ELSEVIER

Catalysis Today 27 (1996) 71–78

CATALYSIS TODAY

Pulse study on reactivity of ethene adsorbed on Cu-MFI with nitrogen oxides and oxygen

Masakazu Iwamoto *, Hiroshi Takeda

Catalysis Research Center, Hokkaido University, Sapporo, 060, Japan

Abstract

The mechanism of selective catalytic reduction of NO by C_2H_4 over Cu-MFI zeolite has been studied by a pulse technique, in which the reactivity of ethene, NO_x, nitrogen- or oxygen-containing compounds has been determined. It follows that the major route to form N_2 is the reaction of the mixture of NO and O_2 with surface adsorbates of C_2H_4. Ethene adsorbed on Cu-MFI is classified into two kinds of hydrocarbon species. One is active for the reaction with NO_x and another is inert. Oxygen molecules are effective to increase the amount of the active hydrocarbon species for NO_x. NO as well as NO_2 would directly be included in the selective reduction as an active NO_x species.

Keywords: Ethene reactivity; Copper-MFI zeolite; Nitrogen oxides; Oxygen

1. Introduction

It is widely accepted that the newly developed selective catalytic reduction of NO by hydrocarbons (SCR-HC) is a potential method to remove NO practically in excess O_2 [1]. Much effort, therefore, has been devoted to development of active catalysts and elucidation of reaction mechanisms. Many kinds of reaction mechanisms have been suggested, which could be classified into three categories; (1) selective reaction of some partially oxidized intermediates (dehydrogenated hydrocarbons, radicals, carbonaceous adsorbates, etc.) with NO_x to give N_2 [2–4], (2) oxidation of NO to NO_2 by O_2 and subsequent reaction of NO_2 with hydrocarbons to give N_2 [5–11], (3) combination of decomposition of NO to N_2 and reaction of the resulting oxygen adsorbates with hydrocarbons [12,13]. The reaction mechanism of the SCR-HC is still controversial. Here we have studied first the reactivity or role of C_2H_4, NO_x and O_2 in the SCR-HC, and then the reactivity of various oxygen- and nitrogen-containing compounds by a pulse technique.

2. Experimental

Cu-MFI catalyst was prepared by the ion exchange of Na-MFI ($SiO_2/Al_2O_3 = 23.3$) in an aqueous solution of copper acetate [14]. The exchange level of Cu^{2+} ion was 105% (the amount of Cu^{2+}, 637 μmol g cat^{-1}), which was determined by atomic absorption spectroscopy. Cu-MFI catalyst was pretreated at 773 K in a He flow for 4 h before the pulse experiment.

The pulse experiment was carried out at 573 K on 5 mg of Cu-MFI, which was mounted in a

* Corresponding author.

0920-5861/96/$32.00
SSDI 0920-5861(95)00206-5

microreactor connected to a gas chromatograph. The reaction apparatus used was similar to that of Choudhary et al. [15]. A constant stream of helium of 50 $cm^3\ min^{-1}$ (GHSV, 300 000 h^{-1}) was employed as a carrier gas. Pulses of 1.36 cm^3 (12.1 mmol g cat^{-1}) was introduced at intervals of 20 min. Unless otherwise stated, the concentration of reductants was 1.0%, and those of NO_x and O_2 were 1.0% and 10.0%, respectively. A Porapak Q and Molecular Sieve 5A columns were used to separate N_2O, CO_2, C_2H_4, O_2, N_2 and CO. Subsequently to the pulse experiment the catalyst was heated from 573 to 773 K at 2 K min^{-1} in a 100 $cm^3\ min^{-1}$ flow of 1% O_2 and 99% He to evaluate the residue on Cu-MFI at 573 K (TPO). Ethene and various oxygen- and nitrogen-containing compounds were used as reductants without any purification.

