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Selective catalytic reduction of NO by ethene in excess oxygen over platinum ion-exchanged MFI zeolites

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Abstract

Various noble metal ion-exchanged MFI zeolites have been examined as catalysts for the selective reduction of NO by ethene in the presence of excess oxygen. Of the catalysts ion-exchanged for Ru, Rh, Pd, Ir, and Pt, Pt-MFI zeolite showed the highest catalytic activity for the conversion of NO into N_2. The catalytic activity was not reduced upon the addition of 8.6 vol.-% water vapor or 300 ppm sulfur dioxide in the reactant stream. It was hardly changed during the continuous experiment of 1000 h except for the initial period of use, indicating the high durability of Pt-MFI. Temperature-programmed decomposition and dynamic XRD measurements over Pt-MFI revealed that metallic platinum particles were formed through the decomposition of tetraammineplatinum ion during the pre-treatment around 673 K in helium atmosphere. The sizes of platinum particles were confirmed by TEM to be about 3 and 13 nm and did not change after use in the catalytic run.

1. Introduction

The removal of nitrogen oxides, particularly nitrogen monoxide (NO), from exhaust is a reaction of social interest for the prevention of air pollution and acid rain. Ammonia had been thought to be the only reductant for the selective reduction of NO_x in the presence of excess oxygen before it has been reported that hydrocarbons can also reduce NO selectively under oxidizing conditions [1,2]. Since the discovery, various zeolites and oxides have been reported to be effective for the selective catalytic reduction of NO by hydrocarbons (SCR by HC). At temperatures below 573 K copper ion-and iron ion-exchanged zeolites [3,4] or supported platinum catalysts [5–8] have been shown to be active. The activities of the copper and iron catalysts are still too low to be used for the actual emissions and greatly decreased in the presence of water vapor or sulfur dioxide [9,10]. On the other hand, the Pt catalysts, Pt-MFI [5], Pt/B_2O_3–SiO_2–Al_2O_3 [6], Pt/Al_2O_3 [7,8], and Pt/SiO_2 [8] have been reported to maintain a high activity in H_2O or SO_2.

The results suggest the possibility that Pt-containing catalysts might be employed in practice; therefore, we have systematically investigated the selective reduction of NO with ethene on various noble metal ion-exchanged MFI zeolites. The effect of SO_2 and water vapor in the reactant stream on the SCR by HC has also been investigated over platinum ion-exchanged MFI zeolites in more detail. The durability of Pt-MFI was also tested in water vapor for 1000 h. In addition, the

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state of platinum introduced to MFI zeolite was clarified by temperature-programmed decomposition, dynamic X-ray diffraction (XRD), and transmittance electron micrograph (TEM) measurements.

2. Experimental

2.1. Preparation of catalyst

Parent zeolite, ZSM-5 ($SiO_2/Al_2O_3 = 23.3$, abbreviated as MFI), was supplied by Tosoh Corporation. Approximately 20 g of zeolite was washed in 2 dm^3 of dilute $NaNO_3$ solution and then ion-exchanged in 1 dm^3 of $[Ru(NH_3)_5Cl]Cl_3$, $[Rh(NH_3)_5Cl]Cl_2$, $[Pd(NH_3)_4](NO_3)_2$, $[IrCl(NH_3)_5]Cl_2$, or $[Pt(NH_3)_4](NO_3)_2$ solution with 10 mmol dm^{-3} overnight. After filtration, the resulting cake was washed and dried for 12 h at 383 K. Then, the catalyst was pressed and sieved. The resultant pellet sizes ranged between 173 and 290 μm.

The amount of noble metal ion in the zeolite was determined by ICP (SPS-1100, Seiko Instruments and Electronics). The degree of ion exchange was calculated by (oxidation number of cation) × (number of cation) / (number of Al ion in the zeolite), where the number of aluminum ions was measured by chemical analysis. The oxidation number of platinum or palladium ion was defined as 2+ and that of iridium, rhodium, or ruthenium ion was defined as 3+ on the basis of the numbers in the ammine complex salts. Hereafter the sample is abbreviated as Pt-MFI-97 (cation-zeolite structure-degree of ion exchange).

In the present experiment, we failed in the attempt to make the ion-exchange levels of zeolite samples even with each other due to the difficulty of the ion exchange of Ru and Ir. Here the study was carried out on the samples prepared under the same ion-exchange conditions.

