

Synthesis of PVP-Ru amphiphilic microreactors with Ru nanocatalysts and their application in the fast hydrogenation of unsaturated compounds in aqueous media

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Received 14 January 2007; received in revised form 12 February 2007; accepted 12 February 2007
Available online 16 February 2007

Abstract

PVP-Ru amphiphilic microreactors with Ru nanocatalysts have been synthesized by reducing the complex of Ru ions with poly(*N*-vinyl-2-pyrrolidone) (PVP) in aqueous media. Microscope and TEM images verified the formation of PVP (K90)-Ru-10 microreactor with 100 μm in length, and Ru nanocatalysts, which were entrapped inside the microreactors, with 1–3 nm in diameter, 20–80 nm in length. The Ru nanoparticles could be protected from aggregation by adjusting the average molecular weight of PVP. The obtained PVP-Ru amphiphilic microreactor system showed high activity in the hydrogenation of unsaturated organic compounds in aqueous media. High turnover frequency (TOF) value of 45,000 h^{-1} was achieved in hydrogenation of benzene in aqueous media, at 353 K, under 4 MPa hydrogen pressure. All the hydrogenation TOF values of investigated arenes, olefins and carbonyl compounds exceeded 1000 h^{-1} . The recovered aqueous phase containing PVP-Ru microreactor could be reused for at least three times without any significant loss in their catalytic activity.

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Keywords: Aqueous; Catalysis; Hydrogenation; Ruthenium; Unsaturated compounds

1. Introduction

Water is important as a typical solvent in physiological processes and is also a favored solvent in green chemistry compared with organic solvents [1,2]. In essence, water is an interesting and useful solvent in organic chemistry, but the reaction rate is too slow to use as a commercial process when the interaction between the organic substrates and catalysts immobilized in water is difficult [3,4]. To circumvent this problem, a variety of strategies have been reported. For example, metal nanoparticles have a characteristic high surface-to-volume ratio compared with its bulk counterpart, and consequently a large fraction of the metal atoms that are exposed at the surfaces are accessible to reactant molecules and available for catalysis [5,6]. Many methods have been developed to prepare nanoparticles, for example the polymers anchored on the surfaces of the metal

nanoparticles can control particle size and prevent them from agglomeration [7,8]. Another promising approach to increase the interaction between catalysts and substrates is the use of amphiphilic microreactor, which is made up of amphiphilic reagents, such as surfactant, cyclodextrin, the ligands with alkyl chains and quaternized aminoalkyl groups, calyx [4] arene ligands with phosphane-containing groups, etc., that can form micelle, vesicle or cavity structure [9–17]. In this way, significant rate enhancement has been observed because substrates and catalysts are brought in close proximity in the hydrophobic interior of the microreactor.

Hydrogenation using Ru catalysts is one of the most important processes in chemical industry, clean fuel and wastewater treatment [18–20]. For example, hydrogenations of arenes are difficult reactions to catalyze and represent important industrial processes in particular with the increasing demand for low-aromatic diesel fuels for environmental constraints [21,22]. Hydrogenation of double-bond-containing compounds such as olefins and carbonyls is also very important process in chemical industries [23,24]. However, the reported hydrogenation TOF

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values of unsaturated compounds usually ranged from several to hundreds using Ru catalysts in aqueous media, only very few arrived to thousands [25–29].

In our previous work, we synthesized the PVP-Ru amphiphilic microreactors with Ru nanocatalysts which were made up of poly(*N*-vinyl-2-pyrrolidone) (PVP) and ruthenium. In this PVP-Ru microreactor system, PVP formed the framework of the microreactor, provided hydrophobic microenvironment in water and prevented the nanoparticles from aggregation. The hydrophobic microenvironment benefited enriching poorly water-soluble reactants. Ru nanoparticles acted as high active catalysts for hydrogenation of arenes, olefins, carbonyl compounds. In addition, substrates and catalysts were confined in the microreactor which could enhance the contact between them. For the protocol described here, fast hydrogenation of arenes, olefins and carbonyl compounds might occur by using this PVP-Ru microreactor system in aqueous media.

