Adsorption properties of oxygen and methane on Ga-ZSM-5; the origin of the selectivity of NOx reduction using methane

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The adsorption properties of oxygen and methane on Ga-ZSM-5 and Cu-ZSM-5 catalysts were examined by a TPD method to clarify the extraordinary selectivity of HC-SCR using methane on Ga-ZSM-5. It was observed that Ga-ZSM-5 did not adsorb oxygen but adsorbed methane dissociatively, while on Cu-ZSM-5 oxygen was dissociatively adsorbed and reacted with adsorbed ethylene.

Keywords: methane; ethylene; dissociative adsorption; gallium; copper; NOx; selective reduction; zeolite; ZSM-5; TPD

1. Introduction

NOx emission control is one of the most important problems for environmental protection. Recently, it has been reported that the selective catalytic reduction of NOx using hydrocarbons or alcohols (HC-SCR), instead of ammonia, occurs even in the presence of excess oxygen on metal ion-exchanged zeolite, H-form zeolite, and alumina [1–5]. Among these catalysts, Cu ion-exchanged ZSM-5 (Cu-ZSM-5) shows the highest activity using propene or ethylene as a reductant [2,3]. However, in the case of HC-SCR, reductant hydrocarbons react not only with NOx but also with oxygen. Thus, the selectivity of NOx reduction by hydrocarbon, versus hydrocarbon oxidation by oxygen, is important, as putting this reaction into practical use with less consumption of reductant hydrocarbons is economically beneficial. When the exhaust from a natural gas-fueled appliance is considered, methane is the only available hydrocarbon to reduce NOx. Unfortunately, methane is less effective and of less selectivity as compared to other alkanes and alkenes on the Cu-ZSM-5 catalyst [2]. Quite recently, HC-SCR using methane proceeds on some catalysts such as Co ion-exchanged zeolite (Co-ZSM-5) [6–8], gamma alumina [9], and Ga ion-exchanged ZSM-5 (Ga-ZSM-5) [10].

On Co-ZSM-5, the NOx reduction selectivity (defined as the molar ratio of reacted NO to consumed carbon) is about 1 or less in the presence of excess oxygen at a range of oxygen concentration of 0.5–5% at 400°C [7]. This value is similar to that of HC-SCR using propane on Ga, Al, Zn, In, or Sn ion-exchanged ZSM-5 at 300°C [11] and Ga- or H-ferrierite, below 400°C, and less than Cu-ZSM-5 [12]. However, on the Ga-ZSM-5 catalyst, the NOx reduction selectivity is about 2 using methane as a reductant even under the conditions of $O_2 = 10\%$ and $T = 500°C$, while the selectivity using higher alkane or alkene is lower [10,13]. In this study, adsorption properties of reactant gas on Ga-ZSM-5 were examined by a temperature programmed desorption (TPD) method to clarify the extraordinarily high selectivity of NOx reduction using methane.

2. Experimental

A Ga-ZSM-5 sample was prepared from the ammonium form ZSM-5 ($SiO_2/Al_2O_3 = 50$) by an ion exchange in an aqueous solution of $Ga(NO_3)_3{\cdot}9H_2O$ (ca. 0.002 M; which contained the equivalent quantity of Ga^{3+} to the ion exchange capacity) for 24 h at 80°C without pH control, followed by calcination at 500°C. The resultant Ga-ZSM-5 involved 1.20 wt% Ga (88% in ion exchange ratio). The gallium ion is theoretically small enough to be introduced into the micropore of ZSM-5, and Ga_2O_3 was not detected by XRD in the sample. Therefore, gallium is thought to be dispersed by ion exchange. Cu-ZSM-5 ($SiO_2/Al_2O_3 = 50$, 104% in ion exchange ratio) was prepared according to the method by Iwamoto et al. [14] for a reference sample.

The temperature programmed desorption (TPD) was performed in an ultra high vacuum system (base pressure was ca. 1×10^{-6} Pa). Catalyst sample powder (15 mg) was placed at the center of a quartz tube directly connected to the vacuum system. To eliminate the residual organic compounds, the sample was first oxidized by ca. 2×10^4 Pa O_2 at 500°C for 1 h, followed by evacuation at the same temperature for 1 h.

