Formation and reactivity of isocyanate (NCO) species on Ag/Al_2O_3

Satosi Sumiya,[a] Hong He,[a] Akira Abe,[a] Nobutsune Takezawa[b] and Kiyohide Yoshida[a]

[a] *Research and Development Division, Riken Corporation, 4-14-1 Suehiro, Kumagaya, Saitama, 360-8522, Japan*

[b] *Division of Materials Science and Engineering, Graduate School of Engineering, Hokkaido University, West 8, North 13, Sapporo, Hokkaido 060, Japan*

The formation of the reactivity of isocyanate species have been studied over Ag/Al_2O_3 by IR spectroscopy and mass spectrometry. Adsorbed $C_xH_yNO_z$ and NO_3^- species are produced by reaction among NO, O_2 and C_3H_6 at room temperature. Thermal decomposition of adsorbed $C_xH_yNO_z$ species leads to the formation of two types of NCO species (NCO on Ag and NCO on Al_2O_3) above 423 K. These NCO species are thermally stable in vacuum at 673 K, while adsorbed NO_3^- species decompose completely. The NCO species are highly reactive toward NO + O_2 at room temperature, being converted into N_2, CO_2, CO and a small amount of N_2O. The NCO species are less active in NO or O_2 alone than in the mixture of NO and O_2. Thus, excess oxygen added in the NO reduction by C_3H_6 plays an important role in the formation of adsorbed $C_xH_yNO_z$ species and in the reaction of adsorbed NCO with NO. It is suggested that the formation of adsorbed $C_xH_yNO_z$ and adsorbed NCO is essential for the progress of the NO reduction with C_3H_6 in the presence of O_2 under the present experimental conditions.

Introduction

Catalytic reduction of lean NO_x with hydrocarbons has been investigated on a number of catalysts.[1–8] Various hydrocarbons were used as reducing agents for the NO_x reduction. The reduction of NO_x is greatly enhanced in the presence of O_2.[3] However, the activity of the catalyst is largely suppressed in the presence of water vapor and SO_2.[4] Prominent catalysts for the reduction of lean NO_x have been developed.

In recent IR studies, surface species such as isocyanate,[9–13] $(N_xO_y)_z$,[11] CN,[12,13] nitro[14] and nitrite species[14] have been observed on various supported catalysts in the reduction of lean NO_x. Isocyanate species (—NCO) were detected on alumina-supported Cu and Ag catalysts in the reaction among NO, hydrocarbons and O_2.[9,10] It was suggested that NCO species were produced through the decomposition of 'precursors', $C_xH_yNO_z$ complexes, which were formed in reactions among NO, O_2 and hydrocarbons.[9] N_2 and CO_2 were formed in the reaction between NCO species and NO on Cu/Al_2O_3.[9] The reduction of NO_x and the formation of NCO species are suppressed in the reaction among NO, hydrocarbons and O_2 in the presence of water vapor.[15] These results suggest that NCO species were important intermediates in the lean NO_x reduction. However, no experiments were carried out for the reaction of NCO with NO in the presence of O_2, although excess oxygen is essential for lean NO_x reduction.

In the present paper, the formation and the reactivity of NCO species on Ag/Al_2O_3 are studied by IR spectroscopy and mass spectrometry, and the role of O_2 in the reduction of lean NO_x is also discussed.

Experimental

An alumina-supported silver catalyst (denoted Ag/Al_2O_3) was prepared by an impregnation method employed in previous experiments.[4] Silver loading was 5.0 wt.%. FTIR spectra of adsorbed species were obtained using a Nicolet Magna 550 spectrophotometer with a resolution of 2 cm^{-1}. An IR cell made of Pyrex glass was fitted with a sample holder, an electronic heater and BaF_2 windows. The sample holder can be moved from the heater section to the window section in the cell. The IR sample was prepared by pressing catalyst powder ground in an agate mortar into a wafer of *ca.* 20 mg cm^{-2}. Prior to the experiment, the sample was heated at 573 K in vacuum (10^{-5} Torr) for 30 min and then oxidized in 50 Torr of O_2 at 573 K for 30 min followed by brief pumping at room temperature. All IR measurements were carried out at room temperature. The reactivity of adsorbed species formed in the reaction was also evaluated over 0.4 g of Ag/Al_2O_3 catalyst in a closed vessel, and the gaseous, products using ^{15}NO as a reactant were analyzed by mass spectrometry.

