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THE REDUCTION OF DISSOLVED OXYGEN BY HYDRAZINE OVER PLATINUM CATALYST SUPPORTED ON DISORDERED MESOPOROUS MATERIALS

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Abstract – Catalytic reduction of dissolved oxygen by hydrazine at room temperature was investigated on Pt catalysts supported on KIT-1 mesoporous material and Y and ZSM-5 zeolites. Pt catalyst supported on AlKIT-1 mesoporous material exhibited high performance ascribed to the high dispersion of Pt and the large diameter lowering diffusion restriction.

Key words : KIT-1 Mesoporous Material, Zeolite, Platinum, Dissolved Oxygen

INTRODUCTION

The concentration of oxygen saturated in water from air is about 8 ppm at room temperature. Even though the concentration of dissolved oxygen is low, it can cause serious metal corrosion. Therefore, oxygen concentration in cooling water in a nuclear power plant should be regulated to remain below 5-10 ppb [Harhay and Wolfe, 1987]. The dissolved oxygen may be degassed by various physical methods such as evacuation and heating. However, physical methods are ineffective due to high operating costs and large construction investments. A chemical method of removing the dissolved oxygen through catalytic reduction using hydrazine is much more effective for meeting the regulation limit for large-scale plant operations [Dickerson, 1985].

Noble metals such as platinum and palladium are most frequently used as an active phase of catalyst for the removal of the dissolved oxygen. The palladium catalyst supported on ion exchange resin exhibits high performance in a swelled state, resulting in rapid removal of the dissolved oxygen even at room temperature [Harhay and Wolfe, 1987]. The small resistance of water transfer in the ion exchange resin enhances the removal rate of dissolved oxygen, compared with other catalyst supports with small pores.

Recently, mesoporous materials with a uniform cross-sectional diameter in the mesopore range of 2-10 nm have been found [Kresge et al., 1992; Beck et al., 1992]. Mesoporous materials attract much attention in catalysis because of the remarkable increase in the pore diameter compared with those of zeolites, which are less than 1.5 nm [Sayari, 1996]. The specific surface area of mesoporous materials depends on the pore diameter but, in general, varies in the range of 800-1,200 $m^2 \cdot g^{-1}$. The large pore diameter with a large specific surface area is expected to cause low diffusion limitation as a catalyst support, resulting in high catalytic activity of the reduction of dissolved oxygen.

In this study, the possibility of mesoporous material as catalyst support for the removal of dissolved oxygen in water using hydrazine was investigated. A catalyst was prepared for this purpose by supporting platinum on a disordered mesoporous material designated KIT-1 [Ryoo et al., 1996a], constructed by the interconnection of mesoporous channels of 3 nm in diameter in a three-dimensional disordered way. KIT-1 was selected as the catalyst support since it exhibits outstanding hydrothermal stability among mesoporous materials found recently [Ryoo et al., 1996b]. Moreover, the three-dimensional channel texture has the advantage of facile diffusion of a reaction mixture, compared with the best known mesoporous molecular sieve designated MCM-41, which is constructed by ordered hexagonal arrays of one-dimensional channels.

EXPERIMENT

1. Synthesis of Mesoporous Materials and Zeolites

Pure silica form of KIT-1 mesoporous material was obtained by hydrothermal synthesis using sodium silicate, hexadecyltrimethylammonium chloride (HTACl) and ethylenediaminetetraacetic tetrasodium salt (Na_4EDTA) [Ryoo et al., 1996a, b]. Then 14.3 g of a colloidal silica Ludox HS40 (39.5 wt% SiO_2, 0.4 wt% Na_2O, 60.1 wt% H_2O, Du Pont) was added to 46.9 g of 1.0 M aqueous NaOH solution preheated to 353 K with stirring. Continuous stirring of the resulting gel mixture at 353 K gave a clear solution with Na/Si=0.5. The sodium silicate solution was dropwise added to a polypropylene bottle containing a mixture of 0.29 g of 28 wt% aqueous NH_3

