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Remarkable Difference between the Kinetic Parameters of a Selective Catalytic Reduction of NO by Ethene on a Copper Ion-Exchanged MFI Zeolite and Al_2O_3

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The kinetic parameters have been determined in reaction systems of $NO+O_2+C_2H_4$, $NO_2+O_2+C_2H_4$, $NO+O_2$, and $O_2+C_2H_4$ over a copper ion-exchanged MFI zeolite (Cu-MFI) and Al_2O_3. The rate equations for the N_2 formation in the $NO+O_2+C_2H_4$ system on Cu-MFI (553—593 K) and Al_2O_3 (673—773 K) were expressed by $r_{N_2}=kP_{NO}^{2.0}P_{O_2}^{0.6}P_{C_2H_4}^{-1.0}\exp(-168000/RT)$ and $r_{N_2}=kP_{NO}^{1.1}P_{O_2}^{0.5}P_{C_2H_4}^{0.1}\exp(-294000/RT)$, respectively. The significant difference between the equations reveals that the reaction mechanisms or rate-determining steps on Cu-MFI and Al_2O_3 greatly differ. In addition, the rate equations for N_2 and CO_2 production were the same on Cu-MFI, while they were different on Al_2O_3. The reaction mechanism is discussed based on the equations.

Many catalysts have been reported to be active for the selective catalytic reduction of NO by hydrocarbons in an oxidizing atmosphere (SCR-HC).[1,2] Among them, a copper ion-exchanged MFI zeolite (Cu-MFI) and Al_2O_3 are typical catalysts for the reaction as a metal ion-exchanged zeolite catalyst and a solid acid catalyst;[2] the former shows high catalytic activity and moderate selectivity to N_2 formation at 523—673 K, while the later is moderately active and highly selective. On the Cu-MFI system, three kinds of reaction mechanisms have previously been suggested: a selective reduction of NO by active surface intermediates,[3—6] oxidation of NO to NO_2 by O_2 and a subsequent reaction of NO_2 with hydrocarbons to give N_2,[7] and decomposition of NO to N_2 and surface oxygen species and a reaction of the resulting oxygen adsorbates with hydrocarbons.[8] Very recently, it has also been reported that the NO_2 species on the surface[9,10] or in the gas phase[11] reacts with hydrocarbons to give an active intermediate for the selective reduction. This suggestion is a combination of the first and second mechanisms previously reported. On the other hand, the second mechanism has been preferentially proposed on the Al_2O_3 system.[6] Thus, the reaction mechanism has been extensively discussed.

In this study, the kinetic parameters of the SCR-HC on Cu-MFI and Al_2O_3 were systematically studied to clarify the difference between the reaction mechanisms on Cu-MFI and Al_2O_3. Several papers have already reported on the kinetics of the SCR-HC on various catalysts.[4,10,12] The results, however, are insufficient to discuss the reaction mechanism on Cu-MFI or Al_2O_3, since they were obtained at high conversion levels of NO_x and hydrocarbons, the concentrations of reactants were much higher than those in a practical system, or the activities of the catalysts employed were much lower than those of Cu-MFI and Al_2O_3. The present study was carried out at the conversion levels of reactants below 10% and at 1000 ppm of NO.

Experimental

The Cu-MFI catalyst was prepared by the same method as that reported previously.[5] The SiO_2/Al_2O_3 molar ratio and the exchange level of the Cu^{2+} ion were 23.3 and 103%, respectively. Al_2O_3 (JRC-ALO-4) was obtained from the Catalysis Society of Japan. All of the kinetic parameters were evaluated using a fixed-bed flow reactor. The reactants and products were analyzed by a gas chromatograph (TCD) with a molecular sieve 5A column for N_2 and CO and a Porapak Q column for N_2O, CO_2, and C_2H_4. NO_x (NO and NO_2) was analyzed by a chemiliminescence NO_x analyzer. The concentrations of the reactants were changed in the range 0—1600 ppm for NO (NO_2), 1.5—3.0% for O_2, and 0—1600 ppm for C_2H_4 (helium balance). The total flow rate was 150—300 $cm^3\ min^{-1}$. The catalyst weight was 0.005—0.500 g. Unless otherwise stated, the standard reaction conditions were P_{NO}=1000 ppm, P_{O_2}=2.0%, $P_{C_2H_4}$=1000 ppm, total flow rate=300 $cm^3\ min^{-1}$, and catalyst weight=0.015 g. The conversions of the reactants were less than 10% under the present conditions.