Results and Discussion

Preparation of NCO on Ag/Al_2O_3

Fig. 1 shows FTIR spectra of Ag/Al_2O_3 subjected to various treatments in O_2, a mixture of C_3H_6 and NO, or in a mixture of C_3H_6, NO and O_2. When Ag/Al_2O_3 is exposed to a mixture of C_3H_6 (11 Torr) and NO (14 Torr) at room temperature, weak absorption bands are discerned at 2860, 2920

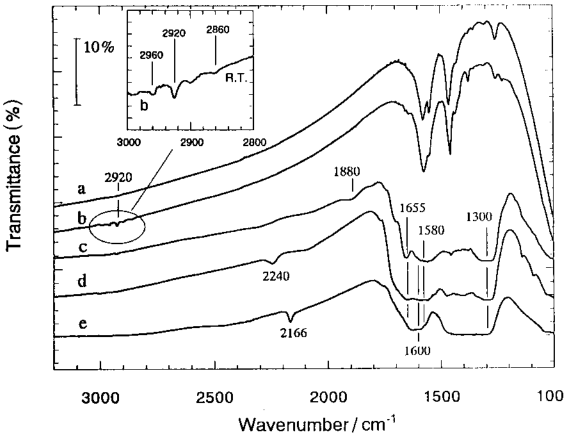

Fig. 1 FTIR spectra of Ag/Al_2O_3 after (a), oxidation treatment, (b), exposure to a mixture of NO (14 Torr) + C_3H_6 (11 Torr) at room temperature, (c), exposure to a mixture of C_3H_6 (11 Torr) + NO (14 Torr) + O_2 (15 Torr) at room temperature, (d), heating (c) at 423 K in the gas mixture for 15 min, and (e), heating (d) at 573 K in the gas mixture for 15 min

and 2960 cm^{-1}, as shown in Fig. 1(b). According to Sheppard,[16] the bands are assigned to C—H stretching modes for adsorbed C_3H_6. When O_2 is added to the mixture of NO and C_3H_6, various absorption bands appear in the region 1200–2000 cm^{-1} as shown in Fig. 1(c). The band observed at 1655 cm^{-1} is ascribable to organic compounds. $C_xH_yNO_z$, formed by reaction among NO, O_2 and C_3H_6.[9] Other bands can be assigned to physisorbed NO (1880 cm^{-1})[9,17] and NO_3^- (1580, 1300 cm^{-1}) localized on Al_2O_3 surface.[9,17–20] Tanaka and Okuhara previously assigned the IR band at *ca.* 1655 cm^{-1} to an N—O stretching mode of RONO in lean NO_x reduction on Pt/SiO_2.[14] Thus, we conclude that the $C_xH_yNO_z$ species are organic nitrites formed on the catalyst surface.

Tanaka and Okuhara also found an IR band at 1565 cm^{-1} and assigned it to RNO_2.[14] Haneda *et al.* recently observed an IR band at 1580 cm^{-1} by reaction among NO, O_2 and C_3H_6 over Ag/TiO_2-ZrO_2 and assigned it to RNO_2.[21] Fig. 1(d) and (e) show IR spectra for Ag/Al_2O_3 heated in a mixture of NO, C_3H_6 and O_2 at 423 K and 573 K for 15 min, respectively. The band at 1655 cm^{-1} decreases at 423 K, while a weak and broad band resulting from NCO species[22] appears at *ca.* 2240 cm^{-1}. After heating to 573 K, the IR spectrum changes drastically. The IR band at *ca.* 2240 cm^{-1} diminishes while a weak band for CN species[12,13,17] is newly detected at 2166 cm^{-1}.

Fig. 2 shows the IR spectra observed after evacuation of a mixture of NO (14 Torr), C_3H_6 (11 Torr) and O_2 (15 Torr) at room temperature and then heating stepwise to various temperatures for 15 min. For the sample heated to 373 K for 15 min, bands appear in the region 1200–2000 cm^{-1} as shown in Fig. 2(a). The absorption band at 1655 cm^{-1} decreases slightly at 423 K, and a weak band appears at 2230 cm^{-1}. After heating to 523 K, the IR spectra change drastically. The IR band at 1655 cm^{-1} almost disappears and a new IR band grows at 2260 cm^{-1} on a shoulder of the band at 2230 cm^{-1} as shown in Fig. 2(d). The absorption bands at 1580 and 1300 cm^{-1} for NO_3^- species still remained. The IR band at 2230 cm^{-1} was assigned to NCO species bound to Ag, Ag—NCO, while the band at 2260 cm^{-1} was assigned to Al—NCO species.[22–24] Hence, NCO species preferably occupy Ag sites and then Al_2O_3 sites. Heating to 623 K leads to the decomposition of NO_3^- and the growth of intense IR bands at 2230 and 2260 cm^{-1} [Fig. 2(f)]. The peak intensities for these NCO species further increase on heating at 673 K for 15 min, while the bands for NO_3^- at 1580 and 1300 cm^{-1} decrease greatly. This suggests that Ag—NCO and Al—NCO species are thermally more stable than NO_3^- species in a vacuum. Hence, these NCO species were selectively produced on heating the sample in a vacuum at 673 K. These results suggest that a broad IR band at *ca.* 2240 cm^{-1} reported above consists of two types of IR bands, at 2230 and 2260 cm^{-1}.

