Magnetically Retrievable Palladium/Maghemite Nanocomposite Catalysts Prepared by Sonochemical Reduction Method

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Nanocomposite catalysts, consisting of Pd and magnetic maghemite, prepared by sonochemical reduction method showed high catalytic activities for the reduction of nitrobenzene. The used catalysts could be readily retrieved by magnets and be employed for further repetitive tests and verified the durability of the catalytic performance.

The demands of noble metals, which are indispensable for IT industries and environmental protections such as automobile catalysts, have been extensively increasing. In uses of these noble metals, it is important to develop sustainable processes lightening the burdens on the environment.

It is a general strategy to fabricate nanosized noble metals to enhance the catalytic activities. The fatal drawback of the nanoparticles is the difficulty in retrieving them from the reaction system. Further, remaining nanoparticles in the reaction system contaminate the reaction products. From the view point of recycle of noble metals, it is necessary to establish the effective methodology for retrieving the noble metal as reusable catalysts.

In this study, we demonstrate the magnetically retrievable novel nanocatalysts consisting of Pd and magnetic maghemite (γ-Fe_2O_3) prepared by sonochemical reduction method, and the catalytic activities were evaluated by a reduction of nitrobenzene (NB). Further, the catalysts were retrieved by a neodymium magnet, and its activities were repeatedly evaluated to assess the durability. Recently, some researches focusing on "the magnetically retrievable heterogeneous catalysts" have been reported.[1] Unlike conventional methods such as impregnation, the sonochemical method can reduce noble metal ions and concurrently immobilize the formed nanoparticles on the surface of supports without rising temperatures.[2]

An aqueous solution containing 0.5 mM of Na_2PdCl_4, γ-Fe_2O_3 nanoparticles (NanoTek™, C. I. Kasei) and poly(ethylene glycol) monostearate (PEG-MS, $n \approx 40$) was purged by Ar prior to sonication. In the sonochemical reduction, PEG-MS is the precursor of the reducing agents.[3] The weight ratio of Pd to γ-Fe_2O_3 was 1/5, 1/10, and 1/20. The sample solution was sonicated in a closed glass vessel with 200 kHz and 6 W cm^{-2} by a multiwave ultrasound generator (Kaijo TA-4021) with a PZT oscillator (Kaijo type 4611). The details of the sonication setup were described in previous papers.[4]

When the sample solution was sonicated, the color of the solution was changed from reddish-brown originating from pure γ-Fe_2O_3 to dark brown, indicating formation of Pd nanoparticles[5] by the reduction of Pd ions. After 15 min of sonication, the sample solution was separated into magnetic and nonmagnetic fractions by a neodymium magnet.

The magnetic fractions were redispersed in pure water, and the dispersion was dropped on a collodion-covered copper mesh and then dried for TEM specimens. The morphologies of the magnetic fractions were analyzed by a scanning-transmission electron microscope (STEM), FEI Titan 80–300 operated at 300 kV, which is equipped with a high-angle annular dark field detector (HAADF). The image of the obtained Pd/γ-Fe_2O_3 nanocomposite catalysts is shown in Figure 1, wherein the contrast of HAADF images is proportional to square of the atomic numbers. The atomic numbers of Pd and Fe are 42 and 26, respectively, so that it is concluded that the smaller particles with bright contrast are Pd nanoparticles, and the larger particles with dark contrasts are γ-Fe_2O_3. The distributions of the constituent elements were analyzed by EDX mappings, revealing that the Pd nanoparticles are immobilized on the surface of γ-Fe_2O_3 and that the average diameter of Pd is 3.8 nm. The average diameters of the immobilized Pd nanoparticles prepared by different conditions are tabulated in Table 1. The amounts of immobilized Pd derived from the differences between the fed and the remaining Pd in nonmagnetic fraction determined by a colorimetric method[6] are included in the table. We proposed the mechanism for the sonochemical immobilization of noble metal nanoparticles such that noble metal ions were reduced in the bulk solution to form the nuclei of the particles, and then they were immobilized on the surface of the supports.[7] Significant dependency of the sizes and amounts of Pd on the amounts of γ-Fe_2O_3 is not observed, which is consistent with the proposed mechanism.

The catalytic activities of the nanocatalysts were investigated by the reduction of NB under the reaction condition reported by Lu et al.[8] A 0.01-g portion of the sonochemically prepared catalysts was added to 30 mL of ethanol containing 0.3 mmol of NB. The reduction of NB was conducted at 25 °C under 1 atm of hydrogen. The solution was periodically sampled, and trace of the magnetic fraction was removed from the solution using a neodymium magnet prior to the HPLC analyses. The progress of the reaction was monitored by the amounts of formed aniline (AN) and consumed NB measured by HPLC. The fed NB

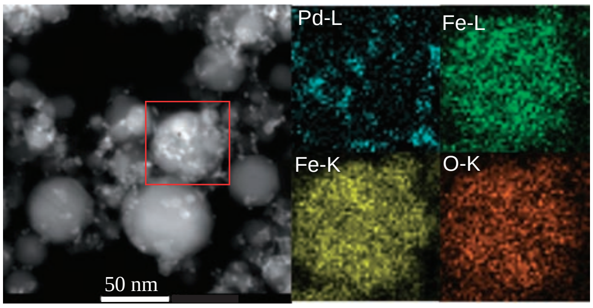

Figure 1. HAADF-STEM image of un-used Pd/γ-Fe_2O_3 nanocomposite catalysts and corresponding EDX mappings.