The material balances of nitrogen atoms (B_N) and oxygen atoms (B_O) during the reaction were calculated as follows:

$$B_N = 2([\text{amount of } N_2 \text{ formed}] + [\text{amount of } N_2O \text{ formed}]) - ([\text{amount of NO consumed}])$$

$$B_O = ([\text{amount of } N_2O \text{ formed}] + 2[\text{amount of } CO_2 \text{ formed}] + [\text{amount of } H_2O\text{formed}]) - ([\text{amount of NO consumed}])$$

Here the amount of NO_2 was not included in the calculation because the concentration of NO_2 could not be determined by a gas chromatograph. The amount of H_2O formed was calculated from the amount of CO_2 on the assumption of complete combustion of C_2H_4.

3. Results

In order to clarify the route to form N_2, the product distribution was measured in three kinds of pulse systems. The results of alternate introduction of NO and $O_2+C_2H_4$, $NO+O_2$ and C_2H_4, or O_2 and $NO+C_2H_4$ have been shown in Fig. 1A, Fig. 1B and Fig. 1C, respectively. In each reaction system, the N_2 formation was observed only when NO or the NO-containing mixture was introduced onto the catalyst bed. The amounts of N_2 produced in the above three pulse systems were 3, 35 and 1 μmol g cat^{-1}, respectively. The results indicate that the major route to form N_2 on Cu-MFI is the reaction of surface adsorbates of C_2H_4 with $NO+O_2$. The reactivity of preadsorbed C_2H_4 with NO_x or NO_x+O_2, therefore, has been studied in more detail.

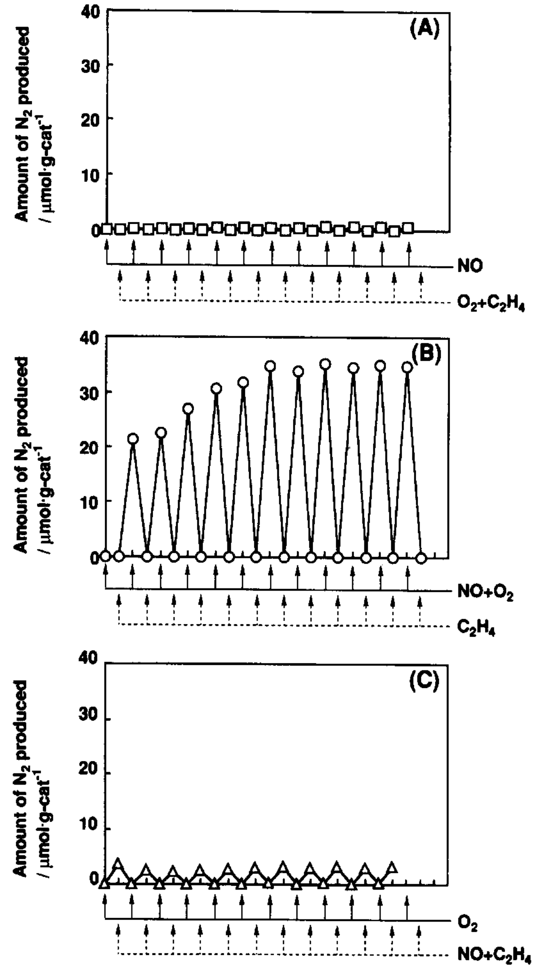


Fig. 1. Change in N_2 formation with the gas compositions introduced. The alternate introduction of (A) NO and $O_2+C_2H_4$, (B) $NO+O_2$ and C_2H_4 or (C) O_2 and $NO+C_2H_4$ onto the Cu-MFI catalyst.

When C_2H_4, NO and O_2 were introduced in series onto Cu-MFI, the amounts of reactants consumed, products formed, and the B_N and B_O values

