NO Reduction by CH_4 over Well-Structured Pt Nanocrystal Supported on γ-Al_2O_3

Ioan Balint,[†]* Akane Miyazaki,[††] and Ken-ichi Aika[††]
[†]*Institute of Physical Chemistry, Romanian Academy, Spl. Independentei 202, 77208 Bucharest, Romania*
[††]*Department of Environmental Chemistry and Engineering, Interdisciplinary Graduate School of Science and Technology,*
Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8502

(Received July 11, 2001; CL-010645)

Platinum nanocrystals, having mainly (100) structure, have been prepared by a colloid method and then supported on γ-Al_2O_3. The catalytic test of Pt(100)/Al_2O_3 for the NO/CH_4 reaction showed that the formation of NH_3 and CO side products was prevented in contrast to the conventional Pt/γ-Al_2O_3 catalyst that gives relatively high selectivity to NH_3 and CO.

The use of CH_4 as a reductant is an efficient way to remove nitrogen oxides. Platinum supported on alumina is a very active catalyst for NO conversion but exhibits high selectivity to CO and NH_3.[1] In a structural sensitive reaction, such as the conversion of NO to N_2,[2] the control of the morphology of the supported Pt particles is essential to improve the catalytic activity and the selectivity to the desired reaction products. A convenient way to prepare monodispersed and well-defined metal particles is the colloid method. An additional advantage is that the support effect on the metallic active phase is minimized.[3] Not only the particle size but also the crystal structure of the metal nanoparticles can be, to some extent, controlled by using appropriate structure-directing polymers.[4]

From general point of view our investigation intend to bridge the gap existing between the science of well-defined single crystal surfaces under high vacuum condition and the word of more practical interest of real catalysis. The particular aims of our research are (I) to prevent the formation of undesired products (CO and NH_3) during the catalytic reduction of NO with CH_4 and (II) to get a better understanding of the relationship existing between the structure of supported Pt and the reaction selectivity to various products. Our approach to the above-mentioned goals was to prepare well-defined Pt nanocrystals by using the colloid method, to support them on alumina and to test the catalytic activity and selectivity to various products for the NO/CH_4 reaction.

The Pt nanoparticles were prepared by following the method of Miyazaki et al.[4] The water dissolved K_2PtCl_4 (10^{-4} M) was reduced in the presence of a structure directing agent NIPA (10^{-3} M) (the polymer of *N*-isopropylacrylamide) with H_2 at 40 °C for 12 h. The resulted colloidal Pt nanocrystals were supported on γ-alumina (Aerosil, 73 $m^2\ g^{-1}$) (the loading of Pt on alumina was 1%). The catalytic test for NO/CH_4 reaction was performed in a quartz microreactor, after freeze-drying and calcination (500 °C, 10 h) steps. The GHSV (Gas Hour Space Velocity) of the reactant gas mixture (1% NO, 0.6% CH_4 and balance Ar) was 60000 h^{-1}.

Typically, the colloidal Pt nanoparticles formed at 40 °C, using as directing agent NIPA, were cubic in shape (around 70%) (Figure 1). Small amounts of round, hexagonal, triangular and irregular Pt crystals have been formed too.

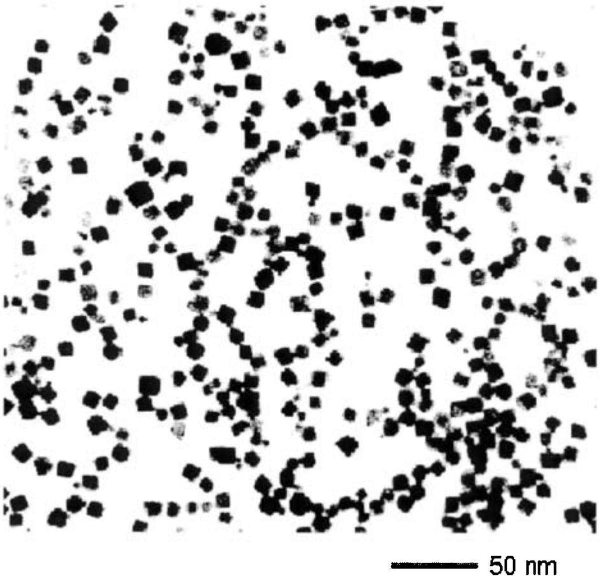

Figure 1. The TEM micrograph of the Pt(100) nanocrystals formed by reduction of K_2PtCl_4 with H_2 in the presence of the structure directing polymer NIPA.

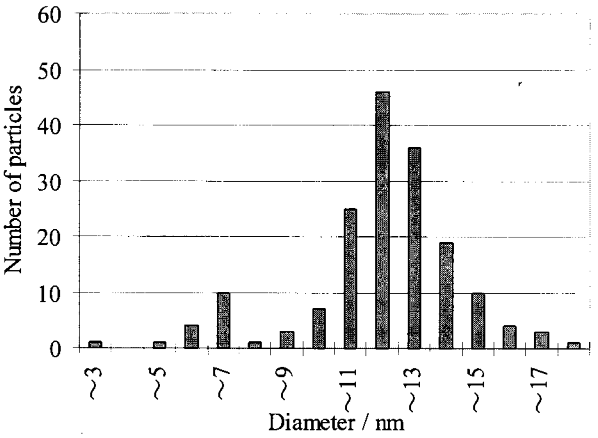

Figure 2. The size distribution of the Pt nanoparticles as it was determined from TEM micrograph.