Results and Discussion

Since it is well known that NO_2 might be formed in a gaseous mixture of NO and O_2,[13] the effect of a mixing chamber (45 cm^3) of the reactants on the kinetics measurement was examined first. When NO, O_2, and C_2H_4 were mixed in the mixer and then introduced into the reactor with the Cu-MFI catalyst, N_2 formation was observed above 503 K under the standard reaction condition. Without the mixer the reaction was detected only above 533 K. One of the authors has already reported that the reaction of $NO_2+O_2+C_2H_4$ system was observed at a lower temperature than that of $NO+O_2+C_2H_4$.[1] The observations indicate that there is a formation of NO_2 in the mixer and the resulting NO_2 affects the kinetics of the $NO+O_2+C_2H_4$ reaction. Therefore the mixer was not used here, and the respective reactants were mixed just before the reactor. Without the mixer there is the possibility that mixing of the reactants is insufficient. At present, however, it is very difficult for us to verify the status of mixing; a measurement under the formation of a smaller amount of NO_2 would be better for studying the kinetics because most of NO_x in real exhausts is well known to be in the form of NO.

Typical examples of kinetics measurements in the $NO+O_2+C_2H_4$ system on Cu-MFI are shown in Figs. 1 and 2. The conversion of NO to N_2 is plotted as a function of the reaction temperature in Fig. 1A. Arrhenius plots of the N_2 formation rate (r_{N_2}) are shown in Fig. 1B. It is clear that when the conversion levels of NO to N_2 became 20% or greater the Arrhenius plots for N_2 formation strayed from the linear correlation line. The activation energy for N_2 formation on Cu-MFI was evaluated to be 168 kJ mol^{-1}. Figure 2 shows ln–ln plots of the rate of N_2 formation against the partial pressure of NO, O_2, or C_2H_4 ($P_{NO,O_2,or\,C_2H_4}$) in the $NO+O_2+C_2H_4$ reaction on Cu-MFI. We could obtain linear correlations within the present experimental conditions. The reaction orders with respect to NO, O_2, and C_2H_4 (α, β, and γ) for the N_2 formation were 2.0, 0.6, and −1.0, respectively.