In order to confirm that no desorption species was observed without exposure of some adsorbate gas, the sample was pretreated before each experiment by evacuation at 500 or 600°C, corresponding to the final temperature of the TPD experiment to be performed. Although fresh catalyst was not utilized for each experiment, reproducibility independent of the experiment order and times was obtained by this pretreatment. After the pretreatment, the adsorbate gas was exposed typically at 1.3×10^{-4} Pa for 5 min (300 langmuir (L); $1\ L = 1.3 \times 10^{-4}$ Pa s) at room temperature. After the base pressure was decreased to a steady state level, the temperature was raised at a rate of 100 K/min by an infrared furnace and desorbed molecules were detected by a quadrupole mass spectrometer (QMS; Nichiden Anelva AQA-200). A blank test was carried out before each experiment run in order to confirm that there was no adsorbed species to be desorbed. The TPD spectra in this report are described by raw mass spectrum ion current without sensitivity correction between the different species.

The isotope exchange experiment was performed in a closed circulation system made of glass (total dead volume is 193 ml). 0.5 g of the Ga-ZSM-5 sample which had been pressed into a thick tablet and then crushed into 1–2 mm pieces, was placed in a quartz cell and pretreated in the same manner as the TPD experiment. The experiment gas initially consisted of 1.9×10^3 Pa CH_4 and 1.9×10^3 Pa CD_4 (isotopic purity $>99\%$), and the gas phase was sampled at an appropriate interval to analyze its isotopic distribution by QMS.

3. Results and discussion

Fig. 1 shows the TPD spectrum of oxygen from Cu-ZSM-5. Two adsorbate species can be easily observed below 150°C (A) and above 450°C (B). Although no desorption species were observed in the blank test after this TPD experiment, species B seems not to be completely desorbed at the end of the experiment. In fact, desorption of oxygen was observed at a higher temperature when the blank test was carried out higher than 600°C. Species B is considered to be dissociatively adsorbed oxygen, since oxygen ($M/Z = 32$) desorption at the temperature range was observed from NO exposed Cu-ZSM-5 as a product of direct decomposition of NO ($2NO \rightarrow N_2 + O_2$) and since isotopic merged species ($^{16}O^{18}O$) was observed after $^{18}O_2$ exposure. However, its desorption temperature is apparently higher than the values from other studies [15,16]. Since samples were exposed to adsorbate gas

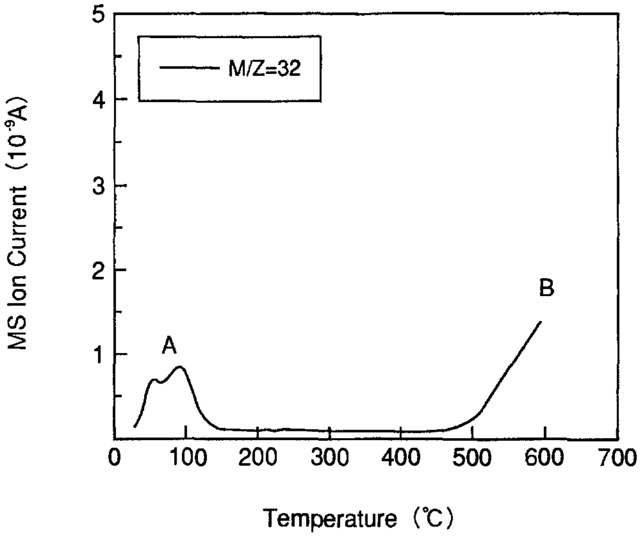

Fig. 1. TPD spectrum from oxygen exposed Cu-ZSM-5. Adsorption temperature 33°C, exposure 292 L, sample weight 10.3 mg, heating rate 100 K/min.

under quite low pressure in the experiments in this paper, coverage of adsorbate might be lower than the saturated value. Furthermore, since the heating rate was rapid, the desorption temperature was higher than in the other studies. Other TPD data in this paper are considered under the same condition.

