The role of K_2O in the selective reduction of NO with NH_3 over a $V_2O_5(WO_3)/TiO_2$ commercial selective catalytic reduction catalyst

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Abstract

To elucidate the nature of the acid sites of the $V_2O_5(WO_3)/TiO_2$ catalyst upon K_2O addition and its relation to the selective reduction of NO with NH_3, measurements were made by means of infrared and Raman spectroscopy, NH_3 chemisorption, and NO reduction measurements as a function of the K_2O loading. The catalytic activity was found to decrease rapidly with the K_2O loading, irrespective of the similar textural properties of all samples. Addition of K_2O modified the vanadium species on the catalyst surface. For large additions of K_2O, the potassium partially reacted with V_2O_5 to form KVO_3. The amount of NH_3 chemisorbed on the catalyst was observed to decrease with both the loading of K_2O and the temperature. The adsorption of NH_3 on both Brønsted and Lewis acid sites was confirmed. The strength and the number of Brønsted acid sites decrease largely with the loading of K_2O in parallel with the decrease of the SCR activity, suggesting that the SCR reaction involves NH_3 adsorption on the Brønsted acid sites. At low surface coverage of NH_3, the isosteric heat of NH_3 chemisorption was determined to be 370 kJ/mol for 0 wt.% K_2O addition. With increasing K_2O amount, the heat of adsorption decreased and was 150 kJ/mol for the catalyst with higher amounts of K_2O addition. The results obtained imply that potassium disturbs the formation of the active ammonia intermediates, NH_4^+, resulting in deactivation of the catalyst. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The selective catalytic reduction (SCR) of nitric oxide (NO) with ammonia as reductant is the most successful method to eliminate NO from waste gases of stationary sources [1]. As commercial SCR catalysts for this purpose, mixed oxides of V_2O_5 and WO_3 or MoO_3 sup-

ported on TiO_2 are commonly used because of their high catalytic activity. Their thermal stability and retardation of the SO_2 oxidation [2,3] also make them suited for practical use. Besides ordinary power plants, waste incineration plants are also possible sources for nitrogen oxides emission. To establish high performance and reliability of the SCR process, especially for incineration plants, it is necessary to design a catalyst that is resistant to deactivation by poi-

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soning, because the flue gas contains several kinds of compounds with metals, e.g., alkaline metals [4,5].

The effect of alkaline metals on the performance of V_2O_5/TiO_2 catalysts has been reported by some investigators [6–10] because of its practical interest. Shikada and Fujimoto [6] and Kasaoka et al. [7] reported an effect on the catalytic activity of V_2O_5/TiO_2 by different kinds of alkaline salt. Bosch et al. [8] suggested that an alkaline metal such as lithium stabilizes the presence of tetra-valent vanadium, resulting in an increase of the NO reduction activity. For alkaline added V_2O_5/TiO_2 catalysts, a correlation between the amount of acid sites and the NO reduction activity has been suggested. Chen and Yang [9] found a correlation between the SCR activity and the Brønsted acidity for a catalyst which was poisoned by alkaline metal oxides. Lietti et al. [10] suggested that potassium decreases the amount of ammonia adsorbed on V_2O_5/TiO_2, explaining the decrease of both the number of acid sites on the catalyst and the activity of NO reduction. However, how alkaline metals interact with the SCR catalyst, especially on a commercial $V_2O_5(WO_3)/TiO_2$ catalyst, and the changes in the reaction process have not yet been clarified.

The purpose of the present study was to examine how potassium oxide affects the SCR activity of a commercial $V_2O_5(WO_3)/TiO_2$ catalyst. Therefore, we have studied such a catalyst with various K_2O loadings by means of infrared and Raman spectroscopy, adsorption of NH_3, and activity measurements. The changes in the reduction mechanism of NO with NH_3 that are caused by K_2O addition are also discussed.

2. Experimental

2.1. Catalysts

The catalysts used in this study were obtained by gently crushing and sieving a commercial honeycomb monolith into particles of 100–180 μm in diameter. The chemical composition of the catalyst was determined by a Perkin-Elmer Plasma 2000 ICP-AES according to the ASTM D3682 method. The composition of the catalyst without K_2O addition is as follows; 1 wt.% V_2O_5–8 wt.% WO_3–TiO_2 (V:W:Ti = 0.012:0.028:0.96 in atomic ratio) with silica–alumina based material as a fiber, which is approximately 10 wt.% of the total. From X-ray diffraction analysis, only the anatase structure of TiO_2 was confirmed. The peaks of crystalline V_2O_5 and WO_3 were not observed.

