COMMUNICATION

ChemComm
www.rsc.org/chemcomm

Catalytic hydrogenation of arenes with rhodium nanoparticles in a water-in-supercritical CO_2 microemulsion

Mariko Ohde, Hiroyuki Ohde and Chien M. Wai*
Department of Chemistry, University of Idaho, Moscow, Idaho 83844, USA. E-mail: cwai@uidaho.edu; Fax: +1 208 885 6173; Tel: +1 208 885 6173

Received (in Corvallis, OR, USA) 18th June 2002, Accepted 3rd September 2002

Rhodium nanoparticles dispersed by a CO_2 microemulsion are effective catalysts for rapid hydrogenation of arenes in supercritical CO_2.

In a recent communication, we reported the hydrogenation of olefins in supercritical carbon dioxide catalyzed by palladium nanoparticles synthesized in a water-in-CO_2 microemulsion.[1] The Pd nanoparticles were prepared by hydrogen reduction of Pd^{2+} ions (a $PdCl_2$ solution) dissolved in the water core of the microemulsion. The metal nanoparticles so produced are uniformly dispersed in the supercritical fluid phase and are stable over an extended period of time for catalysis experiments. The CO_2 microemulsion system provides a unique environment for homogenization of conventional heterogeneous catalysis utilizing metal nanoparticles in supercritical fluid CO_2. Reduction of metal ions to its elemental state using hydrogen gas is a simple, clean, and effective way of producing nanometer-sized metal particles in the microemulsion. This method is particularly interesting for studying hydrogenation reactions in supercritical CO_2 because hydrogen gas, which is miscible with CO_2, can serve both as a reducing agent for metal nanoparticle formation as well as a starting material for subsequent hydrogenation reactions. The advantages of performing hydrogenation reactions in supercritical CO_2 compared with conventional solvent systems are described in the literature.[2,3] High solubility of hydrogen gas and enhanced diffusion rate in supercritical CO_2 often result in faster and more efficient processes. Tunable solvation strength of supercritical CO_2, easy separation of solvent from products, and minimization of waste generation are attractive features of conducting chemical synthesis in CO_2. Based on our previous study, the Pd nanoparticles synthesized in the CO_2 microemulsion are not effective for hydrogenation of aromatic compounds.

Developing effective processes for hydrogenation of arenes is of considerable interest because of increasing industrial demands including production of low-aromatic diesel fuels.[4] The hydrogenation of arenes is conventionally carried out with heterogeneous catalysts. A new approach reported in the recent literature is to use colloidal metallic particles such as rhodium as catalysts in biphasic systems (water–organic) for hydrogenation of arenes.[5] In this approach, the Rh particles are stabilized in the aqueous phase using surfactants to prevent aggregation, and the arenes are dissolved in the organic phase. Hydrogenation of arenes typically requires 7 h to complete in such a biphasic system. Using a similar approach, Bonilla *et al*. reported Rh colloids catalyzed hydrogenation of arenes in a water–supercritical ethane biphasic system.[6] Hydrogenation occurred well in this biphasic system with excellent results obtained for a number of arenes after 62 h of reaction time. We have recently explored the possibility of making rhodium nanoparticles in a water-in-CO_2 microemulsion using the hydrogen gas reduction method. In this paper we report for the first time the hydrogenation of arenes in supercritical CO_2 catalyzed by Rh nanoparticles synthesized in a water-in-CO_2 microemulsion.

Two home-made high-pressure vessels were used for this research. One vessel (54.3 ml volume) was equipped with a fiber optic system (3 mm pathlength) connected to a CCD array UV-Vis spectrometer for *in situ* spectroscopic measurements.[7] The other vessel with a volume of 6.8 ml was used to store hydrogen gas and the selected arene.