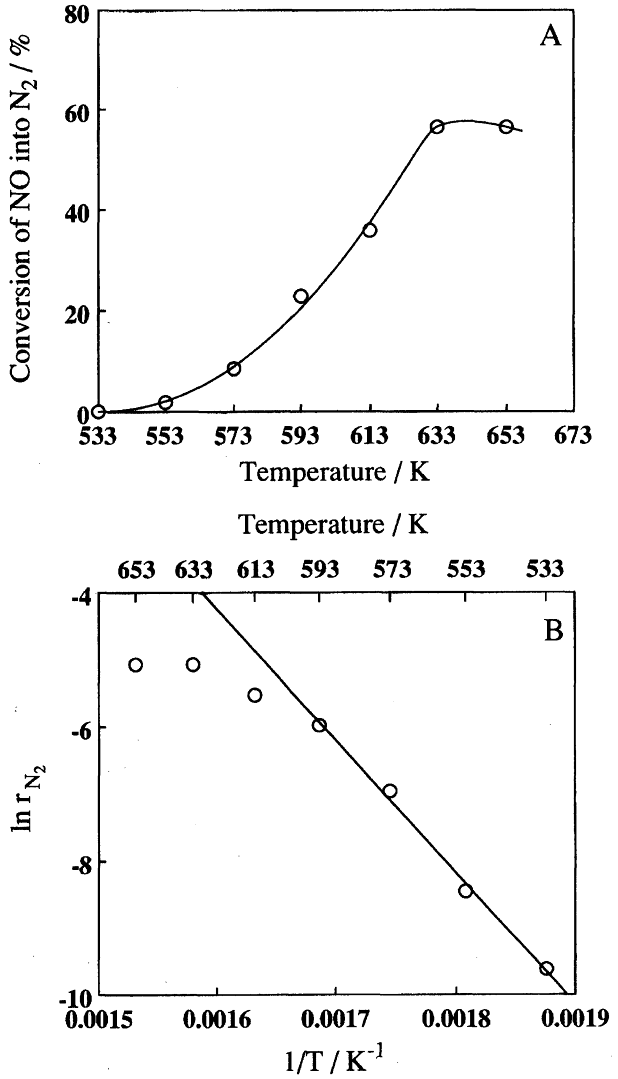

Fig. 1. Temperature dependence of conversion of NO into N_2 in the $NO+O_2+C_2H_4$ reaction system on Cu-MFI (A) and the Arrhenius plots (B). NO 1000 ppm, O_2 2.0%, C_2H_4 1000 ppm, catalyst weight 0.015 g total flow rate 300 cm^3 min^{-1}.

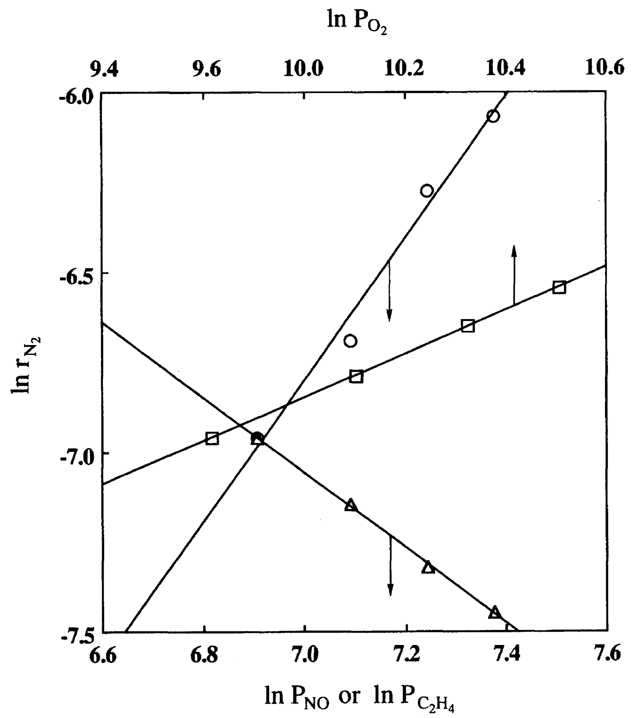

Fig. 2. Dependence of the N_2 formation rate in the $NO+O_2+C_2H_4$ reaction system on Cu-MFI on the partial pressures of reactants. ○, NO 1000—1600 ppm; □, O_2 1.5—3.0%; △, C_2H_4 1000—1600 ppm; Standard condition, NO 1000 ppm, O_2 2.0%, C_2H_4 1000 ppm, catalyst weight 0.015 g, total flow rate 300 cm^3 min^{-1}.

It would be worthy to note that the mass balance of carbon and nitrogen before and after the reaction was 0.95—1.01 and 0.96—0.99, respectively in all of the experiments. It has been reported that HCN and HNCO were formed as byproducts during the $NO+O_2+C_2H_4$ reaction on several catalysts.[14] Although the byproducts were not analyzed in the present experiments, the very good carbon and nitrogen balances indicate a negligible formation of the byproducts.

