

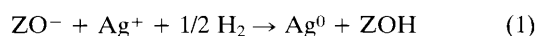
Reversible Interconversion of Silver Cations and Silver Metal Particles in Ag-Y Zeolite

Toshihide Baba, Noboru Akinaka, Mamoru Nomura and Yoshio Ono*

Department of Chemical Engineering, Tokyo Institute of Technology, Ookayama, Meguro-ku, 152 Tokyo, Japan

X-Ray diffraction (XRD) gives clear evidence of the reversible transformation between silver cations and silver metal particles in Ag-Y zeolite partially reduced with hydrogen at 303 K.

The process of reduction of Ag⁺ in various zeolites has been extensively studied by various techniques such as optical spectroscopy.¹⁻⁷ In general, the hydrogen reduction of Ag⁺ in zeolites (ZO⁻) to the metallic state can be represented as shown in eqn. (1).



Beyer *et al.*¹ reported that the reduction of Ag⁺-exchanged Y zeolite (Ag-Y) at low temperatures results in the formation of highly dispersed silver clusters containing unreduced silver cations such as Ag_n⁺ with concomitant formation of acidic OH groups.¹ Moreover, Jacobs *et al.*² reported that the reaction in eqn. (1) in Ag-Y was partially reversible. Thus, only the silver metal clusters, which could not be detected by XRD measurement, were reversibly interconverted to silver cations by hydrogen degassing at 813 K, while silver crystallites which were detected by XRD measurement remained unaltered. However, their XRD measurements were carried out only in the absence of hydrogen after exposing the samples to air, and were thus unable to give any direct XRD evidence of the reversible transformation between silver metal particles and silver cations upon introduction and withdrawal of hydrogen.

We have reported that silver metal particles are reversibly transformed back into Ag⁺ cations by evacuating Ag₃PW₁₂O₄₀ partially reduced with hydrogen.⁸ In this work, we demonstrate that silver metal particles in a partially reduced Ag-Y zeolite are transformed to silver cations by

removing hydrogen from the system and are reversibly regenerated by reintroducing hydrogen to the system at 303 K. This reversible interconversion of Ag⁺ cations and silver metal particles is also supported by IR measurement of CO chemisorbed on Ag⁺ cations.

Na-Y zeolite with Si:Al of 2.8 was obtained from TOSOH. Silver cation exchanged Y-zeolite was prepared by ion exchange from an aqueous solution of AgNO₃ (0.1 mol dm⁻³). The degree of Ag⁺ exchange, determined by atomic absorption analysis, was 100%.

Ag-Y was partially reduced by contacting it with hydrogen at 303 K after evacuating Ag-Y at 303 K for 4 h. The hydrogen adsorption was measured at 303 K in a conventional closed-circulating reactor with a dead volume of 253 cm³.

After prescribed treatment, samples of Ag-Y for X-ray measurements were transferred into quartz tubes of 1 mm (internal diameter) and sealed without exposing the sample to air. IR spectra of CO adsorbed on Ag⁺ were recorded at room temperature by using an infrared cell connected to a conventional high-vacuum system.

The transformation of silver metal particles back into Ag⁺ cations was demonstrated by the XRD measurements of silver metal particles in Ag-Y. When Ag-Y was reduced with 13.3 kPa of hydrogen at 303 K for 25 min after evacuating the Ag-Y at 303 K for 4 h, the amount of hydrogen consumption was 2.78 × 10⁻² mmol g⁻¹ (first hydrogen consumption), which is equal to 19.2% reduction of Ag⁺. The partially

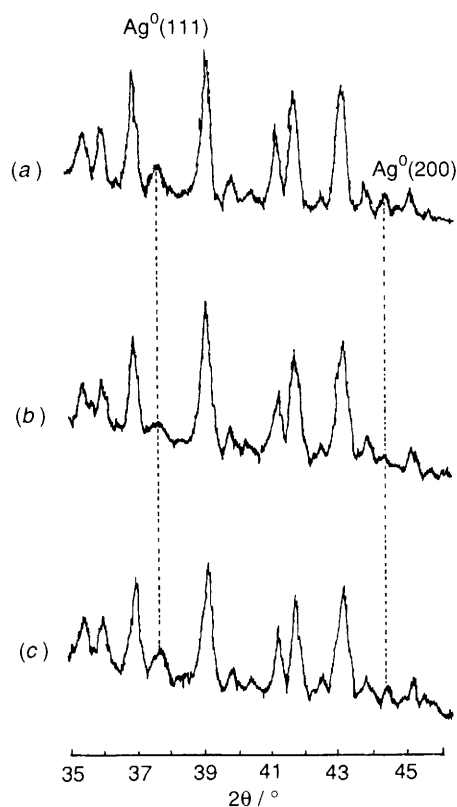


Fig. 1 X-Ray diffraction patterns of silver metal particles. (a): Ag-Y heated under vacuum at 303 K for 4 h followed by reduction with hydrogen (13.3 kPa) at 303 K for 25 min (R-Ag-Y). 13.3 kPa of hydrogen present in the system. (b): R-Ag-Y evacuated at 303 K for 3 h (O-Ag-Y). (c): O-Ag-Y reexposed to hydrogen (16.6 kPa) at 303 K for 25 min.

reduced Ag-Y under the above conditions will be designated hereafter as R-Ag-Y. The XRD spectrum of R-Ag-Y was taken in the presence of 13.3 kPa of hydrogen. As shown in Fig. 1(a), the main diffraction peaks due to silver metal particles were observed at 37.6 and 44.2°, Miller indexes being (111) and (200), respectively.

