

N₂O Removal by Catalytic Decomposition and Reduction with CH₄ over Fe/Al₂O₃

Masaaki Haneda,* Manabu Shinriki,[†] Yukinori Nagao,[†] Yoshiaki Kintaichi, and Hideaki Hamada

Research Institute for Green Technology, National Institute of Advanced Industrial Science and Technology (AIST), AIST Tsukuba Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565

[†]Faculty of Science and Technology, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-8510

Received July 11, 2003; E-mail: m.haneda@aist.go.jp

N₂O removal by catalytic decomposition and reduction with CH₄ over Fe/Al₂O₃ was investigated. The catalytic conversion of N₂O to N₂ over Fe/Al₂O₃ was effectively promoted by the addition of CH₄. The activity of Fe/Al₂O₃ normalized on a TOF basis for N₂O decomposition increased linearly with the Fe loading, whereas that for N₂O reduction increased with an increase in Fe loading up to 2 wt %, then subsequently decreased. Structural characterization by UV–vis and TPR revealed the presence of two types of Fe species, Fe₂O₃ and FeAlO₃, in Fe/Al₂O₃. It was proposed that the catalytically active species for N₂O decomposition and N₂O reduction are Fe₂O₃ and FeAlO₃, respectively.

Nitrous oxide (N₂O) has a strong greenhouse effect, with a global-warming potential per molecule of about 310-times that of CO₂, and contributes to catalytic depletion of the stratospheric ozone layer.¹ N₂O originates from both natural sources and human contributions, such as the production of adipic acid and nitric acid. According to a recent study,² the contribution from vehicles (especially gasoline-fueled) has increased by a factor of 3 over the past 10 years. In this regard, catalytic removal of N₂O has attracted much attention recently. The simplest way to remove N₂O is decomposition to N₂ and O₂, for which various types of catalysts, such as ion-exchanged zeolites,^{3–6} metal oxides,^{7–9} and noble metals,^{9–11} have been reported. For example, Li and Armor³ examined various ion-exchanged zeolites, and found that Cu- and Co-exchanged ZSM-5 are active in N₂O decomposition. A high catalytic performance of Co–ZSM-5 was also reported by Tabata et al.⁴ and Kapteijn et al.⁵ Kapteijn et al.¹¹ also reviewed the decomposition of N₂O over solid catalysts, especially unsupported and supported metal oxides. They showed that some Co-containing mixed oxides, such as Co–La and Co–Mg binary oxides, are catalytically more active than Co–ZSM-5.

As another catalytic N₂O removal method, the reduction of N₂O with hydrocarbons is attracting great interest in both applied and fundamental research. Since the first reports of Segawa and coworkers^{12–15} on the high catalytic performance of Fe–ZSM-5 for N₂O reduction with C₃H₆ in the presence of H₂O and O₂, numerous investigations have focused on Fe ion-exchanged zeolites.¹⁶ In contrast to N₂O decomposition, however, few investigations of N₂O reduction on metal oxide catalysts have been performed so far. In view of a recent report on Fe/ZSM-5 catalysts,¹⁷ suggesting that isolated Fe³⁺ ions are responsible for the catalytic activity in N₂O reduction with C₃H₆, supported catalysts, including highly dispersed Fe species, would also show good performance for N₂O reduction.

In the present study, we investigated the catalytic removal of

N₂O by decomposition and reduction with CH₄ over Fe/Al₂O₃ in which the formation of a highly dispersed Fe species can be expected. The objective of using CH₄ as a reductant was to achieve a simultaneous abatement of greenhouse gas, due to the fact that its global-warming potential per molecule is about 21-times that of CO₂. To specify the active species on Fe/Al₂O₃ for N₂O decomposition and N₂O reduction with CH₄, the structural properties of supported Fe species were characterized by means of UV–vis and temperature-programmed reduction (TPR).

Experimental

The alumina used in this study was supplied by Mizusawa Chemical (GB-45). Fe/Al₂O₃ catalysts were prepared by impregnating Al₂O₃ with an aqueous solution of Fe(NO₃)₂·9H₂O, followed by drying at 383 K and calcination at 873 K for 5 h in air. The loading of Fe was changed from 1 to 10 wt %. Unsupported Fe₂O₃ was prepared by mixing an aqueous solution of Fe(NO₃)₃·9H₂O with an aqueous solution of Na₂CO₃, followed by washing the resulting precipitation with distilled water, drying at 383 K, and calcination at 873 K for 5 h in air.