The kinetic parameters observed are summarized in Table 1. We wish to discuss the kinetics of the SCR-HC on Cu-MFI. The rate equations for N_2 and CO_2 formations in the $NO+O_2+C_2H_4$ reaction were as follows:

$$r_{N_2} = kP_{NO}^{2.0}P_{O_2}^{0.6}P_{C_2H_4}^{-1.0}\exp(-168000/RT) \quad (1)$$

and

$$r_{CO_2} = kP_{NO}^{2.0}P_{O_2}^{0.7}P_{C_2H_4}^{-1.0}\exp(-175000/RT). \quad (2)$$

The kinetic orders and activation energies in both equations were very similar, which suggests that N_2 and CO_2 would be produced through the same rate-determining step in the $NO+O_2+C_2H_4$ system. It should be noted that the value of α for N_2 formation in the $NO+O_2+C_2H_4$ system was 2.0, probably suggesting that N_2 was formed in the reaction of

Table 1. Kinetic Parameters of Selective Reduction of NO by Ethene over Cu-MFI and Al_2O_3 Catalysts[a)]

Catalyst	Reaction system	Temp/ K	Product	Kinetic parameters[b)]			
				α	β	γ	E_a[c)]
Cu-MFI	$NO+O_2+C_2H_4$[d)]	553—593	N_2	2.0	0.6	−1.0	168
			N_2O	0.8	−0.1	−0.6	86
			CO_2	2.0	0.7	−1.0	175
			CO	—	—	—	—
	$NO_2+O_2+C_2H_4$[d)]	563—613	N_2	1.0	0.0	−1.0	105
			N_2O	0.0	0.0	−0.1	152
			CO_2	1.1	0.2	−1.0	144
			CO	1.0	0.0	−1.0	69
	$NO+O_2$[e)]	473—573	NO_2	1.0	0.0	—	36
	$O_2+C_2H_4$[f)]	523—593	CO_2	—	0.5	0.1	247
Al_2O_3	$NO+O_2+C_2H_4$[d)]	673—733	N_2	1.1	0.5	0.1	294
			N_2O	1.0	0.1	0.1	236
			CO_2	0.2	0.7	0.0	316
			CO	0.1	0.6	0.0	210
	$NO_2+O_2+C_2H_4$[d)]	653—713	N_2	1.1	0.0	0.1	272
			N_2O	—	—	—	—
			CO_2	1.1	0.1	0.1	293
			CO	0.1	0.7	0.1	184
	$NO+O_2$[g)]	623—773	NO_2	1.0	0.0	—	11
	$O_2+C_2H_4$[f)]	753—813	CO_2	—	0.5	0.0	268

a) Standard reaction condition, NO_x 1000 ppm, O_2 2.0%, C_2H_4 1000 ppm, catalyst weight 0.015 g, total flow rate 300 $cm^3\ min^{-1}$. The symbol "—" indicates that the value could not be evaluated. b) $r = kP_{NO_x}^{\alpha}P_{O_2}^{\beta}P_{C_2H_4}^{\gamma}\exp(-E_a/RT)$, mol g-cat^{-1}min^{-1}. c) Activation energy, kJ mol^{-1}. d) NO_x 800—1600 ppm, O_2 1.5—3.0%, C_2H_4 1000—1600 ppm. e) Catalyst weight 0.005 g, NO 1000—1600 ppm, O_2 1.5—3.0%. f) O_2 1.5—3.0%, C_2H_4 1000—1600 ppm. g) Catalyst weight 0.101 g, total flow rate 150 $cm^3\ min^{-1}$, NO 1000—1600 ppm, O_2 1.5—3.0%.

the nitrogen-containing compounds with NO_x. In fact, it was reported that N_2 was formed in the reaction of isocyanate species with NO_x[15)] or that nitrogen-containing compounds such as CH_3NO_2 and $C_2H_5NO_2$ were active for the reaction with the mixture of $NO+O_2$ to give N_2 selectively.[5)]

The value of β for N_2 formation in the $NO+O_2+C_2H_4$ system was 0.6, indicating that the higher pressure of O_2 accelerates the NO reduction to N_2. Li and Hall[16)] reported that the rate equation for NO decomposition on Cu-MFI is

$$r_{N_2} = kP_{NO}^{0.9—1.1}P_{O_2}^{-0.4—-0.2}\exp(-71000— -121000/RT). \quad (3)$$

The reaction orders of NO and O_2 for NO decomposition are quite different from those of the $NO+O_2+C_2H_4$ reaction. The rate-determining step in the selective reduction of NO by hydrocarbons would not include the catalytic decomposition processes of NO.

