DOI: 10.1002/chem.200802697

Enhanced Pd-Catalyzed Hydrogenation of Olefins within Polymeric Microreactors under Organic/Aqueous Biphasic Conditions

Yang Lan, Minchao Zhang, Wangqing Zhang,* and Li Yang^[a]

The hydrogenation of olefins has fundamental importance in both academic and industrial fields.^[1] Batch hydrogenation carried out in industry or the academic laboratory basically uses homogeneous or heterogeneous catalysts.^[2,3] Homogeneous catalysts generally have high activity, but with the disadvantage of hard product separation and catalyst recyclability.^[2] On the other hand, besides low activity, heterogeneous catalysts need to be removed from the reaction system by filtration, which may take as long as the chemical reaction itself.^[3] Therefore, research into more efficient catalytic system has been converted to organic/aqueous multiphase catalysis, which combines the advantages of both homogeneous and heterogeneous catalysis.^[4,5] Organic/aqueous biphasic catalysis employing water-soluble transition-metal complexes or metal nanocatalysts has become popular over the past few decades,^[6-12] because it is easy to realize catalyst recyclability and product separation by simple means of decantation, since the catalyst is dispersed in aqueous phase and the product in organic phase. However, while the biphasic conditions facilitate catalyst/product separation, it also introduces a kinetic barrier due to mass-transport limitations between the two phases.^[4,5] To promote mass transportation, several approaches including addition of co-solvent,^[13] surfactant^[14] and the use of phase-transfer catalysts^[15] and amphiphilic catalysts,^[16] have been proposed.

Reactions within a suitable micro- or nanoreactor^[17] can be promoted possibly due to high local concentration of reactants.^[18] Herein, we propose a microreactor of a watersoluble hollow polymeric microsphere with Pd nanoparticles immobilized in the wall for the hydrogenation of olefins under organic/aqueous biphasic conditions. The present microreactor possesses an important advantage in that it has the ability to encapsulate and enrich hydrophobic organic substrates in the aqueous phase. Therefore, there is no need to add a co-solvent or surfactant, and hydrogenation occurs efficiently within the microreactor with high local concentration of reactants. Additionally, the microreactor is stable and can be possibly used in practical applications for continuous hydrogenation of olefins on a technical scale without deactivation in activity.

The microreactor schematically shown in Figure 1a is composed of three parts: 1) the outer corona of polyacrylamide (PAM), which is hydrophilic and keeps the microreactor suspending in aqueous phase; 2) the cross-linked and hydrophobic wall of poly[styrene-co-2-(acetoacetoxy)ethylmethacrylate] (PS-co-PAEMA), which maintains the body of the hollow microsphere; and 3) 3.9 nm Pd nanoparticles, which are immobilized in the wall of the hollow microsphere. The microreactor was synthesized by two general steps (Figure S1 in the Supporting Information). First, hollow microspheres were constructed by using several procedures of seed polymerization and followed by removal of the seed. The synthesis was tracked by IR (Figure S2 in the Supporting Information) and solid-state ¹³C CPMAS NMR spectroscopy (Figure S3 in the Supporting Information), as well as TEM (Figure S4 in the Supporting Information). Second, Pd ions were firstly conjugated with the chelate ligands of PAEMA^[19] and subsequently reduced by NaBH₄ aqueous solution, which consequently resulted in formation of 3.9 nm Pd nanoparticles immobilized in the walls of the hollow microspheres (Figure 1). Herein, it is deduced that the Pd nanoparticles are selectively embedded in the wall of the hollow microspheres, since the chelate segment of PAEMA is located predominantly at the wall of the hollow microspheres. Powder X-ray diffraction (XRD) patterns (Figure S7 in the Supporting Information) also confirm the formation of Pd nanoparticles.

The microreactor can be easily dispersed in aqueous phase due to the hydrophilic PAM corona (Figure S6 in the Supporting Information). Besides, the unique structure of the microreactor endows itself with an important advantage; that is, the microreactor can encapsulate and enrich organic





© 2009 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

 [[]a] Y. Lan, M. Zhang, Prof. W. Zhang, L. Yang Key Laboratory of Functional Polymer Materials of Ministry of Education Institute of Polymer Chemistry, Nankai University Tianjin 300071 (P.R. China) Fax: (+86)22-23503510

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200802697.