2.2. Activity measurement

The catalytic reduction of NO was carried out with a fixed-bed flow reactor system. The reactor with a I.D. of 8.5 mm or 4.8 mm was made of quartz. Unless otherwise stated, the former was used. The reaction temperature was varied between 423 to 723 K and was controlled by using a temperature programmer with the thermocouple inserted in the catalyst bed. The reactant gas contained 1000 ppm of NO, 1000 ppm of C_2H_4 and 2% of O_2 with or without 8.6 vol.-% of water vapor or 300 ppm of sulfur dioxide. Helium was used as the balance gas. The total flow rate was 150 $cm^3\ min^{-1}$ and GHSV was 72000 h^{-1}. The reaction products were analyzed by a gas chromatograph (GC-8A, Shimadzu) with molecular sieve 5A and Porapak Q columns.

The durability of the Pt-MFI catalyst in the presence of water vapor was tested for 1000 h. The apparatus was equipped with computer-controlled automatic sampling system for G.C. The reactant gas contained 500 ppm of NO, 500 ppm of C_2H_4, 10% of O_2, 1% of CO_2, and 10 vol.-% of H_2O. The other reaction conditions are the same as the above.

The catalyst was pre-treated in helium before the reaction: the sample was heated to 773 K with a heating rate of 2 $K \cdot min^{-1}$ and maintained for 4 h at 773 K, and then cooled to the desired temperature. Sufficient time was allowed for steady state to be attained at each temperature. The conversion of NO into N_2 or N_2O was determined by 2 × (conc. of N_2 or N_2O)/(conc. of NO at the inlet) at steady state.

2.3. Characterization

Dynamic XRD measurements were performed in the essentially same apparatus as that reported previously [11]. It consisted of a powder diffractometer (MXP3, MAC Science) and a flow-through, platinum hot stage. Cu Kα radiation and a nickel filter were used. The XRD pattern during the pre-treatment of the Pt-MFI catalyst was measured under helium atmosphere with an interval of 100 K.

Temperature-programmed decomposition of the ammine complex salts during the pre-treatment of Pt-MFI was traced in the apparatus used for the above catalytic run. Instead of the gas chromatograph, a mass spectrometer (MIG-061, Anelva) was used for the analysis of the effluent gas. The peaks at *m/e* of 15, 17, 18, 28, 30, 46, and 62 were collected, each of which corresponds to the detection of NH, NH_3 or OH, H_2O, N_2, NO, NO_2, and NO_3.

The sizes of platinum particles in Pt-MFI after pre-treatment and after reaction were measured by using a transmission electron microscope (H-9000UHR, Hitachi). The radii of at least 150 platinum particles were measured to determine the particle size distribution.

3. Results and discussion

3.1. Catalytic activity of nobel metal ion-exchanged MFI zeolites

Fig. 1 shows the catalytic activities of the noble metal ion-exchanged MFI zeolites for the selective reduction of NO in the absence of water vapor. Pt-MFI-97 showed the highest conversion of NO into N_2 at a temperature as low as 485 K. Rh-MFI-17 showed the second highest conversion, but the active temperature was 673 K, much higher than that on Pt-MFI-97. A strict comparison of the catalytic activities, however, was difficult at present because of the difference of the respective ion-exchange levels. The conversion into N_2 over Pt-MFI-97 at 485 K, 19.8%, was six times greater than that on copper ion-exchanged MFI zeolite at the same temperature [1], though the latter value increased at higher temperatures. It follows that Pt-MFI-97 is much more active at low temperatures than the other metal ion-exchanged MFI zeolites.

N_2O was produced as a by-product over all the catalysts tested as shown in Fig. 1b. The active temperatures for conversion of NO into N_2O were almost the same as those for conversion into N_2. Nitrous oxide is well known as a global warming gas and a destroyer of the ozone layer; therefore, the conversion of NO to N_2O is a disadvantage of the noble metal-MFI zeolites.

The conversion of ethene reached 100% at 485, 523, 623, 673, and 723 K on Pt-MFI-97, Pd-MFI-101, Ru-MFI-23, Ir-MFI-9, and Rh-MFI-17, respectively, as shown in Fig. 1. The temperatures were in good agreement with those for the maximum conversions into N_2 and N_2O, suggesting that the catalytic activity for the oxidation of hydrocarbon is one of the important factors controlling the NO reduction. CO_2 was generally the only product from ethene over all the catalysts.