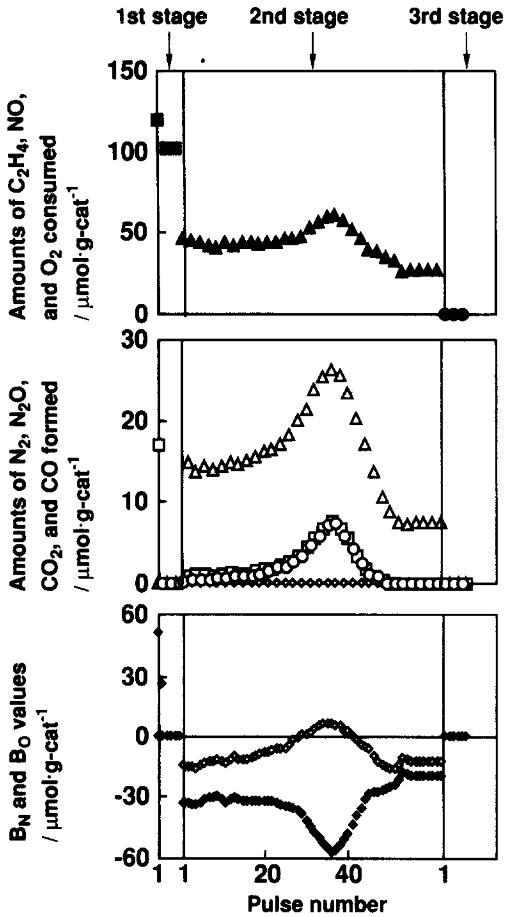


Fig. 2. Product distribution during the NO pulses onto the C_2H_4-preadsorbed Cu-MFI catalyst. In the 1st stage C_2H_4 (1.0%) was pulsed, and in the 2nd and 3rd stages NO (1.0%) and O_2 (1.0%) were introduced, respectively. ■, C_2H_4; ▲, NO; ●, O_2; □, CO_2; △, N_2O; ○, N_2; ◇, CO; ◇, B_N; ♦, B_O.

were greatly changed with the number of pulses as shown in Fig. 2. The total amount of C_2H_4 adsorbed in the 1st stage (6 pulses) was 701 μmol g cat^{-1}. During the 2nd stage (NO pulses), a long-term induction period was observed in N_2 and CO_2 formation. The maximum yields of N_2 and CO_2 were recognized at the 37th pulse of NO in the 2nd stage. On the other hand, N_2O was formed all through the 2nd stage though the amount was changed with the pulse number. It should be noted that a constant amount of N_2O was produced at 54th–62nd pulses without any formation of N_2 and CO_2. The ratio of the amount of NO consumed to that of N_2O generated was approximately 3 during 54th–62nd pulses. It was confirmed separately that the disproportionation reaction ($3NO \rightarrow N_2O + NO_2$) proceeds at a similar extent in a continuous flow experiment on Cu-MFI. It follows that there occurred disproportionation during the pulse experiment. The amount of N_2O formed in the present pulse experiments was thus evaluated by the subtraction of the amount generated by the disproportionation reaction from the total amount.

After the 2nd stage, O_2 was introduced but no product was observed (the 3rd stage in Fig. 2). In the subsequent TPO experiment CO_2 was formed and the amount was 1207 μmol g cat^{-1}.

Various NO_x or $NO_x + O_2$ mixtures were introduced onto the C_2H_4 adsorbates in a similar manner to that of Fig. 1. The N_2 formation profiles are shown as a function of the pulse number in Fig. 3. The amount of C_2H_4 adsorbates in each system was made even at 710 ± 10 μmol g cat^{-1}. The N_2 formation profiles can be classified into the three types; (1) in case of the NO system there was a long induction period for the N_2 formation, (2) in the NO_2 and $NO + NO_2$ systems the amount of N_2 formed at each pulse was almost constant during the 1st–12th NO_x pulses and (3) in the pulse system containing O_2 a lot of N_2 was produced at 1st–4th pulses. The product distribution in the pulse