The size distribution of the Pt nanoparticles, statistically determined from the TEM micrographs (Transmission Electron Microscopy-Philips CM20), is a Gaussian having the maximum located at around 12 nm. There was also a tiny fraction of very small Pt nanoparticles whose size is centered at around 7 nm (Figure 2). The TEM investigations showed that the morphology of Pt nanoparticles did not change after deposition on alumina (Pt nanoparticles retain their initial cubic shape).

The catalytic activity of the Pt(100)/Al_2O_3 for the reduction of NO with CH_4 as a function of temperature is presented in Figure 3. The NO is completely converted (reduced by CH_4) to N_2 and N_2O starting from 400 °C. The selectivity of the reaction to N_2 has a maximum at 500 °C (around 73%). The highest selectivity to N_2O, decreasing with increasing temperature, was observed at 350 °C (around 64%). As interesting facts it should be noted that, below 600 °C the formation of NH_3 could not be observed and the only product of the methane oxidation was CO_2 (the formation of CO could not be detected at any reaction temperature).

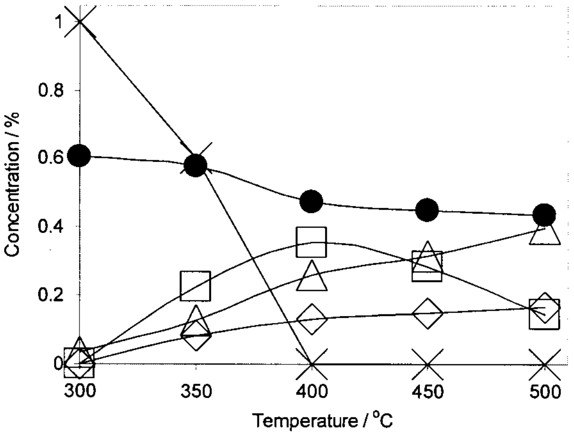

Figure 3. The conversion of NO and CH_4 to all products as a function of temperature for Pt(100)/Al_2O_3 catalyst: NO (×); CH_4 (●); N_2 (△); N_2O (□); CO_2 (◇) (reactant mixture: 1% NO, 0.6% CH_4 and balance Ar).

The influence of the Pt particle morphology on the catalytic reduction of NO with CH_4 is of great interest from a practical and theoretical point of view. Therefore, a comparison between the conventionally prepared Pt/Al_2O_3 catalyst[1] and our well-defined Pt(100) nanocrystals supported on alumina for the conversion of NO and CH_4 and for the selectivity to various products at 500 °C is presented in Figure 4. In this manner the observed differences would be ascribed to the structural effects of the Pt particles on the reaction between NO and CH_4. The conventional 1% Pt/Al_2O_3 catalyst was prepared by incipient wetness method from $Pt(NO_3)_2(NH_3)_2$ precursor.[1] The BET surface area of Al_2O_3 was 180 m^2g^{-1}. The average metal particle diameter of 1.8 nm was calculated from H_2 chemisorption data assuming a spherical geometry.

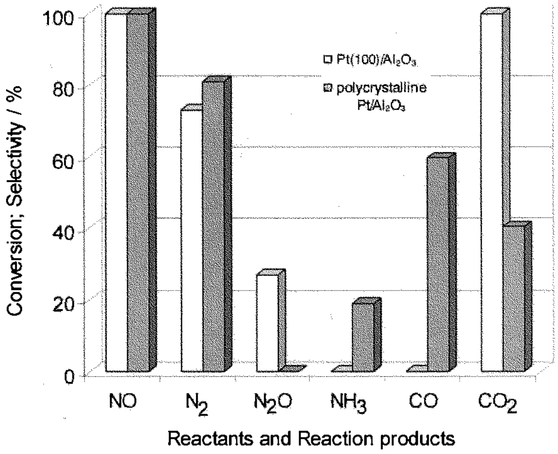

Figure 4. Comparison between Pt(100)/Al_2O_3 and the conventionally prepared Pt/Al_2O_3[1] for the conversion of NO and CH_4 and selectivity to various products at 500 °C.

In the case of well-structured Pt(100) nanoparticles supported on alumina the formation of CO as well as of NH_3 is suppressed. On the other hand, selectivity to N_2O is higher than that observed for the classically prepared Pt/Al_2O_3 (Figure 4).

It seems that, on the surface of Pt(100) nanocrystals the O_{ads} species (from NO decomposition) rapidly react with CH_x species (derived from CH_4) to give selectively CO_2 and H_2O. The concentration of CH_x on Pt(100) is kept low by the high activity of O_{ads} and that is why formation of ammonia, via N_{ads} (from NO) + H_{ads} (originating from CH_4) reaction, is prevented.[5] The higher selectivity to N_2O observed for supported Pt(100) can be explained by the lower activity of Pt(100) to dissociate NO as compared with other crystalline faces. Therefore, the reaction between N_{ads} and NO_{ads} to give N_2O is favored.[6]

A research fund from Japanese Society for the Promotion of Science (No. P00136) is greatly appreciated.

References

1 R. Burch and A. Ramli, *Appl. Catal. B*, **15**, 49 (1998).
2 B. C. Gates, *Chem. Rev.*, **95**, 511 (1995).
3 I. Balint, A. Miyazaki and K-i. Aika, *Chem. Mater.*, **13**, 932 (2001).
4 A. Miyazaki and Y. Nakano, *Langmuir*, **16**, 7109 (2000).
5 R. Burch and A. Ramli, *Appl. Catal. B*, **15**, 63 (1998).
6 A. Fritz and V. Pitchon, *Appl. Catal.* B, **13**, 1 (1997).