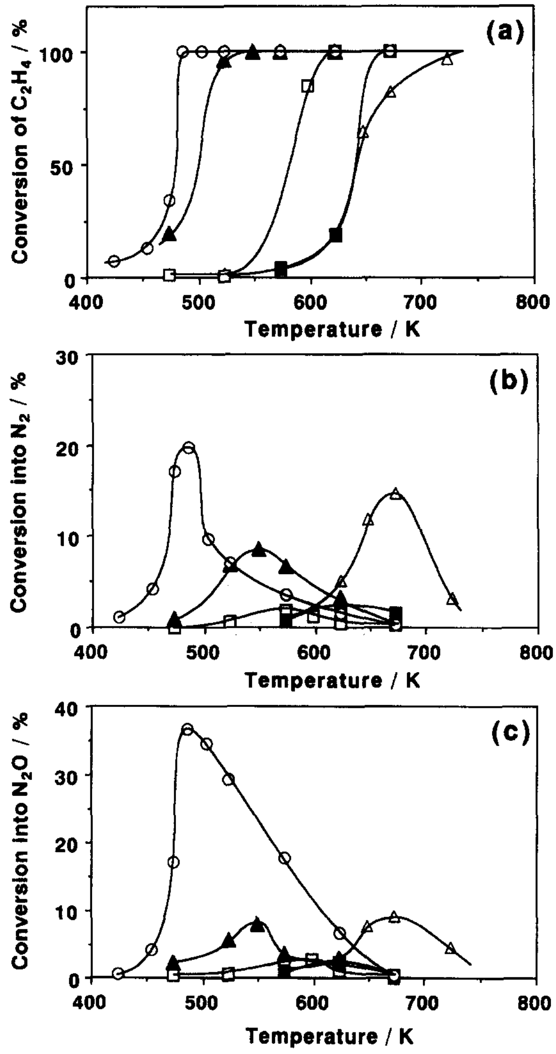

Fig. 1. Temperature dependence of the conversions of C_2H_4 (a) and of NO into N_2 (b) and N_2O (c) over noble metal ion-exchanged MFI catalysts. Symbols ○, ▲, □, ■, and △ are for Pt-MFI-97, Pd-MFI-23, Ir-MFI-9, and Rh-MFI-17, respectively. NO = 1000 ppm, C_2H_4 = 1000 ppm, O_2 = 2.0%, GHSV = 72000 h^{-1}.

3.2. Pt-MFI zeolites

The catalytic property of Pt-MFI-97 was investigated in more detail. Fig. 2 shows the effect of the addition of 8.6 vol.-% water vapor on the catalytic activity. The conversion of NO into N_2 was little changed upon the introduction of water vapor at 423–673 K. This is in contrast to the fact that the activities of Cu-MFI and Fe-mordenite were reduced nearly to 0% at 485 K on the addition of water vapor [5]. Taking the abundance of water vapor in real exhaust gas into consideration, Pt-MFI would be a promising catalyst in practice. The addition of 8.6 vol.-% water vapor affected somewhat the conversion of NO into N_2O as shown in Fig. 2b. The formation of N_2O was slightly enhanced below 485 K, while it was reduced at or above 485 K. It should be noted that the effect of water addition on the N_2O formation was different from that on the N_2 formation. The discrepancy probably suggests the difference between the pathways to give N_2 and N_2O. The change in selectivity to N_2 upon the addition of water was also reported in the selective reduction of NO by ammonia over V_2O_5/SiO_2–TiO_2 [12] and V_2O_5/TiO_2 catalyst [13].