COMMUNICATION



Figure 1. Schematic structure (a) and TEM images (b and c) of the microreactor.

reactants since the hollow microsphere provides hydrophobic microenvironment for organic reactants in water. Herein the encapsulation of a poorly water-soluble cinnamic alcohol (CA) and a hydrophobic styrene is typically introduced. After the hollow microspheres are introduced into the saturated CA aqueous solution and stirred for 1 h, the CA concentration located in the hollow microspheres is almost 270 times higher than that in water, and the encapsulated CA takes up about 52% of vacancy volume of the hollow microsphere (Figure S5 in the Supporting Information). For the more hydrophobic styrene, the corresponding values are 5070 times and 100%, respectively. The difference in encapsulation and enrichment of CA and styrene may be attributed to their polarity disparity.

The merits mentioned above make the microreactor a potential candidate for organic/aqueous biphasic catalysis. The entire concept of hydrogenation within the microreactor under organic/aqueous biphasic condition is pictorially shown in Figure 2. The olefin forms one phase, meanwhile



Figure 2. Schematic hydrogenation within the microreactor under organic/aqueous biphasic conditions.

water that contains the microreactor forms the other. The molecules of olefin firstly diffuse into water and then are encapsulated and concentrated into the microreactor, in which the hydrogenation takes place. Then the product diffuses into water and is further extracted into the organic phase. Clearly, the hollow microspheres accelerate the diffusing of the reactants from the organic phase to the aqueous phase and further concentrate them within the microreactor through encapsulation, which is the reason for efficient hydrogenation.

To explore hydrogenation within the microreactor under organic/aqueous biphasic condition, the hydrogenation of CA with H₂ at 35 °C was evaluated as a typical example. It is found that the conversion increases almost linearly along with time, showing a quasi-zero-order kinetics to CA concentration (Figure 3). This phenomenon can be explained by the fact that the local concentration of CA encapsulated within the microreactor is high enough during the process of

Chem. Eur. J. 2009, 15, 3670-3673

© 2009 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

www.chemeurj.org

- 3671



Figure 3. Time-dependence conversion of CA within the microreactor under organic/aqueous biphasic conditions. Reaction conditions: aqueous dispersion of the microreactor (20.0 mL) containing the Pd catalyst (1.67×10^{-5} mol); CA (4.47 g, ≈ 4.3 mL, 3.33×10^{-2} mol); 35 °C; 1 atm H₂.

hydrogenation under the present organic/aqueous biphasic conditions.

Hydrogenation of several typical aliphatic, aromatic, and alicyclic olefins within the microreactor under organic/aqueous biphasic conditions at 35°C was further explored. All hydrogenation reactions were performed at 35°C, since all olefins used in the present study are liquid at this temperature. Hydrogenation of all the olefins proceeded efficiently and almost quantitive yields were achieved (Table 1). For aliphatic olefins, butyl methacrylate is totally converted to butyl butyrate in 3 h, and the butyl acrylate, which has less hindered double bonds, is converted to butyl propionate in 1 h (entries 1 and 2). Of all the aromatic olefins, styrene, the polarity of which is the smallest, possesses the fastest conversion rate and the highest turnover frequency (TOF; entries 4-10). Compared the activity of the present microreactor with several reference metal nanocatalysts of Pd^[20,21] and $Pt^{[3e]}$ and even the $Rh^{[22]}$ catalyst under other similar conditions, the present microreactor is very competitive (entries 5-8 and 12). It is deemed that the efficient hydrogenation is ascribed to the high local concentration of olefins encapsulated within the microreactor. To confirm this hypothesis, hydrogenation of styrene employing the reference catalyst of 4.1 nm Pd nanoparticles immobilized on the solid microsphere (Figure S8 in the Supporting Information) under other similar conditions was tested, resulting in a much lower TOF than those of the microreactor (entry 5). Furthermore, the present microreactor used in hydrogenation under organic/aqueous biphasic conditions has an advantage that it avoids the bothersome separation of catalyst or the product purification, which is usually necessary in the batch hydrogenation employing a typical heterogeneous Pd catalysts, such as Pd/C^[23] and Pd nanoparticles deposited on mesoporous silicas,^[24-26] or in the hydrogenation under multiphasic condition employing a phase-transfer catalyst^[27,28] (Figure S9 in the Supporting Information). In the present experiment, after the hydrogenation is completed, the organic phase just contains the product, which can be separatTable 1. Hydrogenation of olefins within the microreactor under organic/ aqueous biphasic conditions. $^{\left[a\right] }$

