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Comparative studies of TPD and TPR of the adsorbed NO_3 species formed on copper oxide and ion-exchanged copper mordenite from nitrogen dioxide

Masahide Shimokawabe *, Kenya Itoh, Nobutsune Takezawa

Division of Materials Science and Engineering, Faculty of Engineering, Hokkaido University, Sapporo 060, Japan

Abstract

The catalytic reduction of NO_2 with C_3H_6 in the presence of O_2 was studied over CuO and Cu/mordenite (Cu/M) by the use of the temperature programmed desorption (TPD) and the temperature programmed reduction (TPR) methods. It was found that the reduction of NO_2 with C_3H_6 over CuO was greatly suppressed in the presence of O_2, whereas over Cu ion exchanged mordenite the conversion of NO_2 to N_2 was enhanced by the presence of O_2. It was suggested that NO_3 type adsorbed species were effectively involved in the reaction over Cu/M.

Keywords: NO_3-type adsorbed species; Reduction (selective); Nitrogen dioxide; Copper/mordenite; Copper oxide

1. Introduction

In our previous work [1], we showed that the catalytic properties of metal oxides on the reduction of NO_2 with C_3H_6 in the presence of O_2 were classified into two groups by the values of $-\Delta H$ of metal oxide formation. Over metal oxides (Co_3O_4, CuO, SnO_2, ZnO, CeO_2, and TiO_2: Group I) with $-\Delta H$ values lower than 700 kJ/mol, the redox cycle with C_3H_6 and O_2 was suggested to proceed more rapidly than that with C_3H_6 and NO_2 in the reaction with the mixture of $C_3H_6/NO_2/O_2$, whereas over metal oxides (SiO_2, ZrO_2, Al_2O_3, MgO, La_2O_3, and CaO) with $-\Delta H$ values higher than 700 kJ/mol, the reduction of NO_2 with C_3H_6 took place presumably through an adsorption type mechanism.

It is well known that the ion exchanged Cu/ZSM-5 [2–6], Ce/ZSM-5 [7,8] and Co/ZSM-5 [9,10] exhibit high performance in the catalytic reduction of NO by hydrocarbons in the presence of O_2. The oxides of copper, cerium, and cobalt were assigned to Group I metal oxides according to their $-\Delta H$ values. Hence, the redox cycle with C_3H_6 and O_2 would proceed more rapidly than the reaction of C_3H_6 and NO_2 on these metal oxides in contrast to the observations over Cu/ZSM-5, Ce/ZSM-5, and Co/ZSM-5.

In the present work, the difference in the reaction behaviour over CuO and Cu/M is investigated for elucidation of the role of mordenite in the NO_2 reduction with C_3H_6 in the presence of O_2. Involvement of the NO_3 type

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[*] Corresponding author.

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adsorbed species in the reduction of NO_2 by C_3H_6 on Cu/M is discussed.

2. Experimental

2.1. Catalyst preparation

CuO, and CeO_2 were prepared by calcination of $CuCO_3 \cdot Cu(OH)_2 \cdot H_2O$, and $Ce(CH_3COO)_3 \cdot 3H_2O$ in air at 773K for 3h, respectively. The other metal oxides used (Co_3O_4, SnO_2, ZnO, TiO_2, SiO_2, ZrO_2, Al_2O_3, MgO, La_2O_3, and CaO) were prepared in the similar manner as those used in the previous paper [11]. Cu/mordenite (Cu/M: Cu = 3.1 wt.%) was prepared by an ion exchange method at room temperature in an aqueous solution of copper(II) acetate (Wako Pure Chemicals, extra pure grade) and an aqueous solution of ammonia for 20h under continuous stirring. The final pH value of the solution was 10.5. The ion-exchanged mordenite was then filtered out, washed with distilled water and dried at 383K for 12h, and was further calcined in air at 773K for 3h. Mordenite (JRC-Z-M-20) was supplied from the Catalysis Society of Japan. Some experiments were carried out over Ce/mordenite (Ce/M:Ce = 3.0 wt.%). Ce/M was prepared by an ion exchange method in an aqueous solution of cerium(III)nitrate (Wako Pure Chemicals, extra pure grade) and an aqueous solution of ammonia and further treated in a similar manner to Cu/M.