The catalytic activity was measured with a fixed-bed flow reactor. The reaction gas containing N₂O (1000 ppm), CH₄ (0 or 1000 ppm), and helium as a balance gas was fed to 0.05 g of catalyst at a rate of 60 cm³ min^{–1}. Before the activity measurement, the catalysts were treated in situ at 873 K for 1.5 h in flowing helium. The reaction temperature was first decreased from 873 to 673 K in steps of 50 K, and then increased from 873 to 973 K. The effluent gas was analyzed by two on-line gas chromatographs equipped with a Molecular Sieve 5A column (for the analysis of O₂, N₂, CH₄, and CO) and a Porapak Q column (for that of N₂O and CO₂). The reaction rates of N₂ formation were also measured under nearly differential reaction conditions, giving N₂O conversion of less than 30% by controlling the catalyst weight.

The amount of chemisorbed NO was measured by a pulse method. A sample (0.05 g) was first treated at 873 K in flowing

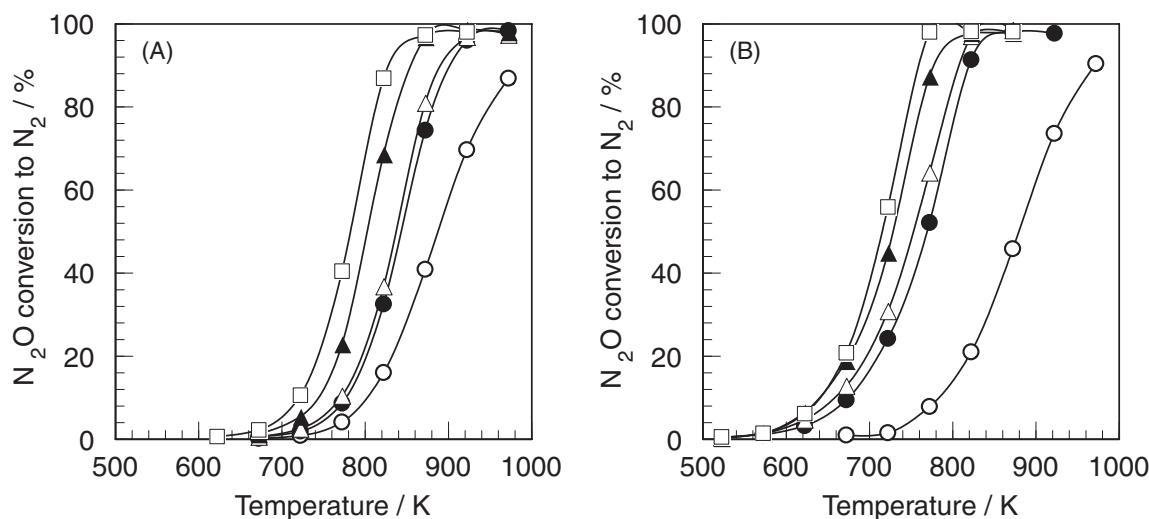


Fig. 1. Temperature dependence of N_2O conversion to N_2 over $\text{Fe}/\text{Al}_2\text{O}_3$ in (A) decomposition and (B) reduction with CH_4 in the absence of O_2 . Reaction conditions: N_2O = 1000 ppm, CH_4 = 0 or 1000 ppm, catalyst weight = 0.05 g, gas flow rate = $60 \text{ cm}^3 \text{ min}^{-1}$. (○) Al_2O_3 , (●) 1% $\text{Fe}/\text{Al}_2\text{O}_3$, (△) 2% $\text{Fe}/\text{Al}_2\text{O}_3$, (▲) 5% $\text{Fe}/\text{Al}_2\text{O}_3$, and (□) 10% $\text{Fe}/\text{Al}_2\text{O}_3$.

