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Effects of preparation methods for V_2O_5-TiO_2 aerogel catalysts on the selective catalytic reduction of NO with NH_3

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Abstract−A series of V_2O_5-TiO_2 aerogel catalysts were prepared by the sol-gel method with subsequent supercritical drying with CO_2. The main variables in the sol-gel method were the amounts of V_2O_5 and when the vanadium precursor was introduced. V_2O_5-TiO_2 xerogel and V_2O_5/TiO_2 (P-25) were also prepared for comparison. The V_2O_5-TiO_2 aerogel catalysts showed much higher surface areas and total pore volumes than V_2O_5-TiO_2 xerogel and impregnated V_2O_5/TiO_2 (P-25) catalysts. The catalysts were characterized by N_2 physisorption, X-ray diffraction (XRD), FT-Raman spectroscopy, temperature-programmed reduction with H_2 (H_2-TPR), and temperature-programmed desorption of ammonia (NH_3-TPD). The selective catalytic reduction of NOx with ammonia in the presence of excess O_2 was studied over these catalysts. Among various V_2O_5-TiO_2 catalysts, V_2O_5 supported on aerogel TiO_2 showed a wide temperature window exhibiting high NOx conversions. This superior catalytic activity is closely related to the large amounts of strong acidic sites as well as the surface vanadium species with characteristics such as easy reducibility and monomeric and polymeric vanadia surface species.

Key words: Selective Catalytic Reduction, NOx, V_2O_5-TiO_2, NH_3, Aerogel, Catalyst

INTRODUCTION

The emission of nitrogen oxides (NO, NO_2 and N_2O) produced during high temperature combustion processes, from both mobile and stationary sources, is one of the most important current environmental issues that concerns the scientific community. The main problems emerging from NOx emissions into the atmosphere are their contribution to acid rain and photochemical smog [1-3]. Selective catalytic reduction (SCR) is one of the most effective post- treatments for the abatement of NOx emission to the atmosphere. As this reaction takes place in an oxidative environment, ammonia is used as a reducing agent owing to its preferential selectivity for reacting with NO instead of oxygen. This selective catalytic reduction of NOx with ammonia is called NH_3-SCR. Among NH_3-SCR catalysts, V_2O_5 supported on TiO_2 is generally recognized as the most active and selective catalyst. Supported vanadia catalysts have been widely employed for catalyzing partial oxidation, ammoxidation, alkylation reactions, and SCR of NOx etc. [4]. Commercial supports such as alumina, silica, zirconia and titania have been commonly employed for dispersing the active vanadia species on their surface [4]. It is well-known that TiO_2 can be obtained only with a relatively low specific surface area and less thermal and mechanical resistance than other oxides, such as for example silica [4,5]. To overcome this, the sol-gel method has been proposed as an alternative to synthesize catalysts with a high surface area and stable active phase [6-8]. In this view point, aerogels which can be prepared via the sol-gel method and the subsequent removal of solvent by supercritical drying have attracted much attention as catalyst supports [6-9]. Until now, some works have been reported on applying titania-based aerogels to NH_3-SCR. Schneider et al. [10] prepared the vanadia-titania aerogels by a two-stage sol-gel process with ensuing high-temperature supercritical drying and applied them to NH_3-SCR. Engweiler and Baiker prepared vanadia supported on titania aerogel catalysts by chemical vapor deposition (CVD) or by grafting in non-aqueous solution, using vanadyl triisopropoxide as a vanadium precursor [11]. Reiche et al. prepared V_2O_5/TiO_2 using the multi-step grafting techniques from vanadyl triisopropoxide and titania aerogel synthesized by the solution sol-gel method and a subsequent low-temperature supercritical drying with CO_2 [12]. V_2O_5-TiO_2 nanoparticles using flame aerosol method were also reported to be active for SCR of NO with NH_3 [13].