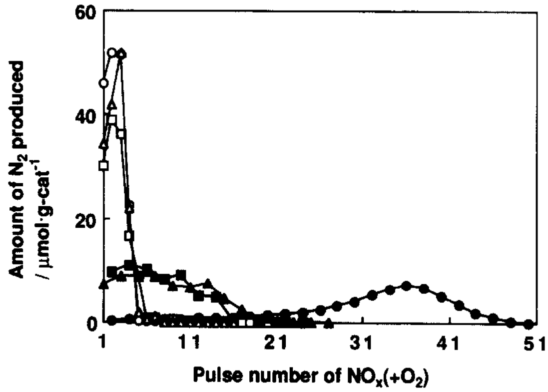


Fig. 3. Change in N_2 formation profile with the gas composition introduced onto the C_2H_4 preadsorbed Cu-MFI catalyst. Amount of C_2H_4 adsorbed, 701–720 μmol g cat^{-1}; catalyst weight, 5 mg; carrier gas flow rate, 50 cm^3 min^{-1} (GHSV, 300 000 h^{-1}); temperature, 573 K; pulse size, 1.36 cm^3 (12.1 mmol g cat^{-1}); pulse interval, 20 min. ●, NO (1.0%); ■, NO_2 (1.0%); ▲, NO (0.5%) + NO_2 (0.5%); ○, NO (1.0%) + O_2 (10.0%); □, NO_2 (1.0%) + O_2 (10.0%); △, NO (0.5%) + NO_2 (0.5%) + O_2 (10.0%).

Table 1
Product distribution in the pulse and TPO experiments over Cu-MFI catalyst[a]

Gases pulsed	Product distribution (μmol g cat^{-1})				CO_2 in TPO[b]
	N_2	N_2O[c]	CO_2	CO	
NO	117	507	131	0	1207
NO_2	121	97	285	0	1079
$NO+NO_2$	120	94	182	0	1182
$NO+O_2$	173	10	833	11	561
NO_2+O_2	135	10	814	19	553
$NO+NO_2+O_2$	154	17	838	19	577
O_2[d]	0	0	829	15	565

[a] The experimental conditions were the same as those in Fig. 3. The amounts of C_2H_4 adsorbed were 710 ± 10 μmol g cat^{-1}.
[b] Amount of CO_2 formed in the TPO experiment, μmol g cat^{-1}. No formation of N_2, N_2O and CO was observed.
[c] The contribution of disproportionation was subtracted from the total amount.
[d] O_2(10.0%).

experiments and the subsequent TPO experiments are summarized in Table 1.

The mass balance of carbon could be calculated. The amounts of CO_2 or CO produced in the pulse and the TPO experiments in Table 1 were varied with the reaction systems but the sums of them were 1386 ± 48 μmol g cat^{-1}. The amounts were in good correspondence to those of C_2H_4 adsorbed (710 ± 48 μmol g cat^{-1}). The same stoichiometry was observed in all experiments, indicating that all ethene molecules on the Cu-MFI surface could be completely oxidized within the present experimental conditions.

To evaluate the effect of O_2 a desired amount of O_2 was pulsed onto the C_2H_4 adsorbates and then NO pulses were introduced until the amount of N_2 formed became zero. The results are plotted in Fig. 4, where the number of O_2 pulses is plotted as abscissa and the numbers on the ordinate indicate the amounts of N_2 formed during the NO pulses. Fig. 4 reveals that the introduction of O_2 before the NO pulses increased the yield of N_2. The maximum value was 143 μmol g cat^{-1}, which was greater than that of the NO system in Table 1.

The effect of the amount of C_2H_4 adsorbates on the product distribution was examined in the $NO+O_2$ system and is summarized in Table 2. The amounts of N_2 and CO_2 produced in the pulse experiment increased with increasing the amount of C_2H_4 adsorbed and leveled off at 701 μmol g cat^{-1}. On the other hand, the amount of CO_2 formed in the TPO experiment was zero at the small amount of C_2H_4 adsorbates and increased at the larger amount.