The TPD spectra from C_2H_4 exposed Cu-ZSM-5 is described in fig. 2. The ion current at $M/Z = 28$ contains signals due to $C_2H_4^+$ and CO^+, while $M/Z = 27$ contains only $C_2H_3^+$, and $M/Z = 44$ contains only CO_2^+. Therefore, the peak A in $M/Z = 28$ is identified as the desorption of ethylene and the peak B as CO. That is, adsorbed C_2H_4 on Cu-ZSM-5 was desorbed as C_2H_4 below 300°C, but C_2H_4 was oxidized and desorbed as CO or CO_2 above 400°C. These results mean that the adsorbed C_2H_4 reacted above 400°C not with gaseous oxygen but rather dissociatively adsorbed oxygen which remained on Cu-ZSM-5 even after evacuation at 600°C. This fact corresponds to the result that ethylene works as a selective reductant of NOx effectively below 300°C but only burns at a higher temperature on Cu-ZSM-5 [2]. Hence, it is considered that the oxidation of C_2H_4 by oxygen is also catalyzed on Cu-ZSM-5 at a temperature at which dissociatively adsorbed oxygen is activated enough to attack reductants since Cu-ZSM-5 has a strong ability to adsorb oxygen dissociatively.

On the other hand, fig. 3 shows that oxygen was not adsorbed on Ga-ZSM-5 by exposure at room temperature. Desorptions of CO, CO_2 and H_2O that would have been observed if oxygen had been consumed with residual reductants were not observed except for the slight increase in $M/Z = 18$ due to unavoidable adsorption of background H_2O. Although the exposure temperature was increased up to 400°C, desorption of oxygen was not observed below 620°C. These facts indicate

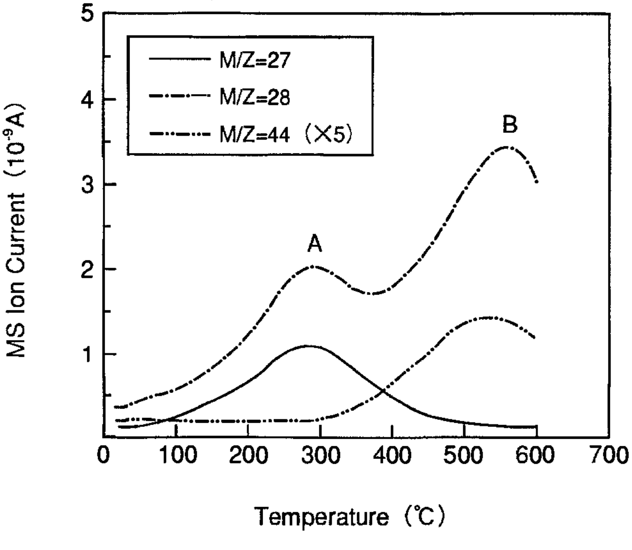

Fig. 2. TPD spectra from C_2H_4 exposed Cu-ZSM-5. Adsorption temperature 25°C, exposure 295 L, sample weight 18.7 mg, heating rate 100 K/min.

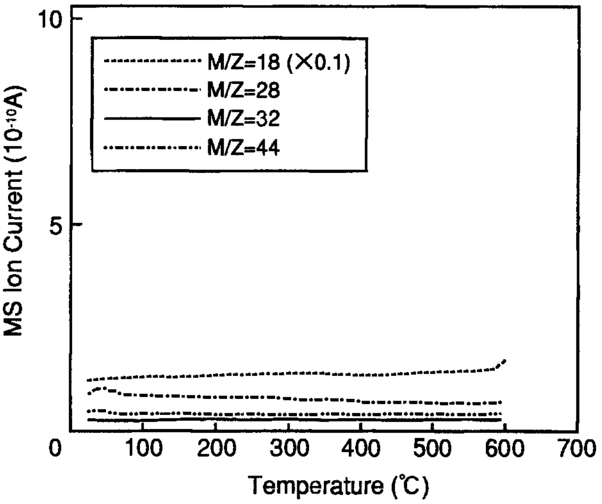

Fig. 3. TPD spectra from oxygen exposed Ga-ZSM-5. Adsorption temperature 33°C, exposure 290 L, sample weight 13.5 mg, heating rate 100 K/min.

that a reversible adsorption of oxygen does not occur on Ga-ZSM-5, at least in the temperature range at which we consider HC-SCR.