The water-in-CO_2 microemulsions were prepared by mixing an aqueous Rh^{3+} solution (0.1 M $RhCl_3$ solution) and a mixture of surfactants containing sodium bis(2-ethylhexyl) sulfosuccinate [AOT] (13.6 mM) and a cosurfactant perfluoropolyether phosphate [PFPE-PO_4] (27.2 mM) in the 54.3 ml fiber optic cell. The solution was stirred for one hour in CO_2 at 180 atm to ensure the formation of an optically transparent microemulsion. The supercritical fluid solution showed a slightly orange color indicating the presence of Rh^{3+} ions in the water core that is uniformly dispersed in the fluid phase. Below 180 atm, the solution was somewhat cloudy indicating formation of water-in-CO_2 microemulsion was not achieved. Formation of Rh nanoparticles was studied by injecting only H_2 gas into the fiber optic cell containing the microemulsion (water-to-surfactant ratio $W = 30$) with a 0.1 M Rh^{3+} solution in the water core. The total amount of Rh in the reaction cell was 4.0×10^{-2} mmol. A UV-Vis spectrum of the microemulsion before the hydrogen injection is shown in Fig. 1(a) (spectrum 1). After the injection of H_2, the solution became colorless indicating reduction of Rh^{3+} in the system. The UV-Vis spectrum shown in Fig. 1(a) (spectrum 2) is consistent with the formation of Rh nanoparticles, which are known to absorb in the UV region with virtually no structure at all.[8] The supercritical fluid solution was depressurized and collected in hexane by the RESS (rapid expansion of supercritical solution) method.[9] A TEM micrograph of the hexane solution (Fig. 1(b)) showed 3–5 nm-sized Rh particles with some aggregation of individual particles. Without the H_2 injection, these nanoparticles were not found in the supercritical fluid solution.

Naphthalene was selected as a CO_2-soluble arene for this hydrogenation study because it absorbs in the UV region that could be monitored *in situ* by the fiber optic cell. Naphthalene and hydrogen (10 atm) were dissolved in CO_2 at a total pressure of 240 atm. This mixture was injected into the fiber optic cell containing the Rh^{3+} ions dissolved in the water core of the CO_2 microemulsion at a pressure of 240 atm controlled by the pump. Fig. 2(a) shows the variation of the UV-Vis spectra of naphthalene with time after the injection of hydrogen and naphthalene into the fiber optic cell at 50 °C and 240 atm. In this experiment, the amount of naphthalene injected into the fiber optic reactor was about 1.4×10^{-1} mmol and the system was stirred with a magnet bar. The spectrometer was turned on 20 seconds after the injection. Fig. 2(b) shows the decrease of absorption at 265 nm with time. In the first 2 min, the absorption

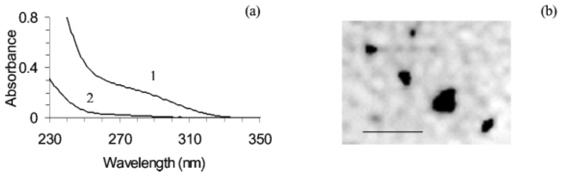


Fig. 1 (a) UV-Vis spectra of Rh^{3+} in the water-in-CO_2 microemulsion before (spectrum 1) and after (spectrum 2) injection of H_2 gas. (b) A TEM micrograph of Rh nanoparticles collected in hexane using the RESS method (scale = 20 nm).

DOI: 10.1039/b205993m

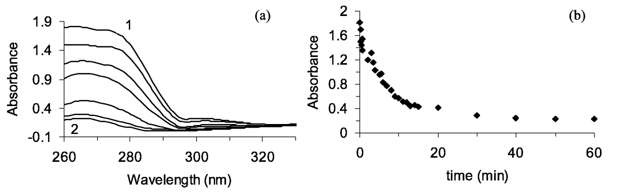
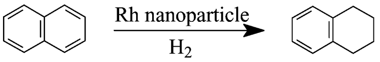


Fig. 2 (a) Variation of UV-Vis spectra of naphthalene with time during hydrogenation process in CO_2 at 50 °C and 240 atm. Each spectrum was taken at zero time (spectrum 1), 10 s, 1 min, 5 min, 10 min, 20 min and 60 min (spectrum 2) from top spectrum to bottom spectrum, respectively. (b) Variation of absorbance of naphthalene at 265 nm with time at 50 °C and 240 atm.