2.2. NO_2 reduction with C_3H_6 in the presence and in the absence of O_2

The reactant gases, C_3H_6, NO_2 and O_2 used were all diluted to 1000 ppm with helium from each standard gas (1 vol.%) in the cylinders. O_2 impurity contained in the He cylinder was less than 9 ppm. The reaction was carried out in a conventional flow reactor at W/F [W = weight of the catalyst (g); F = total flow rate (cm^3/s)] of 8×10^{-2} g s cm^{-3} and at 773K. The reactor was made of 12 mm diameter quartz tubing in which the catalyst sample of 0.2 g was mounted on loosely packed quartz wool. The concentrations of NO, N_2O, N_2, O_2, CO, CO_2, C_3H_6 and other hydrocarbons in the outflow gas were determined by gas chromatography (Hitachi Model 663) with porapak Q and molecular sieve 5A columns. The concentration of NO_2 was monitored by a UV/VIS spectrophotometer (Hitachi Model 100–50). Because of the low concentrations of NO_2 and C_3H_6 in the outflow, the total flow rate was practically constant throughout the catalyst bed. The conversion of NO_2 or C_3H_6 was estimated from the concentrations of NO_2 or C_3H_6 at the inlet and the outlet of the catalyst bed.

2.3. Temperature Programmed Desorption (TPD) and Temperature Programmed Reduction (TPR)

Prior to the TPD and TPR runs, the catalyst (0.5 g) was treated in a stream of He at 773K for 3h. NO_2 diluted with He (5000 ppm) was then fed over the catalyst at room temperature for given periods of time, and was purged by a pure He stream until no NO_2 was detected in the outflow. Programmed heating was started from room temperature to 773K at a rate of 10K/min in a stream of He for the TPD experiments. For the TPR experiments, programmed heating was carried out in a He and 5000 ppm C_3H_6 mixture, or He, 5000 ppm C_3H_6 and 5000 ppm O_2 mixture. Gases evolved during the course of TPD or TPR heating were monitored by gas chromatography and UV/VIS spectrophotometer. The amount of gases desorbed was estimated from the peak area of TPD or TPR profiles.

2.4. Infrared diffuse reflectance spectroscopy

The adsorbed nitrogen oxide species were analyzed by IR diffuse reflectance spectroscopy. The infrared spectra of adsorbed NO species were recorded on a Fourier transform-infrared

(FT-IR) spectrophotometer (Nihon Bunko FT-IR5M) with a diffuse reflectance attachment (Nihon Bunko DG-500/H). The assignment of IR spectra was referred to the literature data [12,13].

3. Results and discussion

3.1. NO_2 reduction with C_3H_6 in the presence and in the absence of O_2

In the catalytic reduction of NO_2 with C_3H_6 in the presence and in the absence of O_2, the products such as N_2, NO, H_2O, CO_2, and CO were observed together with a trace amount of C_2H_4. Table 1 shows the conversion levels of NO_2 to N_2 and of O_2 along with that of C_3H_6 to CO_x (sum of CO and CO_2 produced) for the mixture of $C_3H_6/NO_2/O_2$, those of NO_2 to N_2 and C_3H_6 to CO_x for the mixture of C_3H_6/NO_2, and the ratio, R, of the conversion of NO_2 to N_2 to that of O_2 for the mixture of $C_3H_6/NO_2/O_2$.