helium for 0.5 h, followed by cooling to room temperature. Several pulses of NO were introduced onto the sample until no more adsorption was observed. The crystal structure was identified by measurements using an X-ray diffraction (XRD) system (Shimadzu, XD-D1) with $\text{Cu K}\alpha$ radiation at 40 kV and 40 mA. UV-vis diffuse reflectance spectra of the catalysts were recorded in the range of 200–800 nm with a resolution of 2 nm using a UV-vis spectrometer (Shimadzu, UV-2400PC) equipped with an integrating sphere attachment. The reduction behavior of supported-Fe species was examined by TPR with H_2 . Before each TPR measurement, a sample (0.05 g) was heated in flowing air at 873 K for 1 h, and then cooled to room temperature in the same atmosphere. The sample was then heated to 1173 K at a rate of 10 K min^{-1} in a flow of 10 vol % H_2 -Ar gas mixture at a flow rate of $30 \text{ cm}^3 \text{ min}^{-1}$. Reduction of CuO to metallic copper was measured to calibrate the amount of H_2 consumed.

Results and Discussion

N_2O Decomposition and N_2O Reduction with CH_4 . N_2O decomposition and N_2O reduction with CH_4 were carried out over $\text{Fe}/\text{Al}_2\text{O}_3$ with different Fe loadings. Figures 1(A) and 1(B) show the temperature dependence of N_2O conversion for the decomposition and reduction, respectively. N_2 , CO_2 , and traces of CO were detected as the products in N_2O reduction with CH_4 . Although Al_2O_3 , itself, catalyzed both reactions at high temperatures, the addition of Fe caused an enhancement of N_2O conversion at low temperatures. Figure 2 shows the Fe loading dependence of the reaction rates of N_2 formation for N_2O decomposition and N_2O reduction at 723 K. The reaction rate for N_2O reduction is clearly much faster than that for N_2O decomposition, indicating that the addition of CH_4 is effective in promoting the catalytic conversion of N_2O . It was also found that the N_2 formation rates for both reactions increased with increasing Fe loading. This suggests that the supported Fe acts as catalytically active sites for both reactions. However, the effect of Fe loading on the reaction rate was quite different in the two reactions. An almost linear correlation was observed up to 10 wt % for N_2O decomposition. For N_2O reduction, on the other hand, the N_2 formation rate increased with Fe loading up to 5

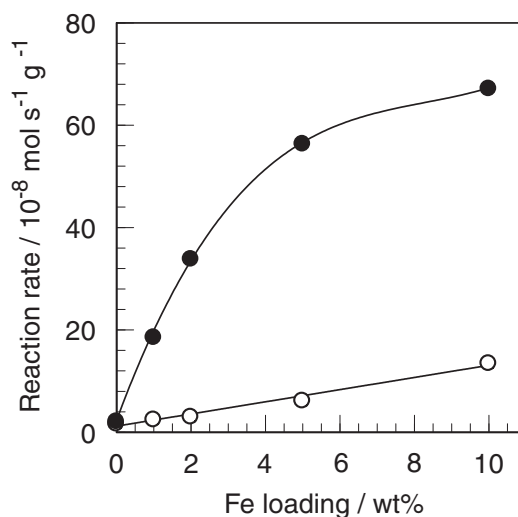


Fig. 2. Changes in the activity of $\text{Fe}/\text{Al}_2\text{O}_3$ for N_2O decomposition (○) and N_2O reduction with CH_4 (●) in the absence of O_2 at 723 K as a function of Fe loading. Reaction conditions: N_2O = 1000 ppm, CH_4 = 0 or 1000 ppm, catalyst weight = 0.015–0.2 g, gas flow rate = $60 \text{ cm}^3 \text{ min}^{-1}$.

wt %, while a prominent increase was not observed above 5 wt % Fe loading. This suggests that the number of active sites for N_2O reduction does not increase linearly with Fe loading. Therefore, the active sites for N_2O reduction should be different from that for N_2O decomposition.