In fig. 4, the TPD spectra from CH_4 exposed Ga-ZSM-5 are described. $M/Z = 16$ involves the signal of CH_4^+ as well as O^+ due to background or desorbed H_2O, while $M/Z = 15$ involves only CH_3^+. The spectra clearly show that Ga-ZSM-5 can adsorb methane even at room temperature. Besides, desorption of CO was not observed in fig. 4, contrary to fig. 2, and the same results were obtained by the

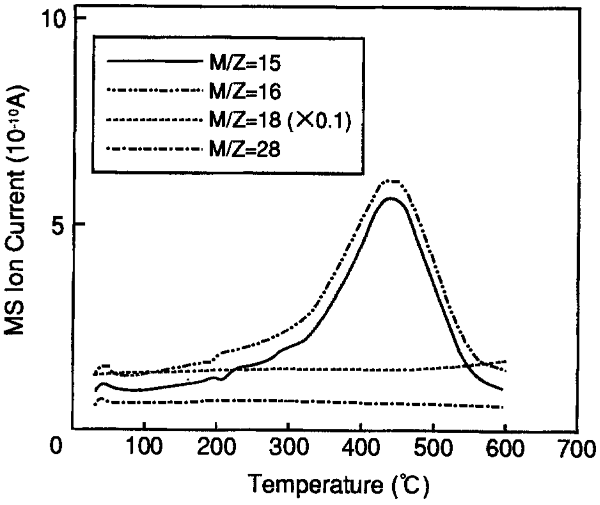

Fig. 4. TPD spectra from CH_4 exposed Ga-ZSM-5. Adsorption temperature 32°C, exposure 292 L, sample weight 13.5 mg, heating rate 100 K/min.

sequential exposure of oxygen and CH_4 and vice versa. Therefore this supports that there is not adsorbed oxygen which could attack methane on Ga-ZSM-5.

To clarify whether methane was adsorbed dissociatively, a TPD experiment using CD_4 was also carried out and the result is shown in fig. 5. Although $M/Z = 20$ is parent CD_4^+, only a small peak below 50°C was observed, which is considered physisorption or very weak chemisorption which was also observed and in the same quantity as in fig. 4. However, a clear desorption peak was observed in $M/Z = 19$ around the same temperature (ca. 430°C) as the desorption peak in fig. 4. The peak in $M/Z = 19$ is assigned to CHD_3^+ formed by the exchange reaction with H from H_2O or H_2 which may be adsorbed on Ga-ZSM-5 or exist in a gaseous background. The assignment to CHD_3^+ is because the peak shape is quite different from the $M/Z = 18$ signal which would have a signal similar to that of the $M/Z = 19$ if $M/Z = 19$ had mainly consisted of HDO^+.

However, the peak height in $M/Z = 19$ is lower than that in $M/Z = 16$ in fig. 4, especially, at a higher temperature compared to the shoulder around 250–300°C. Furthermore, the other contribution besides HO^+ (which would show the same peak shape as in $M/Z = 18$) was observed around 430°C in $M/Z = 17$, and this peak is considered to be due to CHD_2^+ or CH_3D^+. The peak temperature in $M/Z = 17$ seems to be a little higher than in $M/Z = 19$. Since the contribution of CHD_2^+ from CHD_3 molecule must show the same peak shape as in $M/Z = 19$, the contributions of CHD_2^+ from CH_2D_2 molecule and CH_3D^+ come to be observed at a higher temperature than CHD_3. Similarly, the signal in $M/Z = 16$ showed the highest peak temperature and this must be due to CH_4. For, although the signal in $M/Z = 16$ consists of O^+ (from H_2O molecule), CD_2^+ (from CD_4, CHD_3 or CH_2D_2 molecule), CH_2D^+ from CH_2D_2 or CH_3D molecule, and CH_4^+, the signal of