2. Experimental

2.1. Materials

Benzene was chromatography reagent, and all the other chemicals were analytical reagent. They were purchased from commercial source and used without further purification. Hydrogen (99.99%) supplied in a high-pressure cylinder was used through reducing valve without further treatment.

2.2. Preparation of the amphiphilic microreactor system

The aqueous solution of PVP-Ru microreactors were prepared from Ru salt and PVP with various alkyl chain lengths, e.g. K90, K15 (average $M_w = 1,250,000$ and 7000). Prepared amphiphilic microreactor system was denoted as PVP (K90)-Ru-10 when PVP-K90 was used in the preparation process with the mole ratio of the repeating units of PVP to Ru is 10/1. RuCl₃ (0.1 mmol) and PVP (0.22 g) were both dissolved in 60 ml distilled water with constant stirring at 353 K, and the stirring was allowed to continue for 2 h. A dark-brown transparent solution was obtained where Ru^{III} ions were complex with PVP. After PVP-Ru^{III} aqueous solution was treated with 4.0 MPa H₂ in a 500 ml stainless steel autoclave with a Teflon liner at 353 K for 2 h, catalytic microreactor system was obtained.

2.3. Characterization of amphiphilic microreactor system

PVP-Ru^{III} solution and fresh reduced PVP-Ru solution were characterized by Microscopy (Nikon Eclipse 80i microscope), and transmission electron microscope (TEM) on a JEM-2000EX (JEOL) electron microscope operating at 120 kV. PVP, PVP-Ru^{III} and PVP-Ru solution samples, which were in dehydrated membrane forms after being dried overnight at 353 K, were analyzed by an Avatar370 E.S.P. FT-IR spectrometer, Nicolet continuum infrared microscope. Freshly prepared aqueous solution of PVP (K15)-Ru was investigated by a Coulter N4plus instrument for dynamic light scattering.

2.4. Hydrogenation of arenes, olefins and carbonyl compounds

After PVP-Ru microreactor system was prepared (0.1 mmol Ru) in the autoclave, substrate (Ru/substrate mole ratio = 1/3000) and 60 ml diluent (cyclohexane or decane) were added directly. Considering the possibility of the polymerization of long-chain alkenes during their hydrogenation process, the amount of Ru catalyst was reduced to 0.02 mmol, cyclohexane as diluent was added to 100 ml and the Ru/substrate mole ratio was 1/1000. After air was flushed out of the reactor, the autoclave was heated to 353 K and then was pressurized with H₂ to 4.0 MPa. Then the mixture was stirred at 1000 rpm and the reaction was considered to start.

2.5. Analysis of the products

Samples were periodically taken from the product phase after the stirring was interrupted to separate the organic phase and the aqueous phase. The samples were qualitatively analyzed by GC–MS on an Agilent 6890 GC equipped with an Agilent 5973 mass selective detector. Quantitative analysis was performed on an Agilent 4890 GC equipped with a FID and a HP-5 (30 m × 0.53 mm × 0.6 μm) capillary column or an OV-1 (30 m × 0.32 mm × 0.8 μm) capillary column by the area normalization method. The amount of Ru in the organic phase after hydrogenation was analyzed by using PLASAM-SPEC-II inductively coupled plasma emission spectroscopy. The detection limit of the equipment to Ru is 0.03 ppm.

2.6. Recycling experiments

After the reaction, the autoclave was depressurized and the contents were transferred to the separatory funnels. Cyclohexane (50 ml) was used to extract the 1-heptane from the aqueous phase. The separated aqueous PVP (K90)-Ru microreactor solution was then put into the autoclave for the next cycle.

2.7. Measurement of benzene solubility

Benzene (60 ml) and the prepared aqueous solution of PVP-Ru microreactor (200 ml) were introduced into a 500 ml stainless steel autoclave with a Teflon liner. The mixture was stirred at 1000 rpm under 0.1 MPa N₂ at 298 K for 4 h. About 6 ml of the mixture was taken from the autoclave and was left to stand for about 1 h until the organic and aqueous phases were separated. The concentration of benzene in the dark-brown layer was analyzed by an Agilent 4890 GC equipped with a FID and an OV-1 capillary column. Toluene was used as the internal standard. For comparison, benzene solubility in the PVP (K90)-Ru^{III} aqueous solution and pure water was measured at the same conditions.