The present work focuses on the preparation of V_2O_5-TiO_2 aerosol catalysts by sol-gel method with subsequent supercritical drying with CO_2. The catalytic performance of the aerosol catalysts, which were prepared by various methods, was studied for the selective catalytic reduction of NO with NH_3 in the presence of excess O_2. V_2O_5-TiO_2 xerogel and V_2O_5-impregnated TiO_2 (P-25) catalysts were also prepared to compare their catalytic activities with the aerosol catalysts.

EXPERIMENTAL

1. Catalyst Preparation

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The sol-gel process was employed to synthesize V_2O_5-TiO_2 catalysts. In the synthesis, titanium (IV) butoxide ($Ti[O(CH_2)_3CH_3]_4$, Aldrich), vanadium oxytriisopropoxide ($[(CH_3)_2CHO]_3VO$, Gelest), nitric acid, and water were mixed in ethanol and stirred until gelation occurred. The molar ratio of ethanol, water and nitric acid to the metal precursor was adjusted to be 30, 4 and 0.1, respectively. The gels were aged and supercritically dried with carbon dioxide at 333 K and 24 MPa for aerogel [denoted as V_2O_5-TiO_2 (A1)] or dried in an oven at 353 K for xerogel [denoted as V_2O_5-TiO_2 (X)]. Dried gel were thermally treated at 573 K under He for 2 h and calcined at 383 K for 1 h and 773 K for 4 h in oxygen environment. The V_2O_5-TiO_2 (A2) catalyst was prepared by dissolving titanium butoxide in a mixture of ethanol and nitric acid and then adding vanadium oxytriisopropoxide. Aerosol TiO_2 was synthesized by same method except adding to vanadium oxytriisopropoxide. The impregnated V_2O_5/TiO_2 (A3) catalyst was prepared by impregnating an aerosol TiO_2 with an appropriate amount of ammonium metavanadate aqueous solution, evaporated by rotary evaporator, then dried at 373 K overnight, calcined at 773 K for 4 h. For comparison, V_2O_5/TiO_2 (P) was prepared by a simple impregnation method from TiO_2 (P-25, Degussa) and the aqueous ammonium metavanadate solution. The mixture was then evaporated and dried at 373 K overnight, calcined at 773 K for 4 h.

2. Catalyst Characterization

X-Ray diffraction (XRD) patterns were recorded on a Rigaku D/MAC-III using Cu Kα radiation (λ=0.15406 nm), operated at 50 kV and 30 mA (1.5 kW) in a step scan mode with narrow divergence slits. BET surface areas were calculated from N_2 adsorption data that were obtained by using the Autosorb-1 apparatus (Quantachrome) at liquid N_2 temperature. Before the measurement, samples were degassed for 12 h at 323 K.

Temperature programmed desorption of NH_3 (NH_3-TPD) was performed by using a TPD apparatus (AutoChem 2705, Micromeritics). The sample was pretreated in He at 523 K for 1 h, cooled to 298 K and exposed to NH_3 until saturation. After purge at the same temperature for 1 h, the TPD measurement was carried out between 298 K and 773 K in a 30 ml/min flow of He at a heating rate of 5 K/min. The quantitative analysis of TPD patterns was done by using the PeakFit software package (SPSS, version 4.11). Temperature programmed reduction was performed with 100 mg of catalysts in a 10 vol% H_2/Ar stream from 313 K to 1,000 K at a heating rate of 5 K/min, monitoring TCD signals after samples were pretreated with He at 573 K for 1 h.

The Raman (Jobin-Yvon T64000) spectra were taken by using 50 mW of the 514.5 nm line of an Ar ion laser. The signal was dispersed by a Spex 0.6 m triple spectrometer and detected with a charge-coupled device detector.

3. Activity Measurements

Catalytic activities were measured over a fixed bed of catalysts in a tubular flow reactor (8 mm internal diameter). Reactant gases were fed to the reactor by means of an electronic mass flow controller (MKS). The total flow rate of gases was maintained at 200 ml/min at room temperature with a resulting GHSV of 50,000 h^{-1}. The reactant gas typically consisted of 500 ppm NO, 500 ppm NH_3 and 5 vol% O_2 in N_2 flow. The NOx concentration in the inlet and outlet gas was analyzed by means of a NO/NO_2 combustion gas analyzer (Euroton). The steady-state NOx conversion was measured at each reaction temperature.

