Nitrite reduction on morphologically controlled Pt nanoparticles

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On the surface of morphologically controlled Pt nanoparticles, statistically rich in [100] crystalline facet, nitrite ions were reduced by H_2 to N_2 with high selectivity.

In many countries, drinking water, especially that coming from ground water, is at risk from nitrate contamination. The removal of nitrate from drinking water is a challenge because of the ion's high stability and soluble nature. Although a number of treatment technologies have been applied, the inability of conventional physicochemical methods to remove nitrate (*e.g.*, ion exchange, electrodialysis, and reverse osmosis) has made evident the need for new, compact, and more efficient systems. One of the most promising techniques for nitrate removal is liquid phase hydrogenation using noble metal catalysts.[1] Palladium-based catalysts have proved to be the most active and selective for nitrate reduction.[2] The only drawback of these catalysts is the formation of ammonia as a by-product, which is undesirable in drinking water.

Liquid phase hydrogenation over noble metal catalysts proceeds by a two-step process: reduction of nitrate to nitrite, and reduction of nitrite to nitrogen and/or ammonia. In the case of a bimetallic platinum–copper catalyst, copper and platinum were found to catalyse the reduction of nitrate and nitrite respectively.[3] The first step, *i.e.*, the nitrate reduction to nitrite, is a structure-insensitive reaction.[4] On the other hand, the nitrite reduction can be structure-sensitive because it involves N–N bond formation (N_2 is a reaction product).[5] For structure-sensitive reactions, the activity and selectivity of Pt/Al_2O_3 can be tuned by controlling the morphology (size and dominant crystalline facets) of the supported Pt particles. There is currently little information regarding the structure sensitivity of nitrite reduction over supported Pt. In this paper, we aim to investigate the effect of Pt morphology on the activity and selectivity of nitrite reduction to nitrogen.

The morphologically controlled Pt nanoparticles (Fig. 1) were prepared by following a previously reported method.[6] Briefly, a 10^{-4} M K_2PtCl_4 aqueous solution was reduced by H_2 in the presence of a protecting polymer. Morphological analysis of the Pt nanoparticles was undertaken by counting more than 100 particles in colloidal solution, observed by TEM (Fig. 1 (a)). 60% of the particles were cubic shaped, with a surface of [100] crystallographic orientation (Fig. 1 (b)). An adequate amount of γ-Al_2O_3 (Aerosil) was suspended in the colloidal solution obtained, and water eliminated by freeze drying. In order to remove any remaining polymer, the obtained catalyst was treated at 300 °C in the air for 1 h. It was confirmed that the Pt particles supported by this method maintained their original morphology observed in colloidal solution (Fig. 1 (c)). The catalysts obtained by supporting shape-controlled Pt particles are referred to here-onwards as Pt-cubic-*x*/Al_2O_3 (*x* indicates the wt% loading of Pt). For comparison, Pt/Al_2O_3 catalysts were prepared by the conventional impregnation method. 1 g of the γ-Al_2O_3 was suspended in an aqueous solution of K_2PtCl_4. After shaking for 2 h, the water was removed using a rotary evaporator. The solid obtained was reduced in a H_2 flow at 400 °C for 1 h (Fig. 1 (d)). The catalysts obtained by the conventional impregnation method are referred to as Pt-*y*/Al_2O_3 (*y* indicates the wt% loading of Pt). Since the two kinds of catalyst (morphologically controlled and conventionally impregnated) were prepared using the same precursor and support, the observed differences in their catalytic behavior can be ascribed to the morphological differences between their supported platinum particles.

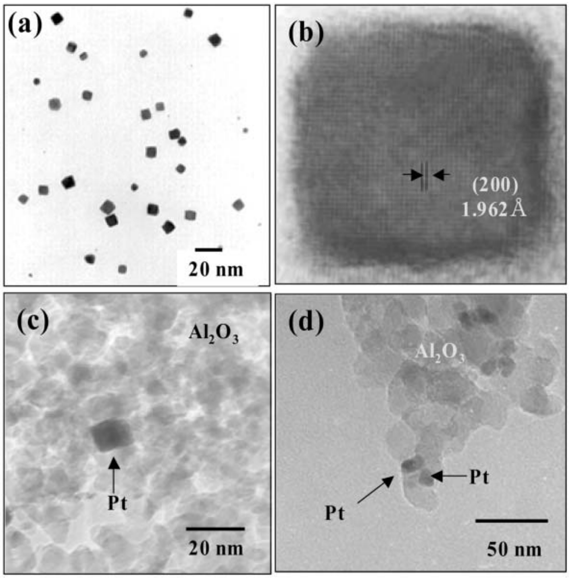

Fig. 1 (a) TEM image of the morphologically controlled Pt nanoparticles, (b) HR-TEM image of a cubic Pt nanoparticle, (c) TEM image of Pt-cubic-1/Al_2O_3, (d) TEM image of Pt-2/Al_2O_3.