Next the reactivity of adsorbed oxygen- and nitrogen-containing compounds with the $NO+O_2$ mixture were studied to clarify the active intermediates on the surface. Table 3 summarized the product distribution in the pulse and the TPO experiments. It is clear that the absolute amounts of N_2 produced were dependent not only on the reactivity of compounds but also on the quantities of compounds adsorbed, since the amounts of CO_2 formed greatly varied. The activity of the reductants for the NO reduction, therefore, should be evaluated by the N_2/CO_x ratio which was calculated by the number of N_2 formed/the number of CO_x formed during the $NO+O_2$ pulses. The values are summarized in Table 3. With the nitrogen-containing compounds, the N_2/CO_x values should be recalculated because of containing of a nitrogen atom in the reductants. Half amounts of N atoms in the nitrogen-containing compounds (the amounts of N_2 from the compounds) were subtracted from the amounts of N_2 formed. The cor-

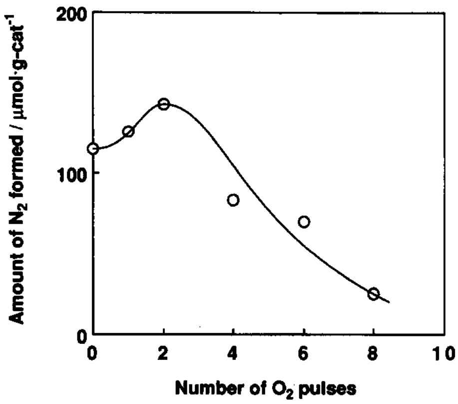


Fig. 4. The amount of N_2 generated in the NO pulses as a function of the number of O_2 pulses. A desired amount of O_2 was introduced onto the C_2H_4-preadsorbed Cu-MFI and then NO was pulsed onto the sample. The other experimental conditions were the same as those of Fig. 3 except that the partial pressures of O_2 and NO were 1.0% and 5.0%, respectively.

Table 2
Dependence of the product distribution in the pulse and TPO experiments on the amount of C_2H_4 adsorbates[a]

Amount of $C_2H_4^b$	Product distribution in $NO+O_2$ pulse (μmol g cat^{-1})				CO_2 in TPO[b]
	N_2	N_2O	CO_2	CO	
0	0	0	0	0	0
232	98	4	445	10	0
701	173	10	833	11	561
1454	172	9	883	8	1896

[a] The experimental conditions are the same as those of the $NO+O_2$ system in Fig. 3.
[b] μmol g cat^{-1}.

rected N_2/CO_x values are described in the parentheses of Table 3.

