Influence of local structure on the catalytic activity of gallium oxide for the selective reduction of NO by CH_4

Ken-ichi Shimizu,* Mikio Takamatsu, Koji Nishi, Hisao Yoshida, Atsushi Satsuma and Tadashi Hattori

Department of Applied Chemistry, School of Engineering, Nagoya University, Chikusa-ku, Nagoya 464-01, Japan

NO selective reduction by CH_4 over Ga_2O_3 catalysts is a structure-sensitive reaction depending on the local structure of Ga_2O_3; low-coordinate Ga ions are responsible for higher activity.

Lean NO_x catalysis is a chemically challenging problem as it requires the hydrocarbon reductant to react selectively with NO in the presence of a large excess of O_2. In particular, gallium containing catalysts such as Ga/H-ZSM-5 are among the few catalysts that are active and selective for NO reduction by hydrocarbons, particularly methane.[1] However, very little is known about the structure of the active sites of these catalysts. Although computational studies[2] have suggested that low coordination around Ga is responsible for the high performance of Ga/H-ZSM-5, there is, as yet, no experimental evidence.

Investigation of structure sensitivity in a catalytic reaction is known to provide very important information about the nature of active sites.[3] In the present study, NO reduction by CH_4 over unsupported and supported gallium oxide catalysts were investigated from the standpoint of structure sensitivity, and the local structure required for this reaction was discussed.

Supported Ga_2O_3 catalysts were prepared by impregnating Al_2O_3 (a reference catalyst of the Catalysis Society of Japan,[4] JRC-ALO-1A) or SiO_2 (JRC-SIO-8) with an aqueous solution of gallium nitrate followed by evaporation to dryness and calcination at 823 K. Unsupported α-Ga_2O_3 was prepared by calcination of gallium hydroxide ($Ga_2O_3 \cdot xH_2O$) at 823 K. β-Ga_2O_3 was purchased from Mitsuwa Chemicals.

The crystal phase of bulk Ga_2O_3 was confirmed by XRD. Ga L-edge X-ray absorption spectra measurements were performed at BL-7A of the UVSOR facility, Institute for Molecular Science, using a beryl double-crystal monochromator. The absorption spectra were recorded by monitoring total photoelectron yield.[5] Each XANES spectrum was normalized by the absorbance at 1126 eV.

Catalytic tests were performed with a flow reactor by passing a mixture of 1000 ppm NO, 1000 ppm CH_4 and 6.7% O_2 in helium at a rate of 42 ml min^{-1} over 0.04–1.5 g catalyst. After reaching steady-state conditions, effluent gas was analysed by gas chromatography and by NO_x chemiluminescence. The catalytic activity was evaluated in terms of the rate of NO conversion into N_2 under differential conditions where conversion was $< 30\%$.

Fig. 1 shows Ga L_{III}-edge XANES spectra of various gallium oxide catalysts. α- and β-Ga_2O_3 exhibited distinct XANES spectra which gave information on the local structure of the Ga ions. It is well known that β-Ga_2O_3 has a defect spinel structure, containing both tetrahedral and octahedral Ga ions,[6] whereas α-Ga_2O_3 has a corundum structure, containing only octahedral Ga ions[7] and the XANES spectra could be interpreted in terms of the expected local structures.[8] Although the crystal phase of Ga_2O_3 supported on SiO_2 could not be identified, the XRD patterns exhibiting only very shadowy peaks, the XANES spectrum was similar to that of α-Ga_2O_3. This indicates that the local structure of Ga_2O_3 on SiO_2 is similar to that of octahedral α-Ga_2O_3. The XANES spectrum of Ga_2O_3/Al_2O_3 however, did not resemble the above spectra indicating that Ga ions have a specific local structure as a consequence of a strong interaction with the Al_2O_3 support.

Table 1 shows the rate and turnover frequency (TF) for the selective reduction of NO by CH_4. For bulk Ga_2O_3, the number of surface Ga ions was estimated from the BET surface area combined with the theoretical surface density of Ga. The values of the latter were estimated as 11.3 nm^{-2} for the (100) face of β-Ga_2O_3 and 14.0 nm^{-2} for the (001) face of α-Ga_2O_3. The number of surface Ga ions on Ga_2O_3/SiO_2 was calculated in the same way as for α-Ga_2O_3 on the basis of the exposed Ga_2O_3 surface area obtained by a BAT (benzaldehyde–ammonia titration)[9] method. Catalytic activity was evaluated in terms of TF defined as the rate of NO reduction divided by the determined number of surface Ga ions.

