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Role of oxygen in selective reduction of nitrogen monoxide by propane over zeolite and alumina-based catalysts

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The role of coexisting oxygen in the selective reduction of nitrogen monoxide by propane on H-zeolites, alumina, Cu–ZSM-5 zeolite and Pt/Al_2O_3 catalysts was investigated. In the case of H-zeolites and alumina, oxidation of NO to NO_2 played an important role for the overall selective reduction of NO. On the other hand, the initial reaction step was considered to be partial oxidation of propane over Cu–ZSM-5 and Pt/Al_2O_3.

Keywords: Nitrogen monoxide; selective reduction; propane; oxidizing atmosphere; oxygen effect; H-zeolite; Cu–ZSM-5; alumina; Pt/alumina

1. Introduction

Selective reduction of nitrogen monoxide (NO) by hydrocarbon in oxidizing atmosphere has been reported over various catalysts recently. Copper ion-exchanged ZSM-5 (Cu-ZSM-5) shows high activity as reported by Held et al. [1] and Iwamoto et al. [2,3]. We have found independently that the selective reduction also occurs over solid acid-type catalysts such as H-zeolites [4], alumina [5], sulfuric acid-pretreated TiO_2 and ZrO_2 [6], etc., including no active transition metal species. Although the catalytic active sites have not been clarified yet, the solid acid-type catalysts are characterized by high selectivity in oxygen-rich atmospheres, that is, efficiency of hydrocarbon for NO reduction, while transition metal-containing catalysts such as Cu-ZSM-5 [7] and transition metal-promoted alumina [8,9] show high activity at relatively low temperatures.

It is obvious that the oxidation of hydrocarbon by oxygen to CO and CO_2 is a side reaction lowering the reduction selectivity. The presence of oxygen, however, usually promotes NO reduction as reported by many researchers [2,10]. With respect to the effect of oxygen, Iwamoto et al. speculated that NO reduction over Cu-ZSM-5 results from partial oxidation of hydrocarbon [11]. On the other hand, we have found [10] that nitrogen dioxide (NO_2) is reduced more easily than NO over H-ZSM-5 and alumina catalyst. Thus, the effect of oxygen could be attributed to either partial oxidation of hydrocarbon or oxidation of NO to NO_2.

In this paper, the role of oxygen in the selective reduction of NO by propane was investigated in detail for H-zeolites, Al_2O_3, Cu-ZSM-5 and Pt/Al_2O_3 catalysts, by examining the catalytic activities for the oxidation of propane and NO.

2. Experimental

H-form zeolites (H-ZSM-5, H-mordenite and H-USY) are the same samples as those used in our previous report [4]. Alumina (pellet, 0.8 mm in diameter) was purchased from Catalysts & Chemicals. Cu-ZSM-5 was prepared by ion-exchanging Na-ZSM-5 with a copper acetate solution. Pt/Al_2O_3 was prepared by impregnation of alumina with a H_2PtCl_6 solution.

The propane oxidation reaction was carried out with a fixed bed flow reactor by passing a mixture of propane and O_2 in helium over a catalyst. A small amount of NO or NO_2 was added to the feed gas for the purpose of performing selective reduction of NO or NO_2. The analysis of N_2, propane, CO and CO_2 in the effluent gas was made by gas chromatography. The oxidation reaction of NO to NO_2 was carried out by using a mixture of NO and O_2 as a reactant gas. In this case, the content of NO and NO_2 in the effluent was analyzed with a chemiluminescence NO_x analyzer.

3. Results and discussion

The experimental results of propane oxidation reaction by oxygen over the present catalysts are summarized in table 1, along with those of the selective reduction of NO (and NO_2) by propane.

The H-zeolites showed catalytic activity for the oxidation of propane to CO and CO_2. The conversion of propane to CO_x was almost 100% at 873 K over H-ZSM-5 and H-mordenite. The activity of H-USY was lower than that of H-ZSM-5 and H-mordenite. When NO or NO_2 was added to the feed gas, the oxidation of propane was further promoted. For example, the propane conversion over H-ZSM-5 was only 1.5% at 573 K in the absence of NO_x, whereas the conversion was about 80% when NO_x was present in a small amount. It should be noted that the reduction of NO or NO_2 to N_2 occurred simultaneously with the oxidation of propane over H-zeolites, indicating selective reduction of NO. Since NO reduction occurred under the conditions on which propane oxidation hardly proceeded over H-zeolites, it seems that the formation of N_2 results from direct reaction of propane and NO_2, formed by oxidation of NO. This specula-

Table 1
Catalytic activities for the oxidation of propane and the selective reduction of NO or NO_2 by propane [a]