Reduction experiments were performed in a semi-batch reactor using 0.3 g of catalyst and 150 ml of 2.0 mM $NaNO_2$ as the reactant solution. The reactor was kept at 25 °C and H_2 bubbled into the solution at a rate of 10 ml min^{-1}. The reaction solution was sampled every 30 min, preliminary experiments proving that the products of the NO_2^-/H_2 reaction were only NH_4^+ and N_2.

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The concentration of NH_4^+ and NO_2^- ions were determined spectrophotometrically using indophenol and Griess–Romijin's reagents respectively. The yield of N_2 was calculated from the difference between the decrease in NO_2^- concentration and the amount of formed NH_4^+.

The activity of the catalyst is defined as the percentage conversion of the NO_2^- ions, $X(NO_2^-)(\%)$ (eqn. (1)). The subscripts "i" indicate the initial concentration of NO_2^- ions in the reaction solution. The reaction selectivity to forming nitrogen, $S(N_2)(\%)$, was defined by eqn. (2).

$$X(\mathrm{NO_2}^-)(\%) = \frac{[\mathrm{NO_2}^-]_\mathrm{i} - [\mathrm{NO_2}^-]}{[\mathrm{NO_2}^-]_\mathrm{i}} \times 100 \qquad (1)$$

$$S(\mathrm{N_2})(\%) = \frac{[\mathrm{NO_2}^-]_\mathrm{i} - [\mathrm{NO_2}^-] - [\mathrm{NH_4}^+]}{[\mathrm{NO_2}^-]_\mathrm{i} - [\mathrm{NO_2}^-]} \times 100 \qquad (2)$$

Table 1 shows the characterization data for the catalysts used in the NO_2^-/H_2 reaction. The Pt metal particle sizes, measured by CO chemisorption (ChemBET, Yuasa Ionics), were in good agreement with TEM observations. The activities and the reaction selectivities to forming nitrogen are shown in Fig. 2 and Fig. 3 respectively. As can be seen in Fig. 2, the conversion over Pt-cubic/Al_2O_3 was lower than that over the conventionally prepared Pt/Al_2O_3. The conversion after 190 min reaction time over Pt-1/Al_2O_3 was 41%, whereas over Pt-cubic-1/Al_2O_3 it was only around 20%. The TOF values for Pt/Al_2O_3 catalysts were affected by particle size (see Table 1), clearly proving the structure sensitivity on the NO_2^-/H_2 reaction. On the other hand, the TOF for the morphologically controlled Pt particles was independent of metal loading. The TOF values over Pt-cubic-1/Al_2O_3 and Pt-cubic-2/Al_2O_3 were almost identical ($\approx 3 \times 10^{-3}$ s^{-1}). Although the particle sizes for Pt-cubic/Al_2O_3 catalysts are close to that of Pt-2/Al_2O_3, their TOF values are clearly different. This proves that the catalytic behavior in the NO_2^-/H_2 reaction is related to the morphology of the supported Pt particles.

The effect of morphology was also observed in the selectivity of N_2 formation over Pt catalysts (Fig. 3). It is noteworthy that the selectivity over morphologically controlled Pt particles remained constant at around 65%. On the other hand, the selectivity over the conventionally prepared catalysts decreased with time. For example, the selectivity of N_2 formation over Pt-2/Al_2O_3 and Pt-5/Al_2O_3 decreased from 90% to $\approx$20%. The decrease is very obvious for Pt-1/Al_2O_3, which has the smallest Pt particle size (1.4 nm). It is interesting to observe that the decrease in selectivity of N_2 formation over the conventional catalysts was not accompanied by a decrease in their catalytic activity. The NO_2^- conversion shown in Fig. 2 follows a first order kinetic with respect to NO_2^- concentration. The structure sensitivity of NO_2^- reduction has already been discussed for Pd based catalysts.[7] The differences in selectivity of N_2 formation, depending on the composition of Pd–Cu bimetal, was proposed to be caused by the differing hydrogenation activities of the surface sites. Since the edge and corner sites of polycrystalline Pd possess high hydrogenation activity, these sites are believed to be responsible for deep hydrogenation of NO_2^- to NH_4^+. On the other hand, the formation of N_2 would be favoured on the terrace sites of the Pd crystalites because these sites have mild hydrogenation capabilities. The results shown in Fig. 3 apparently support the explanation proposed for Pd-based catalysts, although the precious metal used in this study is Pt, not Pd. The Pt-cubic/Al_2O_3 catalysts were statistically rich in Pt nanocrystals, bounded by low index surfaces relatively free of defects. Over these catalysts, higher selectivities of N_2 formation were observed. In contrast, the Pt/Al_2O_3 catalysts, showing higher selectivities of NH_4^+ formation, were composed of polycrystalline Pt particles, rich in high index planes and surface defects. At present it is difficult to explain the progressive decrease in the selectivity of N_2 formation of the Pt/Al_2O_3 catalysts. The CO chemisorption measurements indicated that the metal dispersion was not affected after the catalytic reaction, as for Pt-2/Al_2O_3, the dispersions before and after the reaction were 9.57 and 9.60 respectively. Thus, the number of active sites remains constant. It