Table 1. The specific surface area and the pore volume of TiO_2 supports and V_2O_5-TiO_2 catalysts

Materials	V_2O_5 (wt%)	S_{BET} (m^2/g)	V_P (cc/g)
TiO_2 (aerogel)	0	179.2	0.62
TiO_2 (P-25)	0	51.4	0.43
V_2O_5-TiO_2 (A1)	2	161.8	0.66
V_2O_5-TiO_2 (A1)	5	122.7	0.50
V_2O_5-TiO_2 (A1)	15	70.2	0.45
V_2O_5-TiO_2 (A1)	10	98.0	0.49
V_2O_5-TiO_2 (A2)	10	51.5	0.56
V_2O_5/TiO_2 (A3)	10	117.0	0.51
V_2O_5-TiO_2 (X)	10	21.6	0.07
V_2O_5/TiO_2 (P)	10	49.3	0.52

RESULTS AND DISCUSSION

The chemical composition, the specific surface area, and the pore volume of the TiO_2 support and various V_2O_5-TiO_2 catalysts are given in Table 1. The pure TiO_2 aerogel has a very high surface area that is three times larger than that of TiO_2 (P-25). After the incorporation of vanadium species, the specific surface area of V_2O_5-TiO_2 (A1), V_2O_5-TiO_2 (A2) and V_2O_5/TiO_2 (A3) catalysts decreased to 98.0, 51.5, and 117 m^2/g, respectively. These results reveal that the size of primary particles of the V_2O_5-TiO_2 (A1) and V_2O_5-TiO_2 (A2) catalysts increased due to the addition of vanadium precursor in the sol-gel solutions. In the case of the V_2O_5/TiO_2 (A3), the surface areas decreased as the result of the impregnation of the vanadium precursor. However, all V_2O_5-TiO_2 (A) catalysts show much higher surface areas and total pore volumes than V_2O_5-TiO_2(X) and V_2O_5/TiO_2 (P) catalysts.

Fig. 1 shows the catalytic activity for NH_3-SCR over V_2O_5-TiO_2 (A1) containing different amounts of V_2O_5 as a function of the reac-

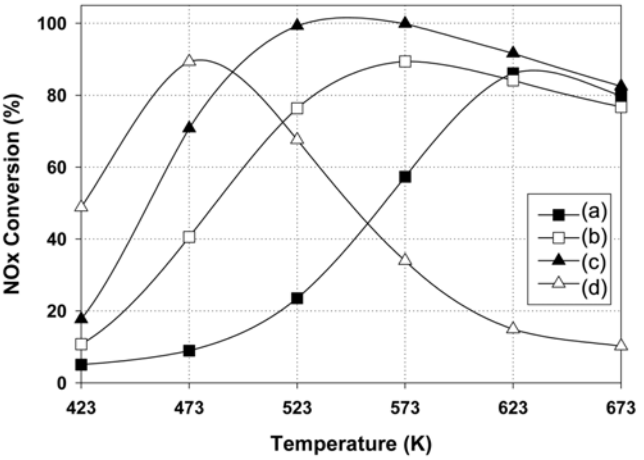

Fig. 1. The NOx conversion during the NH_3-SCR over various V_2O_5-TiO_2 (A1) catalysts containing 2 wt% (a), 5 wt% (b), 10 wt% (c), and 15 wt% (d) V_2O_5. Reactants; 500 ppm NO, 500 ppm NH_3 and 5 vol% O_2 in N_2. The gas hourly space velocity (GHSV) was 50,000 h^{-1}.

tion temperature. The reaction temperature showing the maximum NOx conversion was shifted to the lower temperature, and the NOx conversions at low reaction temperatures were continuously increased as the V_2O_5 content of the catalyst increased up to 10%. In the case of the 15 wt% V_2O_5-TiO_2 (A1) catalyst, the low-temperature NH_3-SCR activity increased further, which is in line with the general trend. However, it presents a rather narrow temperature window showing high NOx conversions, which is not desirable for the NH_3-SCR catalyst. Therefore, the optimum content of V_2O_5 was chosen as 10 wt% for further studies.