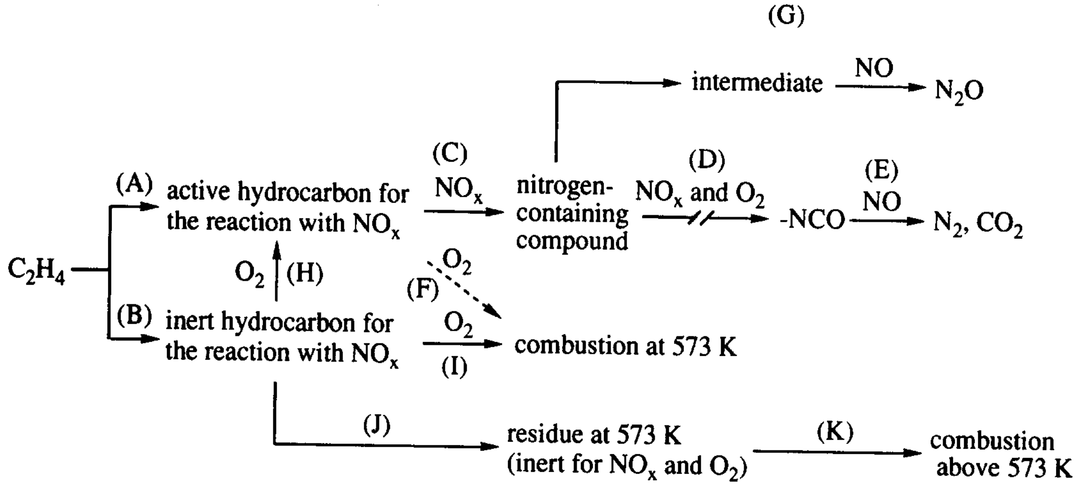
4. Discussion

The hypothetical reaction mechanism of the SCR-HC over Cu-MFI is presented first in Scheme 1 to make it easy for readers to understand the discussion. Ethene adsorbed on Cu-MFI could be classified into the two kinds of hydrocarbon species. One is active for the reaction with NO_x and another is inert (paths A and B). The active hydrocarbon species react with NO_x to yield nitrogen-containing compounds (path C), which further react with NO or O_2 to form -NCO adsorbates (path D). Finally, the -NCO species give N_2 and CO_2 by the reaction with NO (path E). When O_2 was absent, the nitrogen-containing compounds also give N_2O by the reaction with NO (path G). With O_2 in the fed gases, a part of the active hydrocarbon species is subjected to combustion (path F). When O_2 is admitted onto the inert hydrocarbon adsorbates, a part can be converted to the active species for NO_x (path H), a part is lost through combustion (path I) and the remain-

Table 3
Reactivity of various oxygen- and nitrogen-containing compounds adsorbed on Cu-MFI catalyst with the $NO+O_2$ mixture[a]

Reductant	Product distribution at $NO+O_2$ pulse (μmol g cat^{-1})				CO_2 in TPO[b]	N_2/CO_x^c
	N_2	N_2O	CO_2	CO		
C_2H_4	173	10	833	11	561	0.20
CH_3OH	7	3	210	0	0	0.03
C_2H_5OH	113	6	1142	8	143	0.10
CH_3CHO	2	1	20	0	610	0.10
CH_3COOH	86	8	890	67	243	0.09
$HO(CH_2)_2OH$	169	12	985	49	0	0.16
C_3H_7OH	98	16	707	59	0	0.13
$C_2H_5OC_2H_5$	66	4	391	8	0	0.17
CH_3NO_2	650	18	347	3	0	1.86(1.36[d])
$C_2H_5NO_2$	595	113	1003	54	0	0.56(0.31[d])
CH_3CN	442	114	884	38	0	0.46(0.23[d])
CH_3CHNOH	431	135	892	40	0	0.46(0.21[d])

[a] The amount of reductants introduced were $7.6–8.4\times10^{20}$ atom C g cat^{-1}. The other experimental conditions were the same as those in Table 2.
[b] μmol g cat^{-1}.
[c] N_2/CO_x = (the amount of N_2 formed) / (the amount of CO_x formed in the $NO+O_2$ pulse).
[d] N_2/CO_x = ((the amount of N_2 formed) − (the amount of N_2 involved in the nitrogen-containing compounds)) / (the amount of CO_x formed in the $NO+O_2$ pulse).



Scheme 1. Proposed reaction mechanism of the SCR-HC on Cu-MFI.

der is not reactive for NO_x or O_2 at 573 K (path J). The last species can be oxidized at higher temperature (path K).

As shown in Fig. 3, the N_2 formation profile in the NO pulse system was quite different from those in the NO_2 and $NO+NO_2$ systems. The results indicate the lower reactivity of NO than that of NO_2 and $NO+NO_2$. It should be noted, however, that the amount of N_2 produced in the former was the almost the same as those in the latter as shown in Table 1. It follows that the amount of active hydrocarbon species giving N_2 remains constant in the absence of O_2. The amount of N_2O generated was the greatest when NO alone was pulsed on the C_2H_4 adsorbates. This suggests that a part of nitrogen-containing compounds react with NO to form N_2O and that NO_2 or O_2 prevents the production of N_2O. It would be worthy to note that just after the 36th introduction of NO in the experiment of Fig. 2, N_2O was introduced as a pulse onto the sample but there was no formation of N_2. It is clear that N_2O is not the main intermediate to form N_2 in the SCR-HC.

The addition of O_2 onto the NO_x system significantly varied the product distribution. The amounts of N_2 in the O_2-containing system were greater than those without O_2. The order of the amount of N_2 produced was $NO + O_2 > NO + NO_2 + O_2 > NO_2 + O_2 > NO_2 \approx NO + NO_2 \approx NO$. It is noteworthy that the amount of N_2 in the $NO+O_2$ system was the largest among those in the present experiments. The observations conclude first that the reaction of the C_2H_4 adsorbates with O_2 increased the amount of active species for the N_2 formation and second that NO is directly included in the SCR-HC reaction as an active species. The first point can be supported by the results of Fig. 4. Here the introduction of O_2 onto the C_2H_4 adsorbates before the NO pulses increased the amount of N_2 formed. It follows that the reaction of C_2H_4 adsorbates with O_2 increases the amount of the active hydrocarbon species for N_2 formation. These findings indicate the presence of path H.