For the reduction of NO_2 with C_3H_6 in the presence of O_2, metal oxides can be classified into two groups on the basis of the reactivity of NO_2 and O_2 with C_3H_6. Over SiO_2, ZrO_2 and La_2O_3 with the $-\Delta H$ values of metal oxide formation higher than 700 kJ/mol (referred to as Group II metal oxides), higher conversion of NO_2 to N_2 was achieved as compared with the conversion of O_2. These metal oxides exhibit R-values in a range of 2–4. In contrast, over Co_3O_4, CuO and CeO_2 with the $-\Delta H$ values lower than 700 kJ/mol (referred to as Group I metal oxides), the conversion of O_2 exceeds that of NO_2 to N_2. The conversion levels of O_2 over Group I metal oxides are much higher than those over Group II metal oxides. Complete conversion of O_2 was observed. R-values for these metal oxides are smaller than 0.89.

For Cu and Ce loaded on mordenite, the conversion levels of NO_2 to N_2 for the mixture of $C_3H_6/NO_2/O_2$ greatly exceed those for the mixture of C_3H_6/NO_2. The conversion of NO_2 to N_2 increases markedly by the presence of O_2. This contrasts with the results over CuO and CeO_2 for which the conversion of NO_2 to N_2 is appreciably suppressed in the presence of O_2. This indicates the performance of Cu and Ce catalysts for the selective reduction of NO_2 with C_3H_6 in the presence of O_2 was greatly improved upon loading in mordenite.

Table 1
Catalytic reduction of NO_2 with C_3H_6 in the presence and in the absence of O_2 over various catalysts at 773K

Catalyst	Conversion (%)					R [a] (−)	$-\Delta H_f$ (kJ/mol)
	$C_3H_6/NO_2/O_2$			C_3H_6/NO_2			
	NO_2 to N_2	O_2	C_3H_6 to CO_x	NO_2 to N_2	C_3H_6 to CO_x		
[Group I metal oxides]							
Co_3O_4	34.2	100	40.4	58.4	23.0	0.34	382.2
CuO	89.2	100	33.2	92.2	17.6	0.89	390.8
CeO_2	24.6	100	45.2	42.4	27.2	0.25	604.3
[Ion-exchanged mordenite]							
Cu/M	76.0	100	37.1	31.4	13.6	0.76	–
Ce/M	37.0	100	33.3	16.4	13.6	0.37	–
Mordenite	9.7	0	8.5	5.5	8.2	∞	–
[Group II metal oxides]							
SiO_2	8.6	3.7	4.0	7.1	6.3	2.3	675.6
ZrO_2	62.9	17.1	33.1	55.0	20.0	3.7	794.3
La_2O_3	33.6	13.0	14.7	23.2	11.7	2.6	846.6

C_3H_6: 1000 ppm/NO_2: 1000 ppm/O_2: 1000 or 0 ppm.

[a] R represents the ratio of the conversion of NO_2 to N_2 to that of O_2 for the mixture of $C_3H_6/NO_2/O_2$.

3.2. TPD studies for adsorbed NOx species on Cu / mordenite and CuO

Fig. 1 shows TPD curves of adsorbed NO_x species formed on mordenite and Cu/M upon contact with 5000 ppm NO_2 for 1h at room temperature. For mordenite alone (Fig. 1A), the desorption of NO_2 was observed around 373K and 473K in addition to the desorption of NO at 373K. For Cu/M (Fig. 1B), NO_2 and NO peaks occurred at 373K, 473K, and 673K, while O_2 peak was observed at 673K. Comparison with Fig. 1A and Fig. 1B suggests that the peaks of NO_2, NO, and O_2 at 673K arose from the species adsorbed on Cu loaded on mordenite, whereas other peaks at 373K and 473K were ascribed to the species primarily adsorbed on the surface sites of mordenite. Inspection of the peaks showed that O/N atomic ratio calculated from the amounts of NO_2, NO, and O_2 desorbed for the peak at 673K were estimated to be around 3, strongly suggesting that NO_3 species were produced on Cu/M. By IR spectroscopy, it was confirmed that the NO_3 species were formed on the adsorption of NO_2. This suggests that NO_3 species produced on Cu/M decomposed to NO_2, NO, and O_2 around 673K in the TPD runs.