The catalysts added with potassium were prepared by impregnation of the sieved material with aqueous solutions of KNO_3. The impregnation was performed in small containers over night to obtain homogeneous distribution of potassium throughout the particles before drying at room temperature. Then the samples were first dried at 383 K and then calcined under a stream of dry air at 723 K for 4 h in a tubular electrical furnace to form potassium oxide.

2.2. Characterization

The textural properties of the catalyst were determined by N_2 adsorption at 77 K (Miromeritics, ASAP 2400). Before the measurements, degassing was performed at 623 K for 16 h. The obtained results were evaluated by the BET method for the total surface area, and the average pore diameter was calculated from the total surface area and the pore volume.

Raman spectra were recorded with a Bruker IFS66 FTIR spectrometer equipped with an FRA106 Raman device, with a resolution of 4 cm^{-1}. The laser power was set to 50 mW. Measurements were carried out on the particles under ambient conditions. For the measurements, samples were partially crushed.

Ammonia adsorption was examined by infrared spectroscopy (DRIFT) and volumetric chemisorption measurement. The infrared spectra were collected using a Mattson Polaris™ spectrometer with a heatable reaction cell, with a resolution of 4 cm^{-1}. The catalyst powder

was preheated in the reaction cell at 593 K for 3 h under a stream of helium before adsorption was carried out. After being cooled to room temperature, the catalyst was exposed to a gas mixture of 1% NH_3 and argon for 30 min before being purged by helium for another 30 min. All spectra were recorded at room temperature after the catalyst had been heated in the range 373–573 K under a stream of helium in the reaction cell.

The amount of adsorbed NH_3 was measured by the volumetric method (ASAP 2010C, Miromeritics). Before the measurements, the catalyst was degassed by evacuation at 723 K for 16 h in the degassing station to remove water and other contaminations on it. Then the catalyst was put into a quartz tube in the measuring station and was heated again to 723 K in vacuo for 240 min. Subsequently the catalyst was exposed to gaseous NH_3 at various temperatures ranging from 373 to 573 K for measurement of the NH_3 adsorption isotherm (first measurement). To determine the amount of chemisorbed NH_3, the catalyst was evacuated again at the same temperature for 150 min, and subsequently was exposed to gaseous NH_3 for an isothermal measurement (second measurement). The difference in the amount of NH_3 adsorbed between the first and the second measurement is the chemisorbed NH_3.

2.3. Catalytic activity measurement

Measurements of the catalytic activity were carried out at steady-state conditions in a plug-flow microreactor (5 mm in diameter). The apparatus was essentially the same as is described in literature [11]. The flows of NH_3 and O_2/NO were preheated in an electric oven and were then mixed at the reaction temperature before reaching the reactor. The concentration of reactants and products was determined by a mass spectrometer (Balzers, type QMG 311). The fragmentation patterns were determined experimentally. Argon was used as an internal standard. The operating conditions were: total flow rate (STP) 900 ml/min; catalyst weight 0.08 g; total pressure approximately 0.12 MPa; and reaction temperature 533–673 K. The inlet concentration of reactants were as follows: 600 ppm NO, 700 ppm NH_3, ∼ 3000 ppm Ar, 2% O_2, and He as balance. The pressure drop over the catalyst bed was measured by two high precision pressure meters which were connected to the reactor before and after the bed. To maintain the pressure in the reactor, the valve downstream of the apparatus was manually controlled. The conversion of NO, X_{NO}, is defined by

$$X_{NO} = \left[C_{NO}^{in} - C_{NO}^{out} \right] / C_{NO}^{in} \tag{1}$$

where C_{NO}^{in} and C_{NO}^{out} are the NO concentration in the inlet and exit streams, respectively. The formation of N_2O is less than 10 ppm up to 673 K for each catalyst tested.

3. Results and discussion

3.1. Textural properties

The textural properties of the catalysts with different K_2O contents are almost constant up to 1 wt.% K_2O addition: the specific surface area 66.4 ± 0.4 m^2/g; the total pore volume 0.289 ± 0.002 cc/g; and the average pore diameter 174 ± 2 Å. For the highest potassium loading, 2 wt.% K_2O, the surface area and the pore volume are decreased to 61.2 m^2/g and 0.275 cc/g, respectively. Average pore diameter correspondingly increases to 182 Å. It suggests that K_2O addition does not affect the pore structure of the $V_2O_5(WO_3)/TiO_2$ catalyst up to 1 wt.% K_2O addition. At higher amounts of K_2O loading, such as 2 wt.%, K_2O tends to modify the pore structure of the catalyst.