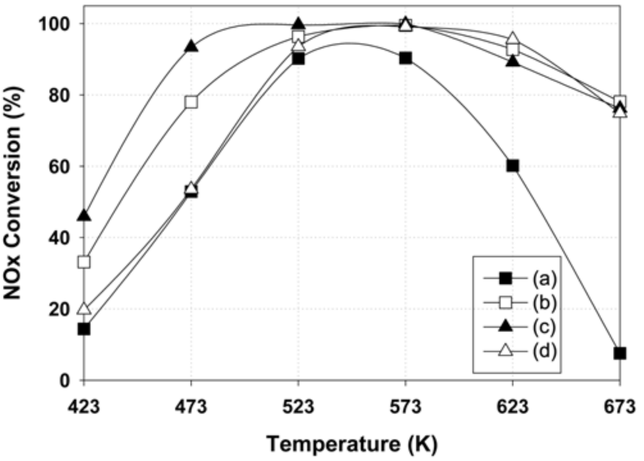

Fig. 2. The NOx conversion during the NH_3-SCR over various 10 wt% V_2O_5-TiO_2 catalysts such as V_2O_5-TiO_2 (X) (a), V_2O_5-TiO_2 (A2) (b), V_2O_5/TiO_2 (A3) (c), and V_2O_5/TiO_2 (P) (d). Reactants; 500 ppm NO, 500 ppm NH_3 and 5 vol% O_2 in N_2. The gas hourly space velocity (GHSV) was 50,000 h^{-1}.

The catalytic activity for NO reduction with NH_3 over 10 wt% V_2O_5-TiO_2 catalysts prepared via different ways is compared as shown in Fig. 2. This indicates that the catalytic activity order among catalysts at 473 K is as follows: V_2O_5/TiO_2 (A3)>V_2O_5-TiO_2 (A2)>V_2O_5-TiO_2 (A1)>V_2O_5-TiO_2 (X)≈V_2O_5/TiO_2 (P). Although both V_2O_5-TiO_2 (A2) and V_2O_5-TiO_2 (A1) were prepared by a similar sol-gel method, these catalysts show different de-NOx activities. The sequential addition of vanadium precursor after the titania gelation seems to be superior to the co-gelation of titania and vanadium precursors. The V_2O_5/TiO_2 (A3) catalyst shows the highest activity in the low temperature range of 473-573 K.

The X-ray diffraction patterns of V_2O_5-TiO_2 catalysts are illustrated in Fig. 3. As usual, both anatase and rutile phases were observed in TiO_2 (P-25). However, the anatase phase was observed as the only crystallographic phase in TiO_2 (aerogel). X-ray diffraction patterns indicate the coexistence of crystalline anatase and rutile phases in V_2O_5-TiO_2 (A1), V_2O_5-TiO_2 (A2), and V_2O_5-TiO_2 (X). This implies that the addition of the vanadium precursor during the gelation of titania promotes the formation of the rutile phase. This result

