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A novel method to immobilize Ru nanoparticles on SBA-15 firmly by ionic liquid and hydrogenation of arene

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A novel support of the Ru nanoparticles was achieved by combination of electrostatic force and coordination. The Ru catalyst was used as heterogeneous catalyst for hydrogenation of arene. This catalyst is very active for the hydrogenation of benzene to cyclohexane even under mild conditions. The TOF of this Ru catalyst is 85.3 mol mol^{-1} h^{-1} at 20 °C and 1.0 MPa for complete hydrogenation of benzene. The catalytic activity did not decrease after other five runs. The excellent performance of this catalyst demonstrated that there existed synergistic effects among 1,1,3,3-tetramethylguanidinium, mesoporous SBA-15, and Ru nanoparticles.

KEY WORDS: support; Ru nanoparticles; catalyst; hydrogenation; arene.

1. Introduction

Nanoparticles have properties intermediate between those of bulk and single particles. The application of transition-metal nanoparticles in catalysis has attracted much attention because they are expected to be suitable candidates for the design of highly active and selective catalysts [1]. It is well known that nanoparticles tend to aggregate to form larger particles due to their large surface area. Therefore, stabilization of the nanocatalysts by different methods has been studied extensively [2]. For example, many supported nanoparticles on molecular sieves have been used as catalysts, and incipient-wetness method is commonly used [3]. Ligand protected nanoparticles supported on molecular sieves [4] and nanoclusters on SiO_2 [5] have also been used as catalysts and high activities were achieved, although the stabilities were not satisfactory. Some nanoparticles stabilized by polyoxoanion and tetrabutylammonium were synthesized, characterized, and applied as catalysts for the hydrogenation of arene or olefins in organic solvents or water [1d–i]. Recently, many metallic nanostructured materials were synthesized and some of them were used directly as catalysts for various reactions with satisfactory results [6].

Room-temperature ionic liquids (ILs, low-temperature molten salts) possess many unusual properties, such as extremely low vapour pressure. They can be used as environmentally benign solvents for different chemical processes, such as separations [7] and reactions [8]. ILs are also attractive media to stabilize metal nanoparticles [6, 9]. It is known that guanidine has considerable coordination ability [10] to form coordinated complexes. Recently, we have conducted olefin hydrogenation with Pd nanopaiticle catalyst immobilized on molecule sieve by IL 1,1,3,3-tetramethylguanidinium lactate (TMGL) [11]. The catalyst was very active although the thin IL film might exist on the surface of the Pd nanoparticles.

It is well known that arene hydrogenation is of great interest due to increasing industrial demand for low aromatic diesel, and for conventional conversion of benzene to cyclohexane [1g]. In this work, we explored a new way to apply ILs, and developed a new route to prepared nanocatalyst for hydrogenation of arene. Ru nanoparticles were immobilized onto the wall of the channels of the SBA-15 by cations of an ionic liquid. Benzene was selected as the objective arene substrate to test and characterize the Ru nanocatalyst, and excellent activity and durability were achieved.

2. Experimental section

The SBA-15 silica was synthesized using the procedures reported by Zhao *et al.* [12]. In the experiment, 4.0 g Pluronic P123 was dissolved in 150 g of 1.6 M HC1 solution. Then, 8.50 g of tetraethyl orthosilicate (TEOS) was added. The resulting mixture was stirred for 5 min and then kept at 308 K for 24 h without stirring, and then aged for 2 days at 353 K. The solid product was filtered, and dried in an oven for 4 h at 413 K. To completely remove organic materials, the as-synthesized product was subsequently calcined at 823 K for 6 h in the air. The surface area, pore diameter, and pore volume were 750 m^2 g^{-1}, 6.3 nm, and 1.1 cm^3 g^{-1}, respectively.

The IL TMGL was synthesized directly by neutralization of 1,1,3,3-tetramethylguanidine and lactic acid.

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[11] To prepare the Ru catalyst, 0.25 g IL TMGL was added to a solution of 0.021 g $RuCl_3$ in 20 mL methanol. 1.0 g SBA-15 was added, and slurry was obtained. The slurry was dried at 50 °C under vacuum for 10 h to obtain the powder catalyst. The Ru in the powders was reduced by H_2 at 150 °C for 2 h and then heated up to 220 °C for 3 h to decompose the ionic liquid TMGL, and then the 1.0% mass percent Ru catalyst was obtained as black powders.

The hydrogenation was carried out in a 20 mL stainless steel autoclave with a magnetic stirrer. In a typical experiment, 0.20 g Ru catalyst and 1.2 g benzene was charged into the autoclave, and the air was replaced by H_2. The reaction system was stirred by the magnetic stirrer (300 rpm) at desired temperature, and the pressure of hydrogen was maintained at a pressure of interest. The products were analyzed by GC (Agilent 4890 D).