A weak band for CN species appears at 573 K in the presence or the absence of a mixture of NO, C_3H_6 and O_2. In Fig. 1(d), it was shown that the weak and broad band at *ca.* 2240 cm^{-1} for NCO surface species appeared at 423 K. The band disappeared at 573 K when the Ag/Al_2O_3 was heated in the presence of a mixture of NO, C_3H_6 and O_2 [Fig. 1(e)]. In contrast to the NCO species, the CN species was stable at 573 K in the presence of a mixture of NO, C_3H_6 and O_2, suggesting that CN species were less active toward a mixture of NO, C_3H_6 and O_2 than the NCO species. The mechanism of the formation of the CN species is not clear at present. Bell *et al.*[25] recently proposed that CN species were formed by decomposition of CH_3NO in NO reduction by CH_4. Hence, it is probable that the $C_xH_yNO_z$ species are involved in the formation of CN species in the present experiments.

Reaction of $NCO/Ag/Al_2O_3$ with O_2, NO or a mixture of NO and O_2

Surface NCO species (Ag—NCO and Al—NCO) were prepared on heating in a vacuum at 673 K after exposing Ag/Al_2O_3 to a mixture of NO (14 Torr), C_3H_6 (11 Torr) and O_2 (15 Torr) at room temperature. The reactivity of the NCO species was then tested with O_2, NO or a mixture of NO and O_2. Fig. 3 shows the variation of the NCO species in the presence of O_2 on Ag/Al_2O_3 at various temperatures. The bands for Ag—NCO and Al—NCO species decrease greatly in intensity after heating to 523 K. Heating to 523 K results in the disappearance of the NCO species. By mass spectrometric measurements, it was found that CO_2 and N_2 were produced in a molar ratio of *ca.* 2 : 1, suggesting that the reaction $2NCO + O_2 \rightarrow 2CO_2 + N_2$ took place.

In a similar fashion, the reactivity of adsorbed NCO was inspected in the presence of NO. No reaction occurred below 573 K. The absorption bands for Ag—NCO and Al—NCO disappeared around 623 K.

Fig. 4 shows the interaction between adsorbed NCO species (Ag—NCO and Al—NCO) prepared at 673 K and a mixture of NO (14 Torr) and O_2 (15 Torr). When the NCO species is exposed to the mixture of NO and O_2, the bands ascribed to Al—NCO and Ag—NCO species decrease markedly even at room temperature (298 K). A band remains at 2245 cm^{-1} with a weak shoulder at *ca.* 2230 cm^{-1}. These results suggest that the position of the band for Al—NCO species shifts to 2245 cm^{-1} in the course of the reaction in the presence of NO and O_2. The IR bands attributed to Al—NCO and Ag—NCO

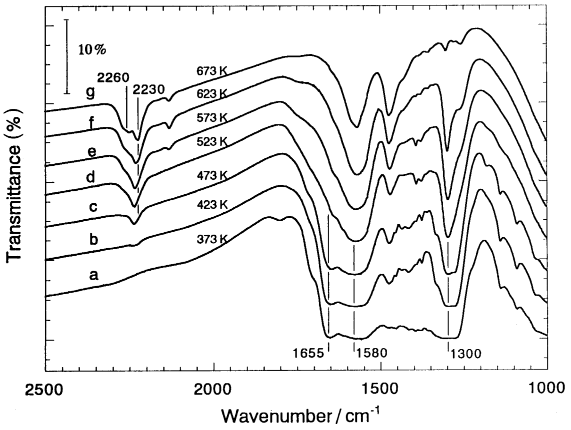

Fig. 2 FTIR spectra of Ag/Al_2O_3 after evacuating a mixture of NO (14 Torr) + C_3H_6 (11 Torr) + O_2 (15 Torr) at room temperature and heating to various temperatures in a vacuum for 15 min; (a) 373 K, (b) 423 K, (c) 473 K, (d) 523 K, (e) 573 K, (f) 623 K, (g) 673 K