The CO_2 formation was observed in the TPO experiments, revealing that the inert hydrocarbon species at 573 K can react with O_2 to yield CO_2 above 573 K (path J and K). Similar results have already been reported by d'Itri and Sachtler [16]. The constant value of the reactive C_2H_4 adsorbates at 573 K independent of the amount of C_2H_4 adsorbed (Table 2) implies the possibility that specific ethene adsorbates on the copper ions might react with NO_x to form N_2. In a separate experiment the reaction of C_2H_4 adsorbates with $NO+O_2$ mixture were performed on H-MFI but there was no formation of N_2 due to the small amount of C_2H_4 adsorbed. It follows that copper ions are essential to the SCR-HC under the present experimental conditions.

The role of NO_2 is discussed here. The oxidation of NO to NO_2 is well recognized on Al_2O_3 [17], Pt/SiO_2 [18], Cu–ZrO_2 [11], H-MFI [19], Cu-MFI [5,8,10,11,20,21], Co-FER [22], Ce-MFI [6] and Ga-MFI [7] catalysts. Taking the results in Fig. 3 into consideration, it is likely that NO_2 included in the SCR-HC as an active nitrogen compound. On the other hand, the greater amount of N_2 formed in the $NO + O_2$ system than that in the $NO_2 + O_2$ system (Table 1) clearly concludes that NO directly reacts in the SCR-HC as an active species. The conclusions are consistent with the report of Chajar et al. [20] in which they claimed that NO_2, formed during the reduction of NO by propane in O_2, does not play a predominant role in the catalytic process. It was also reported by Liu and Robota [23] that NO reacts with the activated hydrocarbon species adsorbed on Cu^+.

Finally, the surface species to generate N_2 molecules would be discussed. In Fig. 2 the B_N values increased at 28th–40th pulses and then decreased at 41st–50th pulses. The behavior suggests that the nitrogen-containing compounds were accumulated on the catalyst surface and then reacted with NO to give N_2 and N_2O.

The reactivity of various compounds are summarized in Table 3. Three interesting phenomena can be pointed out. First, $C_2H_5NO_2$, CH_3CN and CH_3CHNOH gave a lot of N_2O. This probably suggests that one of the adsorbates resulting from these reductants is active for the formation of N_2O. Second, the N_2/CO_x values of oxygen-containing compounds were smaller than that of C_2H_4. This would be due to that the oxygen-containing groups are little active for the reduction of NO_x. The suggestion is supported by the results of Montreuil and Shelef [24] in which the oxygen-containing compounds were found not to be so effective reductants as propene in the SCR-HC on Cu-MFI. Third, the corrected N_2/CO_x values of CH_3CN and CH_3CHNOH were essentially the same as that of C_2H_4, while those of the nitro compounds were greater. Especially, CH_3NO_2 was very effective for the selective reduction of NO to N_2. This suggests the possibility that the nitro compounds are the active intermediates for the SCR-HC.

Many investigators have reported that the isocyanate (–NCO) species formed on the catalyst surface during the SCR-HC [12,25–29]. It was confirmed in a separate experiment that the adsorbates derived from cyanuric acid, $(HOCN)_3$, at 573 K on Cu-MFI could react with NO to give N_2 and CO_2 selectively. This suggest that the final step to form N_2 is the reaction of surface isocyanate species with NO.

5. Conclusions

The reaction mechanism of the SCR-HC on Cu-MFI catalyst at 573 K has been proposed. Ethene adsorbs on Cu-MFI in two kinds of species. One is active for the reaction with NO_x and another is inert. A part of the latter can be converted to the active species through the reaction with oxygen. The active species reacts with NO_x and O_2 to form a nitrogen-containing compound and then an isocyanate species. The –NCO species would give N_2 by the reaction with NO. NO as well as NO_2 is directly included in the selective reduction as an active species. Very recently Beutel et al. have reported the reaction of surface NO_x species with C_3H_8 to form active intermediates at 473 K [10]. The difference between their and the present conclusions would be due to the distinction of the reaction temperatures and the low adsorbability of C_3H_8.