Catalyst	Reactant	Conversion of C_3H_8 to CO, CO_2 (%)										Conversion of NO, NO_2 to N_2 (%)				
		873 K		773 K		673 K		573 K		523 K		873 K	773 K	673 K	573 K	523 K
		CO	CO_2	CO	CO_2	CO	CO_2	CO	CO_2	CO	CO_2					
H-ZSM-5	$C_3H_8+O_2$	21	77	11	60	4	17	0	1.5				–	–	–	
($SiO_2/Al_2O_3=34$)	$C_3H_8+O_2+NO$			7	90	15	83	21	61				43	62	60	
	$C_3H_8+O_2+NO_2$			1	96	35	62	36	44				38	65	51	
H-mordenite	$C_3H_8+O_2$	17	76	11	57	4	22	0	3				–	–	–	
($SiO_2/Al_2O_3=20$)	$C_3H_8+O_2+NO$			1	103	4	98	5	71				48	65	58	
H-USY	$C_3H_8+O_2$	22	28	8	11	1	1					–	–	–		
($SiO_2/Al_2O_3=20$)	$C_3H_8+O_2+NO$	5	89	25	25	9	15					27	21	15		
alumina	$C_3H_8+O_2$	17	78	38	40	25	18					–	–	–		
	$C_3H_8+O_2+NO$	0	97	26	68	13	8					18	35	15		
	$C_3H_8+O_2+NO_2$	0	100	5	94	26	38					22	36	33		
Cu-ZSM-5																
(Cu = 3.2%)	$C_3H_8+O_2$					0	99	0	99	0	68			–	–	–
($SiO_2/Al_2O_3=34$)	$C_3H_8+O_2+NO$					0	97	0	97	0	65			9	12	15
Pt/Al_2O_3																
(Pt = 0.5%)	$C_3H_8+O_2$			0	97	0	97	0	22				–	–	–	
	$C_3H_8+O_2+NO$			0	99	0	98	0	22				10	26	3	
	$C_3H_8+O_2+NO_2$			0	97	0	95	0	25				11	24	10	

[a] Reaction conditions: $C_3H_8+O_2$; $O_2=9\%$, $C_3H_8=400$ ppm, catalyst weight = 1 g, gas flow rate = 62 cm^3 min^{-1}. $C_3H_8+O_2+NO$; $O_2=10\%$, $C_3H_8=323$ ppm, NO = 1079 ppm, catalyst weight = 1 g, gas flow rate = 62 cm^3 min^{-1}. $C_3H_8+O_2+NO_2$; $O_2=10\%$, $C_3H_8=323$ ppm, $NO_2=1123$ ppm, catalyst weight = 1 g, gas flow rate = 62 cm^3 min^{-1}.

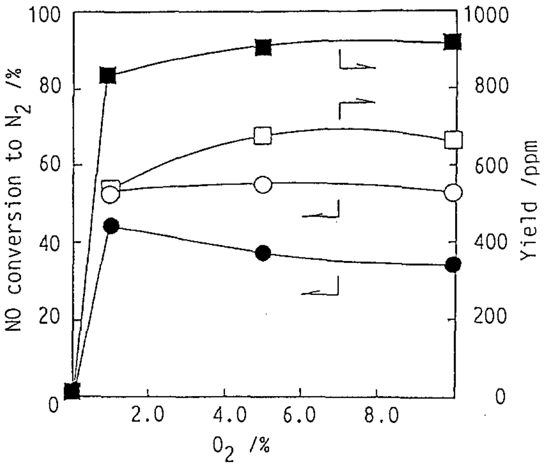

Fig. 1. Effect of oxygen in the reduction of NO by propane over H-ZSM-5 ($SiO_2/Al_2O_3 = 64$). (○) Conversion of NO to N_2 (673 K), (●) conversion of NO to N_2 (773 K), (□) yield of CO_2 (673 K), (■) yield of CO_2 (773 K). Reaction conditions: NO = 1079 ppm, $C_3H_8 = 323$ ppm, catalyst weight = 1 g, gas flow rate = 62 cm^3 min^{-1}.

tion is supported by the fact that NO is not reduced to N_2 by direct reaction with propane at such low temperatures as 673 K and that NO reduction is promoted by the presence of oxygen at the same temperatures, as shown by fig. 1. Another point to be noted for the reaction system of propane–O_2–NO_x over H-ZSM-5 is that no difference was observed in the reactivity of NO and NO_2 under the reaction conditions of the table.

Alumina also showed catalytic activity for propane oxidation and gave similar results to H-zeolites. However, the behavior with respect to the effect of NO_x addition was somewhat different. Namely, the increase in the extent of propane oxidation by NO addition was not so remarkable as that by NO_2 addition, although the reduction of NO to N_2 was observed as well as that of NO_2. It is also noted that reduction of NO_2 occurred more effectively than that of NO.