Entry	Substrate	Product	Conditions S/C ^[b] /t [h]/ T [°C]	Yield [%] ^[c]	$\begin{array}{c} TOF \\ [h^{-1}]^{[d]} \end{array}$
1			2000/3/35	100	930
2		$\sim 0 \sim 0$	2000/1/35	100	2150
3 ^[e]			2000/1/35	100	2150
4			2000/2/35	100	1449
5 ^[f]			2000/6/35	100	204
6 ^[g]			122/5/80	99	_
7 ^[h]			449/4/50	100	448
8 ^[i]			4000/1/90	100	2000
9	ОН	ОН	2000/14/35	99.5	219
10	CI	CI	2000/2/35	100	1099
11		\bigcirc	2000/2/35	100	1136
12 ^[j]			5000/1/75	91	-

[a] Reaction conditions: aqueous dispersion of the microreactor (20.0 mL) containing the Pd catalyst $(1.67 \times 10^{-5} \text{ mol})$; substrate (3.33 × $10^{-2} \text{ mol})$; 35 °C; 1 atm H₂. [b] S/C= the molar ratio of substrate to catalyst. [c] Yield measured by ¹H NMR spectroscopy or HPLC. [d] TOF is measured as moles hydrogenated olefin per mole Pd per hour from the initial reaction time. [e] Yield at the eighth catalyst cycle. [f] The reference catalyst of 4.1 nm Pd nanoparticles immobilized on the solid microsphere (Figure S8 in the Supporting Information). [g] The reference Pd catalyst in reference [20]. [h] The reference Pd catalyst in reference Pt catalyst in reference [21]; [i] The reference Rh catalyst in reference Pt catalyst in reference [3e].

ed simply by decantation and no further purification is needed; therefore it has possible practical application for continuous hydrogenation of olefins on technical scale (Figure S9 in the Supporting Information).

The reusability of the microreactor was also tested by using the hydrogenation of butyl acrylate as a typical example. After 1 h the hydrogenation was completed (Figure S10 in the Supporting Information), the organic phase was removed by simple decantation, and butyl acrylate was reloaded. It is found that the microreactor can be used for at least eight times without any decrease in activity (entry 3 in Table 1, and Table S1 in the Supporting Information). The organic phase was analyzed by atomic absorption spectroscopy (AAS) and no Pd catalyst, which might have leached into the organic phase, was detected. Moreover, the longtime endurance of the microreactor is also judged by the hydrogenation of CA when the CA/Pd ratio is increased to 40000, which affords a turnover number (TON, mole product per mol Pd) of 14400 in 240 h (Figure S11 in the Supporting Information).

In conclusion, a microreactor of hollow polymeric microsphere with Pd nanoparticles immobilized in the wall has

been designed for efficient hydrogenation of olefin under organic/aqueous biphasic conditions. The fact that the microreactor can encapsulate and concentrate the hydrophobic olefin into the cavity of the microreactor in aqueous phase brings a new way for the design of organic/aqueous biphasic catalysts. Work on the design of similar microreactors for use in chemoselective hydrogenation and aerobic alcohol oxidation is in progress.

Experimental Section

Detailed experimental procedures are reported in the Supporting Information.

Acknowledgements

The authors thank the financial support by National Science Foundation of China (No. 20504016) and the Program for New Century Excellent Talents in University (No. NCET-06-0216).

Keywords: biphasic catalysis • hydrogenation microreactors • nanoparticles • palladium

- [1] N. B. Johnson, I. C. Lennon, P. H. Moran, J. Ramsden, Acc. Chem. Res. 2007, 40, 1291.
- [2] B. Chen, U. Dingerdissen, J. G. E. Krauter, H. G. J. Lansink Rotgerink, K. Möbus, D. J. Ostgard, P. Panster, T. H. Riermeier, S. Seebald, T. Tacke, H. Trauthwein, *Appl. Catal. A* 2005, 280, 17.
- [3] a) Y. Jiang, Q. Gao, J. Am. Chem. Soc. 2006, 128, 716; b) R. Nakao, H. Rhee, Y. Uozumi, Org. Lett. 2005, 7, 163; c) N. Erathodiyil, S. Ooi, A. M. Seayad, Y. Han, S. S. Lee, J. Y. Ying, Chem. Eur. J. 2008, 14, 3118; d) T. Ueno, M. Suzuki, T. Goto, T. Matsumoto, K. Nagayama, Y. Watanabe, Angew. Chem. 2004, 116, 2581; Angew. Chem. Int. Ed. 2004, 43, 2527; e) S. Ikeda, S. Ishino, T. Harada, N. Okamoto, T. Sakata, H. Mori, S. Kuwabata, T. Torimoto, M. Matsumura, Angew.