Fig. 2A illustrates TPD curves of the adsorbed species on CuO formed in a flow of 5000 ppm NO_2 for 1h at room temperature. Broad peaks of NO_2 are observed along with those of O_2 in temperature ranges between 373K and 573K, and 573K and 773K. Fig. 2B illustrates TPD curves obtained after removing the species desorbed below 573K in a He flow up to 573K. The peaks of NO_2 and O_2 are also observed in a temperature range of 573K and 773K. The O/N atomic ratio calculated from the amounts of NO_2 and O_2 desorbed were also estimated to be around 3. This suggests that NO_3 species also produced on CuO and decomposed between 573K and 773K, giving NO_2 and O_2 in the TPD runs.

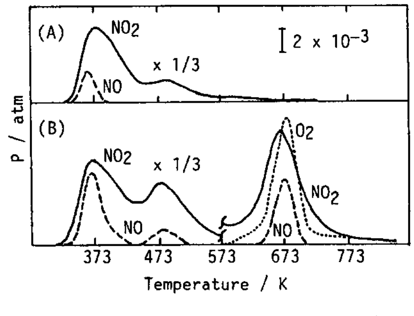

Fig. 1. TPD curves of adsorbed NO_x species formed on mordenite and Cu/M by NO_2 adsorption at room temperature. (A) mordenite; (B) Cu/M.

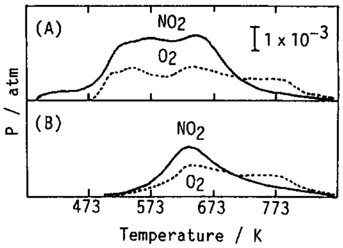

Fig. 2. TPD curves of adsorbed NO_x species formed on CuO. (A) NO_2 adsorbed at room temperature; (B) CuO was heated up to 573K in a stream of He after NO_2 adsorption.

3.3. TPR studies for Cu / mordenite and CuO with C_3H_6

Fig. 3 illustrates TPR curves of Cu/M and CuO with C_3H_6. No peak was observed over Cu/M (Fig. 3A). By contrast, CO_2 was evolved rapidly above 523K over CuO (Fig. 3B). Hence, CuO was easily reduced with C_3H_6 whereas ion exchanged copper was hardly reduced with C_3H_6.

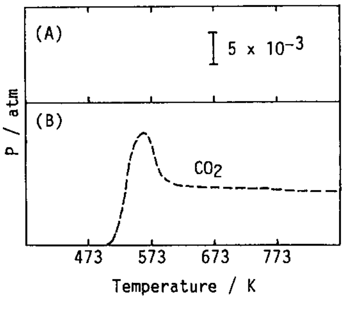

Fig. 3. TPR curves of Cu/M and CuO heated in a stream of C_3H_6. (A) Cu/M; (B) CuO.

3.4. TPR studies for adsorbed NO_x species on Cu/mordenite and CuO with C_3H_6 in the absence and in the presence of O_2

NO_3 type adsorbed species were prepared by heating Cu/M previously treated with NO_2 at room temperature in a stream of He up to 573K. TPR of the NO_3 species was then conducted in a stream of C_3H_6 or C_3H_6–O_2. Fig. 4A illustrates TPR curves of NO_3 type species on Cu/M heated in a stream of C_3H_6. The peaks of NO, N_2, CO_2, and CO appear around 483K. The temperature at which the products evolved was lower than the decomposition temperature of NO_3 type species by 200K. This strongly suggests that the NO_3 type species were directly involved in the reaction with C_3H_6 without decomposition to NO_2, NO and O_2. Other NO_x species, which desorbed around 373K and 473K (Fig. 1B), were heated together with NO_3 type species in a stream of C_3H_6. It was shown that the reduction of NO_2 to NO with C_3H_6 also occurred to some extent below 473K. By comparison of the amount of each desorbed species in TPD run (Fig. 1B) with the amount of the corresponding evolved species in TPR run, it indicates that most of adsorbed species other than NO_3 type species evolved as NO_2 and NO below 473K.