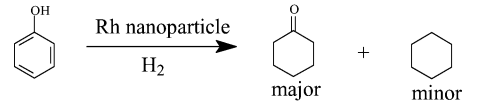
at 265 nm dropped rapidly probably due to mixing after injection because the detector was located at the inlet of the injection line. After this period of time, the decrease in absorbance at 265 nm more or less followed first order kinetics and reached a near constant value ($A = 0.2$) after 20 min. Tetralin absorbs at 265 nm (spectrum 2 in Fig. 2(a)) but its molar absorption coefficient (5.5×10^2) is about one order of magnitude smaller than that of naphthalene. After one hour, the system was depressurized and the materials in the CO_2 phase were collected in $CDCl_3$ for NMR measurements. The reactor was washed with $CDCl_3$ to remove all residual materials for a separate NMR measurement. The NMR results indicated that nearly all of the original naphthalene (> 96%) injected into the reactor were reacted to form tetralin (eqn. (1)). The NMR results also showed that AOT was not affected by the catalyst. The cosurfactant PFPE-PO_4 does not contain any functional group acceptable to hydrogenation. In the absence of $RhCl_3$ or H_2 gas, the hydrogenation of naphthalene was not observed.



(1)

When the amount of naphthalene was increased to 7.7×10^{-1} mmol, the % conversion to tetralin was about 82% after 1 h. A plot of the % conversion of naphthalene to tetralin in logarithmic scale *versus* time indicated the curve was near linear in the first 20 min but tended to deviate from a straight line (curved to the right) with further increase in time. The rate constant obtained from the slope was about 1.0×10^{-3} s^{-1}. The reaction rate depended on stirring. Without stirring, the reaction rate was much slower. The Rh nanoparticles formed in the water core of the microemulsion are obviously very reactive and consequently less stable than the Pd nanoparticles formed in the same microemulsion system.

Phenol was selected as a water-soluble arene for this hydrogenation study. Phenol is actually soluble both in supercritical CO_2 and in water.[10] In this experiment (18.2 mM AOT, 36.4 mM PFPE-PO_4 and $W = 30$), phenol was dissolved in the water core of the microemulsion together with Rh^{3+} (3.3×10^{-1} mmol phenol and 1.7×10^{-2} mmol Rh^{3+}). The water-in-CO_2 microemulsion was prepared in the same way as the naphthalene experiments. The hydrogenation experiments with phenol were carried out at 50 °C and 240 atm with 10 atm of H_2 gas injected from the 6.8 ml cell into the microemulsion system. This system does not show any characteristic absorptions in the UV-Vis region, therefore only NMR measurements of the initial and the final solutions of the experiments were used for quantification. After 5 min, the products were collected in $CDCl_3$ for NMR measurements. After depressurization, the compounds remaining in the fiber optic cell were also collected by washing with a $CDCl_3$ solution. The ^{1}H-NMR spectrum of the product solution showed that the two groups of peaks (from 6.78 to 7.19 ppm) belonging to phenol were virtually undetectable (Fig. 3(a)). The major product was cyclohexanone as indicated by its characteristic NMR peaks (1.65, 1.79 and 2.26 ppm) and the minor product was cyclohexane (the 1.36 ppm peak) (eqn. (2)). The ratio of cyclohexanone to cyclohexane calculated from the NMR peaks intensities is about 15:1. The conversion of phenol estimated from the detection limit of the NMR peak was > 92%. In control experiments performed in the absence of $RhCl_3$ or H_2 gas, the hydrogenation of phenol was not observed.