The solubility was calculated according to the following equation:

$$\alpha = \frac{m_{\text{toluene}} \times f_{\text{benzene}} \times A_{\text{benzene}}}{V_{\text{solution}} \times A_{\text{toluene}} \times f_{\text{toluene}}}$$

In this equation, α (g/l) is the solubility of benzene, m (g) represents mass, V_{solution} (l) the volume of sample solution, A the peak area, and f is the calibration factor to heptane.

3. Results and discussion

3.1. Characterization of PVP-Ru amphiphilic microreactor system with Ru nanocatalysts

The PVP-Ru amphiphilic microreactor system was synthesized by reducing the complex of Ru ions with PVP (PVP-Ru^{III}) in water with hydrogen. Micrograph and TEM images for the synthesized products of PVP (K90)-Ru-10 are shown in Fig. 1. Fig. 1A clearly shows that the microreactors, about 100 μm in length, were formed in the PVP (K90)-Ru aqueous solution (after reduction by hydrogen), whereas no microreactor was observed in the PVP (K90)-Ru^{III} aqueous solution (before reduction). From Fig. 1B, it can be seen that black Ru particles were entrapped inside the PVP (K90)-Ru microreactors. Fig. 1C shows more details of the Ru morphology in microreactors. They are chain-like Ru nanoparticle arrays, 1–3 nm in diameter and ~ 40 nm in length. In this case, the products in the dark-brown transparent solution were stable for months without noticeable precipitation. The resultant products (Fig. 1D), which yielded a black precipitate after 1 day at room temperature, were totally cross-linked, and the Ru nanoparticle arrays were 1–3 nm in diameter. From Fig. 1, it would be possible to protect the Ru nanoparticles from aggregation by using PVP with high average M_w .

Table 1
Benzene solubility in the PVP-Ru microreactor system

Samples	Size of the microreactor (μm)	Benzene solubility (g/l)	Enrich time (min)
Pure water	None	1.1	–
PVP-Ru ^{III}	None	1.5	–
PVP (K15)-Ru	0.8	470	240
PVP (K90)-Ru	100	470	50

3.2. Benzene solubility in the PVP-Ru microreactor system

The obtained microreactors existed in water were based on the hydrogen bonds formed between PVP and water, since PVP is an amphiphilic water-soluble polymer with pyrrolidone as the hydrophilic groups. On the other hand, the alkyl chains of PVP formed the confined hydrophobic microenvironment inside the microreactors in water. The main advantage of this hydrophobic microenvironment was an anticipated increase in the solubility of organic substrates in aqueous phase. Here, we investigated the solubility of poorly water-soluble benzene in aqueous phase in the presence of microreactors. The results are shown in Table 1.

From Table 1, after benzene was added to PVP-Ru microreactor system and stirred for 4 h, the concentration of benzene in aqueous phase containing microreactors reached 470 g/l, which is significantly higher than the benzene solubility in pure water (1.1 g/l, under the same conditions). The remarkable color change was observed in aqueous phase which was dark-brown transparent solution originally. The color of lower layer in aqueous solution changed from dark-brown to colorless, whereas, the color of upper layer in aqueous solution changed from clear