3.2. NO reduction activity

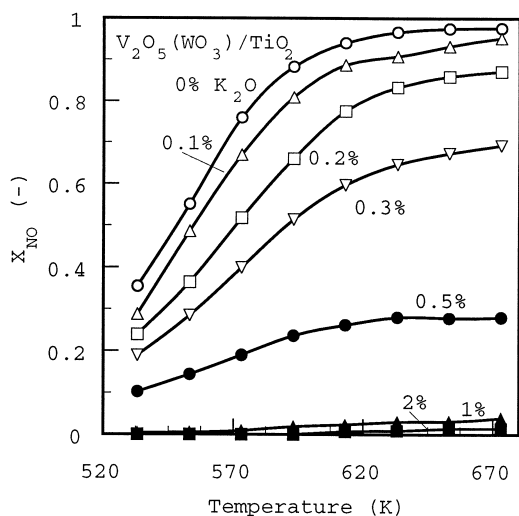Fig. 1 shows the temperature dependence of the conversion of NO for the catalysts with

Fig. 1. Temperature dependence of NO conversion, X_{NO}, for $V_2O_5(WO_3)/TiO_2$ catalysts with different K_2O contents. Experimental conditions were: total flow rate (STP) 900 ml/min (600 ppm NO, 700 ppm NH_3, ~ 3000 ppm Ar, 2% O_2, and He as balance); catalyst weight 0.08 g; and total pressure approximately 0.12 MPa.

different K_2O loadings. For the catalyst without K_2O addition, the conversion increases with increasing temperature up to 0.98 at 673 K. With increasing amount of K_2O addition, the activity rapidly decreases. For the catalyst with 2 wt.% K_2O, the activity for the NO reduction is almost zero at all temperatures. As mentioned above, since the textural properties of the catalyst are almost constant up to 1 wt.% K_2O addition, the large decrease of the activity upon potassium addition is not due to plugging by precipitated K_2O, but is due to the chemical interaction between K_2O and the V_2O_5-$(WO_3)/TiO_2$ catalyst. From the unit cell dimensions of K_2O, a value for the loading corresponding to a complete monolayer on the $V_2O_5(WO_3)/TiO_2$ catalyst can be calculated to be approximately 11 wt.%. Therefore, the preparations studied on have K_2O contents corresponding to less than a theoretical monolayer. The large effect on the activity suggests that potassium added to the catalyst preferentially coordinates to specific sites on the catalyst surface which are the most active for the SCR reaction.

3.3. Spectroscopic study of the chemical character of the catalyst

As shown in Fig. 2, the Raman spectrum of the catalyst without K_2O addition shows typical features of $V_2O_5(WO_3)/TiO_2$ catalyst with relatively high amounts of WO_3 under ambient conditions [12,13]. Two broad bands at 983 and 797 cm^{-1} have been assigned to the symmetric V=O stretching modes of two dimensional surface vanadium species and to the titanium–oxygen vibration of TiO_2, respectively. Compared to the results of V_2O_5/TiO_2 with different V_2O_5 amounts [12], hydrated decavanadate species might be predominant on the catalyst without K_2O addition under ambient conditions. The Raman band of tungsten oxide species is not observed in this study because of their lower intensity compared to that of the V = O groups [12]. For the catalysts with lower amounts of K_2O, the spectra do not show the crystalline feature of V_2O_5 and WO_3. With increasing K_2O amount, the position of the band due to V=O
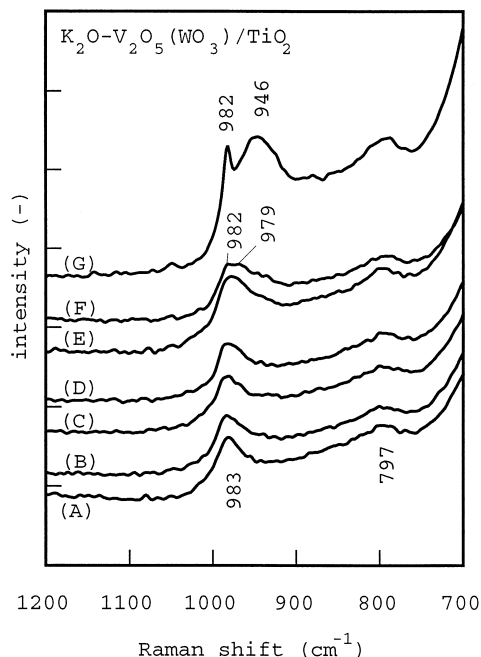