Table 1 clearly shows the great difference between the kinetic parameters for the N_2 and N_2O formations in the $NO+O_2+C_2H_4$ system on Cu-MFI. It has already been reported by Li and Armor[17)] that the decomposition of N_2O to give N_2 is well catalyzed on Cu-MFI; therefore, if N_2 was mainly generated through the N_2O decomposition in the $NO+O_2+C_2H_4$ system, the kinetic parameters of N_2 and N_2O formations should be the same. The difference in the rate equations suggests that the pathway of the N_2O formation is distinct from that of N_2.

The rate equation of N_2 formation in the $NO_2+O_2+C_2H_4$ system was clearly different from that in the $NO+O_2+C_2H_4$ system. This observation reveals that the reduction mechanism of NO on Cu-MFI is not the same as that of NO_2.[1)] In addition, the values of γ for N_2 formation in the NO (or NO_2)$+O_2+C_2H_4$ system were −1.0, indicating that C_2H_4 strongly adsorbs on the active site of Cu-MFI. The activation energy of CO_2 formation on Cu-MFI was found to be in the order $O_2+C_2H_4 > NO+O_2+C_2H_4 > NO_2+O_2+C_2H_4$. This clarifies that the oxidation of C_2H_4 on Cu-MFI is enhanced by the presence of NO_x.

With Al_2O_3 used as a catalyst, it should first be noted that the active temperature regions for all reaction systems were much higher than those on Cu-MFI. This indicates the low activity of Al_2O_3 for the oxidation of C_2H_4 or the reduction of NO_x. The rate equation of N_2 formation in the $NO+O_2+C_2H_4$ system on Al_2O_3 is described by

$$r_{N_2} = kP_{NO}^{1.1}P_{O_2}^{0.5}P_{C_2H_4}^{0.1}\exp(-294000/RT). \quad (4)$$

The equation is entirely different from Eq. 1 on Cu-MFI. In addition, Eq. 4 is distinct from that of CO_2 on Al_2O_3. It follows that the rate-determining step of N_2 formation is different from either that of N_2 formation on Cu-MFI or that of CO_2 on Al_2O_3. It should further be noteworthy that the order on NO for the N_2 formation in the $NO+O_2+C_2H_4$ system was the same as that on NO_2 in the $NO_2+O_2+C_2H_4$ system, which is a different phenomenon from that on Cu-MFI. The findings suggest that NO_2 would easily be formed on Al_2O_3 and the resulting NO_2 might participate in the SCR-HC. The idea is partly consistent with the suggestion of Hamada et al.[6] that the oxidation of NO to NO_2 is a key step and NO_2 can preferentially react with hydrocarbons. It should be noted, however, that there are great differences between the values of α and β for the CO_2 formation in the $NO+O_2+C_2H_4$ and the $NO_2+O_2+C_2H_4$ systems. Clearly the role of oxygen added into the $NO+C_2H_4$ mixture is not limited to the oxidation of NO to NO_2.

Recently Vannice and co-workers have reported the following rate equation for N_2 formation in the $NO+O_2+CH_4$ reaction on a Sr/La_2O_3 catalyst:[10]

$$r_{N_2} = kP_{NO}^{0.87}P_{O_2}^{0.55}P_{CH_4}^{0.26}\exp(-109000/RT). \tag{5}$$

The similarity in the values of α and β on the catalyst to those on Al_2O_3 (Eq. 4) might indicate that the formation of NO_2 would be the key step on both catalysts.[10] The difference between the values of γ on Sr/La_2O_3 and on Al_2O_3 is probably due to the different adsorbabilities of CH_4 and C_2H_4.

At present it is very difficult for us to propose reaction mechanisms on the basis of the above kinetic parameters because of the complex rate equations. These results, however, would be very promising data for understanding the difference between the catalyses of Cu-MFI and Al_2O_3, and useful for clarifying the reaction mechanisms.

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