COMMUNICATION

Chem. **2006**, *118*, 7221; *Angew. Chem. Int. Ed.* **2006**, *45*, 7063; f) R. Abu-Reziq, D. Wang, M. Post, H. Alper, *Adv. Synth. Catal.* **2007**, *349*, 2145; g) G. Sharma, Y. Mei, Y. Lu, M. Ballauff, T. Irrgang, S. Proch, R. Kempe, *J. Catal.* **2007**, *246*, 10.

- [4] W. Keim, Green Chem. 2003, 5, 105.
- [5] F. Joó, Acc. Chem. Res. 2002, 35, 738.
- [6] M. Gruber, M. Wagner, R. Heidenreich, J. G. E. Krauter, N. Coskun, K. Köhler, *Catal. Lett.* 2004, 94, 177.
- [7] J. Schulz, A. Roucoux, H. Patin, Chem. Eur. J. 2000, 6, 618.
- [8] F. Lu, J. Liu, J. Xu, Adv. Synth. Catal. 2006, 348, 857.
- [9] S. S. Zinovyev, A. Perosa, P. Tundo, J. Catal. 2004, 226, 9.
- [10] S. L. Vinson, M. R. Gagné, Chem. Commun. 2001, 1130.
- [11] R. Zhang, W. Ding, B. Tu, D. Zhao, Chem. Mater. 2007, 19, 4379.
- [12] D. E. Bergbreiter, S. D. Sung, Adv. Synth. Catal. 2006, 348, 1352.
- [13] C. Bianchini, A. Meli, V. Patinec, V. Sernau, F. Vizza, J. Am. Chem. Soc. 1997, 119, 4945.
- [14] B. Boyer, A. Hambardzoumian, J.-P. Roque, N. Beylerian, *Tetrahe*dron 2000, 56, 303.
- [15] S. Tilloy, H. Bricout, E. Monflier, Green Chem. 2002, 4, 188.
- [16] M. S. Goedheijt, B. E. Hanson, J. N. H. Reek, P. C. J. Kamer, P. W. N. M. v. Leeuwen, J. Am. Chem. Soc. 2000, 122, 1650.
- [17] D. M. Vriezema, M. C. Aragones, J. A. A. W. Elemans, J. L. M. Cornelissen, A. E. Rowan, R. J. M. Nolte, *Chem. Rev.* 2005, 105, 1445.
- [18] S. M. Leeder, M. R. Gagné, J. Am. Chem. Soc. 2003, 125, 9048.
- [19] P. Zheng, W. Zhang, J. Catal. 2007, 250, 324.
- [20] M. Vasylyev, G. Maayan, Y. Hovav, A. Haimov, R, Neumann, Org. Lett. 2006, 8, 5445.
- [21] U. R. Pillai, E. Sahle-Demessie, J. Mol. Catal. A 2004, 222, 153.
- [22] D. C. Mudalige, G. L. Rempel, J. Mol. Catal. A 1997, 116, 309.
- [23] S. Domínguez-Domínguez, A. Berenguer-Murcia, B. K. Pradhan, A. Linares-Solano, D. Cazorla-Amoros, J. Phys. Chem. C 2008, 112, 3827.
- [24] Y. Jiang, Q. Gao, J. Am. Chem. Soc. 2006, 128, 716.
- [25] J. Panpranot, K. Pattamakomsan, P. Praserthdam, J. G. Goodwin, Jr., Ind. Eng. Chem. Res. 2004, 43, 6014.
- [26] J.-N. Park, A. J. Forman, W. Tang, J. Cheng, Y.-S. Hu, H. Lin, E. W. McFarland, *Small* **2008**, *4*, 1694.
- [27] J. Schulz, A. Roucoux, H. Patin, Chem. Commun. 1999, 535.
- [28] A. Perosa, P. Tundo, S. Zinovyev, Green Chem. 2002, 4, 492.

Received: December 20, 2008 Published online: February 26, 2009