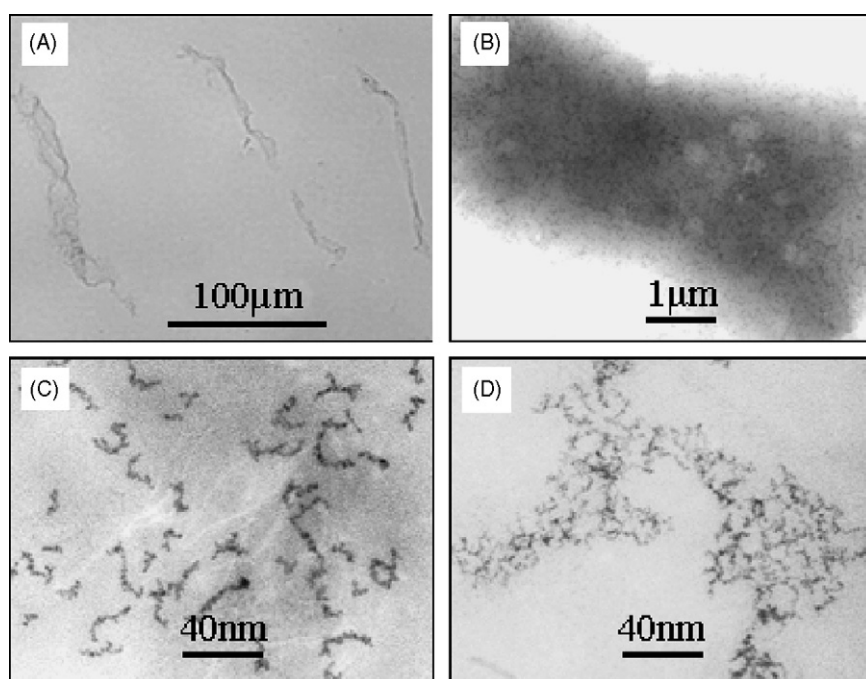


Fig. 1. Microscope and TEM images of the PVP-Ru microreactor system: (A) microscope image of the PVP (K90)-Ru microreactor; (B) TEM image of PVP (K90)-Ru microreactor and Ru particles; (C) TEM image of chain-like Ru nanoparticles arrays inside the PVP (K90)-Ru microreactor; (D) TEM image of cross-linked Ru nanoparticles arrays inside the PVP (K15)-Ru microreactor.

dark-brown to opaque dark and the solution became extremely viscous. Such changes could be explained that the microreactors, which were dark-brown because of containing ruthenium, would expand and then floated up to the upper layer of water when the microreactors enriched a large amount of benzene, while this layer was immiscible with organic phase. Whereas, the solubility of benzene in PVP-Ru^{III} aqueous solution (before reduction process) in the absence of microreactors was only 1.5 g/l under the same condition, much close to the case in water, and no color change was found in the aqueous phase over time.

The microreactor which was made up of PVP (K90)-Ru (100 μm) could enrich benzene completely within 50 min, whereas 4 h was needed for the complete enrichment on PVP (K15)-Ru (800 nm, determined by Dynamic Laser Scattering Technique). These results suggested that the microreactor could enrich a large amount of benzene in aqueous solution due to its hydrophobic microenvironment. Moreover, larger size of the amphiphilic microreactor induced the faster rate of enrichment.

3.3. Effect of microreactor system on the performance of benzene hydrogenation

The hydrogenation of benzene was selected as a modal reaction for the PVP-Ru amphiphilic microreactor system. Catalytic hydrogenation of benzene to cyclohexane was performed at 353 K, under 4 MPa H₂ with Ru/benzene mole ratio of 1/3000. A comparison between the catalytic performance of the PVP (K90)-Ru and PVP (K15)-Ru microreactor system in the hydrogenation of benzene in aqueous media is presented in Fig. 2. It is evident that the PVP (K90)-Ru was much more active than PVP (K15)-Ru for the hydrogenation of benzene. Hydrogenation of benzene using PVP (K90)-Ru microreactor system was completed just after 12 min, corresponding to a catalytic turnover frequency (TOF) of 45,000 h⁻¹ (Table 2, entry 1), defined as number of moles of consumed H₂ per mol of Ru per hour. Although the size of Ru nanoparticle was similar, the initial hydrogenation TOF of benzene using PVP (K15)-Ru microreactor was only 5800 h⁻¹ (Table 2, entry 2). In addition, these