In order to obtain information about the active sites for N_2O decomposition and N_2O reduction, the turnover frequency (TOF) for N_2 formation was calculated based on the number of surface Fe atoms. Here, the number of surface Fe atoms was estimated by NO chemisorption, because NO is known to be adsorbed on Fe(II) and Fe(III) in $\text{Fe}/\text{Al}_2\text{O}_3$ as mononitrosyl species.^{18,19} Since a small amount of NO was adsorbed on Al_2O_3 , the number of exposed Fe atoms was calculated by subtracting the amount of chemisorbed NO on Al_2O_3 from that on

Table 1. Physical Properties of Fe/Al₂O₃

Catalyst	BET surface area /m ² g ⁻¹	Amount of NO chemisorption/mol g ⁻¹	Number of exposed Fe atoms/Fe-atoms g ⁻¹
Al ₂ O ₃	176	1.4×10^{-5}	—
1% Fe/Al ₂ O ₃	169	3.4×10^{-5}	1.2×10^{19}
2% Fe/Al ₂ O ₃	165	3.8×10^{-5}	1.4×10^{19}
5% Fe/Al ₂ O ₃	163	6.5×10^{-5}	3.1×10^{19}
10% Fe/Al ₂ O ₃	156	9.6×10^{-5}	4.9×10^{19}

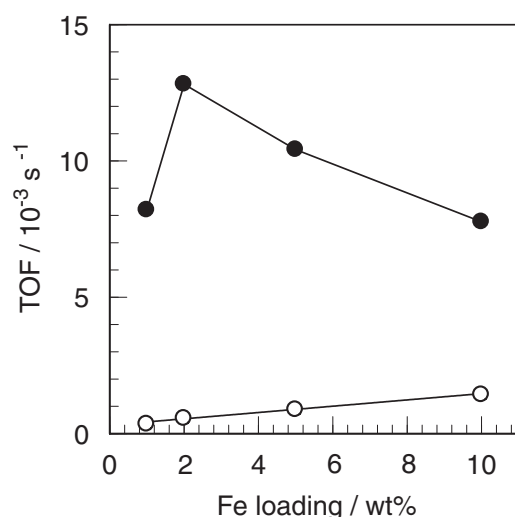


Fig. 3. Changes in the TOF for N₂O decomposition (○) and N₂O reduction by CH₄ (●) over Fe/Al₂O₃ in the absence of O₂ at 723 K as a function of Fe loading. Reaction conditions: N₂O = 1000 ppm, CH₄ = 0 or 1000 ppm, catalyst weight = 0.015–0.2 g, gas flow rate = 60 cm³ min⁻¹.

Fe/Al₂O₃. Table 1 summarizes the amounts of chemisorbed NO on Fe/Al₂O₃ with different Fe loadings as well as their surface areas. The BET surface area of Fe/Al₂O₃ was slightly decreased as Fe loading was increased, suggesting a blockage of the pores of Al₂O₃ by supported Fe. Based on the number of surface Fe atoms, the TOFs for N₂ formation in N₂O decomposition and N₂O reduction were calculated. As shown in Fig. 3, the dependency of the TOF on Fe loading was quite different in the two reactions. The TOF for N₂O decomposition linearly increased with Fe loading, while that for N₂O reduction increased with an increase in Fe loading up to 2 wt %, then subsequently decreased. This suggests that the active site for N₂O reduction is different from that for N₂O decomposition.

Structural Characterization of Fe/Al₂O₃. The XRD patterns of the Fe/Al₂O₃ samples were measured to identify their crystal structures. Only the diffraction peaks assignable to γ -Al₂O₃ were observed for all of the Fe/Al₂O₃ samples with up to 10 wt % Fe loading (results not shown). This suggests that the Fe phases are present in a highly dispersed state or in a solid solution with the support.

UV–vis diffuse reflectance spectra were taken to learn about the details of the state of supported Fe. Figure 4 shows the spectra of Fe/Al₂O₃ with different Fe loadings after subtracting the Al₂O₃ spectrum, along with that of α -Fe₂O₃. Fe/Al₂O₃ showed a distinct absorption band at 300 nm as well as a shoulder band at around 540 nm. From a comparison with

