DOI: 10.1002/adsc.200505444

Fast Aqueous/Organic Hydrogenation of Arenes, Olefins and Carbonyl Compounds by Poly(*N*-Vinylpyrrolidone)-Ru as Amphiphilic Microreactor System

Fang Lu, Jing Liu, Jie Xu*

State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Graduate School of the Chinese Academy of Sciences, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, People's Republic of China
Fax: (+86)-411-84379245, e-mail: xujie@dicp.ac.cn.

Received: November 15, 2005; Accepted: March 2, 2006

Supporting Information for this article is available on the WWW under http://asc.wiley-vch.de/home/.

Abstract: Fast aqueous/organic hydrogenations of arenes, olefins and carbonyl compounds were successfully realized in a PVP-Ru amphiphilic microreactor system. The turnover frequency (TOF) of aqueous/organic hydrogenation of benzene reached 45,000 h^{-1}. All the hydrogenation TOFs of investigated benzene derivatives, olefins and carbonyl compounds exceeded 1000 h^{-1}.

Keywords: arenes; hydrogenation; multiphase catalysis; nanoparticle catalysts; ruthenium; water

Water is important as a typical solvent in physiological processes and is also a favored solvent in green chemistry compared with organic solvents. The use of water-soluble catalysts for various reactions in the aqueous phase is recognized as an effective method for catalyst immobilization, and leads to a very efficient separation of the catalysts from the organic products.[1] This method has been applied commercially on a large scale (600,000 tons per year) in Germany and Korea to the rhodium-catalyzed hydroformylation of propene.[2] However, the major problem is that the reaction rate is too slow to use as a commercial process when this method is extended to poorly water-soluble substrates. One of the promising approaches to improve the solubility of organic substrates in the aqueous phase is the use of an amphiphilic reagent, such as surfactant, ligands with alkyl chains and quaternized aminoalkyl groups, cyclodextrin, and calix[4]arene ligands with phosphane-containing groups, that can form micelle, vesicle or cavity structures.[3–9] In this way, an enhancement of activity is observed because substrates and catalysts are brought in close proximity in the hydrophobic interior of the aggregates. Roucoux et al. have just reported that the hydrogenation of benzene derivatives was realized successfully, at room temperature and under atmospheric hydrogen pressure, in an aqueous/organic system, in the presence of cyclodextrin-stabilized ruthenium nanoparticles.[10]

Hydrogenation of arenes is a difficult reaction to catalyze and represents an important industrial process, in particular with the increasing demand for low-aromatic diesel fuels for environmental constrains.[11,12] Hydrogenation of double bond-containing compounds such as olefins and carbonyls are also very important processes in the chemical industry.[13–15] Ruthenium catalysts are often used in the hydrogenation of arenes, olefins and carbonyl compounds.[16] However, the reported hydrogenation TOF values usually range from several to hundreds using Ru catalysts in aqueous/organic system, only very few reach the thousands, even the amphiphilic reagents are used.[17–19]

In this communication, we report an aggregate formed by water-soluble amphiphilic poly(*N*-vinyl-2-pyrrolidone) (PVP K90, average Mw = 1,250,000) and ruthenium which can serve as a microreactor in the aqueous/organic hydrogenation of arenes, olefins and carbonyl compounds. In this PVP-Ru amphiphilic microreactor system, PVP can form the framework of the microreactor, provide a hydrophobic microenvironment in water and prevent the nanoparticles from aggregation. The hydrophobic microenvironment will benefit the enrichment of poorly water-soluble substrates. Ru nanoparticles can act as highly active catalysts for the hydrogenation. In addition, catalysts and substrates are confined in the microreactor which can enhance the contact between them. With the protocol described here, fast aqueous/organic hydrogenation of arenes, olefins and carbonyl compounds can be achieved using this PVP-Ru microreactor system.