Fig. 2. Raman spectra of $V_2O_5(WO_3)/TiO_2$ with different K_2O contents under ambient conditions. (A) 0, (B) 0.1, (C) 0.2, (D) 0.3, (E) 0.5, (F) 1, and (G) 2 wt.% K_2O.

stretching slightly shifts to lower wavenumber, and possibly splits. In the spectrum of the catalyst with 1 wt.% K_2O, the band splits into two ones at 982 and 979 cm^{-1}, suggesting that K_2O modifies the structure of the surface vanadium species. For V_2O_5/TiO_2 and V_2O_5–WO_3/TiO_2 catalysts, the position of the band due to V=O stretching mode has been found to shift toward higher wavenumber with increasing amount of V_2O_5 and/or WO_3 addition [12–14]. This is due to the change in the structure of the surface vanadium species from metavanadate to decavanadate form with increasing amount of acidic V_2O_5 and WO_3 [12,14]. K_2O, on the contrary, might change the vanadium oxide species from decavanadate to metavanadate form due to its basic properties under ambient conditions. For the catalyst with 2 wt.% K_2O, an intense band appears at 946 cm^{-1} which has been assigned to potassium vanadate, KVO_3 [15]. Preferentially adsorbed K_2O reacts with surface vanadium species to form KVO_3.

From this spectroscopic study, it was shown that the addition of K_2O modifies the structure of the surface vanadium species. K_2O added to the catalyst might also react with surface vanadium oxide species to form KVO_3.

3.4. Characterization of the NH_3 adsorption behavior

3.4.1. Determination of surface acid sites

Regarding the reaction mechanism of NO reduction with NH_3, there have been several reports which suggest that the adsorption of NH_3 plays an important role. Inomata et al. [16] have suggested that NO reacted with strongly adsorbed NH_3 on dual sites, comprising a V–OH surface group and an adjacent V=O group which assists in the activation of NH_3. Gaisor et al. [17] proposed that the SCR reaction proceeds with participation of NH_3 adsorbed on the Brønsted acid site, V–OH groups. Topsøe et al. [18] also suggested that the reaction proceeds through the adsorption of NH_3 on the Brønsted acid site. However, the nature of

the sites for NH_3 adsorption has not yet been clarified. To reveal how the acid sites on the commercial catalyst are affected by K_2O addition and their relation to the NO reduction activity, it is important to examine the change in the NH_3 adsorption behavior with K_2O addition. In the present study this was achieved using infrared spectroscopy.

Typical infrared spectra in the OH region for the catalysts with different K_2O contents are shown in Fig. 3. The catalyst without K_2O addition shows bands at 3742 and 3672 cm^{-1}, which are due to hydroxyl groups on TiO_2 [19]. The band due to the V–OH groups is also confirmed at 3640 cm^{-1} [20] as a shoulder of intense band due to the Ti–OH groups. With increasing amount of K_2O addition, first, the band due to the V–OH groups decrease in intensity. The Ti–OH band also decreases in intensity upon higher amounts of K_2O addition. Upon 2 wt.% K_2O addition, the band due to the OH groups becomes broad. This implies that potassium added to the catalyst coordinates to the V–OH groups preferentially, and then coordinates to the Ti–OH groups.
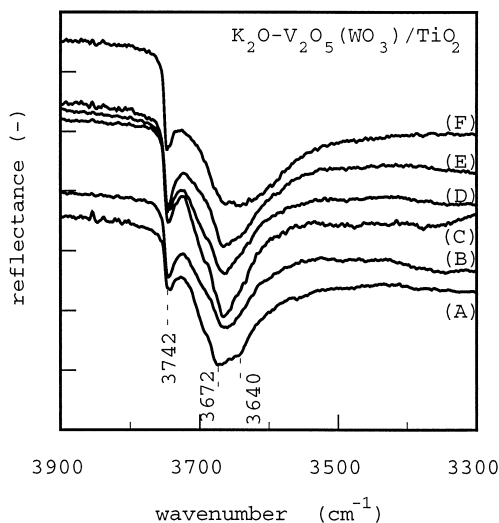

Fig. 3. Infrared spectra in the OH region of $V_2O_5(WO_3)/TiO_2$ with different K_2O contents after being heated at 593 K under a stream of helium for 3 h. (A) 0, (B) 0.2, (C) 0.3, (D) 0.5, (E) 1, and (F) 2 wt.% K_2O.