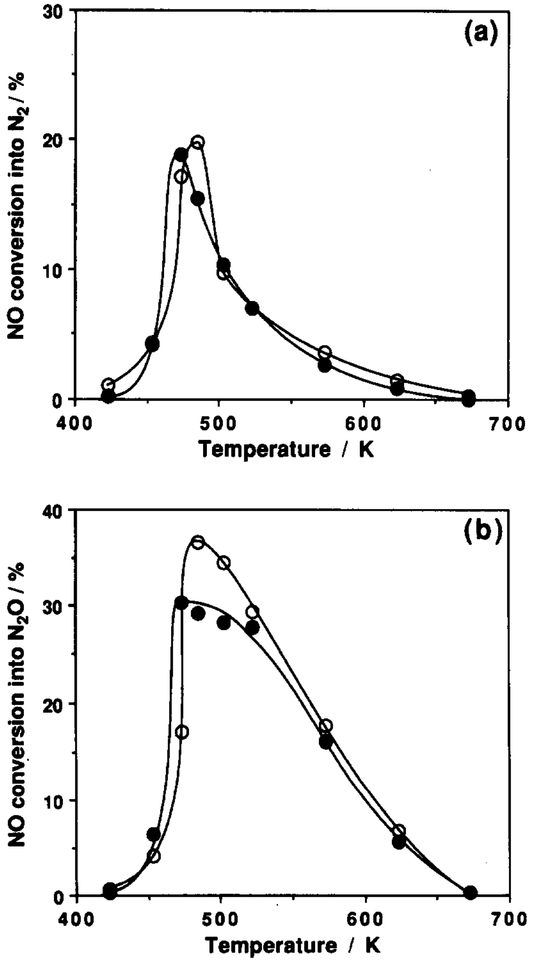

Fig. 2. Effect of sulfur dioxide on the conversions of NO into N_2 (a) and N_2O (b) over Pt-MFI-97 catalyst. NO = 1000 ppm, C_2H_4 = 1000 ppm, O_2 = 2.0%, H_2O = 0 (○) or 8.6% (●), GHSV = 72000 h^{-1}.

It is noteworthy that the oxidation of ethene was enhanced upon the addition of 8.6 vol.-% water vapor. For example, the conversion of ethane increased from 34.4% to 95.6% at 473 K. With the enhancement of ethene conversion, the temperature of maximum conversion of NO into N_2 and N_2O was lowered from 485 to 473 K. This is quite different from the reports that on Co-MFI [14] and Cu-MFI [15] the active temperatures rose upon the addition of water vapor. To clarify the reason for the phenomenon on Pt-MFI, water vapor was introduced into the steady-state reaction where the conversion of ethene to CO_2 was 100% without the addition of water. The CO_2 concentration at the outlet of the reactor steeply increased, gradually decreased, and finally reverted to the original value corresponding to 100% conversion of ethene. This clearly indicates that the water addition resulted in the removal of coke or other residue formed on the catalyst. The decrement of coke formation by the introduction of water has also been reported on Cu-MFI by Kharas et al. [16] Although the reason for the effect of water remains unclear, it is of interest to discuss the reaction mechanism and surface state during the reaction.

Fig. 3 shows the effect of sulfur dioxide on the catalytic activity of Pt-MFI-97. Upon the addition of 300 ppm of SO_2, the maximum conversion of NO into N_2 did not change but the active temperature region rose a little and significantly widened. The conversion of NO into N_2O decreased around 473 K but did not vary at or above 500 K. The temperature at which C_2H_4 conversion reached 100% slightly shifted from 485 to 498 K, which

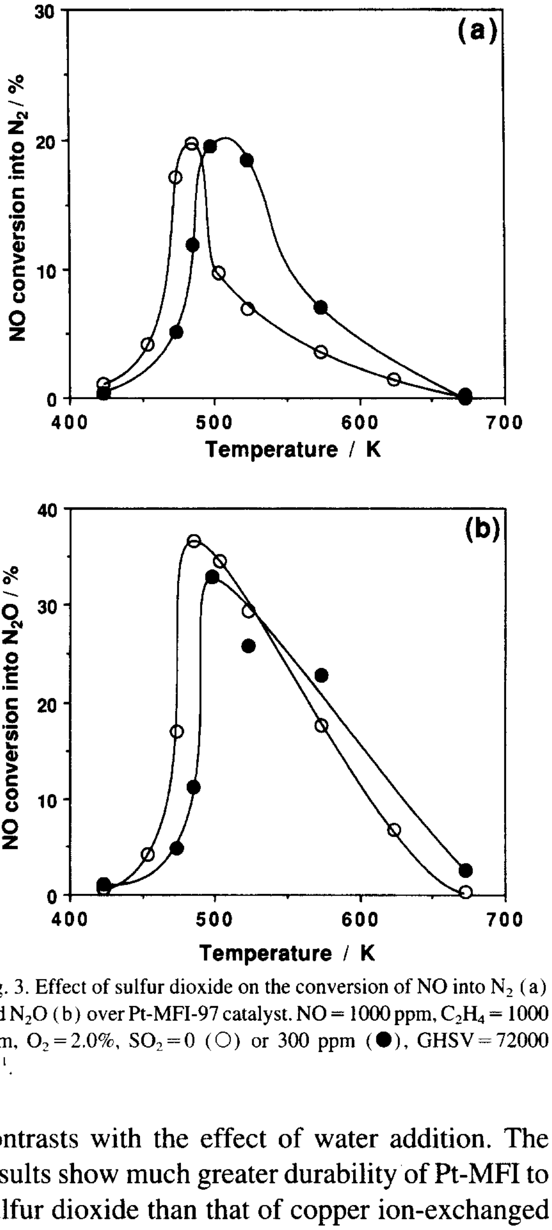

Fig. 3. Effect of sulfur dioxide on the conversion of NO into N_2 (a) and N_2O (b) over Pt-MFI-97 catalyst. NO = 1000 ppm, C_2H_4 = 1000 ppm, O_2 = 2.0%, SO_2 = 0 (○) or 300 ppm (●), GHSV = 72000 h^{-1}.

contrasts with the effect of water addition. The results show much greater durability of Pt-MFI to sulfur dioxide than that of copper ion-exchanged zeolite; for example, the conversion of NO into N_2 on Cu-MFI decreased from ca. 100% to 85% on the introduction of 300 ppm SO_2 [9,10].