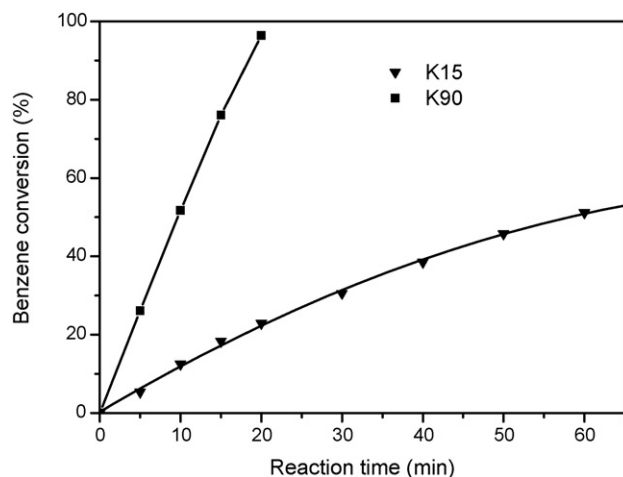


Fig. 2. Compared hydrogenation of benzene in the aqueous solution of PVP (K90)-Ru and PVP (K15)-Ru microreactor system.





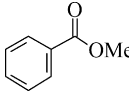
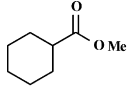








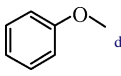


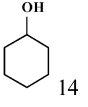
TOF values were much higher than 888 h⁻¹ obtained in a similar system with ~ 1.5 nm Ru nanoparticles where no microreactors were reported [30,31]. It meant that the microreactors made a significant contribution to the high activity besides the small Ru particle size.

As can be visualized from Fig. 2, catalytic transformation of benzene in the presence of the PVP (K90)-Ru amphiphilic microreactor system showed a very different kinetic behavior compared with PVP (K15)-Ru microreactor system. Benzene conversion increased linearly along with the reaction time in the aqueous solution of PVP (K90)-Ru microreactor system. Thus, the benzene conversion rate was independent with benzene concentration, showing kinetics of zero-order to benzene in this system which was in good agreement with that reported in monophasic reactions. In contrast, the conversion of benzene on PVP (K15)-Ru microreactor system depended on the concentration of benzene [32]. Normally, benzene conversion rate was strongly depended on the benzene concentration in benzene hydrogenation in the presence of water because of the low solubility of benzene in pure water [33]. The kinetic difference could be explained that the local benzene concentration inside the PVP (K90)-Ru microreactor was higher than that in pure water and in the PVP (K15)-Ru microreactor, at the same reaction time. Thus, Ru catalyst surface inside the PVP (K90)-Ru amphiphilic microreactor system was largely covered with benzene molecular, regardless of the changes of benzene concentration.

3.4. Effect of hydrogen pressure on the performance of benzene hydrogenation

The influence of the hydrogen pressure on benzene conversion was investigated using PVP (K90)-Ru microreactor system. Experiments were conducted at 1, 2, 3 and 4 MPa, at 353 K with the speed of agitation at 1000 rpm and Ru/benzene mole ratio of 1/6000. The variation of benzene conversion with reaction time is shown in Fig. 3A. The reaction proceeded rather slowly at 1 MPa, the benzene conversion was only 12% after 70 min. However, at 4 MPa, the benzene conversion was 50% at the same time. TOF values of benzene hydrogenation as a function of hydrogen pressure at the given conditions was shown in Fig. 3B. The approximately linear plot of TOF values versus hydrogen pressure indicated the first-order kinetic with respect to hydrogen pressure. This explained that the rates of reaction on catalysts increased with the increasing of the concentration of hydrogen. Thus, different activity of benzene hydrogenation on PVP (K90)-Ru and PVP (K15)-Ru should also be correlated with the solubility of hydrogen in both reaction media. It is known that the solubility of hydrogen in benzene is higher than that in water [34]. Therefore, the aqueous solution of PVP (K90)-Ru microreactor could solubilize more hydrogen than that of PVP (K15)-Ru microreactor at the same time due to its higher enrichment rate of benzene. It was concluded, consequently, that the activity order of PVP (K90)-Ru > PVP (K15)-Ru > Ru (~ 1.5 nm, in the absence of the microreactors) was consistent with the size increment of the microreactors in which both solubilities of benzene and hydrogen increased at the same time.