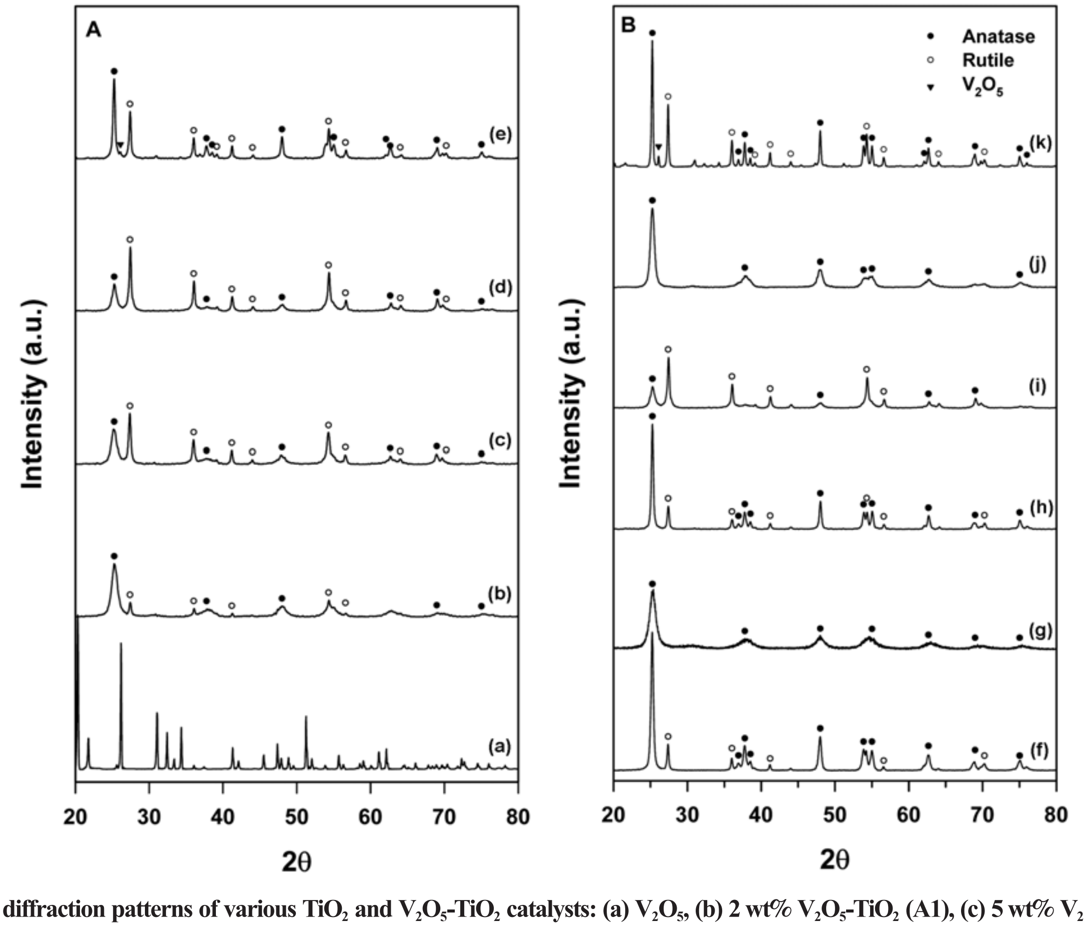

Fig. 3. X-ray diffraction patterns of various TiO_2 and V_2O_5-TiO_2 catalysts: (a) V_2O_5, (b) 2 wt% V_2O_5-TiO_2 (A1), (c) 5 wt% V_2O_5-TiO_2 (A1), (d) 10 wt% V_2O_5-TiO_2 (A1), (e) 15 wt% V_2O_5-TiO_2 (A1), (f) TiO_2 (P-25), (g) TiO_2 (aerogel), (h) 10 wt% V_2O_5-TiO_2 (X), (i) 10 wt% V_2O_5-TiO_2 (A2), (j) 10 wt% V_2O_5/TiO_2 (A3) and (k) 10 wt% V_2O_5/TiO_2 (P).

also excludes the possibility that the drying step can control the crystalline phase of TiO_2 in V_2O_5-TiO_2. The peak intensities due to anatase phase decreased and those from rutile phase decreased with increasing the content of V_2O_5 in V_2O_5-TiO_2 (A1) till 10 wt%. However, the anatase phase appeared to be dominant in 15 wt% V_2O_5-TiO_2 (A1). This implies that the crystalline phase of TiO_2 in V_2O_5-TiO_2 can be affected complicatedly by the composition of metal precursors. Naturally, V_2O_5/TiO_2 (A3) catalyst shows only the anatase phase. In the case of V_2O_5-TiO_2 (A1), no noticeable characteristic peak related to the crystalline V_2O_5 phase can be found until the content of V_2O_5 in V_2O_5-TiO_2 (A1) reaches 10 wt%. A weak peak, which is characteristic of the V_2O_5 phase, can be observed in 15 wt% V_2O_5-TiO_2 (A1). No characteristic peak representing the V_2O_5 phase can be observed in 10 wt% V_2O_5-TiO_2 catalysts except 10 wt% V_2O_5/TiO_2 (P). This result supports that a high dispersion of VOx can be achieved via sol-gel method irrespective of the drying methods. Unfortunately, it is impossible to explain the different NH_3-SCR activity among various 10 wt% V_2O_5-TiO_2 catalysts based on the XRD analysis.