The TF for Ga_2O_3–SiO_2 was almost the same as for α-Ga_2O_3, while the TF for β-Ga_2O_3 was *ca.* 20 times larger than that for α-Ga_2O_3. The activity pattern, *i.e.* Ga_2O_3/SiO_2 = α-Ga_2O_3 < β-Ga_2O_3, corresponds to the fact that Ga_2O_3/SiO_2 and α-Ga_2O_3 have the same local structure, differing from β-Ga_2O_3 which

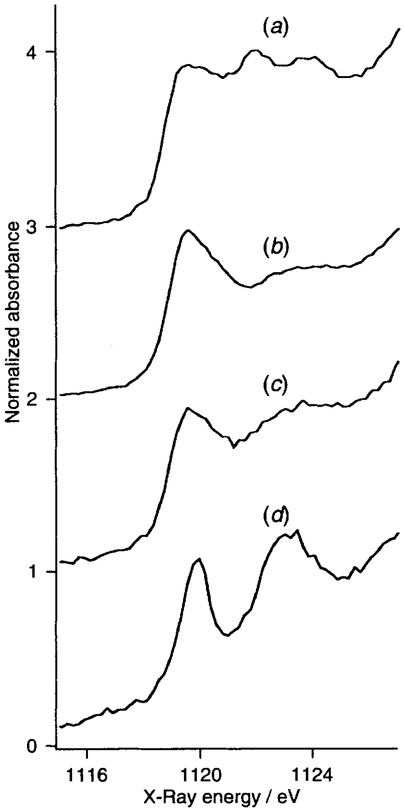

Fig. 1 Ga L_{III}-edge XANES spectra of various Ga_2O_3 catalysts; (*a*) β-Ga_2O_3, (*b*) α-Ga_2O_3, (*c*) 27 mass%Ga_2O_3/SiO_2, (*d*) 27 mass%Ga_2O_3/Al_2O_3

Table 1 Rate and TF for selective reduction of NO by CH_4 on Ga_2O_3 catalysts[a]

Catalyst	Ga_2O_3 content/ mass%	Surface area of Ga_2O_3/m^2 g^{-1}	Number of surface Ga ions/ mmol g^{-1}	Rate/nmol g^{-1} s^{-1}	TF/10^{-6} s^{-1}
β-Ga_2O_3	100	4.8	0.09	4.4	49.1
α-Ga_2O_3	100	69.9	1.62	4.0	2.5
Ga_2O_3/SiO_2	27	35.4	0.82	1.7	2.1
Ga_2O_3/Al_2O_3	0	—	0	8.1	—
	2.7	—	0.29	69.0	240.5
	27	—	2.87	165.3	57.6

[a] *Reaction conditions*: T = 823 K; NO = 1000 ppm; CH_4 = 1000 ppm; O_2 = 6.6%.

has a local structure containing tetrahedrally coordinated Ga ions. This seems to indicate that surface Ga_2O_3 species related to the tetrahedrally coordinated Ga ions of β-GaO_3 are responsible for the higher activity.

The number of surface Ga ions on Ga_2O_3/Al_2O_3 was estimated assuming that Ga_2O_3 forms a monolayer exposing all Ga ions. The TF for Ga_2O_3/Al_2O_3 with high loading content (27 mass%) was much higher than that for α-Ga_2O_3 and Ga_2O_3/SiO_2 and almost the same as that for β-Ga_2O_3. Furthermore, the TF for Ga_2O_3/Al_2O_3 with low mass loading (2.7 mass%) was the highest among the present catalysts. Considering the fact that Ga ions on Ga_2O_3/Al_2O_3 have a specific local structure owing to a strong interaction with the Al_2O_3 support as revealed by XANES, low-coordinated gallium oxide species with a specific local structure may account for the high activity of Ga_2O_3/Al_2O_3.

In conclusion, NO selective reduction by CH_4 on Ga_2O_3 catalysts is a structure-sensitive reaction depending on the local structure; low-coordinated Ga ions are responsible for higher activity and act as active sites to coordinate CH_4 or NO_x molecules leading to transition state species.

References

1 E.Kikuchi and K. Yogo, *Catal. Today*, 1994, **22**, 73; Y. Li and N. Armor, *J. Catal.*, 1994, 145, 1; J. S. Feelry, M. Deeba, R. J. Farrauto, G. Berri and A. Haynes, *Appl. Catal. B*, 1995, **6**, 79.
2 R. Vetrivel, M. Kobo, H. Himei, E. Maruya, M. Katagiri, E. Broclawik and A. Miyamoto, *Stud. Surf. Sci. Catal.*, 1995, **92**, 233; H. Himei, M. Yamadaya, M. Kubo, R. Vetrivel, E. Broclawik and A. Miyamoto, *J. Phys. Chem.*, 1995, **99**, 12461.
3 K. Mori, A. Miyamoto and Y. Murakami, *Appl. Catal.*, 1983, **6**, 209; J. C. Volta, J. M. Tatibouet, C.Phichitkal and J. E. Germain, *Proc. Int. Congr. Catal.*, Verlag Chemie, Weinhein, 1984, vol. IV, p. 451; M. Boudart, *Chem. Rev.*, 1995, **95**, 661.
4 Y. Murakami, *Stud. Surf. Sci. Catal.*, 1983, **16**, 775.
5 T. Yoshida, T. Tanaka, H. Yoshida, T. Funabiki, S. Yoshida and T. Murata, *J. Phys. Chem.*, 1995, **99**, 10890.
6 S. Geller, *J. Chem. Phys.*, 1960, **33**, 676.
7 M. Marezio and J. P. Remeika, *J. Chem. Phys.*, 1967, **46**, 1862.
8 K. Nishi, M. Takamatsu, H. Yoshida and T. Hattori, *UVSOR Activity Rep.*, 1995, in the press.
9 M. Niwa, S. Inagaki and Y. Murakami, *J. Phys.Chem.*, 1985, **89**, 3869.

Received, 14th May 1996; Com. 6/03376H