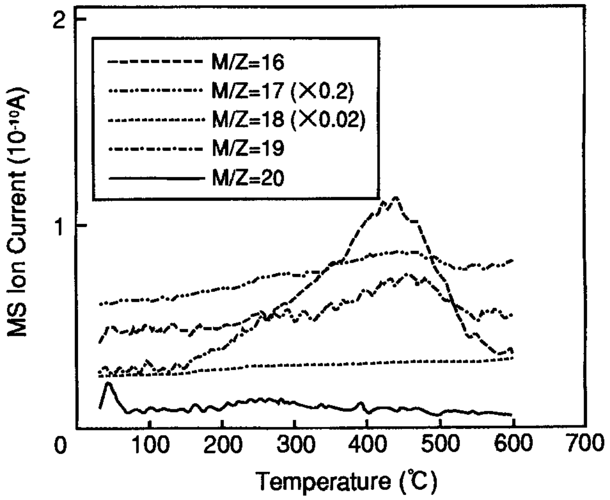

Fig. 5. TPD spectra from CD_4 exposed Ga-ZSM-5. Adsorption temperature 33°C, exposure 289 L, sample weight 13.5 mg, heating rate 100 K/min.

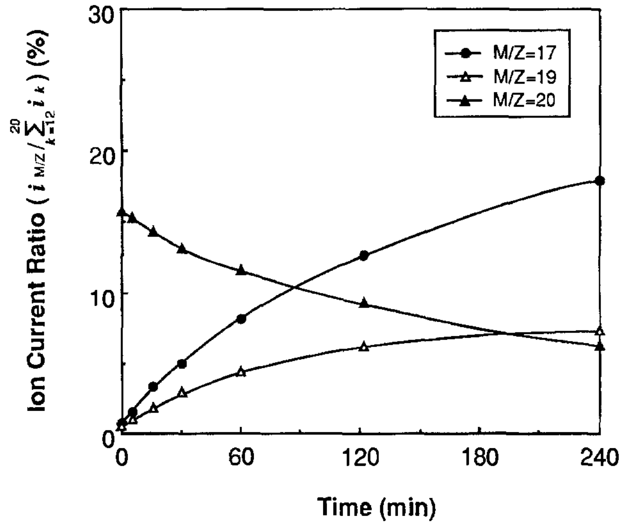

Fig. 6. Isotopic distribution change during CH_4–CD_4 exchange reaction on Ga-ZSM-5. Temperature 200°C, sample weight 0.5 g, total pressure 3.8×10^3 Pa, initial $CH_4 : CD_4 = 1 : 1.01$.

the other molecules except CH_4 contributes to $M/Z = 17$ (CH_2D_2, CH_3D, H_2O), 18 (H_2O), 19 (CHD_3), and 20 (CD_4).

From these results, the phenomenon during TPD may be explained as follows. Adsorbed CD_4 was desorbed as CD_4 below 50°C, but the exchange reaction with H occurred and was accelerated by the ascending temperature. Although CHD_3 was first formed as an isotopic exchange product, multiple exchange products such as CH_2D_2, CH_3D and CH_4 were also produced. Therefore, the desorption temperatures in TPD apparently seem to be in the order of CHD_3 ($M/Z = 19$), CH_2D_2 and CH_3D ($M/Z = 17$) followed by CH_4 ($M/Z = 16$).

An isotopic exchange reaction between CH_4–CD_4 was performed in a closed circulation system to confirm the dissociative adsorption of methane. Though the isotopic distribution was not changed at room temperature, isotopic exchange products were observed at $M/Z = 17$ and $M/Z = 19$ at 200°C as shown in fig. 6. Thus, it was clarified that methane is adsorbed on Ga-ZSM-5 dissociatively, at least at an elevated temperature, although it is still unknown as to whether methane is dissociated at room temperature.

TPD experiments using NO were also performed, but there was no drastic difference observed in NO desorption between Ga-ZSM-5 and Cu-ZSM-5. The great NO adsorption capacities of these catalysts are the common characteristics of zeolite, which has been considered to be the reason why the zeolite catalyst has high activity of HC-SCR reaction. Given the above results, it was clarified that methane is adsorbed on Ga-ZSM-5 dissociatively while oxygen cannot be adsorbed at least reversibly. This may be the reason why the HC-SCR reaction using methane proceeds with extraordinary selectivity on Ga-ZSM-5 catalyst.

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