Cu-ZSM-5 and Pt/Al_2O_3 showed excellent activity for propane oxidation. By using these two catalysts, propane was almost completely oxidized to CO_2 even at 673 K. However, the behavior of the transition metal-containing catalysts with respect to the selective reduction of NO and NO_2 was entirely different from that of H-zeolites and alumina. The addition of NO or NO_2 to the feed did not accelerate propane oxidation at all, yet the selective reduction of NO or NO_2 to N_2 occurred. This indicates that NO or NO_2 was reduced to N_2 over Cu-ZSM-5 and Pt/Al_2O_3 under the reaction conditions where the oxidation of propane proceeded. Consequently, it is speculated that the first reaction step of the overall NO reduction over these catalysts is probably partial oxidation of propane, followed by reaction with NO or NO_2 to form N_2. No difference in reactivity was observed between NO and NO_2 over Pt/Al_2O_3.

Table 2
Catalytic activities for the oxidation of NO to NO_2 [a]

Catalyst	Conversion of NO to NO_2 (%)			
	873 K	773 K	673 K	573 K
without catalyst	16	16	17	17
H-ZSM-5 ($SiO_2/Al_2O_3 = 34$)	17	28	54	84
alumina	20	29	23	15
Cu-ZSM-5 (Cu = 3.2%) ($SiO_2/Al_2O_3 = 34$)	17	30	55	87
Pt/Al_2O_3 (Pt = 0.5%)	18	28	54	69

[a] Reaction conditions: $O_2 = 10\%$, NO = 1032 ppm, catalyst weight = 1 g, gas flow rate = 60 cm^3 min^{-1}.

Catalytic activities of the present catalysts for the oxidation of NO to NO_2 are shown in table 2. It was found that the activity of H-ZSM-5, Cu-ZSM-5 and Pt/Al_2O_3 for NO oxidation was much higher than that of Al_2O_3, as can be seen from the data at 573 and 673 K. The decrease in the extent of NO oxidation with increasing temperature for H-ZSM-5, Cu-ZSM-5 and Pt/Al_2O_3 is attributed to chemical equilibrium of NO oxidation reaction. The difference mentioned before in the effect of NO addition and NO_2 addition over alumina catalyst can be accounted for by the low catalytic activity of alumina for NO oxidation.

In order to get information on the role of CO in the NO reduction, reactions between NO_x and CO were examined. Table 3 shows the experimental results over alumina catalyst. In the absence of oxygen, NO was almost completely reduced to N_2 or N_2O by CO at 673 and 773 K. However, the conversion of NO became almost zero in the presence of 10% oxygen. The situation was almost the same for NO_2–CO reactions except for the activity difference between the NO–CO reaction and NO_2–CO reaction. Although not all results of table 3 are understandable at present, it is evident that CO does not serve as the selective reductant of NO_x in oxidizing atmosphere.

To confirm the role of catalysts, gas phase reactions were examined. The results are presented in table 4. It was found that gas phase oxidation of propane to CO and CO_2 without a catalyst did not occur below 873 K. However, the addition of a small amount of NO or NO_2 to the reactant gas accelerated propane oxidation, as can be seen from the fact that CO and CO_2 were formed in large amounts at 873 K. NO_2 was more effective than NO for the promotion of propane oxidation. However, reduction of NO or NO_2 to N_2 was not observed at all. This fact shows the need of the present catalysts for NO reduction to N_2 to occur.

Table 3
Effect of oxygen in the reduction of NO and NO_2 by CO over Al_2O_3 [a]

Reactant	Recovery of CO and conversion to CO_2 (%)								Conversion of NO, NO_2 to N_2, N_2O (%)							
	873 K		773 K		673 K		573 K		873 K		773 K		673 K		573 K	
	CO	CO_2	CO	CO_2	CO	CO_2	CO	CO_2	N_2	N_2O	N_2	N_2O	N_2	N_2O	N_2	N_2O
CO+NO	70	26	68	28	70	25	87	8	83	0	88	10	70	29	4	48
$CO+O_2+NO$	0	97	0	99	5	93	80	20	0.4	0	0.4	0	0.3	0	0.6	1
$CO+NO_2$	32	63	42	53	65	30	94	3	89	0.5	41	42	0	5	0	0
$CO+O_2+NO_2$	0	100	0	99	41	57	94	4	0	0	0	0	0	0	0	0

[a] Reaction conditions: CO+NO; CO = 3480 ppm, NO = 1032 ppm, catalyst weight = 1 g, gas flow rate = 62 cm^3 min^{-1}. $CO+O_2+NO$; O_2 = 10%, CO = 3484 ppm, NO = 1016 ppm, catalyst weight = 1 g, gas flow rate = 62 cm^3 min^{-1}. $CO+NO_2$; CO = 3480 ppm, NO_2 = 1123 ppm, catalyst weight = 1 g, gas flow rate = 62 cm^3 min^{-1}. $CO+O_2+NO_2$; O_2 = 10%, CO = 3480 ppm, NO_2 = 1123 ppm, catalyst weight = 1 g, gas flow rate = 62 cm^3 min^{-1}.