The microreactor system was synthesized by reducing the complex of Ru ions and PVP (PVP-Ru^{III}) in water with hydrogen. The micrograph (Figure 1A) clearly shows that the microreactors, which are about 100 μm

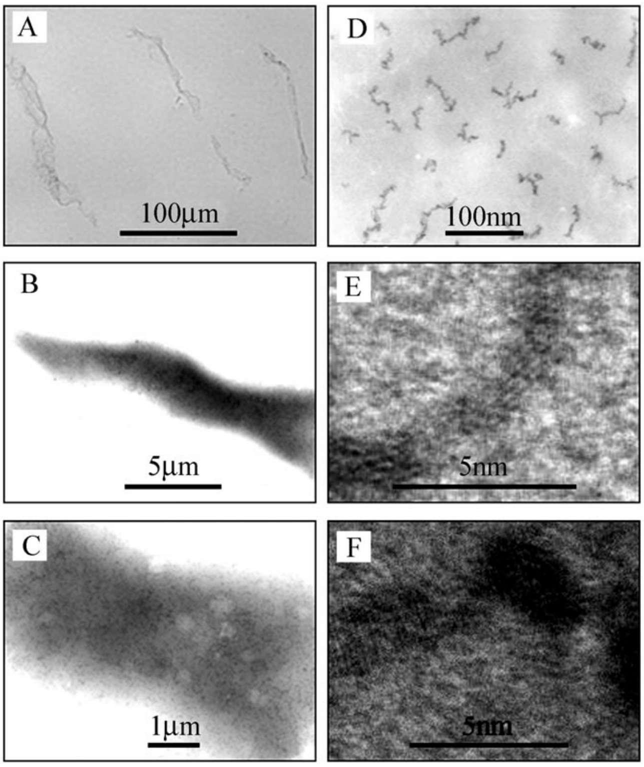


Figure 1. Microscope and (HR-)TEM images of the PVP-Ru microreactor system. **A:** Microscope image of the microreactor; **B:** TEM image of microreactor; **C:** TEM image of microreactor and Ru particles; **D**: TEM image of chain-like Ru nanoparticle arrays; **E:** HR-TEM image of continuous Ru nanowires; **F:** HR-TEM image of discrete Ru nanoparticles.

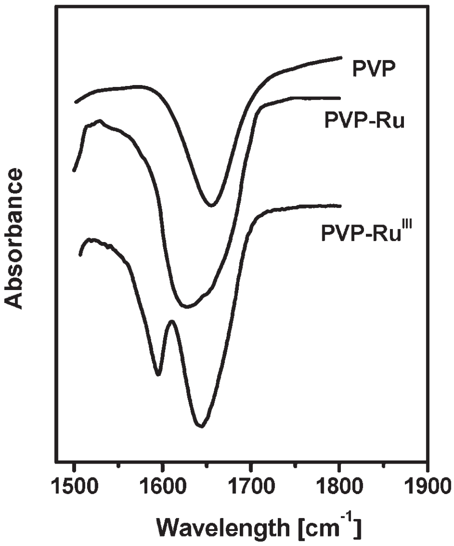


Figure 2. FT-IR spectra of the PVP, PVP-Ru^{III} and PVP-Ru.

in length, are formed in the PVP-Ru aqueous solution (after reduction by hydrogen), whereas no microreactor was observed in the PVP-Ru^{III} aqueous solution. It can be seen from Figures 1B and 1C that Ru particles were entrapped inside the microreactors. Figure 1D shows more details of the morphology of ruthenium in the microreactors. There are chain-like Ru nanoparticle arrays, about 20–80 nm in length and 1–3 nm in diameter. HR-TEM images also show that the chain-like Ru nanoparticle arrays are composed of both continuous Ru nanowires (Figure 1E) and discrete Ru nanoparticles (Figure 1F).

Compared with pure PVP, the Fourier transform infrared spectrum (FT-IR) (Figure 2) of a PVP-Ru^{III} sample exhibits an additional shoulder peak around 1600 cm^{-1} along with a peak for the C=O stretching vibration of the PVP amide unit at 1650 cm^{-1}. The appearance of the shoulder peak suggests that the complex of PVP-Ru^{III} forms by a part of the amide in PVP binding to the ruthenium ion.[20] After the reduction process (PVP-Ru sample), the shoulder peak essentially disappears, while the C=O stretching vibration peak is widened, which may result from bond weakening arising from partial electron donation from the PVP oxygen to the vacant orbitals of ruthenium surface atoms.[21] It is suggested that the interaction between Ru and PVP exists inside the microreactor, which can protect the Ru nanoparticles from aggregation.[22]