It has been reported that vanadia species can be present on a support as different forms such as isolate vanadyl centers, polymeric polyvanadate species, and crystalline V_2O_5. The former two kinds of vanadium species, which cannot be observed with an XRD analysis, can be identified by Raman spectroscopy as shown in Fig. 4. The three peaks at 920, 995, and 1,030 cm^{-1} may originate from polyvanadate, bulk vanadia, and monovanadate, respectively [13]. These three characteristic peaks were observed in the V_2O_5-TiO_2 (A1) and V_2O_5-TiO_2 (A2) catalysts. In the case of V_2O_5/TiO_2 (A3), monovanadate and polyvanadate species can be found and no peak representing bulk vanadia can be observed. However, V_2O_5/TiO_2 (P) catalyst is determined to have only bulk vanadia, which is known to mainly contribute to the oxidation of NH_3 at high temperature [14]. Based on Raman spectroscopy as well as XRD, it can be concluded that the aerogel catalysts have uniform distribution of vanadia clusters in the titania matrix.

The redox property of surface vanadium species was examined with a TPR technique as shown in Fig. 5. The temperature showing the maximum peak in the TPR pattern increase in the following order: V_2O_5/TiO_2 (A3)<V_2O_5-TiO_2 (A2)<V_2O_5-TiO_2 (A1)<V_2O_5/TiO_2 (P). This is in line with the NH_3-SCR activity at low temperatures. Therefore, it can be concluded that the most active catalyst has the easily reducible vanadium species.

The amounts of surface acid sites and the acid strength for various V_2O_5-TiO_2 catalysts were examined with NH_3-TPD method as illustrated in Fig. 6. The broad peak centered at about 400 K may be originating from the physisorbed NH_3, while the rather broad peaks above 450 K is attributed to desorption of the strongly adsorbed ammonia. It is generally accepted that the acidity strength

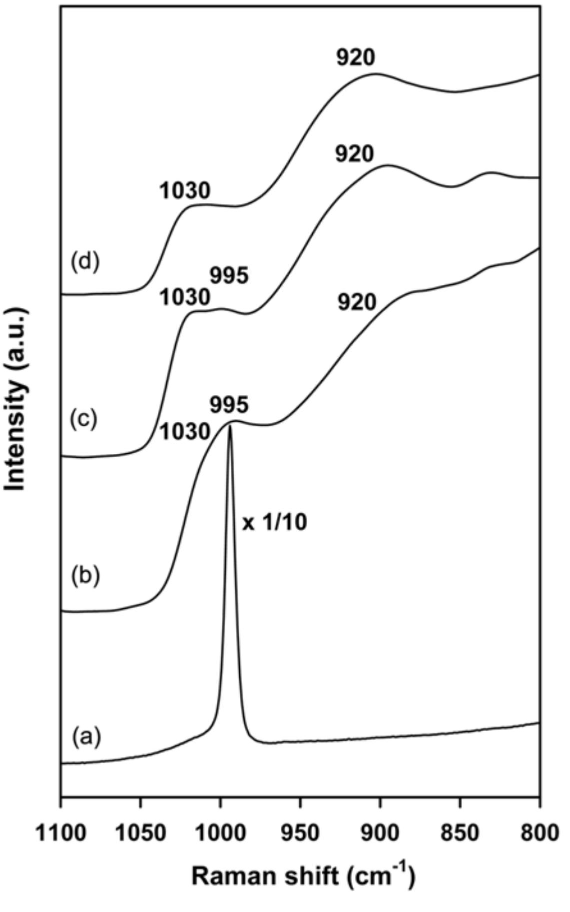

Fig. 4. Raman spectra of various 10 wt% V_2O_5-TiO_2 catalysts: (a) V_2O_5/TiO_2 (P), (b) V_2O_5-TiO_2 (A1), (c) V_2O_5-TiO_2 (A2) and (d) V_2O_5/TiO_2 (A3).