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solution, 23.8 g of Na_4EDTA, 20.0 g of 25 wt% HTACl solution and 28.0 g of doubly distilled water, with vigorous mechanical stirring at room temperature. The resulting gel mixture in the bottle had a molar composition of 4 SiO_2 : 1 HTACl : 4 Na_4EDTA : 1 Na_2O : 0.15 $(NH_4)_2O$: 350 H_2O. After 1 h more of stirring, the gel mixture was heated to 370 K for 2 days. The resulting mixture was cooled to room temperature. Subsequently, the pH of the mixture was adjusted to 10.2 by dropwise addition of 30 wt% acetic acid with vigorous stirring. The raction mixture after the pH adjustment was heated again to 370 K for 2 days. This procedure for pH adjustment to 10.2 and subsequent heating for 2 days was repeated twice more. The precipitated product had a disordered surfactant-silicate mesostructure. The product was filtered, washed with doubly distilled water and dried in an oven at 370 K. The product was then calcined in O_2 flow while temperature was increased from room temperature to 823 K over 10 h and maintained at 823 K for 4 h. The product yield was more than 90 %, based on the silica recovery.

An aluminium-containing KIT-1 (AlKIT-1) sample with Si/Al=40 was prepared by adding 5 wt% aqueous solution of sodium aluminate (Strem, 99.9 % on metal basis) to the above surfactant-silicate gel mixture before heating to 370 K dropwise with vigorous mixing. The reaction mixture was stirred for 30 min more after the addition was completed. The remainder of the synthesis procedure was the same as the preparation of the above pure silica KIT-1.

The NaY zeolite with Si/Al=2.4 was hydrothermally synthesized at 373 K, using Ludox HS40 as the silica source. The HZSM-5 zeolite with Si/Al=25 was obtained from the PQ Corporation.

2. Platinum Support

Typically, 1.0 g of the AlKIT-1 sample was slurried in 100 mL of aqueous solution of $Pt(NH_3)_4(NO_3)_2$ (Aldrich) for 6 h at room temperature, in order to support Pt by the ion exchange of $Pt(NH_3)_4^{2+}$. The concentration of the Pt compound in the solution was given in order to achieve desired Pt wt%, assuming 100 % support. After the ion exchange, the sample was filtered, washed with doubly distilled water and dried in a vacuum oven at room temperature. The resulting Pt/AlKIT-1 sample was calcined in O_2 flow. The calcination temperature was linearly increased from room temperature to 593 K over 12 h and then maintained for 2 h. O_2 gas was dried through a molecular sieve trap. The gas flow rate was 1 $L \cdot min^{-1} \cdot g^{-1}$. After the calcination treatment was over, O_2 gas was evacuated from the reactor at 573 K. Subsequently, the Pt species was reduced with heating in H_2 flow (99.999 %, passed through a MnO/SiO_2 trap). The H_2 flow rate was 200 $mL \cdot min^{-1} \cdot g^{-1}$. The reduction temperature was linearly increased from room temperature to 573 K over 4 h and maintained at 573 K for 2 h.

An impregnation method was used for supporting Pt on KIT-1 since the pure-silica form did not have a sufficient ion exchange capacity to support Pt by the ion exchange. For the Pt impregnation, a 1.0 g of KIT-1 sample was slurried in 50 mL of an aqueous solution containing 4×10^{-2} g of $Pt(NH_3)_4(NO_3)_2$ (Aldrich). The aqueous solution was completely evaporated by using a rotatory evaporator at 443 K. The resulting Pt/KIT-1 sample was calcined in O_2 flow and subsequently reduced in H_2, in the same way used for the above ion exchanged sample.

Platinum supporting on NaY and HZSM-5 zeolites was performed by the ion exchange of $Pt(NH_3)_4^{2+}$ in the same way used for Pt/AlKIT-1.

3. Characterization

Elemental analyses for Si/Al ratio and the Pt content were performed with inductively coupled plasma (ICP) emission spectroscopy (Shimadzu, ICPS-1000III). All samples obtained in the present work had the same aluminum content as the Si/Al ratio and the Pt content given with reactants for the synthesis and Pt supporting, respectively. XRD patterns were obtained with a CuK_α X-ray source using a Rigaku D/MAX-III (3 kW) instrument.