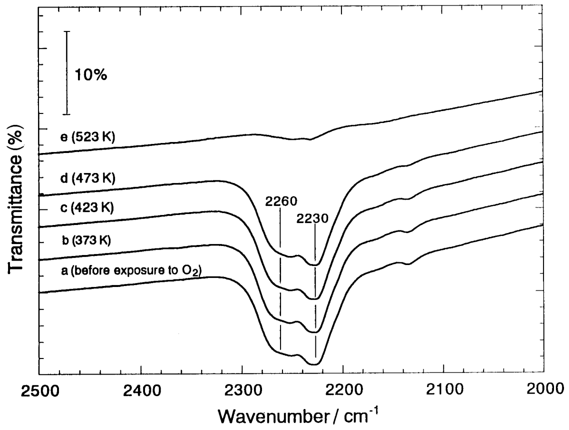

Fig. 3 FTIR spectra of the NCO species on Ag/Al_2O_3. (a) NCO species on Ag/Al_2O_3 after heating to 673 K for 15 min in a vacuum, (b) after exposure to 15 Torr of O_2 at 373 K for 15 min, (c) after heating at 423 K in 15 Torr of O_2 for 15 min, (d) after heating at 473 K in 15 Torr of O_2 for 15 min, (e) after heating at 523 K in 15 Torr of O_2 for 15 min.

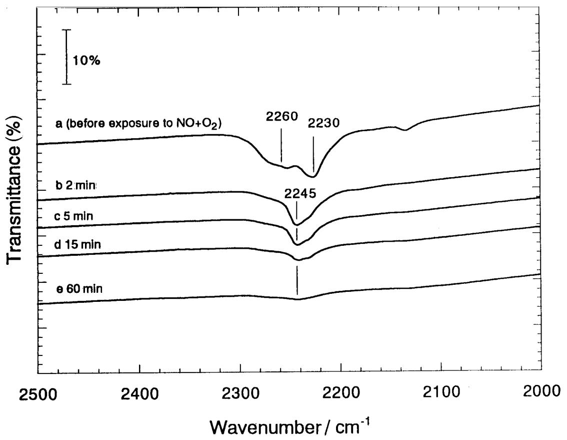

Fig. 4 FTIR spectra of the NCO species on Ag/Al_2O_3. (a) NCO species on Ag/Al_2O_3 after heating to 673 K for 5 min in a vacuum, (b) after exposure to a mixture of NO (14 Torr) + O_2 (15 Torr) at room temperature for 2 min, (c) after exposure to the gas mixture at room temperature for 5 min, (d) after exposure to the gas mixture at room temperature for 15 min, (e) after exposure to the gas mixture at room temperature for 60 min.

species decrease gradually with the progress of the reaction, and finally disappear after 60 min at room temperature. By gas phase analysis, it was found that N_2, CO_2 and CO were produced in a molar ratio of *ca.* 1 : 1 : 0.5 with a small amount of N_2O. Hence, the conversion of Ag—NCO into N_2 in the presence of a mixture of NO and O_2 was extremely rapid as compared with that in a vacuum, or in the presence of O_2 or NO alone. Since NO_2 is formed by the reaction of NO and O_2, the rapid rate of the conversion of NCO species in the presence of the mixture of NO and O_2 is most probably ascribed to the involvement of NO_2 in the conversion of NCO species.

From these results, the steps of NO reduction by hydrocarbons in an oxidizing atmosphere on Ag/Al_2O_3 can be expressed as,

$$NO + O_2 + C_3H_6 \rightarrow C_xH_yNO_z \rightarrow$$

$$NCO(a) \xrightarrow{NO,\ O_2} N_2 + CO_2 + CO$$

It was shown that the organic compounds, $C_xH_yNO_z$, were readily produced on the Ag/Al_2O_3 in a mixture of NO, O_2 and C_3H_6 at room temperature [Fig. 1(c)]. The organic compounds underwent thermal dissociation at *ca.* 600 K in a vacuum to yield NCO species. Because of facile formation of $C_xH_yNO_z$ and high reactivity of NCO species in the presence of NO and O_2, we conclude that the NCO formation is a rate determining step of the NO reduction with C_3H_6 in the presence of O_2 under the present experimental conditions.