(2)

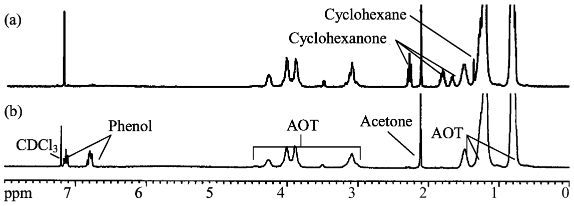


Fig. 3 NMR spectra of (a) the products collected from the phenol hydrogenation experiment in $CDCl_3$ (b) control experiment (phenol, AOT, PFPE-PO_4 and H_2 gas).

Hydrogenation of phenol catalyzed by the dimer of Rh(I) in organic solvents showed products were cyclohexanone and cyclohexanol.[11] Hydrogenation of phenol catalyzed by Rh(III) in dichloroethane showed cyclohexanone as the major product with cyclohexanol and cyclohexane as the minor products.[12] In biphasic hydrogenation systems,[5,6] Rh colloids suspended in the aqueous phase with surfactants converted phenol to cyclohexanol only. Rhodium catalyzed hydrogenation depends on the chemical form of the catalyst and solvation environment. In the hydrogenation of phenol with Rh nanoparticles in the CO_2 microemulsion system, one possible reaction route is the addition of 2 moles of hydrogen to phenol leading to the formation of cyclohexen-1-ol, which undergoes tautomerization to form cyclohexanone. Hydrogenation of cyclohexanone to cyclohexanol is negligible under our reaction conditions according to a separate experiment.

This report demonstrates that Rh nanoparticles can be formed by hydrogen gas reduction of Rh^{3+} ions dissolved in the water core of a water-in-CO_2 microemulsion. The Rh nanoparticles dispersed in the CO_2 phase are capable of catalyzing hydrogenation of CO_2-soluble or water-soluble arenes in supercritical CO_2. The hydrogenation of arenes in supercritical CO_2 catalyzed by the Rh nanoparticles is rapid. The Rh nanoparticles appear stable in the CO_2 microemulsion for about 20–30 min and gradually lose the catalytic capability after that, probably by aggregation. Methods for improving the stability of the Rh nanoparticles in the water-in-CO_2 microemulsion system are currently under investigation.

This work was supported by a DEPSCoR grant (DAAD19-01-0458) from the Army Research Office (ARO) managed by Dr. Stephen Lee of the ARO Chemistry Division.

Notes and references

1 H. Ohde, C. M. Wai, H. Kim, J. Kim and M. Ohde, *J. Am. Chem. Soc.*, 2002, **124**, 4540.
2 P. G. Jessop, T. Ikariya and R. Noyori, *Chem. Rev.*, 1999, **99**, 475.
3 A. Baiker, *Chem. Rev.*, 1999, **99**, 453.
4 A. Stanislaus and B. H. Cooper, *Catal. Rev.*, 1994, **36**, 75.
5 J. Schulz, A. Roucoux and H. Patin, *Chem. Commun.*, 1999, 535.
6 R. J. Bonilla, B. R. James and P. G. Jessop, *Chem. Commun.*, 2000, 941.
7 F. Hunt, H. Ohde and C. M. Wai, *Rev. Sci. Instrum.*, 1999, **70**, 4661.
8 J. A. Creighton and D. G. Eadon, *J. Chem. Soc., Faraday Trans.*, 1991, **87**, 3881.
9 D. W. Matson, J. L. Fulton, R. C. Petersen and R. D. Smith, *Ind. Eng. Chem. Res.*, 1987, **26**, 2298.
10 R. A. Van Leer and M. E. Paulaitis, *J. Chem. Eng. Data*, 1980, **25**, 257.
11 K. R. Jauszkiewicz and H. Alper, *Organometallics*, 1983, **2**, 1055.
12 J. Blum, I. Amer, A. Zoram and Y. Sasson, *Tetrahedron Lett.*, 1983, **24**, 4139.