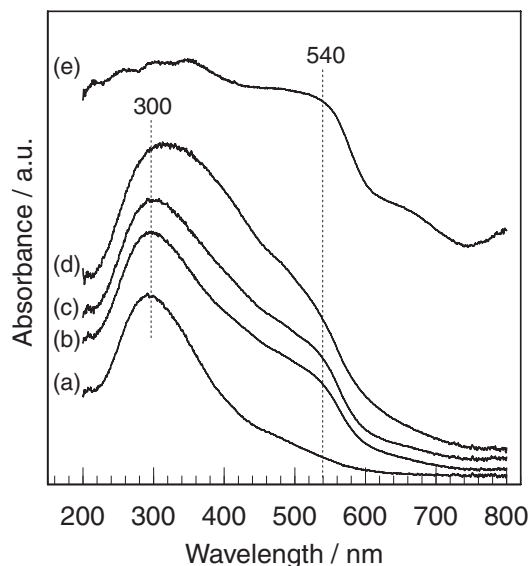


Fig. 4. Diffuse reflectance UV–vis spectra of (a) 1% Fe/Al₂O₃, (b) 2% Fe/Al₂O₃, (c) 5% Fe/Al₂O₃, (d) 10% Fe/Al₂O₃, and (e) Fe₂O₃.

the spectrum of α -Fe₂O₃ (Fig. 4(e)), the absorption band at 540 nm would be assigned to Fe₂O₃ particles. Centi and Vazzana¹⁷ observed absorption bands at 270 and 330 nm in the UV–vis spectra of Fe/ZSM-5 samples prepared by CVD, and assigned these bands to isolated Fe³⁺ species interacting strongly with the support. Accordingly, we can consider the band at 300 nm to be due to Fe³⁺ species interacting strongly with Al₂O₃. A possible candidate for the Fe³⁺ is Fe–Al composite oxide. Hoffmann et al.²⁰ recognized the presence of FeAlO₃ in Fe/Al₂O₃ using XRD, EXAFS, Mössbauer, and ESCA techniques. They also observed an increase in the amount of FeAlO₃ as the Fe loading increased. In accordance with their report, the band intensity at 300 nm increased with an increase in Fe loading. Consequently, we can conclude that the band at 300 nm is assignable to FeAlO₃. It is noteworthy that the absorption band at 300 nm slightly shifted to a higher wavelength as the Fe loading increased to 10 wt %. This is probably due to overlapping of the absorption bands for Fe₂O₃ particles, suggesting that 10 wt % Fe/Al₂O₃ includes a relatively large amount of Fe₂O₃ particles compared with the other Fe/Al₂O₃ samples.

It is known that the reduction behavior of a supported Fe species changes depending on its dispersion and metal–support interaction.^{21–23} TPR measurements were made to obtain information on the dispersion state of the Fe species in the Fe/Al₂O₃ catalysts. Figure 5 shows the TPR profiles of the Fe/Al₂O₃

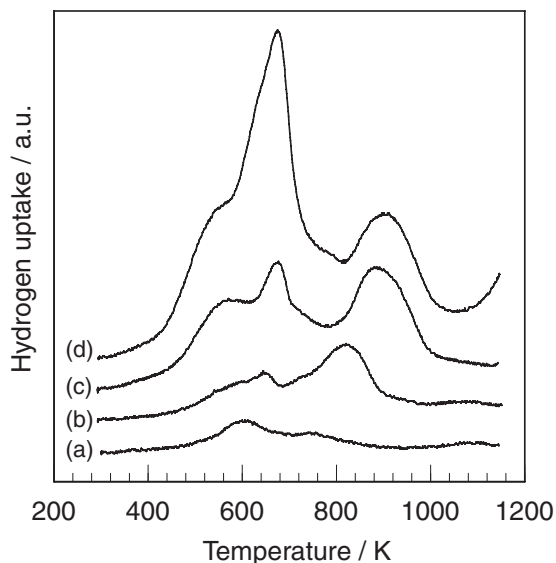


Fig. 5. TPR profiles of (a) 1% Fe/Al_2O_3 , (b) 2% Fe/Al_2O_3 , (c) 5% Fe/Al_2O_3 , and (d) 10% Fe/Al_2O_3 .

samples with different Fe loadings. The Fe/Al_2O_3 samples gave very complicated TPR profiles consisting of two or three reduction peaks, with the peak temperatures differing depending on the Fe loading. According to previous reports,^{21–23} the peaks located below 773 K can be ascribed to the reduction of Fe_2O_3 . The reduction of supported oxide species has been reported to consecutively proceed from the surface to the bulk. For example, CeO_2/Al_2O_3 shows two or three reduction peaks at around 873 and 1073 K, assignable to the reactions of oxygen atoms located at the surface of and inside the CeO_2 particles, respectively.²⁴ A similar phenomenon would take place for Fe_2O_3 supported on Al_2O_3 . Accordingly, the low-temperature peak at around 573 K is due to the surface reduction of Fe_2O_3 particles, and the high-temperature peak at around 673 K is due to bulk reduction. The fact that 1 wt % Fe/Al_2O_3 gave one reduction peak below 773 K suggests that this sample contained only small Fe_2O_3 particles. This is in good agreement with the results of the UV–vis measurements (Fig. 4(a)).