The obtained amphiphilic microreactors exist in water on the basis of the hydrogen bonds formed between the pyrrolidone of PVP and water. On the other hand, the alkyl chains of PVP form the confined hydrophobic microenvironment inside the microreactors in water. The main advantage of this hydrophobic microenvironment is an anticipated increase in the solubility of organic substrates in the aqueous phase. Here, we investigated the solubility of poorly water-soluble benzene in the aqueous phase in the presence of the microreactors. After benzene was added to the PVP-Ru microreactor system and stirred for 1 h, the concentration of benzene in the aqueous phase containing microreactors reached 470 g/L, which is significantly higher than the solubility of benzene in pure water (1.1 g/L, under the same conditions). Additionally, the solubility of benzene in PVP-Ru^{III} aqueous solution (before reduction by hydrogenation) in the absence of microreactors was only 1.5 g/L under the same conditions, much close to the case in pure water. These results suggest that the microreactor can enrich a large amount of benzene in aqueous solution due to its hydrophobic microenvironment.

A series of hydrogenations of arenes, olefins and carbonyl compounds in the PVP-Ru microreactor system was investigated in this work (Table 1). In all the investigated cases, the PVP-Ru microreactor system showed a very high activity and the conversion reached almost 100% within 3 h.

For benzene, the hydrogenation was completed after just 12 min, corresponding to a catalytic turnover frequency (TOF) of 45,000 h^{-1} (entry 1), defined as the number of moles of consumed H_2 per mol of Ru per hour, much higher than the 888 h^{-1} obtained in a similar system with ~1.5 nm Ru nanoparticles where no microreactors were reported.[12,23] This means that the microreactors make a significant contribution to the high reactivity besides the small Ru particle size. It was also found that the conversion of benzene increased linearly along with the reaction time, thus, the rate of benzene conversion is independent of the benzene concentration, showing zero-order kinetics to benzene in this system. However, it is usually reported that the rate of conversion of benzene is strongly dependent on the benzene concentration in the hydrogenation of benzene in the presence of water because of the low solubility of benzene in pure water.[24] The kinetic difference can be explained by the fact that the local benzene concentration inside the microreactors is much higher than that in pure water. The Ru catalyst surface inside the microreactor is largely covered with benzene molecules, regardless of the changes of benzene concentration. Furthermore, reactions defined in micrometer dimensions also improved the reaction activity, which is usually observed in microreactor systems.[25,26]

For benzene derivatives, the hydrogenation TOFs of arenes with electron-donating substituents all exceeded 10,000 h^{-1} (entries 2–4), whereas the hydrogenation TOFs of arenes with electron-withdrawing substituents were about 1000 h^{-1} (entries 5 and 6), resulting from the decrease of the electron density of the aromatic system.

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.[27] Here, the PVP-Ru amphiphilic microreactor system was successfully used in the hydrogenation of terminal higher olefins and cycloolefins in the aqueous/organic system. Although the TOF decreased with increasing the chain length of olefins, the TOF of the extremely water-insoluble 1-hexadecene reached 3000 h^{-1} (entries 7–11). Furthermore, carbonyl compounds were also hydrogenated efficiently using our microreactor system (entries 12 and 13).

In addition to the high hydrogenation reactivity, this microreactor system also had several merits. The PVP-Ru microreactor system can be recycled three times without losing activity. No ruthenium was detected in the product solution after reaction as checked by inductively coupled plasma emission spectroscopy analysis, which could also be noticed by the dark-brown aqueous and colorless organic phases obtained. This meant that no leaching of the Ru occurred. Moreover, the preparation procedure of the microreactor system was quite simple.

In summary, fast aqueous/organic hydrogenation of arenes, olefins and carbonyl compounds was successfully realized in the PVP-Ru amphiphilic microreactor system. The very high TOF values were attributed to the enrichment of poorly water-soluble organic substrates, highly active Ru nanoparticle catalysts and the localized reaction in microscale dimensions. This microreactor system was flexible whereby other metals can substitute for Ru and the polymers could be adjusted to fit the new reaction environment. Thus, high reactivity could also be expected in other aqueous/organic reaction systems.

Experimental Section

Reagents

PVP was of pharmaceutical grade (Shanghai sunpower material co.), Benzene was a chromatography reagent, and all the other chemicals were analytical reagents. They were purchased from commercial sources and used without further purification. Hydrogen (99.99%) supplied in a high-pressure cylinder was used through a reducing valve without further treatment.