The results, that is, no detrimental effect of SO_2 on the selective catalytic reduction of NO on Pt-MFI should be noted, since the detrimental effect of SO_2 has been reported on the practical three-way catalyst. The difference between the effects of SO_2 seems to be due to the reaction conditions, as mentioned bellows. Summers and Baron [17] reported that the detrimental effect of SO_2 on the activity of Pt/Al_2O_3 catalyst became less when the ratio of air to fuel increased. Beck et al. [18] claimed that in a reducing atmosphere SO_2 could dissociate into adsorbed oxygen and sulfur atoms, the latter being strongly bound to the surface to act as poison to the catalyst. In an oxidizing atmosphere, it is well known that platinum acts as a good catalyst for the oxidation of SO_2 to SO_3 [19]. On the basis of these findings it can be proposed that under the present reaction conditions the oxidation of SO_2 into SO_3 is more probable than dissociation, which is the reason why there is no detrimental effect of SO_2 on the present reduction system. Formation of new surface species [19] or retarded mobility of surface species [6] are also possible explanations for the effect of SO_2. Further studies are needed on this phenomenon.

The catalytic activity of Pt-MFI catalyst was studied as a function of the amount of Pt loaded. As shown in Fig. 4, the maximum conversion into N_2 increased with decreasing Pt and the optimum temperature shifted to a higher temperature. In contrast, the maximum conversion into N_2O decreased with the decrement of Pt. As a result, the selectivity to N_2 became higher at the lower ion-exchanged level of Pt. It follows that the activity, the selectivity, and the active temperature are dependent on the Pt content. It may be worth noting that the correlation of Pt contents with the catalytic activity is the reverse of the that reported for the NO–H_2 reaction on Pt/Al_2O_3 [20].

It should be noted that the catalytic activity of Pt-MFI also depended on the shape of the reactor. In the experiments of Fig. 1Fig. 2Fig. 3Fig. 4, a reactor with an I.D. of 8.5 mm was used. The activity increased by using a reactor with a 4.8 mm I.D; for example, the maximum activity to N_2 over Pt-MFI-7 was enhanced from 30.1% on the 8.5 mm reactor to 38.8% on the 4.8 mm reactor under the same conditions. This is due to the change of the interparticle mass transfer and/or the thickness of boundary layer on the catalyst [21]. The results suggest that the design of the reactor is very influential on the quality of the results.

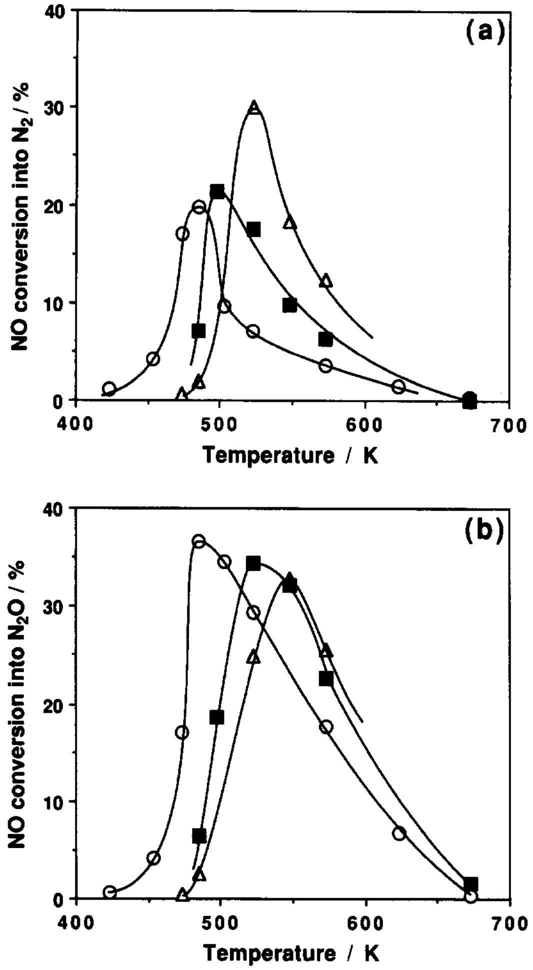

Fig. 4. Catalytic activity of Pt-MFI catalyst as a function of the ion-exchange level of platinum. Symbols △, ■, and ○ are for Pt-MFI-7, Pt-MFI-27, and Pt-MFI-97, respectively. NO = 1000 ppm, C_2H_4 = 1000 ppm, O_2 = 2.0%, GHSV = 72000 h^{-1}.