Fig. 4 shows the infrared spectra of NH_3 adsorbed on the $V_2O_5(WO_3)/TiO_2$ catalyst with different K_2O contents. After the catalysts were exposed to NH_3, bands due to adsorbed NH_3 species appear at 1610, 1417, and 1670 cm^{-1}. Similar bands have been reported previously [21–24], and they can be assigned to the asymmetric bending of coordinated NH_3, $\delta_{as}(NH_3)$, asymmetric bending vibration of NH_4^+, $\delta_{as}(NH_4^+)$, and symmetric bending of NH_4^+, $\delta_s(NH_4^+)$, respectively [21,22]. Upon NH_3 adsorption, the bands at 3258 cm^{-1} due to coordinated NH_3 and around 2800–3000 cm^{-1} due to NH_4^+ are also observed [21,22]. As to the NH_3 adsorption on WO_3/TiO_2, both ammonium ions and coordinatively adsorbed NH_3 have been observed [25]. However, it is difficult to distinguish the NH_3 species adsorbed on WO_3 from those adsorbed on V_2O_5 in a mixed oxide catalyst because of the similar position of the bands. The bands at 1417 and 1670 cm^{-1}, which correspond to $\delta_{as}(NH_4^+)$ and $\delta_s(NH_4^+)$, respectively, decrease in intensity with increasing amount of K_2O addition. Because only Lewis acid sites are confirmed on the TiO_2 surface, the decreases in intensity of $\delta_{as}(NH_4^+)$ and $\delta_s(NH_4^+)$

bands could be due to the decrease of acidity of the V–OH and/or W–OH groups. Lewis acid sites on TiO_2 can be distinguished by their peculiar splitting peaks around 1200 cm^{-1} [26]. However in this study, we could not observe these peaks because of the cut-off limit of the spectra below around 1200 cm^{-1}. For all samples, after heating under a stream of helium, the bands due to ammonium ion decrease in intensity with increasing temperature. A typical result showing this effect for $V_2O_5(WO_3)/TiO_2$ with 0.2 wt.% K_2O addition is shown in Fig. 5. The coordinatively adsorbed NH_3 with bands at 1610 and 3258 cm^{-1} is more stable at high temperature than the ammonium ion (1417, 1670, and 2800–3000 cm^{-1}).

To estimate the strength and the number of both Lewis and Brønsted acid sites, the area of the bands at 1610 and 1417 cm^{-1}, respectively, were calculated. For the calculation, the spectra which were measured after calcination at 593 K under flowing helium, for example spectrum A in Fig. 5a, were used as backgrounds. Fig. 6a and b show the calculated area due to Brønsted and Lewis acid sites as a function of activation temperature. The area representing Brønsted acid sites decreases with increasing activation temperature for all samples. The catalyst without K_2O addition shows Brønsted acidity still after being heated at 573 K. With increasing K_2O amount, the number of Brønsted acid sites readily decreases. For the sample with 2 wt.% K_2O, no Brønsted acidity is observed after activation above 373 K. This suggests that both the number and the strength of Brønsted acid sites on the V_2O_5 surface, and possibly on WO_3 as well, decrease with increasing amount of K_2O. The area representing Lewis acid sites shows no significant change with addition of K_2O. The number of Lewis acid sites decreases slightly with increasing temperature. Compared with the Brønsted acid sites, Lewis acid sites are less sensitive to heat treatment, and are not so much affected by the addition of K_2O. From the comparison of NO reduction activity with the behavior of these acid sites, it is suggested that
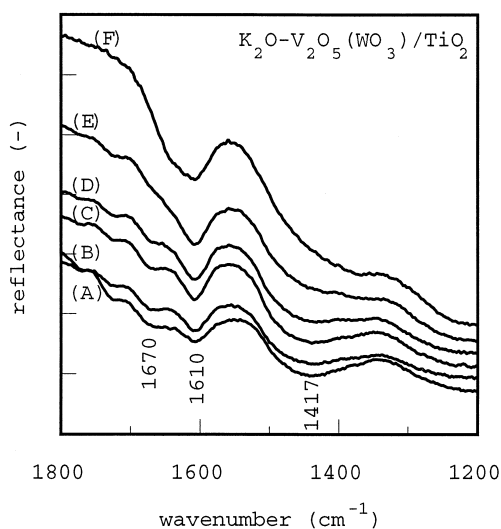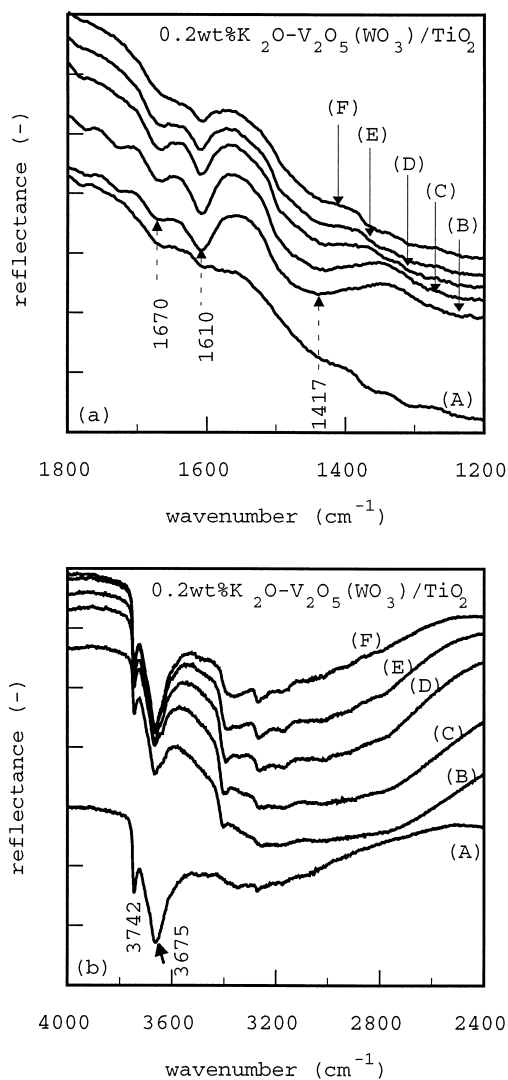