Preparation and Characterization of the Microreactor System

$RuCl_3 \cdot H_2O$ (0.027 g, 0.1 mmol) and PVP (0.11 g, 1 mmol) were dissolved in water (60 mL) in a 100-mL flask, stirred at 353 K for 2 h and a dark-brown transparent solution was obtained where Ru^{III} ions were complexed with PVP. After the PVP-Ru^{III} solution had been treated with 4.0 MPa H_2 in a 500-mL stainless steel autoclave with a Teflon liner at 353 K for 2 h, the catalytic microreactor system was obtained. The PVP-Ru^{III} solution and fresh reduced PVP-Ru solution were characterized by microscopy (Nikon Eclipse 80i microscope), TEM on a JEM-2000EX (JEOL) electron microscope operating at 120 kV and HR-TEM on a Philips 20 TECNAI G2 field emission gun electron microscope operating at 200 kKV. PVP, PVP-Ru^{III} and PVP-Ru solution samples, which were in dehydrated membrane form after being dried overnight at 353 K, were analyzed using an Avatar370 E. S. P. FT-IR spectrometer and a Nicolet continuum infrared microscope.

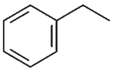
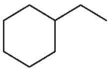
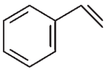
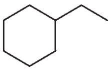
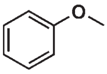
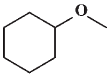
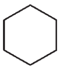
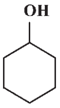
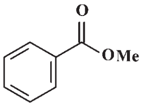
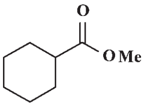
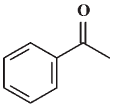
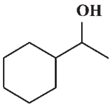
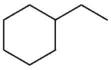
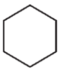
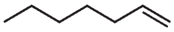
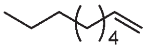
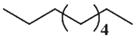
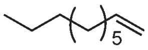
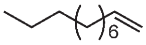
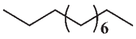
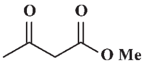
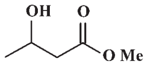
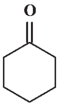
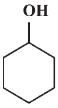
Measurement of the Solubility of Benzene

Benzene (60 mL) and the prepared aqueous solution of PVP-Ru microreactors (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 N_2 at 298 K for 1 hour. About 6 mL of the mixture were taken from the autoclave every 10 min and left to stand for about 1 h until the organic and aqueous phases had separated. The concentration of benzene in the dark-brown layer was analyzed using an Agilent 4890 GC equipped with an FID and an OV-1 capillary column. Toluene was used as the internal standard. For comparison, the solubilities of benzene in the PVP-Ru^{III} aqueous solution and in water were measured under the same conditions.

Hydrogenation Reactions

After the PVP-Ru microreactor system had been prepared (0.1 mmol Ru) in the autoclave, the substrate (Ru/substrate mole ratio = 1/3000) and 60 mL dilutent (cyclohexane or dec-

Table 1. Hydrogenation of arenes, olefins and carbonyl compounds in aqueous PVP-Ru microreactor system.[a]

Entry	Substrate	Product and Selectivity[d] [%]	Initial TOF[e] [h^{-1}]
1	 [b]	 100	45,000
2		 100	30,000
3		 100	29,000
4	 [b]	 70,  16,  14	16,000
5		 100	1100
6		 83,  17	2600
7	 [b]	 100	23,000
8	 [c]	 100	11,800
9	 [c]	 100	5500
10	 [c]	 100	4000
11	 [c]	 100	3800
12		 100	7400
13		 100	7300

---

[a] *Conditions:* microreactor system (0.1 mmol Ru), Ru/substrate = 1/3000. Solvent: cyclohexane (60 mL), *T* (353 K), H_2 (4.0 MPa), agitation rate (1000 rpm).

[b] Solvent: decane (60 mL).

[c] Microreactor system (0.02 mmol Ru), Ru/substrate = 1/1000, solvent: cyclohexane (100 mL).

[d] Determined by GC-MS.

[e] Tested within 5 minutes.

ane) were added directly. Considering the possibility of the polymerization of long-chain alkenes during the hydrogenation process, the amount of Ru catalyst was reduced to 0.02 mmol, cyclohexane as dilutent was added to 100 mL and the Ru/substrate mole ratio was 1/1000. After air had been flushed out of the reactor, the autoclave was heated to 353 K and then was pressurized with H_2 to 4.0 MPa. Then the mixture was stirred at 1000 rpm and the reaction was considered to start. Samples were periodically taken from the organic 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 an FID and an HP-5 capillary column or an OV-1 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.

