

Synthesis of SBA-15 Supported Rh Nanoparticles with High Loading Density and its Catalytic Hydrogenation of Phenol in Supercritical Carbon Dioxide

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Rhodium (Rh) metal is used in a variety of organic reactions, especially in the hydrogenation of arenes which is an important chemical process in the synthesis of fine chemicals. Among diverse hydrogenations, the ring hydrogenation of phenol is considered as an important industrial reaction as its products, cyclohexanol and cyclohexanone, are key intermediates for the manufacture of Nylon-6.6.¹ Although various liquid solvent systems have been mainly employed for such hydrogenation reaction of arenes catalyzed by Rh catalysts, the supercritical carbon dioxide (scCO₂) can be an environmentally benign alternative in chemical technology to avoid the use of organic solvents.² Most of previous hydrogenations of phenol in scCO₂ have been carried out with carbon or alumina supported Rh catalysts which have poor size distribution and dispersion of particles.

The synthesis of nanoparticles on template, such as mesoporous materials, provides an efficient strategy for narrow size distribution and high dispersion of metal nanoparticles.³ The incorporation of small particles in the pores of ordered porous materials have been carried out by using liquid solvents⁴ or chemical vapor deposition techniques.⁵ Compared with these methods, scCO₂ with high diffusivity, low viscosity, controllable solubility, and noncohesiveness⁶ has special advantages for deposition of metal and alloy particles within porous templates.⁷ In this work, we have employed an indirect route using scCO₂ pressure to synthesize SBA-15 supported Rh nanoparticles with high loading density and high dispersion of Rh metal. In comparison with commercial Rh catalysts, Rh/SBA-15 with high loading density revealed significantly enhanced activity for the ring hydrogenation in scCO₂ medium.

Mesoporous SBA-15 was prepared according to the literature procedure.⁸ [Rh(OAc)₃]₂ (Rh; 2.0, 5.0, and 10.0 wt%) was dissolved in THF (10 mL) containing SBA-15. After stirring for 24 h, evaporating, and drying for 4 h, [Rh(OAc)₃]₂/SBA-15 was placed in 200-mL high-pressure stainless steel reactor and equilibrated to 75 °C. Carbon dioxide was then added to 160 bar using a high pressure syringe pump. After standing for 24 h, the recovered powder was calcined in air (400 °C, 2 h) and reduced in a mixed gas (4% H₂, 96% Ar) atmosphere (200 °C, 2 h) to form Rh/SBA-15.

TEM images of Rh/SBA-15 are compared in the function of loading density in Figure 1. X-ray diffraction pattern of Rh/SBA-15 shows characteristic reflections from the (111) and (200) Rh crystal planes (Figure 1e), confirming the existence of well crystallized Rh metals. Rh nanoparticles

(~ 6 nm) loaded by 2 - 10 wt% are well dispersed inside the mesoporous channels of SBA-15. Rh and RhPt alloy nanoparticles of 2.5 wt% have been loaded on the mesoporous HMM-1 and FSM-16 in scCO₂.⁹ The higher loading concentration of metals would be desirable for the practical purposes, but high metal loading frequently results in an aggregation of particles on the external surface or a formation of nanowires in the pores.¹⁰ Thus, the homogeneous inclusion of nanoparticles would be a considerable challenge for an achievement of such high loadings. When the ordered mesoporous silicas are used as supporting materials, significant amounts of metal particles can be formed on the outer surface, depending on the type of silica support.¹¹ It is accordingly noted that excellent dispersion of nanoparticles is maintained even in Rh/SBA-15 with 10 wt% of loading density (Figure 1d).

When we carried out the hydrogenation reaction of phenol

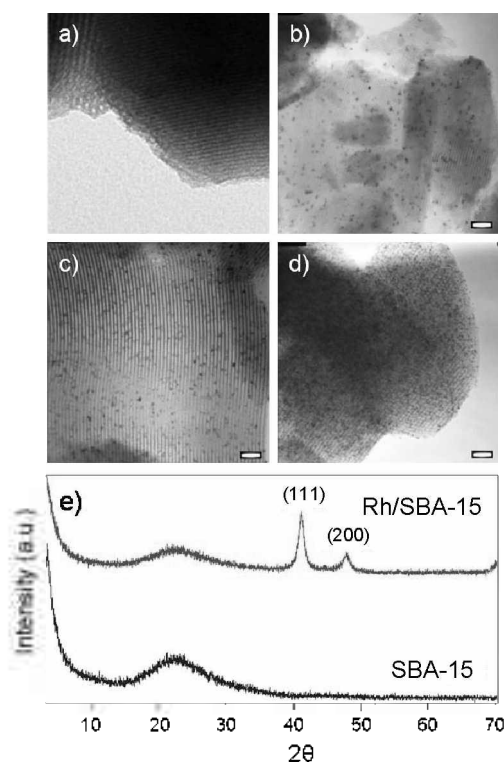
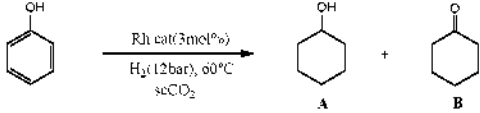


Figure 1. TEM images of (a) SBA-15 and Rh/SBA-15 with Rh concentration of (b) 2.0 wt%, (c) 5.0 wt%, and (d) 10.0 wt% (bar = 50 nm). (e) Wide angle XRD patterns of SBA-15 and Rh/SBA-15. The (111) and (200) diffractions of Rh metal are indicated.