On the other hand, the reduction peaks located above 773 K (Fig. 5(a)–(d)) would be due to the reduction of iron–aluminum oxide species.^{21,23} Taking into account the results of UV–vis measurements mentioned above, the peaks above 773 K can be ascribed to the reduction of $FeAlO_3$. It should be noted that the apparent peak area increased with an increase in Fe loading, suggesting an increase in the amount of $FeAlO_3$. This is in good agreement with the results of the UV–vis measurements. Accordingly, we can conclude that there are two types of Fe species, namely Fe_2O_3 and $FeAlO_3$, in Fe/Al_2O_3 samples.

Specification of Active Sites. From the relationship between the TOF for the conversion of N_2O and Fe loading shown in Fig. 3, the active site for N_2O reduction was presumed to be different from that for N_2O decomposition. Since Al_2O_3 , itself, was almost inactive for the conversion of N_2O , supported Fe should be the active sites. Therefore, there seem to be at least two types of Fe species in the Fe/Al_2O_3 catalysts. In accordance with this idea, UV–vis (Fig. 4) and TPR (Fig. 5) measurements revealed the presence of two types of Fe species with dif-

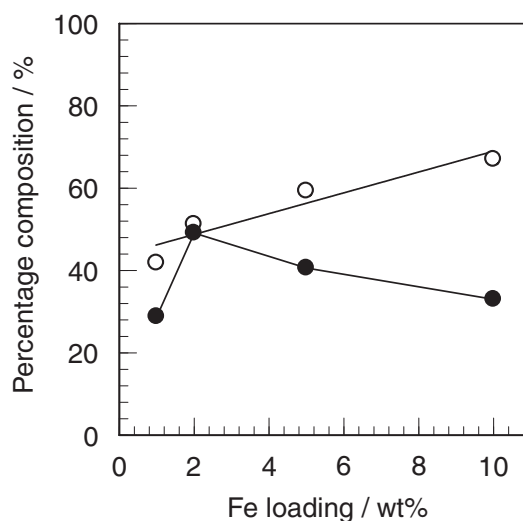


Fig. 6. Percentage composition of Fe_2O_3 (○) and $FeAlO_3$ (●) present in Fe/Al_2O_3 catalysts.

ferent structures, Fe_2O_3 and $FeAlO_3$, in the catalysts. The same conclusion was also reported by Hoffmann et al.²⁰ If Fe_2O_3 and $FeAlO_3$ have different catalytic functions, good correlation between the TOF and the percentage composition of Fe_2O_3 and $FeAlO_3$ in Fe/Al_2O_3 catalysts should be obtained. Figure 6 shows the change in the percentage composition of Fe_2O_3 and $FeAlO_3$ as a function of Fe loading. Here, the percentage composition was calculated by dividing the amounts of Fe_2O_3 and $FeAlO_3$, which were estimated from the H_2 uptake in TPR, by the total Fe content in the catalyst. A comparison of Fig. 3 with Fig. 6 shows a good correlation between the TOF for N_2O reduction and the percentage composition of $FeAlO_3$. It should be noted that the former reflects the surface profile and the latter the subsurface, from the feature of impregnation, whereby Fe is deposited on the surface of Al_2O_3 . If Fe_2O_3 and $FeAlO_3$ phases are present separately on the Al_2O_3 support, the surface and subsurface compositions of the two Fe^{3+} species should be the same. Hoffmann et al.²⁰ prepared Fe/Al_2O_3 samples using the same impregnation method as we employed in the present study, and observed the presence of both Fe_2O_3 and $FeAlO_3$ phases on the surface of Al_2O_3 by means of ESCA. This indicates that Fe_2O_3 and $FeAlO_3$ phases are present separately. Taking into account their report, the composition of Fe_2O_3 and $FeAlO_3$ on the surface of Fe/Al_2O_3 prepared in the present study can be expected to be the same as that in the subsurface. The fact that a good correlation between the TOF and the percentage composition of Fe^{3+} species was observed thus leads us to conclude that the catalytically active species for N_2O reduction is $FeAlO_3$, whereas Fe_2O_3 behaves as a catalytically active species for N_2O decomposition.