Fig. 4B illustrates TPR curves of NO_3 type species on Cu/M in a stream of C_3H_6–O_2. The TPR patterns obtained are greatly different from those obtained in a flow of C_3H_6. New desorption peaks of N_2 and CO_2 were observed at 423K along with the peaks of NO, N_2, CO_2, and CO observed in the flow of C_3H_6 around 483–493K. Thus, the temperature of N_2 formation observed in a stream of C_3H_6–O_2 was lower than that observed in a stream of C_3H_6 alone by 60K. In both cases (Fig. 4A and Fig. 4B), the amount of nitrogen evolved as N_2 and NO was practically equal to that adsorbed as NO_3 type species shown in Fig. 1B. It suggests NO_3 type adsorbed species on Cu/M reacted completely with C_3H_6 to produce N_2, NO, CO_2, and CO. The conversion of adsorbed NO_3 type species to N_2 was calculated on the basis of the amount of NO_3 type adsorbed species (Fig. 1B) and the amount of N_2 formed by the reaction in a stream of C_3H_6 or C_3H_6–O_2 (Fig. 4). The value calculated for the absence of O_2 was 69%, while the value increased to 77% by the presence of O_2. Hence, the formation of N_2 by the reaction between NO_3 type species and C_3H_6 was enhanced by the presence of O_2 on Cu/M. Above 523K, CO_2 was formed by the reaction between C_3H_6 and O_2 on Cu/M.

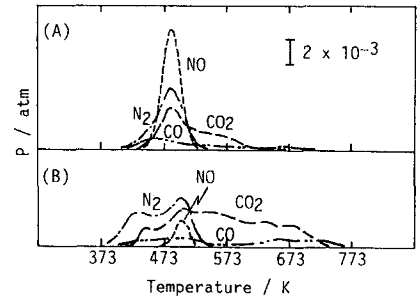

Fig. 4. TPR curves of adsorbed NO_x species on Cu/M with C_3H_6. (A) Heated in a stream of C_3H_6; (B) Heated in a stream of $C_3H_6+O_2$.

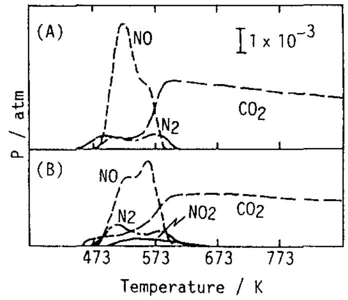

Fig. 5. TPR curves of adsorbed NO_x species on CuO with C_3H_6. (A) Heated in a stream of C_3H_6; (B) Heated in a stream of $C_3H_6+O_2$.

In a similar fashion, experiments were conducted over CuO. Fig. 5A and Fig. 5B show TPR curves of NO_3 type species on CuO heated in a stream of C_3H_6 and C_3H_6–O_2, respectively. In both cases, the adsorbed NO_x species reacted with gaseous C_3H_6 and the evolution of NO and N_2 started around 493K before the reduction of CuO occurred at 523K (Fig. 3B). In the presence of O_2 (Fig. 5B), a small amount of unreacted NO_2 evolved between 503K and 623K. It indicates that the reaction between the NO_3 type adsorbed species and C_3H_6 in TPR run was slightly suppressed in the presence of O_2. The conversion of adsorbed NO_3 to N_2 in the absence and in the presence of O_2 were estimated to be, respectively, 35% and 36% from the TPR profiles of Fig. 5. These values for CuO were much lower than these for Cu/M. Above 593K, the reduction of CuO occurred rapidly. Only CO_2 was produced as observed in the TPR of CuO with C_3H_6 (Fig. 3B).

4. Conclusion

The reduction of NO_2 with C_3H_6 over CuO was greatly suppressed in the presence of O_2, whereas over Cu ion exchanged mordenite the conversion of NO_2 to N_2 increased by the presence of O_2. The catalytic performance of Cu for the selective reduction of NO_2 with C_3H_6 in the presence of O_2 was greatly improved upon loading in mordenite.

From the results of TPD and TPR of adsorbed NO_x species, it was shown that NO_3 type adsorbed species were effectively involved in the reaction over Cu/M.

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