of base-catalyzed hydrogenation of BPA are shown in Table 2. It can be seen that in the absence of base, the hydrogenation of BPA could still be carry out in the neat water system (entry 1 and entry 2). However, after adding 1 equiv of sodium hydroxide, the reaction was dramatically improved (entry 3). This phenomenon may attribute to an increment of solubility of BPA in the aqueous base solution. The photographs of BPA aqueous solutions are shown in Fig 3. According to the literature, the solubility of BPA in water is approximately 10^{-3} to 10^{-5}, which could be considered as an insoluble substance [9]. When the presence of sodium hydroxide, the hydroxyl groups of BPA could be deprotonated by OH^- to form BPA disodium salt, then the BPA disodium salt became totally soluble in this work. This phenomenon suggested that the addition of base could also enhance the reaction rate of BPA (only 1/2 of the reaction time needed

Table 2: Base-catalyzed hydrogenation of BPA.

Entry	Solvent	Time (hr)	Conv. (%)	Product yield (%)
1[a]	Water	2	69.4	20.7
2[a]	Water	4	99.6	91.9
3[b]	Water + NaOH	2	99.7	86.1

[a] BPA: 1 g; Catalyst: 3.7 wt% of Ru/MCM-41: 50 mg; solvent: water 50 g; H_2 pressure: 5 MPa; temperature: 358 K; propeller stir: 500 rpm.
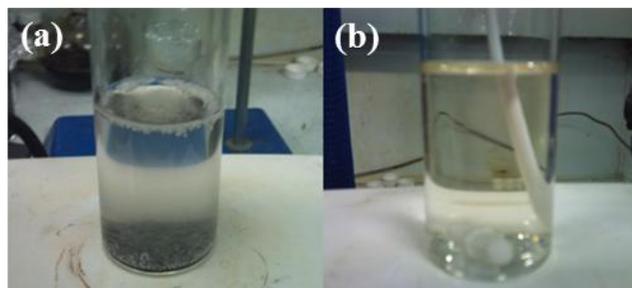[b] NaOH:BPA=1:1 (molar ratio)

Figure 3: Photographs of (a) the BPA aqueous solution at 358 K and (b) the BPA aqueous solution with the addition of 1 equiv NaOH at 358 K after stir for 1 hr.

for total conversion comparing to neat water) while still maintained high product yield.

4 CONCLUSIONS

In conclusion, four key points in this work can be summarized as the following: (i) A simple and green method of depositing Ru nanoparticles on an ordered mesoporous silica support MCM-41 can be achieved by using CFD technique; (ii) water is a suitable solvent for the ring hydrogenation of aromatic compounds such as benzyl alcohol and BPA; (iii) using compressed CO_2/water system or acetic acid solution as solvent could enhance the reaction rate of benzyl alcohol while still maintain high product selectivity; (iv) the addition of alkali base such as sodium hydroxide could significantly improve the reactivity of BPA in water due to the increment of solubility of BPA in water. Last but not least, applying the idea of green environment and sustainable chemistry for hydrogenation reactions remains our primary goal in the near future.

5 ACKNOWLEDGEMENTS

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