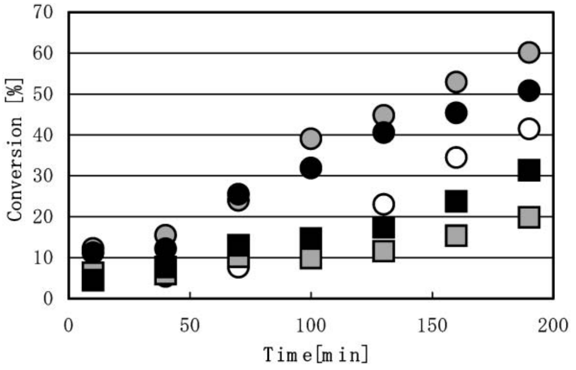

Fig. 2 Conversion of NO_2^- over Pt-cubic-1/Al_2O_3(▨), Pt-cubic-2/Al_2O_3(■), Pt-1/Al_2O_3(○), Pt-2/Al_2O_3(◍) and Pt-5/Al_2O_3(●) catalysts.

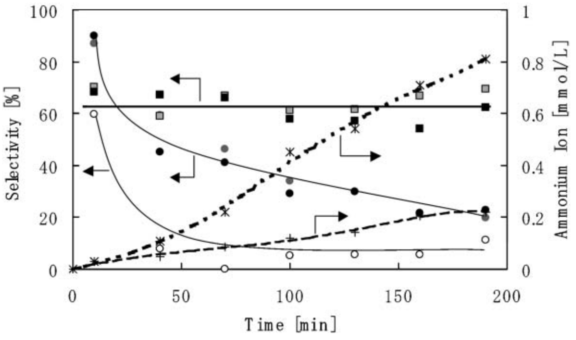

Fig. 3 Selectivity of N_2 formation over Pt-cubic-1/Al_2O_3 (▨), Pt-cubic-2/Al_2O_3 (■), Pt-1/Al_2O_3 (○), Pt-2/Al_2O_3 (◍), and Pt-5/Al_2O_3 (●) catalysts. The formation of ammonium ion over Pt-cubic-2/Al_2O_3 (+) and that over Pt-2/Al_2O_3 (*) are shown together.

Table 1 Catalysts used in the reactions

Catalyst	Pt-cubic-1/Al_2O_3	Pt-cubic-2/Al_2O_3	Pt-1/Al_2O_3	Pt-2/Al_2O_3	Pt-5/Al_2O_3
Pt loading (wt%)	1	2	1	2	5
Average particle size/nm	9.6	12.2	2.1	11.8	36.1
TOF/s^{-1}	3.08×10^{-3}	3.11×10^{-3}	1.40×10^{-3}	8.01×10^{-3}	8.03×10^{-3}

looks like the sites responsible for N_2 formation are gradually converted in time to sites on which NH_4^+ is generated. Although further investigation of this point is necessary, experimental results indicate the possibility that NH_4^+ (reaction product) interacts strongly with the surface of polycrystalline Pt particles, inducing the decrease in selectivity of N_2 formation.

From the above results, nitrite reduction over Pt was proved to be a structure-sensitive reaction, and it was evident that the selectivity of N_2 formation could be improved by better controlling the morphology of the supported Pt particles. Pt metal is known to be inactive for nitrate reduction.[2] In order to promote nitrate reduction, other metals such as Cu should be added. The bimetallic system, based on morphologically controlled Pt metal nanoparticles, can be expected to show improved performance for the selective reduction of nitrate to nitrogen.

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