Table 4
Gas phase reactions without catalysts [a]

Reactant	Conversion of C_3H_8 to CO, CO_2 (%)						Conversion of NO, NO_2 to N_2 (%)		
	873 K		773 K		673 K				
	CO	CO_2	CO	CO_2	CO	CO_2	873 K	773 K	673 K
$C_3H_8+O_2$	0	0	0	0	0	0	–	–	–
$C_3H_8+O_2+NO$	15	2	0	0	0	0	0	0	0
$C_3H_8+O_2+NO_2$	60	13	2	1	0	0	0	0	0

[a] Reaction conditions: $C_3H_8+O_2$; $O_2=9\%$, $C_3H_8=400$ ppm, gas flow rate $=62$ cm^3 min^{-1}. $C_3H_8+O_2+NO$; $O_2=10\%$, $C_3H_8=323$ ppm, $NO=1079$ ppm, gas flow rate $=62$ cm^3 min^{-1}. $C_3H_8+O_2+NO_2$; $O_2=10\%$, $C_3H_8=323$ ppm, $NO_2=1123$ ppm, gas flow rate $=62$ cm^3 min^{-1}.

The conclusions of the present study are summarized as follows. The selective reduction of NO over H-zeolites proceeds probably via the reaction of propane and NO_2 which is formed by the oxidation of NO,

$$NO \xrightarrow{+O_2} NO_2 \xrightarrow{+C_3H_8} (C_xH_yO_z) \xrightarrow{+NO_x} N_2 + CO_x + H_2O. \qquad (1)$$

The high selectivity is probably attributable to the low activity of H-zeolites for propane oxidation by oxygen. The reaction pathway over alumina catalyst is similar to H-zeolites except that the activity of alumina for NO oxidation to NO_2 is low.

On the other hand, the first step of NO reduction over Cu-ZSM-5 and Pt/Al_2O_3, which are highly active catalysts for propane oxidation, seems to be the oxidation of propane to partially oxidized hydrocarbon, which then reacts with NO (or NO_2) to form N_2:

$$\begin{array}{l} C_3H_8 \xrightarrow{+O^*} (C_pH_qO_r) \xrightarrow{+NO\text{ (or }NO_2)} N_2 + CO_x + H_2O \\ \qquad\qquad\qquad\quad \llcorner \xrightarrow{+O^*} CO_x + H_2O. \end{array} \qquad (2)$$

Activated oxygen on transition metal catalysts (O* in eq. (2)) enhances a side reaction lowering the selectivity of NO reduction.

This difference in the reaction mechanism can explain the high efficiency of hydrocarbon in selective NO reduction over solid acid-type catalysts and the high activity of transition metal catalysts at lower temperatures, which is attributable to high activity of hydrocarbon oxidation. However, the determination of the precise mechanism requires further experimental confirmation.

References

[1] W. Held, A. Koenig, T. Richter and L. Puppe, SAE Paper, 900496 (1990).
[2] M. Iwamoto, H. Yahiro, Y. Yu-u, S. Shundo and N. Mizuno, Shokubai (Catalyst) 32 (1990) 430.

[3] M. Iwamoto, H. Yahiro, S. Shundo, Y. Yu-u and N. Mizuno, Appl. Catal. 69 (1991) L15.
[4] H. Hamada, Y. Kintaichi, M. Sasaki, T. Ito and M. Tabata, Appl. Catal. 64 (1990) L1.
[5] Y. Kintaichi, H. Hamada, M. Tabata, M. Sasaki and T. Ito, Catal. Lett. 6 (1990) 239.
[6] H. Hamada, Y. Kintaichi, M. Tabata, M. Sasaki and T. Ito, Chem. Lett. (1991) 2179.
[7] S. Sato, Y. Yu-u, H. Yahiro, N. Mizuno and M. Iwamoto, Appl. Catal. 70 (1991) L1.
[8] H. Hamada, Y. Kintaichi, M. Sasaki, T. Ito and M. Tabata, Appl. Catal. 75 (1991) L1.
[9] Y. Torikai, H. Yahiro, N. Mizuno and M. Iwamoto, Catal. Lett. 9 (1991) 91.
[10] H. Hamada, Y. Kintaichi, M. Sasaki, T. Ito and M. Tabata, Appl. Catal. 70 (1991) L15.
[11] Y. Yu-u, Y. Torikai, S. Sato, H. Hosose, H. Yahiro, N. Mizuno and M. Iwamoto, Shokubai (Catalyst) 33 (1991) 65.