Transmission electron microscopy (TEM) observations were taken on a TECNAI 20 PHILIPS microscope operating at an accelerating voltage of 200 kV. The Ru catalyst were mixed with an epoxy resin distributed between two silicon wafer pieces at 50 °C for 30 min. Cross section TEM samples were pre-thinned mechanically and transferred to a holey carbon grid. The FT-IR and solid state NMR were carried out on Bruker Tensor 27 spectrometer and Brucker spectrometer at 300 MHz, respectively.

3. Results and discussion

We conducted catalytic hydrogenation of benzene with our Ru catalyst at 20 °C and 35 °C maintaining hydrogen pressure at 1.0, 2.0, and 3.0 MPa (runs 1–3, and 6–8). The hydrogenation results of benzene are listed in Table 1. The Ru catalyst is very active for the hydrogenation of benzene to cyclohexane even at mild conditions (20 °C. 1.0 MPa, run 6). Its activity is even comparable or superior to Ru cluster catalysts for the same reaction. For example, the TOF of $[(\eta^6\text{-}C_6FI_6)(\eta^6\text{-}C_6Me_6)_2Ru_3(\mu_3\text{-}O)(\mu_2\text{-}H)_3]^+$ BF_4 at 110 °C and 6.0 Mpa [13a] in ionic liquids were 3644 mol mol^{-1} h^{-1}, which, as far as we know, was the most active Ru catalyst reported. However, the Ru catalyst prepared in this work is a heterogeneous catalyst. It is well known that heterogeneous catalysts have some advantages because they can be easily separated from the products and can be used in fixed bed process.

Table 1
The results of hydrogenation of benzene at different conditions

Run	Benzene/Ru (mol/mol)[a]	T (°C)[b]	P H_2 MPa[c]	Time h[d]	Yield[e] %	TOF[f]
1	750	35	1.0	4	100	187
2	750	35	2.0	1.6	100	469
3	750	35	3.0	1.2	100	625
4	750	35	6.0	0.5	100	1500
5	10000	110	6.0	2.5	100	4000
6	750	20	1.0	8.8	100	85.3
7	750	20	2.0	5.6	100	1.34
8	750	20	3.0	2.8	100	268

Notes: Products were analyzed by GC. [a]The moles of benzene added to the reactor was 750 times of Ru. [c] Hydrogen pressure remained constant in the reaction processes. [d]The time required for all the reactant was converted. [e]Yield of cyclohexane. conversions were 100% and no other products were detected. [f]TOF, turnover frequency was calculated as moles of converted benzene per mol Ru per hour.

The catalyst used in Run 3 was reused 5 runs without any detectable loss of activity, which demonstrated the advantages of applying the novel support for this nanocatalyst. The reasons for the excellent activity and durability are discussed in the following.

We characterized the nanocatalyst by energy-dispersive X-ray spectroscopy (EDS) analysis and TEM examination. The EDS spectrum confirmed the Ru metal nanopartieles in the as synthesized catalyst. The TEM micrograph is shown in figure 1. It can be known from the figure that Ru nanoparticles exist in the channels of SBA-15, and the diameter of the most Ru particles is in the range of 2–5 nm. The small size of the particles is favorable to enhancing the activity.

The stability of ILs depends mainly on the natures of the cations and anions, and the interaction between the ions. Our previous work indicated that the decomposition temperature of TMGL was 191 °C, [14] while the decomposition temperature of 1,1,3,3-tetramethylguanidinium trifluoromethylsulfonate, which had the same cation with TMGL, was 354 °C [14]. It means that the cation (1,1,3,3-tetrarethylguanidinium) of the IL used in this work can be stable at the temperature to prepare the catalyst (220 °C) if it is paired with suitable anions. Although the SBA-15 was a weak acid, the weak acidic nature of lactate acid and the Strong basic nature of TMG resulted in at least partial substitution of TMG$^+$ for H$^+$ of the SBA-15 to form TMG$^+$ –O$^-$ ion pairs on the surface of SBA-15, which may be stable at 220 °C. The replaced H$^+$ and the anion of the IL formed lactate acid, and released either by decomposition or vaporization. At the same time, the excess TMGL (the IL) also

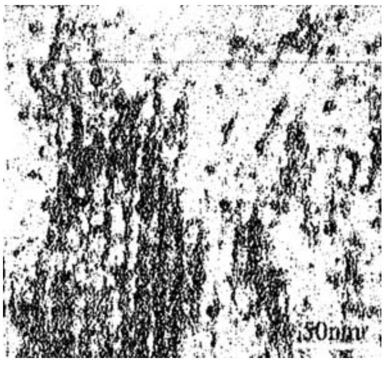

Figure 1. The TEM micrograph of Ru nanopartictes in SBA-15.

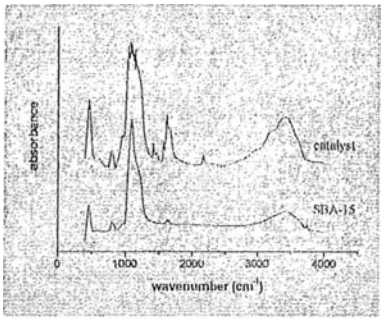

Figure 2. The FTIR of SBA and the as prepared catalyst.