Table 2
Hydrogenation of arenes in aqueous PVP-Ru microreactor system^a

Entry	Substrate	Product and selectivity ^b (%)	TOF ^c (h ⁻¹)
1		 100	45,000
2		 100	5,800
3		 100	1,100
4		 83  17	2,600
5		–	–
6		 100	30,000
7		 100	29,000
8		 70  16  14	16,000

^a Conditions: PVP (K90)-Ru microreactor system (0.1 mmol Ru), Ru/substrate = 1/3000. Solvent: cyclohexane (60 ml), *T* (353 K), H₂ (4.0 MPa), agitation rate (1000 rpm).

^b Determined by GC–MS.

^c Tested within 5 min, defined as number of moles of consumed H₂ per mole of ruthenium per hour, determined by GC.

^d Solvent: decane (60 ml).

^e PVP (K15)-Ru microreactor system.

3.5. Effect of temperature on the performance of benzene hydrogenation

The temperature effect on the activity of hydrogenation of benzene in aqueous solution over PVP (K90)-Ru microreactor system was also investigated. The experiments were conducted

at 343, 353, 363 and 373 K, under 4 MPa hydrogen pressure with the speed of agitation at 1000 rpm and Ru/benzene mole ratio of 1/6000. The variation of benzene conversion with time is shown in Fig. 4A. It could be concluded that higher temperature was favorable for fast benzene hydrogenation to cyclohexane in aqueous media. The temperature effect on the activities of

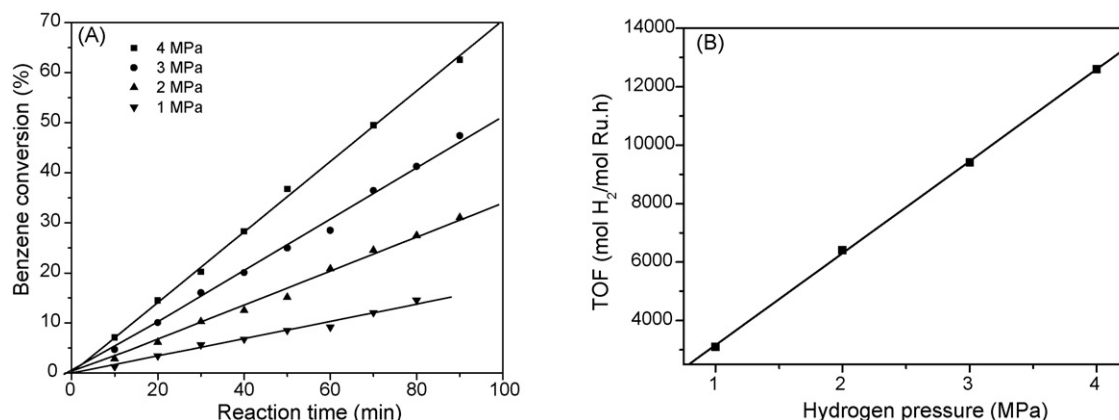


Fig. 3. (A) Conversion curves of benzene hydrogenation using the aqueous solution of PVP (K90)-Ru microreactor system under different hydrogen pressure. (B) Variation of benzene hydrogenation rate at different hydrogen pressure.

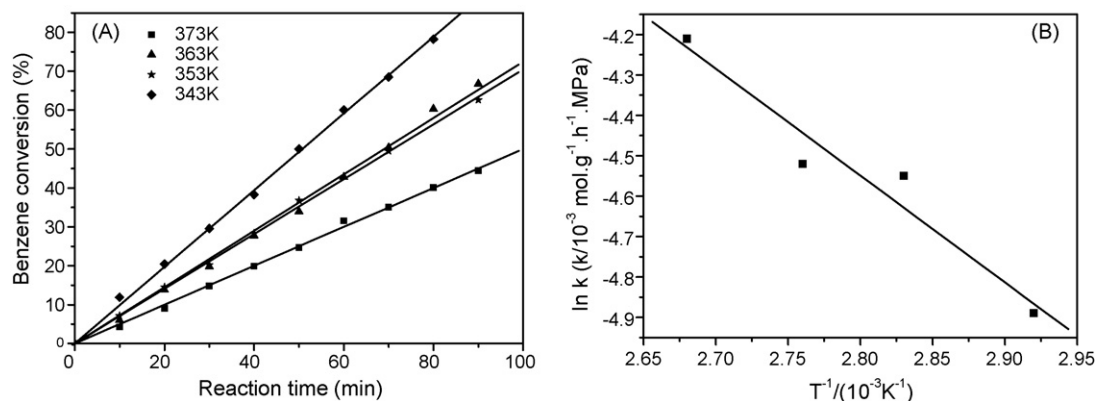


Fig. 4. (A) Conversion curves of benzene hydrogenation using the aqueous solution of PVP (K90)-Ru microreactor system at different reaction temperature. (B) Variation of benzene hydrogenation rate at different reaction temperature.