Finally the time dependence of the activity of Pt-MFI-7 was investigated. The concentrations of NO, ethene, oxygen, CO_2 and H_2O were set at 500 ppm, 500 ppm, 10%, 1% and 10%, respectively, which were similar to those in the actual diesel exhaust except that of CO_2: the concentration of CO_2 was reduced since a lot of CO_2 interfered with the analysis of N_2O by a gas choromatograph. The activity was changed during the initial period of the reaction and it took 150–200 h to reach a steady state. The conversion into N_2 was 16% initially and fell to 10% at the steady state, while that into N_2O increased from 12% to 20%. The activity was maintained more than 800 h. It follows that Pt-MFI shows good durability even in the presence of H_2O.

3.3. Characterization of Pt-MFI catalyst

The state of Pt loaded on the MFI zeolite was studied. Fig. 5 shows the change in XRD profiles during the pre-treatment. The peaks corresponding to the zeolite observed below 583 K. The treatment at elevated temperatures resulted in the appearance of two new peaks at $2\theta = 39.6°$ and 45.9°. These peaks are attributable to platinum metal [22]. The peaks began to appear at 673 K and became greater at higher temperatures and longer treating times. No peak assignable to platinum oxide appeared. Thus, it is clear that Pt^{2+} ions exchanged into MFI zeolite as $[Pt(NH_3)_4]^{2+}$ were reduced to metallic platinum atoms and the resulting metal atoms agglomerated to form large particles. On the other hand, no significant change was recognized in the peaks of the zeolite lattice, indicating that the MFI structure remained unchanged after the pre-treatment at 773 K for 4 h.

The half-height width of the XRD peaks of Pt^0 were used to determine the mean diameter of the particles. The particle size calculated by Scherrer's equation was ca. 14 nm after the pre-treatment. There was no change in the value even after

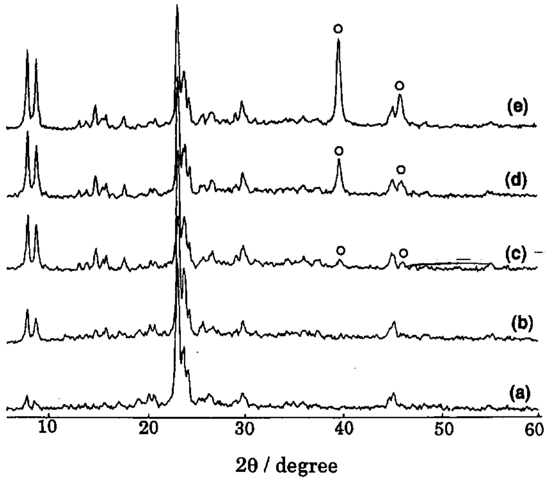

Fig. 5. Standardized XRD profiels of Pt-MFI-90 measured at 373 K (a), 583 K (b), 673 K (c), during heating and after treatment at 773 K for 1 h (d) and 4 h (e) in helium. Heating rate = 2 K min^{-1}.

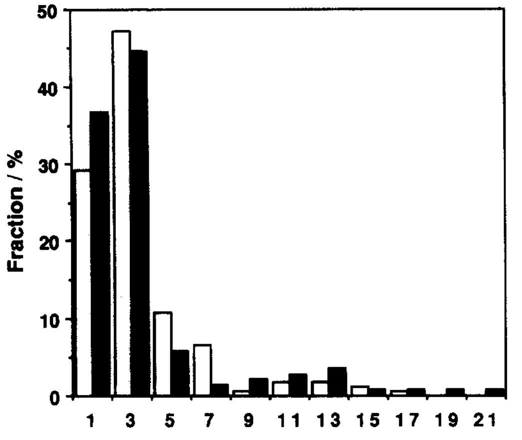

Fig. 6. Size distribution of Pt particles over Pt-MFI-97 after the pre-treatment (□) and after the SCR by HC (■).

several days' service of the catalyst for the selective reduction of NO. The formation of platinum particles was also confirmed by a transmission electron microscope. The sizes of platinum particles could be classified into two groups; one around 3 nm, and the other 13 nm, as shown in Fig. 6. No significant change in the size distribution was observed before and after the reaction, indicating little sintering during the selective catalytic reduction of NO. The sizes of platinum particles were much larger than the diameter of the channels in MFI zeolite, suggesting that the platinum particles existed outside the MFI zeolite particles.