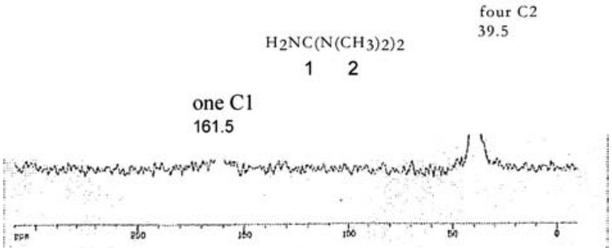

Figure 3. ^{13}C-NMR spectrum of organic monolayers on the surface of the catalyst.

decomposed because its decomposition temperature was 191 °C [14]. In other words, only the TMG$^+$ cations paired with -O$^-$ on the SBA-15 left after the thermal treatment at 220 °C. The TMG$^+$ ions left on the surface of the SBA-15, which had replaced the H$^+$ on the molecular sieve, were fixed on the surface of the molecular sieve by electrostatic force, which should be much stronger than common physical interactions. Furthermore, guanidine had considerable electron-donor ability to stabilize Ru nanoparticles [10]. Therefore, the Ru catalyst was firmly fixed on the surface of the molecular sieve, which enhanced the durability of the catalyst effectively.

The presence of the cation of the IL in the as prepared catalyst is supported by the fact that the catalyst contained 3 wt% organic compound, as determined by TGA. The existence of the TMG cations was also supported by the FTIR spectrum (figure 2). The CH_3 groups specific peaks at 1413 cm^{-1}, 1456 cm^{-1}, and 2945 cm^{-1}, and peak of C=N bond at 1616 cm^{-1} can be observed in the spectrum of the as prepared catalyst.

Figure 3 illustrates the solid-state ^{13}C-NMR spectrum of the catalyst, which shows clearly existence of the TMG cation. The peak at 39.5 ppm was attributed to the four carbons of the methyl groups, and the peak at 161.5 ppm is attributed to the other carbon of the TMG cation. The catalyst did not contain the anion of IL, which is known from the fact the peak of the carbon in carboxyl at 175 ppm cannot be observed in figure 3. The FTIR and solid-state ^{13}C-NMR spectra did not change even after 5 other runs.

On the basis of the discussions above, we suggest a possible structure of the Ru catalyst and the formation mechanism, which can be illustrated using figure 4. The Ru^{3+} diffuses into the channels of the SBA-15 with the help of the TMGL-methanol solution, and Ru(0) particles are formed after reduction of Ru^{3+} by H_2. Some cations of the IL replace the H$^+$ on the surface of molecular sieve. The H$^+$ and excess IL are removed after thermal decomposition of the IL. The TMG$^+$ interacted strongly with surface of the SBA-15 by electrostatic force. At the same time, the cations have electron-donor ability to stabilize Ru nanoparticles. In this way, the novel support of the nanoparticles was achieved by combination of electrostaticf force and coordination. Both the electrostatic and coordination forces are very strong, which avoid leaching of the catalyst effectively. Therefore, the catalyst is very stable. At the same time, the Ru particles are well dispersed and have small size, which is favorable to enhancing the activity of the catalyst. Meanwhile, the reactants can contact directly with the surface of Ru particles in the reaction process due to the removal of the IL by the thermal decomposition, which also enhances the activity of the catalyst. Therefore, the catalyst is very active and stable.

In summary, this work explored a new way to apply ILs. The Ru catalyst immobilized onto SBA-15 by the cations of TMGL was very active and durable catalyst for hydrogenation of benzene. The TMG$^+$, mesoporous SBA-15 and Ru nanoparticles exhibited excellent synergistic effects for the hydrogenation of arene. The nanocatalyst was used completely as heterogeneous catalyst, and apparently, this heterogeneous nanocata-

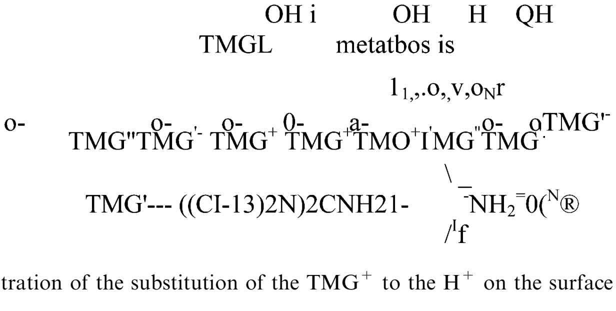

Figure 4. Illustration of the substitution of the TMG$^+$ to the H$^+$ on the surface of the SBA-15.

lyst was more advantageous than conventional suspended nanoparticle catalyst in solution or conventional heterogeneous catalyst. We believe that using this method some other transition metals, such as Rh, Pd, and Ir, may also be supported on the molecular sieve stably and can be used as catalysts.

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