Conclusion

The reduction of NO with C_3H_6 was carried out over Ag/Al_2O_3 in the presence of oxygen by the use of IR spectroscopy and mass spectrometry. Adsorbed $C_xH_yNO_z$ species were produced on Ag/Al_2O_3 by reaction among NO, O_2 and C_3H_6 at room temperature. The NCO species (Ag—NCO and Al—NCO) were formed by the thermal decomposition of $C_xH_yNO_z$. The NCO species were thermally stable up to 673 K in a vacuum. These species were highly reactive in a mixture of NO and O_2 at room temperature, being converted to N_2, CO_2, CO and small amounts of N_2O. Two important contributions of O_2 to the reduction of NO_x by C_3H_6 were suggested in the present experiments; (1) the presence of oxygen is essential for the formation of organic compound $C_xH_yNO_z$ intermediates for NCO species, and (2) oxygen promotes the reaction of NCO with NO. On the basis of the above results, the importance of the formation of $C_xH_yNO_z$ precursors and NCO species was stressed.

References

1 H. Hamada, Y. Kintaichi, M. Sasaki, T. Ito and M. Tabata, *Appl. Catal.*, 1990, **64**, L1.
2 W. Held, A. Koenig, T. Richter and L. Puppe, *SAE paper* 900496, 1990.
3 M. Iwamoto, H. Yahiro, S. Shundo, Y. Yu-u and N. Mizuno, *Appl. Catal.*, 1991, **69**, L15.
4 T. Miyadera and K. Yoshida, *Chem. Lett.*, 1993, 1483.
5 S. Sumiya, G. Muramatsu, N. Matsumura, K. Yoshida and R. Schenck, 1992, *SAE paper* 920853, 1992.
6 Y. Torikai, H. Yahiro, N. Mizuno and M. Iwamoto, *Catal. Lett.*, 1991, **9**, 91.
7 J. O. Petunchi, G. Sill and W. K. Hall, *Appl. Catal. B*, 1993, **2**, 303.
8 G. P. Ansell, A. F. Diwell, S. E. Golunski, J. W. Hayes, R. R. Rajaram, T. J. Truex and A. P. Walker, *Appl. Catal. B*, 1993, **2**, 81.
9 Y. Ukisu, S. Sato, G. Muramatsu and K. Yoshida, *Catal. Lett.*, 1991, **11**, 177.
10 H. Hong, A. Abe, K. Yoshida, S. Sumiya, Y. Ukisu and T. Miyadera, *71st Annual Meeting of Chem. Soc. Jpn.*, 1996, **3P1** and **16.**
11 V. A. Bell, J. S. Feeley, M. Deeba and R. J. Farruto, *J. Catal. Lett.*, 1994, **29**, 15.
12 C. Li, K. A. Bethke, H. H. Kung and M. C. Kung, *J. Chem. Soc., Chem. Commun.*, 1995, 813.
13 G. R. Bamwenda, A. Obuchi, A. Ogata and K. Mizuno, *Chem. Lett.*, 1994, 2109.
14 T. Tanaka and T. Okuhara, *Appl. Catal. B*, 1994, **4**, L1.
15 Y. Ukisu, S. Sato, A. Abe and K. Yoshida, *Appl. Catal. B*, 1993, **2**, 147.
16 N. Sheppard, *Pure Appl. Chem.*, 1962, **4**, 71.
17 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley-Interscience, New York, 4th edn., 1986.
18 J. W. London and A. T. Bell, *J. Catal.*, 1973, **31**, 32.
19 J. W. London and A. T. Bell, *J. Catal.*, 1973, **31**, 96.
20 K. Nakamoto, J. Fujita and H. Murata, *J. Am. Chem. Soc.*, 1976, **98**, 621.
21 M. Haneda, Y. Kintaichi, M. Inaba and H. Hamada, *Shokubai* (*Catalysts*), 1997, **39**, 204.
22 Y. Ukisu, T. Miyadera, A. Abe and K. Yoshida, *Catal. Lett.*, 1996, **39**, 265.
23 F. Solymosi and T. Bansagi, *J. Phys. Chem.*, 1979, **83**, 552.
24 F. Solymosi and J. Sarkany, *Appl. Surf. Sci.*, 1979, **3**, 68.
25 A. T. Bell, L. J. Lobree, A. W. Aylor and J. A. Reimer, *Prepr. Am. Chem. Soc. Div. Pet. Chem.*, 1997, **42**, 815.

Paper 8/01849I; *Received* 6th *March*, 1998