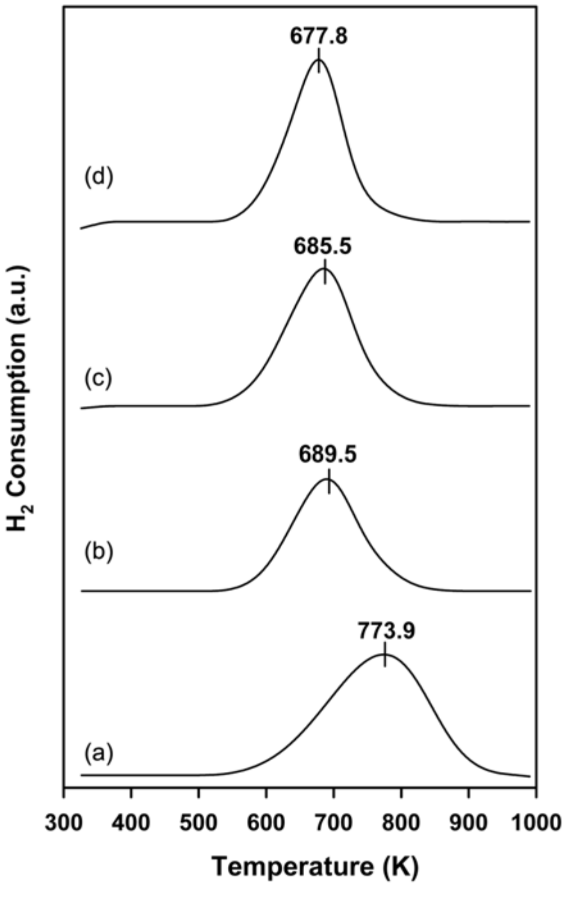

Fig. 5. TPR patterns of various 10 wt% V_2O_5-TiO_2 catalysts: (a) V_2O_5/TiO_2 (P), (b) V_2O_5-TiO_2 (A1), (c) V_2O_5-TiO_2 (A2) and (d) V_2O_5/TiO_2 (A3).

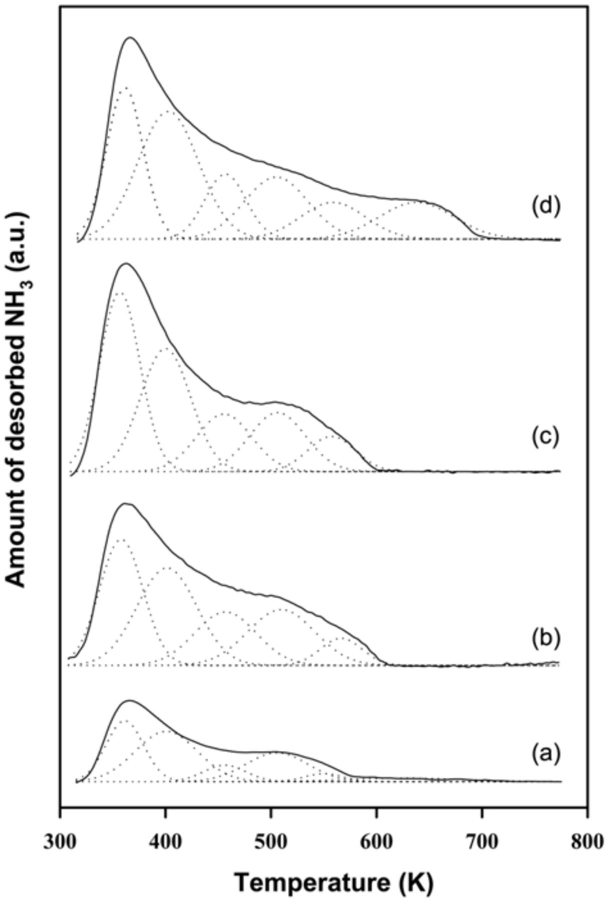

Fig. 6. NH_3-TPD profiles of various 10 wt% V_2O_5-TiO_2 catalysts: (a) V_2O_5/TiO_2 (P), (b) V_2O_5-TiO_2 (A1), (c) V_2O_5-TiO_2 (A2) and (d) V_2O_5/TiO_2 (A3).