The adsorption isotherm of H_2 on the Pt-containing catalyst samples was volumetrically obtained at room temperature after all the preadsorbed hydrogen was desorbed at 673 K and 1×10^{-3} Pa for 1 h. The total number of hydrogen atoms chemisorbed per platinum atom (H/Pt) was determined by extrapolating the medium-pressure linear part of the isotherm of 10-50 kPa to zero pressure.

4. Measurement of Catalytic Activity

The rate of catalytic reduction of dissolved oxygen with hydrazine was measured using a 5-L Pyrex batch reactor at 298 K, in the same way as described elsewhere [Seo et al., 1996]. The amount of water was 5 L, and 0.05 g catalyst in the powder form dispersed in the water. The flow rate of argon was adjusted to 10 $mL \cdot min^{-1}$, in order to minimize the effects of oxygen inflow from air or the degassing of oxygen into the argon gas.

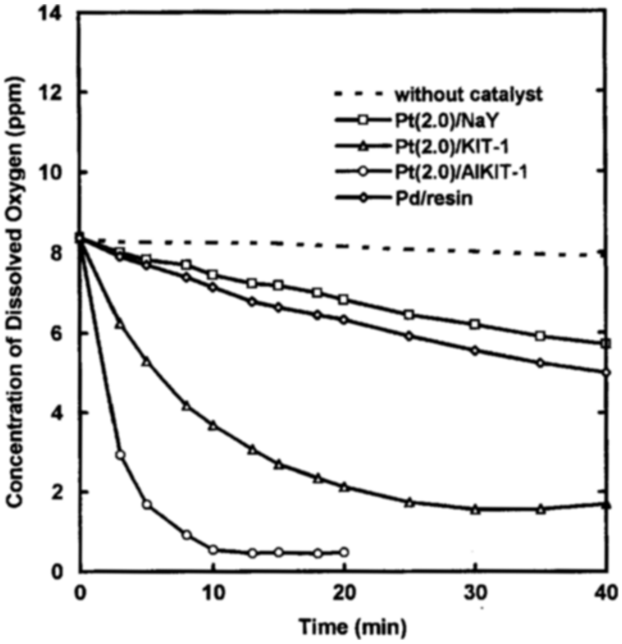

Fig. 1. Reduction reaction of dissolved oxygen (DO) with hydrazine on various catalysts at 25 °C $[N_2H_4]_0/[DO]_0=2.0$, water/catalyst=5 L/0.05 g.

RESULTS AND DISCUSSION

Fig. 1 shows the concentration of dissolved oxygen plotted against catalytic reaction time at 298 K. The concentration of dissolved oxygen changed very little without catalyst during the reaction period of one hour, even in the presence of hydrazine. When catalysts were suspended in the reaction mixture, the oxygen concentration began to show a rapid decrease. However, the reaction rate depended considerably on the catalysts. Both Pt(2.0)/KIT-1 and Pt(2.0)/AlKIT-1 showed very high catalytic activity for the oxygen removal reaction, compared with Pt(2.0)/NaY. The Pt(2.0)/AlKIT-1 catalyst showed a particularly high catalytic activity among the catalysts investigated here.

Table 1 summarizes Pt content, hydrogen chemisorption and catalytic activity of various catalysts investigated in the present study. The Pt wt% given in Table 1 is based on fully dehydrated weight of catalyst after evacuation at 673 K. The hydrogen chemisorption data, given in terms of H/Pt, represents the average number of chemisorbed hydrogen atoms per Pt atom supported on the catalysts. The Pt/NaY catalysts investigated in the present work are the same samples that were characterized by EXAFS and xenon adsorption in the previous work [Ryoo et al., 1993]. The EXAFS and xenon adsorption data indicated that the Pt/NaY catalysts contained Pt clusters of 1-nm diameter. The hydrogen chemisorption data more than 1 H/Pt are due to chemisorption of more than one hydrogen atoms per Pt atom for very small Pt clusters.

All the Pt/AlKIT-1 catalysts show similar H/Pt values to the Pt/NaY catalysts, which indicates that the Pt clusters supported on the Al-containing mesoporous material are about the same size as the Pt/NaY clusters. Compared with the Pt/AlKIT-1 samples, Table 1 shows small hydrogen chemisorption for the Pt/KIT-1 catalyst. The difference between pure-silica support and Al-containing support is similar to a recent result obtained for Pt supported on MCM-41 and AlMCM-41 [Ryoo et al., 1996c]. Platinum can be supported on the Al-containing materials by the ion exchange of $Pt(NH_3)_4^{2+}$, which gives small 1-nm Pt clusters inside the mesoporous channels.