Table 1. Sonochemically prepared Pd/γ-Fe_2O_3 nanocomposite catalysts

	(a)	(b)	(c)
γ-Fe_2O_3/mg	13.3	26.6	53.2
Pd/γ-Fe_2O_3 (w/w)[a]	0.2	0.1	0.05
Immobilized Pd/mg	2.53	2.46	2.31
	(95.40%)	(92.40%)	(86.96%)
Pd size/nm	4.9 ± 0.9	4.0 ± 0.8	3.8 ± 0.9
TOF/h^{-1} [b]	55.3 ± 3.7	70.5 ± 31.7	301 ± 94.3

[a] Fed Pd was 0.5 mM (2.66 mg) in each sample. [b] Average of four times of repetitive tests.

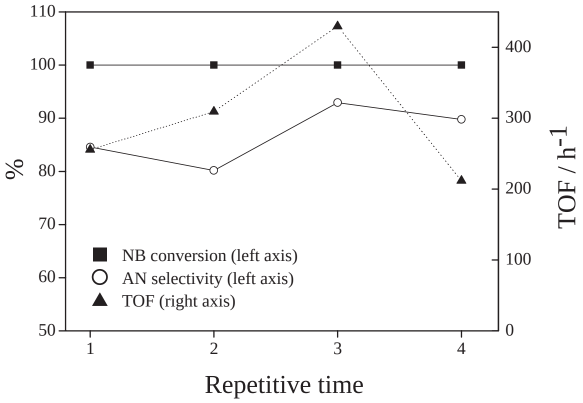

Figure 2. Change in the catalytic activity during the repetitive uses.

was completely consumed within 30 min of the reaction time. In response, AN was formed and the yield was reached the maximum at the 30 min of reaction time. The change in the color of the reaction solution was not observed during 60 min of the reactions, indicating that detachments of Pd nanoparticles did not occur. After 60 min, the nanocatalysts were retrieved by a neodymium magnet and supplied for the next measurements after rinsing with ethanol.

The changes in NB conversion (consumed NB(mol)/fed NB(mol)), AN selectivity (formed AN(mol)/consumed NB(mol)), and TOF of AN formation (formed AN(mol)/immobilized Pd(mol)/reaction time (h)) in the four times of repetitive uses are displayed in Figure 2.[9] On an average, NB conversion and AN selectivity were 100 and 87%, respectively. A spread of TOF as found in Figure 2 is probably due to the state of the dispersion of the catalysts. The maximum TOF was 429.6 h^{-1}, and the average of the four repetitive evaluations was 301.2 h^{-1}. This result is not inferior to the previously reported value, e.g., the activity of Pd/Ni catalysts by Nagaveni et al.[10] Furthermore, the present nanocatalysts exhibits high TOF in spite of repetitive uses, and it is advantageous for practical usages and saving Pd. In addition, magnetic retrieving facilitates the effective purification of the reaction products. STEM observation of the catalysts after four times repetitive evaluations showed no distinct changes in the sizes of the immobilized Pd nanoparticles between before and after evaluation, which is consistent with the maintenance of the initial catalytic activities. TOFs of the catalysts with different compositions are listed in Table 1, wherein the TOFs are the average of four repetitive uses. Faint correlation between TOFs and the sizes of the immobilized Pd nanoparticles is recognized, and it suggests that the catalytic activity of the present catalysts depend not only on the sizes of the Pd but on carrier effect coming from the amount of γ-Fe_2O_3 supports.

In conclusion, Pd/γ-Fe_2O_3 nanocomposite catalysts prepared by the sonochemical reduction method exhibit excellent catalytic activities for the reduction of NB and high durability for repetitive uses.

This study was financially supported by Japan Science and Technology Agency. The authors thank Ms. Y. Matsuda (IMR, Tohoku Univ.) for her helpful assistance in laboratory works.

References and Notes

1 a) D. K. Yi, S. S. Lee, J. Y. Ying, *Chem. Mater.* **2006**, *18*, 2459. b) Z. Wang, P. Xiao, B. Shen, N. He, *Colloids Surf., A* **2006**, *276*, 116. c) D. Guin, B. Baruwati, S. V. Manorama, *Org. Lett.* **2007**, *9*, 1419.
2 K. Okitsu, S. Nagaoka, S. Tanabe, H. Matsumoto, Y. Mizukoshi, Y. Nagata, *Chem. Lett.* **1999**, 271.
3 Y. Mizukoshi, E. Takagi, H. Okuno, R. Oshima, Y. Maeda, Y. Nagata, *Ultrason. Sonochem.* **2001**, *8*, 1.
4 For example, Y. Mizukoshi, R. Oshima, Y. Maeda, Y. Nagata, *Langmuir* **1999**, *15*, 2733.
5 J. A. Creighton, D. G. Eadon, *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 3881.
6 K. Okitsu, H. Bandow, Y. Maeda, Y. Nagata, *Chem. Mater.* **1996**, *8*, 315.
7 Y. Mizukoshi, Y. Tsuru, A. Tominaga, S. Seino, N. Masahashi, S. Tanabe, T. A. Yamamoto, *Ultrason. Sonochem.* **2008**, *15*, 875.
8 P. Lu, T. Teranishi, K. Asakura, M. Miyake, N. Toshima, *J. Phys. Chem. B* **1999**, *103*, 9673.
9 In the calculations of catalytic activities, adsorbed nitrobenzene on catalyst surface and reaction vessel (7% of fed amount), which was determined in a blank test in the absence of hydrogen, was subtracted from the consumption of nitrobenzene.
10 K. Nagaveni, A. Gayen, G. N. Subbanna, M. S. Hegde, *J. Mater. Chem.* **2002**, *12*, 3147.