Fig. 4. Infrared spectra of NH_3 adsorption on $V_2O_5(WO_3)/TiO_2$ with different K_2O contents after exposure to gaseous NH_3 (1% NH_3–Ar) at room temperature. (A) 0, (B) 0.1, (C) 0.2, (D) 0.5, (E) 1, and (F) 2 wt.% K_2O.

Fig. 5. Infrared spectra of NH_3 adsorption on $V_2O_5(WO_3)/TiO_2$ with 0.2 wt.% K_2O. The two spectral region 1800–1200 cm^{-1} and 4000–2400 cm^{-1} are shown in (a) and (b), respectively. (A) after being heated at 593 K in He for 3 h (before NH_3 adsorption), (B) after being exposed to gaseous NH_3 for 30 min and subsequently purged by He for 30 min at room temperature, and (C–F) after being heated at (C) 373 K, (D) 473 K, (E) 523 K, and (F) 573 K under flowing He gas for 30 min at each temperature.

the partial pressure of NH_3 for the $V_2O_5(WO_3)/TiO_2$ catalysts with different K_2O contents. The amount of adsorbed NH_3 decreases with increasing amount of K_2O addition. Almost no ammonia adsorbed on the catalyst with 2 wt.% K_2O. Considering the infrared results on NH_3 adsorption on Lewis and Brønsted acid sites, the large change in the amount of adsorbed ammonia upon K_2O addition is mainly due to NH_3 adsorbed on Brønsted acid sites. Assuming a Langmuir type of adsorption, the amount of adsorbed NH_3 is given by:

$$V_{NH_3} = V_{NH_3}°K_{NH_3}P_{NH_3}\big/\left[1 + K_{NH_3}P_{NH_3}\right] \qquad (2)$$

where $V_{NH_3}°$ and K_{NH_3} are the monolayer capacity of adsorbed NH_3 and the equilibrium constant, respectively. To determine $V_{NH_3}°$ and K_{NH_3}, we fitted Eq. (2) to the observed chemisorption isotherm. The values determined for $V_{NH_3}°$ and K_{NH_3} are shown in Fig. 8a and b

the ammonium ions on Brønsted acid sites is a major intermediate for the reduction of NO.