Table 1. Platinum content, hydrogen chemisorption and catalytic activity for oxygen reduction of various catalysts

Catalyst	Pt wt%	H/Pt[a]	H_2 (10^{-6} $m^3 \cdot g^{-1}$)[b]	O_2 removal (%)[c]
Pt(2.0)/KIT-1	2.0	0.4	0.46	37
Pt(0.5)/AlKIT-1	0.5	1.4	0.40	30
Pt(1.0)/AlKIT-1	1.0	1.3	0.75	45
Pt(2.0)/AlKIT-1	2.0	1.2	1.38	80
Pt(2.0)/NaY	2.0	1.2	1.39	7
Pt(5.0)/NaY	5.0	1.2	3.48	7
Pt(2.0)/MZSM-5	2.0	0.6	0.69	10
Pd/resin[d]	0.3	–	–	6

[a] The number of chemisorbed hydrogen atoms per Pt atom impregnated.

[b] Volume of chemisorbed H_2 per g catalyst at 273 K and 1 atm.

[c] Percent of dissolved oxygen removed by the catalytic reduction during initial 5 min. $[N_2H_4]_0/[O_2]_0=2$, water/catalyst=5 L/0.05 g.

[d] Pd/resin catalyst was commercially available from Bayer.

However, the ion exchange technique fails to support Pt on the pure-silica forms of the mesoporous materials, since the pure-silica mesoporous materials have almost no ion exchange capacity, different from the Al-containing analogues. The impregnation method may be used to support Pt on the pure-silica MCM-41 and KIT-1, instead of the ion exchange technique. Thus, the resulting clusters in the case of the impregnation are much larger than 1 nm and show low dispersion of Pt [Ryoo et al., 1996a]. In the case of the large cluster formation, catalytic activity of the Pt/KIT-1 may decrease not only due to low metal dispersion but also to the diffusion limitation of reactants into the mesoporous channels.

The percentage of dissolved oxygen removed after the reaction of 5 min for various catalysts is also given in Table 1, in order to compare the catalytic activity under the same conditions. In the Pt/AlKIT-1 series, the catalytic activity increased almost linearly with respect to the Pt content. The Pt(0.5)/AlKIT-1 catalyst showed a much more rapid decrease in the oxygen concentration than the Pt(5.0)/NaY zeolite which contained 10 times more Pt. The catalytic activity of the Pt(0.5)/AlKIT-1 was also much higher than that of a commercially available Pd/resin catalyst containing 0.3 wt% Pd supported on a bead-type ion exchange resin. It is not reasonable to evaluate the catalytic activity of two different metal catalysts from these data only, but the point to be stressed here is that the mesoporous material shows remarkable potential for application of the catalyst support for catalytic removal of dissolved oxygen.

Since the concentration of dissolved oxygen is quite low, the treatment amount of water must be very large. So a fast removal of dissolved oxygen is possible when the diffusion limitation is exceptionally small. Therefore, the pore diameter of catalyst support is considerably important, because the pore diameter is a key factor in determining the resistance in restrictive diffusion. The low catalytic activities of Pt(2.0)/NaY and Pt(5.0)/NaY catalysts, in spite of their high metal dispersions, are believed to be due to the small pores of the zeolite. The Pt(2.0)/HZSM-5 catalyst also shows low activity compared with the Pt(1.0)/AlKIT-1 catalyst, though their amount of exposed Pt atoms is similar. This shows that the diffusion resistance must be small on highly active catalysts as well as the high dispersion of metal.