The reduction of Pt^{2+} to Pt^0 was further verified by the mass analysis. Fig. 7 shows the mass spectra of effluent gases during the pre-treatment. Complicated desorption profiles were obtained around 400 and 670 K. Around 403 K the peaks with mass numbers of 17 (OH or NH_3) and 18 (H_2O) were observed. This indicates the desorption of water adsorbed on the zeolite surface because there was no peak of 15 (NH). At higher temperature regions (around 670 K) it is clear that ammonia (17 and 15), water (18 and 17), and molecular nitrogen (28) desorbed.

On the basis of the results of XRD, TEM, and temperature-programmed decomposition, the reduction scheme of platinum during the pre-treatment will be discussed. The evolution of NH_3 in Fig. 7 concludes the decomposition of the $[Pt(NH_3)_4]^{2+}$ complex around 653 K. The temperature of NH_3 desorption was 653 K and higher than the position of the N_2 peak by 15 K. The position of the present NH_3 peak agreed well with the desorption temperature of ammonia adsorbed on H-MFI [23]. These observations suggest that the NH_3 molecules, produced by the decomposition of the ammine complex, first adsorbed as NH_4^+ species and then desorbed as NH_3 molecules at higher temperature. Taking the report of Reagan et al. [24] into consideration, the following reaction could be suggested to proceed.

$$Pt^{2+}(NH_3)_4\text{-}Z + \text{-}Z$$

$$\rightarrow Pt^0 + 2NH_4^+\text{-}Z + \frac{1}{3}N_2 + \frac{4}{3}NH_3 \quad (1)$$

$$2NH_4^+\text{-}Z \rightarrow 2NH_3 + 2H^+\text{-}Z \quad (2)$$

$$2H^+\text{-}Z \rightarrow H_2O + V^{\cdot\cdot}\text{-}Z + \text{-}Z \quad (3)$$

Z, zeolite lattice; -Z, vacant ion-exchange site; $V^{\cdot\cdot}$-Z, lattice oxygen defect).

The temperatures of NH_3 and N_2 evolution in Fig. 7 were in good agreement with that for the formation of platinum particles in Fig. 6. It suggests that the Pt^0 atoms produced by the reaction 1 were not stable at the temperature and gathered to make metallic platinum particles.

To confirm the above reduction process the as-prepared Pt-MFI was heated at 773 K in a H_2 flow

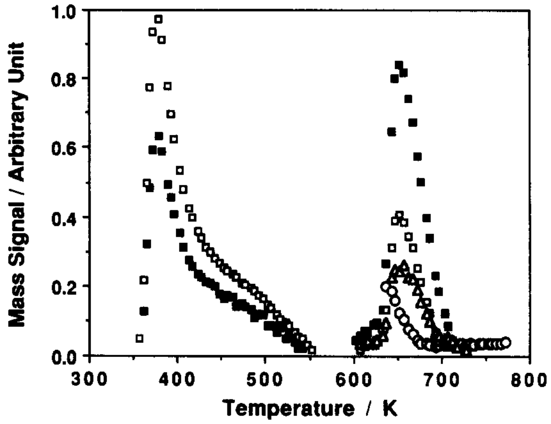

Fig. 7. Mass spectra obtained during the pre-treatment of Pt-MFI-96 under helium stream. Symbols △, ■, □, and ○ indicate the intensities of mass number of 15, 17, 18, and 28, respectively.

and then used as the catalyst. The activity was almost the same as that in Fig. 1. It follows that all Pt atoms loaded on the MFI zeolite were reduced upon the present He-pretreatment.

The decomposition temperature of tetraammineplatinum ion on MFI zeolite, ca. 653 K, is about 100 K higher than that on Y zeolite [24]. This difference results from the stability of the complexes and the resulting Pt particles in zeolites. For example, the reduction of tetraammineplatinum ion to platinum metal during the decomposition in air was reported on Y zeolite [24]. We also confirmed no formation of platinum oxide by XRD after the pre-treatment of tetraammineplatinum ion on MFI in oxygen. On the other hand, platinum oxide was observed on L-type zeolite after the pre-treatment in an oxygen stream [25].