When R-Ag-Y was evacuated at 303 K for 3 h (hereafter referred as O-Ag-Y), the diffraction peaks of silver metal particles almost disappeared as shown in Fig. 1(b). This result indicates that silver metal particles are transformed into Ag⁺ cations by eliminating hydrogen from the system.

When O-Ag-Y was then reexposed to hydrogen (13.3 kPa) at 303 K for 25 min, the diffraction peaks due to silver metal particles reappeared [Fig. 1(c)]. At this stage, the amount of hydrogen consumption was 2.7×10^{-2} mmol g⁻¹, which is equal to that of the first hydrogen consumption. The results of XRD measurements and the amount of hydrogen consumption give clear evidence of the reversible transformation between silver cations and silver metal particles in Ag-Y partially reduced with hydrogen.

This reversible interconversion is also supported by IR measurement of CO chemisorbed on Ag⁺ cations. It is known that the adsorption of CO molecule on Ag⁺ in the supercage of a Y-zeolite, gives a CO stretching IR band at 2174 cm⁻¹.²

Fig. 2 (a)–(c) show the intensity change of this vibrational mode, after each prescribed treatment. When Ag-Y, evacuated at 303 K for 4 h, was contacted with 6.7 kPa of CO at 303 K for 30 min, followed by evacuation of CO for 15 s at the same temperature, the intense IR band indicative of CO adsorption on Ag⁺ cations appeared at 2174 cm⁻¹ [Fig. 2(a)].

R-Ag-Y was contacted with 6.7 kPa of CO at 303 K for 30 min without evacuating hydrogen (13.3 kPa) and then the

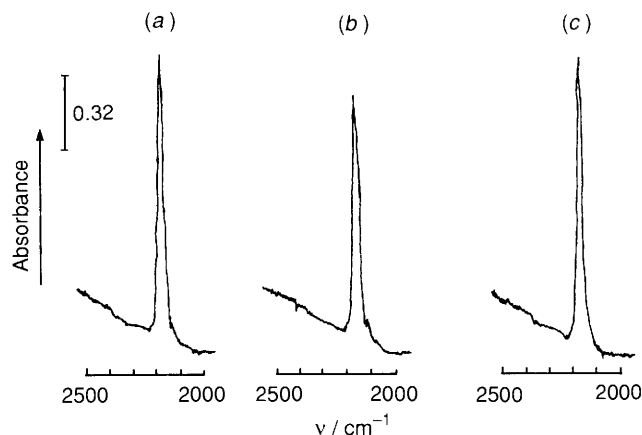


Fig. 2 IR spectra of CO adsorbed on Ag⁺ cations. All spectra recorded at room temperature. (a): Ag-Y evacuated at 303 K for 4 h and contacted with 6.7 kPa of CO at 303 K for 30 min followed by evacuation of CO for 15 s at the same temperature. (b): R-Ag-Y contacted with 6.7 kPa of CO at 303 K for 30 min without evacuating hydrogen (13.3 kPa) from the system, followed by evacuation of the mixture of hydrogen and CO at 303 K for 15 s. (c): O-Ag-Y contacted with 6.7 kPa of CO at 303 K for 30 min followed by evacuation of CO at 303 K for 15 s.

system was evacuated for 15 s. As shown in Fig. 2(b), the intensity of the peak diminished by about 20%. This value is in good agreement with the degree of Ag⁺ reduction, 19.2%, determined in a separate experiment by the amount of hydrogen consumption.

When O-Ag-Y was contacted with CO (6.7 kPa) for 30 min followed by evacuation of CO for 15 s, the intensity of the peak in Fig. 2(c) is restored to that of the original peak in Fig. 2(a). This result indicates that the amount of Ag⁺ cations in R-Ag-Y recovers to that in the original Ag-Y by the reaction of silver metal particles with protons to silver cations and hydrogen molecules. When O-Ag-Y was reexposed to 13.3 kPa of hydrogen at 303 K, the intensity of the peak diminished again 20% as expected. However, an IR experiment showed that the extent of the reversibility decreased as the degree of Ag⁺ reduction increased. Thus, when 30 and 50% of Ag⁺ ions were reduced, only 41 and 17% of the reduced ions were converted back to Ag⁺ cations, respectively, by eliminating hydrogen from the system at 303 K for 3 h.

The XRD measurements of silver metal particles under hydrogen atmosphere revealed clear evidence of the reversible transformation between silver cations and silver metal particles.

Received, 12th November 1991; Com. 1105746D

References

- H. K. Beyer, P. A. Jacobs and J. B. Uytterhoeven, *J. Chem. Soc., Faraday Trans. 1*, 1976, **72**, 674.
- P. A. Jacobs, J. B. Uytterhoeven and H. K. Beyer, *J. Chem. Soc., Faraday Trans. 1*, 1977, **73**, 1745, 1755; 1979, **75**, 56.
- L. R. Gellens, W. J. Mortier and J. B. Uytterhoeven, *Zeolite*, 1981, **1**, 11, 85.
- G. A. Ozin and F. Hughes, *J. Phys. Chem.*, 1983, **87**, 94.
- G. A. Ozin, F. Hughes, S. M. Matter and D. F. McIntosh, *J. Phys. Chem.*, 1983, **87**, 3445.
- M. D. Maker and G. A. Ozin, *J. Phys. Chem.*, 1985, **89**, 305.
- B. Xu and L. Keavan, *J. Phys. Chem.*, 1991, **95**, 1147.
- T. Baba, M. Nomura, Y. Kansaki and Y. Ono, *J. Chem. Soc., Faraday Trans.*, 1992, 71.