Conclusions

The present study has demonstrated that the catalytic removal of N_2O over Fe/Al_2O_3 can be effectively promoted by the addition of CH_4 . It was revealed by UV–vis and TPR measurements that Fe_2O_3 and $FeAlO_3$ phases are present in Fe/Al_2O_3 catalysts. The former acts as a catalytically active species for N_2O decomposition, while the latter acts as that for N_2O reduction.

References

- 1 H. Rodhe, *Science*, **248**, 1217 (1990).
- 2 T. Salvesen, S. Roesch, P. A. Sermon, and P. Kaur, *Top. Catal.*, **16/17**, 381 (2001).
- 3 Y. Li and J. N. Armor, *Appl. Catal., B*, **1**, L21 (1992).
- 4 M. Tabata, H. Hamada, Y. Kintaichi, M. Sasaki, and T. Ito, *Chem. Express*, **7**, 77 (1992).
- 5 F. Kapteijn, G. Marb  n, J. Rodr  guez-Mirasol, and J. A. Moulijn, *J. Catal.*, **167**, 256 (1997).
- 6 R. S. da Cruz, A. J. S. Mascarenhas, and H. M. C. Andrade, *Appl. Catal., B*, **18**, 223 (1998).
- 7 E. R. S. Winter, *J. Catal.*, **19**, 32 (1970).
- 8 A. Satsuma, H. Maeshima, K. Watanabe, and T. Hattori, *Energy Convers. Manage.*, **42**, 1997 (2001).
- 9 J. Oi, A. Obuchi, G. R. Bamwenda, A. Ogata, H. Yagita, S. Kushiyaama, and K. Mizuno, *Appl. Catal., B*, **12**, 277 (1997).
- 10 K. Yuzaki, T. Yarimizu, K. Aoyagi, S. Ito, and K. Kunimori, *Catal. Today*, **45**, 129 (1998).
- 11 F. Kapteijn, J. Rodr  guez-Mirasol, and J. A. Moulijn, *Appl. Catal., B*, **9**, 25 (1996).
- 12 C. Pophal, T. Yogo, K. Tanabe, and K. Segawa, *Catal. Lett.*, **44**, 271 (1997).
- 13 K. Yamada, C. Pophal, and K. Segawa, *Microporous Mesoporous Mater.*, **21**, 549 (1998).
- 14 C. Pophal, T. Yogo, K. Tanabe, and K. Segawa, *Appl. Catal., B*, **16**, 177 (1998).
- 15 K. Yamada, S. Kondo, and K. Segawa, *Microporous Mesoporous Mater.*, **35/36**, 227 (2000).
- 16 S. Kameoka, T. Suzuki, K. Yuzaki, T. Takeda, S. Tanaka, S. Ito, T. Miyadera, and K. Kunimori, *Chem. Commun.*, **2000**, 745, and references therein.
- 17 G. Centi and F. Vazzana, *Catal. Today*, **53**, 683 (1999).
- 18 D. G. Retwisch and J. A. Dumesic, *J. Phys. Chem.*, **90**, 1625 (1986).
- 19 M. Jiang, N. Koizumi, and M. Yamada, *J. Phys. Chem. B*, **104**, 7636 (2000).
- 20 P. Hoffmann, M. Houalla, A. Proctor, M. J. Fay, and D. M. Hercules, *Appl. Spectrosc.*, **46**, 208 (1992).
- 21 X. Gao, J. Shen, Y. Hsia, and Y. Chen, *J. Chem. Soc., Faraday Trans.*, **89**, 1079 (1993).
- 22 A. J. H. M. Kock, H. M. Fortuin, and J. W. Geus, *J. Catal.*, **96**, 261 (1985).
- 23 R.-Y. Tang, S. Zhang, C. Wang, D. Liang, and L. Lin, *J. Catal.*, **106**, 440 (1987).
- 24 H. C. Yao and Y. F. Yu-Yao, *J. Catal.*, **86**, 254 (1984), and references therein.