the PVP-Ru microreactor system is shown by the Arrhenius plots in Fig. 4B. The apparent activation energy for PVP (K90)-Ru microreactor system calculated from this plot was about 22 kJ/mol which was much lower than that reported (about 38 kJ/mol) for liquid benzene hydrogenation to cyclohexane over supported Pd catalysts [35]. Therefore, this PVP (K90)-Ru microreactor system could enhance the mass transfer between catalysts and substrates [36].

3.6. Hydrogenation of functionalized arenes

In all the investigated functionalized arenes, PVP (K90)-Ru microreactor system showed remarkable high activity and the conversion reached almost 100% within 3 h at 353 K under 4 MPa hydrogen pressure in aqueous media. For functionalized arenes, these reactions may be influenced by the electronic effects of arenes substituents. Typically, arenes with electron-withdrawing groups react more slowly, whereas the arenes with electron-donating groups react faster. Here, the hydrogenation TOF values of methyl benzoate and acetophenone (Table 2, entries 3 and 4) were 1100 and 2600 h^{-1} , respectively, resulting from the decrease of the electronic density of the aromatic system. Unfortunately, chlorobenzene was not hydrogenated, as a consequence of catalyst deactivation (Table 2, entry 5). It might be caused by a poisoning effect of the substrate [37].

Electron-donating groups increase the electronic density of the aromatic system, which benefits the catalytic activity. The hydrogenation TOF values of ethyl benzene, styrene and anisole with electron-donating substituents (Table 2, entries 6–8), were 30,000, 29,000 and 16,000 h^{-1} , respectively, exhibiting the highest TOF values except benzene. It might result in the lower solubility in water than benzene.

Although the hydrogenolysis of arenes is almost a general case in the hydrogenation of arenes by soluble transition metal nanoparticles [38], it is much slower than the hydrogenation of arenes. We have observed that the hydrogenolysis products, ethylcyclohexane (17%), cyclohexane (16%) and cyclohexanol (14%), were formed in the hydrogenation of acetophenone and anisole, respectively. In addition, in all investigated substrates, no partial hydrogenation product was detected.

3.7. Hydrogenation of olefins and carbonyl compounds



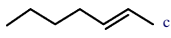
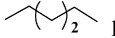
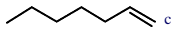
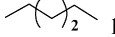
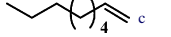
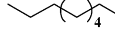
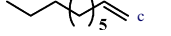
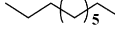
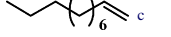
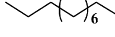
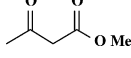
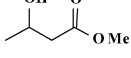


It is well known that the reaction of higher olefins ($>C_{10}$) in conventional aqueous/organic system is far less effective because of their extremely low solubility in water [39,40]. Here, the PVP-Ru microreactor system was successfully used in the hydrogenation of cyclo-olefin, internal olefin and higher terminal olefins in aqueous/organic system, such as 1-hexadecene. All the TOFs exceeded 3000 h^{-1} (Table 3).