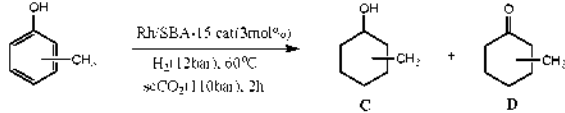
Table 1. Hydrogenation of Phenol catalyzed by Rh metals in scCO₂


| Catalyst | CO ₂ (bar) | Time (min) | Conversion(%) | | |
|-----------------------------------|-----------------------|------------|---------------|----|----|
| | | | Total | A | B |
| Rh/SBA-15 | 83 | 60 | 83 | 81 | 19 |
| Rh/SBA-15 | 110 | 60 | 100 | 80 | 20 |
| Rh/SBA-15 | 130 | 60 | 81 | 79 | 21 |
| Rh/SBA-15 | 110 | 10 | 95 | 36 | 64 |
| Rh/SBA-15 | 110 | 30 | 96 | 71 | 29 |
| Rh/C | 110 | 60 | 82 | 76 | 24 |
| Rh/Al ₂ O ₃ | 110 | 60 | 57 | 52 | 48 |

in hexane using Rh/SBA-15 catalysts. no improvement in catalytic activity and selectivity was observed in comparison with commercial Rh catalysts. The inside of mesopores containing Rh particles would not be easily accessible for the reactant molecules during catalytic reaction in liquid solvents. In contrast, the ability of scCO₂ to penetrate inside the mesochannels can facilitate the access of reactant molecules. In this context, it was expected that the catalytic performance of Rh catalyst with high loading density could be highly improved in scCO₂ reaction medium. Therefore, we explored the ring hydrogenation of phenol in scCO₂ using Rh/SBA-15 with 10 wt% of loading density.

Phenol (0.015 g, 1.6 × 10⁻⁴ mol) and Rh/SBA-15 catalyst (3 mol% Rh) were loaded in a 10 mL high pressure stainless steel reactor.^{7a} After heating the cell to a desired reaction temperature, hydrogen gas was introduced and then the reactor was pressurized. The same procedure was performed using commercially available Rh/C (5 wt% Rh) and Rh/Al₂O₃ (5 wt% Rh) catalysts for comparison. After the reaction, the cell was cooled down to room temperature and then depressurized carefully. The residue collected with acetone was dissolved into CDCl₃ after the simple filtration and evaporation of acetone to determine hydrogenation conversion and product distribution by ¹H NMR measurements.

The results of hydrogenation of phenol catalyzed by Rh/SBA-15, Rh/C, and Rh/Al₂O₃ are summarized in Table 1. It was observed that the optimum condition for the hydrogenation in scCO₂ is 110 bar of CO₂ pressure and 60 °C of reaction temperature. Compared to commercial Rh catalysts, Rh/SBA-15 shows an improved catalytic activity and selectivity for the hydrogenation in scCO₂. Thus, 100% conversion of phenol to cyclohexanol/cyclohexanone mixture was obtained with 80% selectivity of cyclohexanol and 20% selectivity of cyclohexanone over Rh/SBA-15 catalyst, while the commercial Rh/C and Rh/Al₂O₃ resulted in 82 and 57% conversions, respectively, under the same condition. Hydrogenation of cresols, derivatives of phenol, was further explored under the same conditions except an even longer reaction time (Table 2). Rh/SBA-15 catalyst also showed high activities for the ring hydrogenation of cresols to yield corresponding methylcyclohexanone and methylcyclohexanol as products. Among cresols, the catalysts showed the lowest activity for *m*-cresol

Table 2. Hydrogenation of Cresols over Rh/SBA-15 catalyst in scCO₂


| Substrate | Conversion(%) ^a | | |
|---------------------------------------|----------------------------|------------------------|----|
| | Total | C (<i>cis:trans</i>) | D |
| <i>o</i> -cresol (2-CH ₃) | 98 | 47 (90:10) | 53 |
| <i>m</i> -cresol (3-CH ₃) | 89 | 51 (30:70) | 49 |
| <i>p</i> -cresol (4-CH ₃) | 100 | 93 (72:28) | 7 |

hydrogenation, which may be due to the position of methyl group with respect to the hydroxy group.

In conclusion, SBA-15 supported catalyst with high loading density and high dispersion of Rh nanoparticles was successfully synthesized using scCO₂ pressure. We propose this Rh/SBA-15 as an effective catalyst for the ring hydrogenations of phenol and cresols in scCO₂.

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