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan.

References

[1] M. Iwamoto and N. Mizuno, J. Automobile Eng., 207 (1993) 23.

[2] S. Sato, Y. Yu-u, H. Yahiro, N. Mizuno and M. Iwamoto, Appl. Catal., 70 (1991) L1.

[3] J.L. d'Itri and W.M.H. Sachtler, Catal. Lett., 15 (1992) 289.

[4] C.J. Bennett, P.S. Bennett, S.E. Golunski, J.W. Hayes and A.P. Walker, Appl. Catal., 86 (1992) L1.
[5] J.O. Petunchi and W.K. Hall, Appl. Catal. B, 2 (1993) L17.
[6] C. Yokoyama and M. Misono, J. Catal., 150 (1994) 9.
[7] E. Kikuchi and K. Yogo, Catal. Today, 22 (1994) 73.
[8] M. Shelef, C.N. Montreuil and H.W. Jen, Catal. Lett., 26 (1994) 277.
[9] T. Tabata, H. Ohtsuka, M. Koitsu and O. Okada, Bull. Chem. Soc. Jpn., 68 (1995) 1905.
[10] T. Beutel, B.J. Adelman, G.-D. Lei and W.M.H. Sachtler, Catal. Lett., 32 (1995) 83.
[11] K.A. Bathke, C. Li, M.C. Kung, B. Yang and H.H. Kung, Catal. Lett., 31 (1995) 287.
[12] T. Inui, S. Iwamoto, S. Kojo, S. Shimizu and T. Hirabayashi, Catal. Today, 22 (1994) 41.
[13] R. Burch and S. Scire, Appl. Catal. B, 3 (1994) 295.
[14] M. Iwamoto, H. Yahiro, K. Tanda, N. Mizuno, Y. Mine and S. Kagawa, J. Phys. Chem., 95 (1991) 3727.
[15] V.R. Choudhary, S.D. Sansare, A.M. Rajput and D.B. Akolekar, Appl. Catal., 69 (1991) 187.
[16] J.L. d'Itri and W.M.H. Sachtler, Appl. Catal. B, 2 (1993) L7.
[17] H. Hamada, Y. Kintaichi, M. Sasaki and T. Ito, Appl. Catal., 75 (1991) L1.
[18] T. Tanaka, T. Okuhara and M. Misono, Appl. Catal. B, 4 (1994) L1.
[19] H. Hamada, Y. Kintaichi, M. Sasaki and T. Ito, Appl. Catal., 64 (1990) L1.
[20] Z. Chajar, M. Primet, H. Praliaud, M. Chevrier, C. Gauthier and F. Mathis, Appl. Catal. B, 4 (1994) 199.
[21] 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, 2 (1993) 81.
[22] Y. Li, T.L. Slager and J.N. Armor, J. Catal., 150 (1994) 388.
[23] D. Liu and H.J. Robota, Appl. Catal. B, 4 (1994) 155.
[24] C.N. Montreuil and M. Shelef, Appl. Catal. B, 1 (1992) L1.
[25] H. Yahiro, Y. Yu-u, H. Takeda, N. Mizuno and M. Iwamoto, Shokubai, 35 (1993) 130.
[26] Y. Ukisu and S. Sato, Appl. Catal. B, 2 (1993) 147.
[27] C. Li, K.A. Bethke, H.H. Kung and M.C. Kung, J. Chem. Soc., Chem. Commun., (1995) 813.
[28] F. Radtke, R.A. Koeppel and A. Baiker, J. Chem. Soc., Chem. Commun., (1995) 427.
[29] G.R. Bamwenda, A. Obuchi, A. Ogata and K. Mizuno, Chem. Lett., (1994) 2109.