3.4.2. Volumetric measurements of chemisorbed NH_3

Fig. 7 shows the dependence of the amount of NH_3 chemisorbed at 473 K as a function of
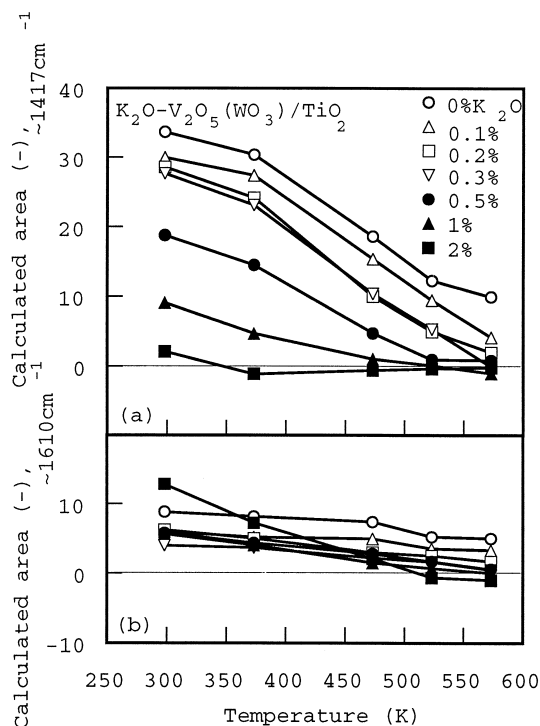

Fig. 6. The calculated area of infrared bands of adsorbed NH_3 due to (a) Brønsted acid sites (1417 cm^{-1}) and (b) Lewis acid sites (1610 cm^{-1}) as a function of the activation temperature.
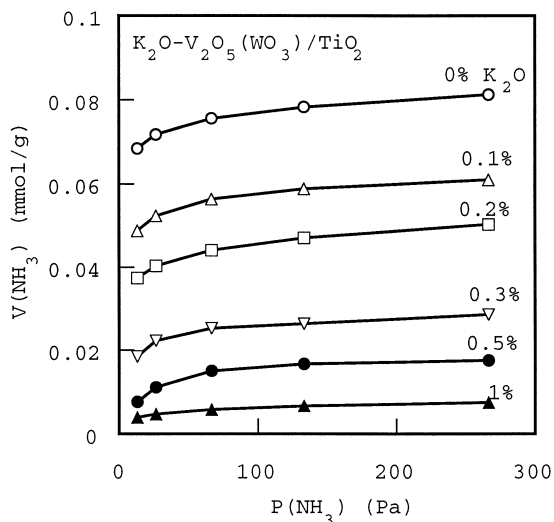
Fig. 7. Influence of the partial pressure of NH_3 on the amount chemisorbed at 473 K for $V_2O_5(WO_3)/TiO_2$ with different K_2O contents.

as a function of temperature, respectively. The monolayer capacity of NH_3, which is a measure of the number of acid sites on the surface, decreases with increasing both amount of K_2O
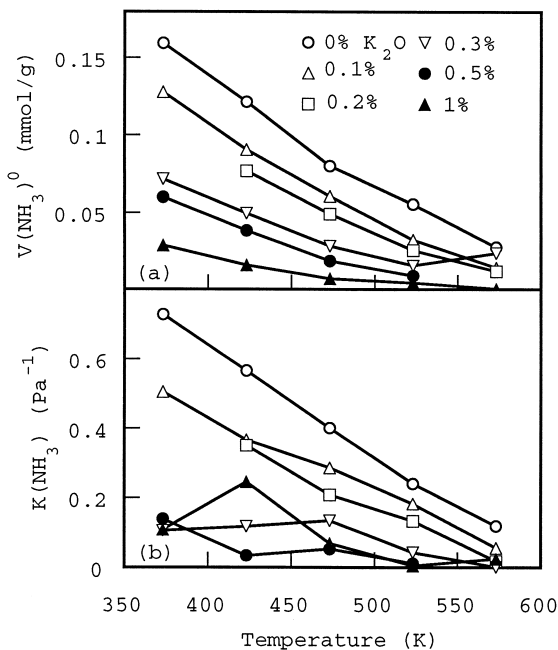

Fig. 8. Temperature dependence of (a) the monolayer capacity for NH_3 adsorption, $V_{NH_3}^{\circ}$, and (b) the adsorption constant, K_{NH_3}, for $V_2O_5(WO_3)/TiO_2$ with different K_2O contents.

content and temperature. The equilibrium constant for NH_3 adsorption also decreases with both K_2O content and temperature, suggesting that the strength of the acid sites also decreases upon K_2O addition. The results are consistent with the spectroscopic data that were presented in the previous paragraph. As the amount of chemisorbed NH_3 is determined within $\pm 5\%$, the error for the samples with high K_2O loading becomes relatively large, especially at higher temperatures. The scattering data in Fig. 8a and b are due to limitations of the experimental accuracy for the NH_3 chemisorption measurements.