Supporting Information

Detailed recycling experiments and benzene conversion profiles are contained in the Supporting Information.

References and Notes

[1] D. J. Cole-Hamilton, *Science* **2003**, *299*, 1702–1706.
[2] R. T. Baker, W. Tumas, *Science* **1999**, *284*, 1477–1479.
[3] M. S. Goedheijt, B. E. Hanson, J. N. H. Reek, P. C. J. Kamer, P. van Leeuwen, *J. Am. Chem. Soc.* **2000**, *122*, 1650–1657.
[4] H. Ding, B. E. Hanson, J. Bakos, *Angew. Chem. Int. Ed.* **1995**, *34*, 1645–1647.
[5] S. Shimizu, S. Shirakawa, Y. Sasaki, C. Hirai, *Angew. Chem. Int. Ed.* **2000**, *39*, 1256–1259.
[6] S. Tilloy, H. Bricout, E. Monflier, *Green Chem.* **2002**, *4*, 188–193.
[7] L. Leclercq, M. Sauthier, Y. Castanet, A. Mortreux, H. Bricout, E. Monflier, *Adv. Synth. Catal.* **2005**, *347*, 55–59.
[8] M. Li, H. Y. Fu, M. Yang, H. J. Zheng, Y. E. He, H. Chen, X. J. Li, *J. Mol. Catal. A: Chem.* **2005**, *235*, 130–136.
[9] H. Chen, Y. Z. Li, R. X. Li, P. M. Cheng, X. J. Li, *J. Mol. Catal. A: Chem.* **2003**, *198*, 1–7.
[10] R. Raja, V. B. Golovko, J. M. Thomas, A. Berenguer-Murcia, W. Z. Zhou, S. H. Xie, B. F. G. Johnson, *Chem. Commun.* **2005**, 2026–2028.
[11] P. J. Dyson, D. J. Ellis, D. G. Parker, T. Welton, *Chem. Commun.* **1999**, 25–26.
[12] C. M. Hagen, L. Vieille-Petit, G. Laurenczy, G. Suss-Fink, R. G. Finke, *Organometallics* **2005**, *24*, 1819–1831.
[13] C. Daguenet, R. Scopelliti, P. J. Dyson, *Organometallics* **2004**, *23*, 4849–4857.
[14] J. W. Yang, M. T. H. Fonseca, B. List, *Angew. Chem. Int. Ed.* **2004**, *43*, 6660–6662.
[15] E. T. Silveira, A. P. Umpierre, L. M. Rossi, G. Machado, J. Morais, G. V. Soares, I. L. R. Baumvol, S. R. Teixeira, P. F. P. Fichtner, J. Dupont, *Chem. Eur. J.* **2004**, *10*, 3734–3740.
[16] J. A. Widegren, R. G. Finke, *J. Mol. Catal. A: Chem.* **2003**, *191*, 187–207.
[17] T. Dwars, G. Oehme, *Adv. Synth. Catal.* **2002**, *344*, 239–260.
[18] N. Pinault, D. W. Bruce, *Coord. Chem. Rev.* **2003**, *241*, 1–25.
[19] F. Joo, *Accounts Chem. Res.* **2002**, *35*, 738–745.
[20] T. Uemura, S. Kitagawa, *J. Am. Chem. Soc.* **2003**, *125*, 7814–7815.
[21] R. Brayner, G. Viau, F. Bozon-Verduraz, *J. Mol. Catal. A: Chem.* **2002**, *182*, 227–238.
[22] R. Narayanan, M. A. El-Sayed, *J. Phys. Chem. B* **2005**, *109*, 12663–12676.
[23] G. Suss-Fink, B. Therrien, L. Vieille-Petit, M. Tschan, V. B. Romakh, T. R. Ward, M. Dadras, G. Laurenczy, *J. Organomet. Chem.* **2004**, *689*, 1362–1369.
[24] L. Ronchin, L. Toniolo, *Appl. Catal. A: Gen.* **2001**, *208*, 77–89.
[25] K. Jahnisch, V. Hessel, H. Lowe, M. Baerns, *Angew. Chem. Int. Ed.* **2004**, *43*, 406–446.
[26] P. Walde, S. Ichikawa, *Biomol. Eng.* **2001**, *18*, 143–177.
[27] E. Monflier, S. Tilloy, G. Fremy, Y. Castanet, A. Mortreux, *Tetrahedron Lett.* **1995**, *36*, 9481–9484.