4. Conclusions

The selective catalytic reduction of NO with ethene was investigated over noble metal ion-exchanged MFI and the followings could be clarified:

(1) Of the catalysts tested, platinum ion-exchanged MFI showed the highest catalytic activity at a temperature as low as 485 K. N_2O was formed in a considerable amount as a by-product over all the noble metal ion-exchanged MFI zeolites tested.

(2) The catalytic activity of Pt-MFI did not decrease in the presence of water vapor or SO_2 in the reactant stream. Moreover, the selectivity into N_2 was slightly enhanced by the presence of SO_2 or water vapor.

(3) The activity of Pt-MFI showed the high durability in H_2O. It took about 200 h to reach a steady state and the activity hardly changed for 1000 h.

(4) Platinum metal was formed via the decomposition of tetraammineplatinum ion. TEM revealed that the sizes of the platinum metal particles were centered on 3 and 13 nm and were not changed during the reaction.

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References

[1] M. Iwamoto, H. Hamada, Catal. Today, 10 (1991) 57. M. Iwamoto and N. Mizuno, J. Automobile Eng., 207 (1993) 23.

[2] W. Held, A. Konig, T.T. Richter and L. Puppe, SAE Paper 900496 (1990).

[3] S. Sato, H. Hirabayashi, H. Yahiro, N. Mizuno and M. Iwamoto, Catal. Lett., 12 (1992) 193.

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

[5] H. Hirabayashi, H. Yahiro, N. Mizuno and M. Iwamoto, Chem. Lett., (1992) 2235.

[6] G. Zhang, T. Yamaguchi, H. Kawakami and T. Suzuki, Appl. Catal. B: Enviromental, 1 (1992) L15.

[7] A. Obuchi, A. Ohi, M. Nakamura, A. Ogata, K. Mizuno and H. Obuchi, Appl. Catal. B: Environmental, 2 (1993) 71.

[8] H. Hamada, Y. Kintaichi, T. Yoshinari, M. Sasaki and T. Ito, Proc. National Meeting of the Catalysis Society of Japan, Niigata, Oct. 1992, 3E216.

[9] M. Iwamoto, H. Yahiro, S. Shundo, Y. Yu-u and N. Mizuno, Appl. Catal., 69 (1991) L15.

[10] M. Iwamoto, H. Yahiro, Y. Yu-u, S. Shundo and N. Mizuno, Shokubai (Catalyst), 32 (1991) 430.

[11] H. Jung and W.J. Thomson, J. Catal., 128 (1991) 218.

[12] C.U.I. Odenbrand, P.L.T. Gabrielsson, J.G.M. Brandin and L.A.H. Andersson, Appl. Catal., 78 (1991) 109.

[13] N.-Y. Topsøe, T. Slabiak, B.S. Clausen, T.Z. Srnak and J.A. Dumesic, J. Catal., 134 (1992) 742.

[14] Y. Li, P.J. Battavio and J.N. Armor, J. Catal., 142 (1993) 561.

[15] R. Gopalakrishnan, P.R. Stafford, J.E. Davidson, W.C. Hecker and H. Bartholomeaw, Appl. Catal. B: Environmental, 2 (1992) 165.

[16] K.C.C. Kharas, H.J. Robota and D.J. Liu, AIChE 1992 Annual Meeting, Nov. 1–6, 1992, Miami Beach, FL, Paper 240b.

[17] J.C. Summers and K. Baron, J. Catal., 57 (1979) 380.

[18] D.D. Beck, M.H. Krueger, D.R. Monroe, SAE Paper 910844 (1991).

[19] E. Xue, K. Seshan and J.G. van Ommen, Appl. Catal. B: Environmental, 2 (1993) 183.

[20] R. Burch, P.J. Millington and A.P. Walker, Appl. Catal. B: Environmental, 4(1994) 65.

[21] J.J. Carberry, Chemical and Catalytic Reaction Engineering, McGraw-Hill, New York, 1976.

[22] R. Jenkins, et al. (Editors), Powder Diffraction File, JCPDS International Center for Diffraction Data, Swarthmore, 1991.

[23] M. Iwamoto, M. Tajima and S. Kagawa, J. Chem. Soc. Chem. Commun., (1986) 598.

[24] W.J. Reagan, A.W. Chester and G.T. Kerr, J. Catal., 69 (1981) 89.

[25] D.J. Ostard, L. Kustov, K.R. Poeppelmeier and W.M.H. Sachtler, J. Catal., 133 (1992) 342.