To elucidate the nature of the surface acid sites, we calculated the heat of sorption of NH_3 using the relationship between amount of NH_3 adsorbed and its partial pressure. Assuming that NH_3 adsorbs on one type of site, the isosteric heat, q_{st}, is given by

$$\left(\partial \ln P_{NH_3} / \partial T \right)_{V_{NH_3}} = q_{st}/RT^2 \qquad (3)$$

where the partial derivative is determined at constant coverage of NH_3. Fig. 9 shows the dependence of q_{st} on the amount of NH_3 adsorbed on the catalyst surface. For all samples, q_{st} decreases with increasing amount of adsorbed NH_3, due to the heterogeneity of the
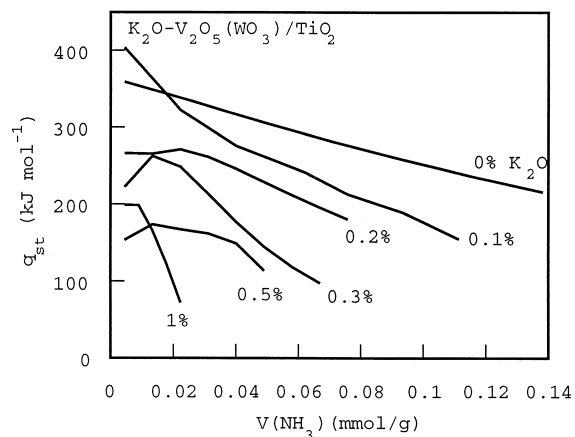

Fig. 9. Relationship between the heat of NH_3 adsorption and the amount of NH_3 chemisorbed on $V_2O_5(WO_3)/TiO_2$ with different K_2O contents.

surface acid sites. For the catalyst without K_2O addition, q_{st} decreases gradually with NH_3 adsorption, from 370 kJ/mol at low surface coverage to 250 kJ/mol at high coverage. The value of q_{st} varies with increasing amount of K_2O content from 370 to 150 kJ/mol at low surface coverage of NH_3. This suggests that K_2O added to the catalyst coordinates preferentially on the adsorption sites of V_2O_5, and probably WO_3, having the highest affinity for NH_3.

The heats of NH_3 adsorption on acid catalysts have been measured by means of calorimetry [27,28] and isothermal adsorption measurement [29]. At low NH_3 coverage, the reported differential heats of NH_3 adsorption are approximately 125 kJ/mol on silica–alumina [27], 100–130 kJ/mol on H–Y zeolite [28], and 80–160 kJ/mol on porous silica–alumina [29]. These values are significantly lower than that determined here for the $V_2O_5(WO_3)/TiO_2$ catalyst. Considering that we determined q_{st} for only the strongly adsorbed NH_3, the value may correspond only to adsorbed NH_3 which chemically interacts with the acid sites on the surface.

Assuming that NH_3 chemisorbs only on the Brønsted acid sites, the number of sites can be estimated to approximately 160 μmol/g for the catalyst without K_2O. The numbers of vanadium and tungsten atoms on the surface are approximately 130 and 300 μmol/g, respectively. This means that the number of the Brønsted acid sites, V–OH groups and probably W–OH groups, is two or three times less than total number of the surface vanadium and tungsten atoms.

With increasing amount of K_2O, both number and strength of Brønsted acid sites decrease in a similar way with the decrease of the NO reduction activity. For example, the sample with 1 wt.% K_2O, which gives almost no SCR activity, the amount of potassium atoms on the surface is approximately 210 μmol/g being enough to cover all the Brønsted acid sites. This suggests that K_2O, which preferentially adsorbed on the V–OH and/or W–OH groups, disturbs the formation of active intermediate for

the NO reduction. The excess amount of potassium on the surface might also play the role to decrease the acid strength of V–OH and W–OH groups. To form active intermediates for the NO reduction, the Brønsted acid sites with q_{st} of above 150–200 kJ/mol might be needed.

4. Conclusions

It was shown that the activity in the reduction of NO with NH_3 over a $V_2O_5(WO_3)/TiO_2$ catalyst is significantly decreased by K_2O addition. Potassium preferentially coordinates to the specific sites on the catalyst surface, namely the hydroxyl groups on V_2O_5 and probably on WO_3. The catalytic activity decreases in similar way with the decrease of both number and strength of the Brønsted acid sites. Consequently, the reaction proceeds through the participation of Brønsted acid sites and NH_3 takes part in the reaction in the form of ammonium ions.

Acknowledgements

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