The rate of hydrogenation of cyclohexene (23,000 h^{-1}) (Table 3, entry 1) was lower than that of benzene (45,000 h^{-1}) which was very unusual since cyclohexene are much easier to hydrogenate than benzene. It could be explained by the cyclohexene solubility in water (0.2 g/l) was lower than that of benzene (1.7 g/l), as reported. From Table 3, it could be seen that the TOF values of 1-heptene, 1-dodecene, 1-tetradecene and 1-hexadecene were 11,800, 5500, 4000 and 3800 h^{-1} , respectively (Table 3, entries 3–6). Although the TOF decreased with the increase of the chain length of terminal olefins, the hydrogenation of extremely water-insoluble 1-hexadecene was still very fast. These results indicated that the solubility of organic substrates in aqueous solution played an important role in aqueous/organic hydrogenation reactions. Increasing the solubility of organic substrates in aqueous solution would benefit for fast aqueous/organic hydrogenation. It was worth noting that the TOF value of 2-heptene (Table 3, entry 2) was much lower than that of 1-heptene. The well-known poor reactivity of internal olefins might contribute to this low reaction rate [41]. Furthermore, carbonyl compounds were also hydrogenated efficiently using this microreactor system (Table 3, entries 7 and 8).

3.8. Catalyst recycles

1-Heptene was used for recycling experiments because olefins were often used in aqueous/organic reactions. After the reaction was complete, the product could be easily separated from catalysts by separatory funnel. No ruthenium was detected in the product solution after reaction by inductively coupled plasma emission spectroscopy analysis, which could also be noticed by colorless organic phases obtained. This meant that

Table 3
Hydrogenation of olefins and carbonyl compounds in aqueous PVP-Ru microreactor system^a

Entry	Substrate	Product and selectivity (%)	Solubility [42] (g/l)	TOF (h ⁻¹)
1		 100	0.2	23,000
2		 100	1.5×10^{-2}	4,200
3		 100	1.5×10^{-2}	11,800
4		 100	8.4×10^{-6d}	5,500
5		 100	6.9×10^{-6d}	4,000
6		 100	6.3×10^{-6d}	3,800
7		 100	–	7,400
8		 100	24.4	7,300

^a Conditions: the same as Table 2.

^b Solvent: decane (60 ml).

^c PVP (K90)-Ru microreactor system (0.02 mmol Ru), Ru/substrate = 1/1000, solvent: cyclohexane (100 ml).

^d Solubility of corresponding alkanes.

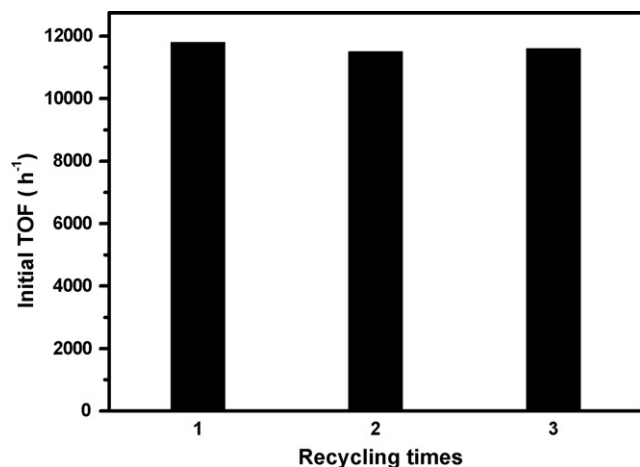


Fig. 5. Durability of the aqueous solution of PVP (K90)-Ru microreactor system in 1-heptene hydrogenation.

no leaching of the Ru occurred. The recovered aqueous phase containing the PVP (K90)-Ru microreactor system was reused in another reaction cycle. By doing so, two more cycles had been performed to demonstrate the separation and reuse of the microreactor system. The aqueous phase containing microreactors could be reused at least three times without any significant changes in the catalytic activity for the hydrogenation of 1-heptene, as shown in Fig. 5.

4. Conclusions

In summary, fast hydrogenation of arenes, olefins and carbonyl compounds were successfully realized in the PVP-Ru

microreactor system in aqueous media. The very high TOF values were contributed to the enrichment of poorly water-soluble organic substrates and hydrogen by hydrophobic microenvironment in microreactor in aqueous phase, and high active Ru nanoparticle catalysts. The recovered aqueous phase which contains PVP-Ru microreactor system could be reused for at least three times without any significant loss in catalytic activity. Moreover, the preparation procedure of the microreactor system was quite simple. Although the amphiphilic property of the microreactor system disturbed the phase boundary in such a system, high activity and much low ligands cost for the aqueous/organic hydrogenation render it attractive and feasible for potential commercialization.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2007.02.010.

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