The hydrophilic nature of zeolite may reduce the catalytic activity in the reduction of dissolved oxygen by hydrazine. Hydrazine adsorbed on catalysts dissociates and produces atomic hydrogen to react with dissolved oxygen. Therefore, wetting the Pt surface on the hydrophilic support induces the inhibition of hydrazine adsorption, resulting in a serious loss of catalytic activity. The Pt(2.0)/HZSM-5 catalyst shows high activity compared with the Pt(2.0)/NaY or the Pt(5.0)/NaY catalysts, even though the metal dispersion of the Pt(2.0)/HZSM-5 catalyst is poor. Since the pore size is also small in HZSM-5 zeolite, there must be another factor in determining the catalytic activity. The Si/Al ratio of the NaY zeolite is 2.4, which is very low compared with Si/Al=25 of the HZSM-5 zeolite or Si/Al=40 of the AlKIT-1 support. Since a low Si/Al ratio represents a high content of Al, NaY has more hydrophilic site than HZSM-5 zeolite. Therefore, it is reasonable that the hydrophilicity of catalyst support influences the catalytic activity, but the significance of the hydrophilicity is considered as to be small compared with that of metal dispersion or the diffusion restriction.

In general, mesoporous materials have very low stability compared with conventional zeolites such as Y and ZSM-5. The hydrothermal stability depends on the synthesis conditions and structures [Ryoo et al., 1996a], ranging from serious losses of structure in water even at room temperature to good stability for 2 days at 373 K. On the other hand, the KIT-1 and AlKIT-1 mesoporous materials used in this study showed good stability overnight in boiling water [Ryoo et al., 1996b]. The Pt catalysts supported on KIT-1 and AlKIT-1 exhibited good long-term stability (5 days) under the reaction condition indicating the possibility of useful catalyst for the removal of dissolved oxygen in water.

In summary, Pt catalysts supported on AlKIT-1 mesoporous material exhibited high performance for the catalytic reduction of dissolved oxygen at room temperature with long-term stability. The high performance is ascribed to the high dispersion of Pt and the large pore diameter which lowers the diffusion restriction.

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REFERENCES

Beck, J. S., Vasrtuli, J. C., Roth, W. J., Leonowicz, M. E., Kresge, C. T., Schmitt, K. D., Chu, C. T.-W., Olson, D. H., Sheppard, E. W., McCullen, S. B., Higgins, J. B. and Schlenker, J. L., "A New Family of Mesoporous Molecular Sieves Prepared with Liquid Crystal Templates," *J. Am. Chem. Soc.*, **144**, 10834 (1992).

DeSilva, S. G., "Process for Removing Dissolved Oxygen from Water using Hydrazine," US Patent, 4574071, 1986.

Dickerson, R. C., "Deoxygenations Process," US Patent, 4556492, 1985.

Harhay, A. J. and Wolfe, C. R., "Catalytic System Deoxygenates Makeup Water to 10 ppb," *Power Engineering*, 24 (1987).

Kresge, C. T., Leonowicz, M. E., Roth, W. J., Vartuli, J. C. and Beck, J. S., "Ordered Mesoporous Molecular Sieves Synthesized by a Liquidcrystal Template Mechanism," *Nature*, **359**, 710 (1992).

Ryoo, R., Cho, S. J., Pak, C. and Lee, J. Y., "Clustering of Platinum Atom into Nanoscale Particle and Network on NaY Zeolite," *Catal. Lett.*, **20**, 107 (1993).

Ryoo, R., Kim, J. M., Ko, C. H. and Shin, C. H., "Disordered Molecular Sieve with Branched Mesoporous Channel Network," *J. Phys. Chem.*, **100**, 17718 (1996a).

Ryoo, R., Kim J. M., Shin, C. H. and Lee, J. Y., "Synthesis and Hydrothermal Stability of a Disordered Mesoporous Molecular Sieve," *Stud. Surf. Sci. Catal.*, **105**, 45 (1996b).

Ryoo, R., Ko, C. H., Kim, J. M., Howe, R., "Preparation of Nanosize Pt Clusters using Ion Exchange of $Pt(NH_3)_4^{2+}$ Inside Mesoporous Channel of MCM-41," *Catal. Lett.*, **37**, 29 (1996c).

Sayari, A., "Periodic Mesoporous Material : Synthesis, Characterization and Potential Applications," *Stud. Surf. Sci. Catal.*, **102**, 1 (1996).

Seo, G., Park, K. J., Moon, J. S. and Park, T. J., "Kinetics of the Reduction Reaction of Dissolved Oxygen by Hydrazine over Pd/C Catalysts," *HWAHAK KONGHAK*, **34**, 671 (1996).