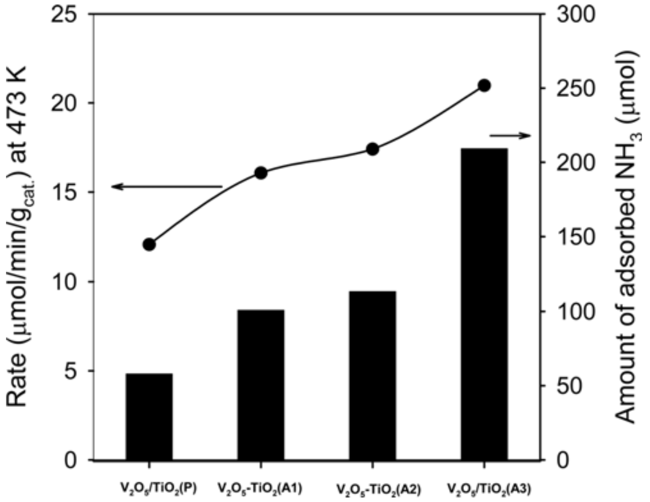

Fig. 7. The relationship between the NH_3-SCR activity at 473 K and the number of strong acid sites.

of the catalyst surface increases with the desorption temperature of chemisorbed NH_3. Therefore, V_2O_5/TiO_2 (A3) seems to have the strongest surface acidity among the examined catalysts. For quantitative analysis, all the TPD peaks that can be discerned by computer software have been integrated to evaluate their individual amounts. The numerical values obtained from the integrated areas are given in Table 2. The total amount of adsorbed NH_3 was proportional to the surface area determined with BET method. Compared with the catalytic activity, it was found that a close correlation existed between the amount of strong acid sites and the NH_3-SCR activity. This close correlation between the low-temperature NH_3-SCR activity and the amounts of strong acid sites which can be calculated from peaks 4,

Table 2. Results of NH_3-TPD analysis of various V_2O_5-TiO_2 catalysts determined in the temperature range from 300 to 800 K

Catalysts	Peak 1		Peak 2		Peak 3		Peak 4		Peak 5		Peak 6		Total NH_3 (μmol)
	Temp. (K)	NH_3 (μmol)	Temp. (K)	NH_3 (μmol)	Temp. (K)	NH_3 (μmol)	Temp. (K)	NH_3 (μmol)	Temp. (K)	NH_3 (μmol)	Temp. (K)	NH_3 (μmol)	
V_2O_5/TiO_2(P)	362	53	401	73	456	15	506	40.3	550	8	627	10	199
V_2O_5-TiO_2(A1)	358	126	401	86	457	136	510	75.6	567	25	-	-	449
V_2O_5-TiO_2(A2)	357	169	400	144	455	73	506	75.6	557	38	-	-	499
V_2O_5/TiO_2(A3)	362	129	403	179	457	63	505	90.7	559	55	638	63	580

Table 3. Performance of various V_2O_5/TiO_2 based catalysts for SCR of NO with NH_3

Catalysts	V_2O_5 (wt%)	S_{BET} (m^2/g)	Feed composition			TOF × 10^4 at 423 K (mol NO/molV/s)	Reference
			NO (ppm)	NH_3 (ppm)	O_2 (%)		
V_2O_5-TiO_2 (A1)	10.0	98.0	500	500	5.0	0.60	In this work
V_2O_5-TiO_2 (A2)	10.0	51.5	500	500	5.0	1.20	In this work
V_2O_5/TiO_2 (A3)	10.0	117.0	500	500	5.0	1.70	In this work
V_2O_5/ TiO_2 (P)	10.0	49.3	500	500	5.0	0.70	In this work
V10 (V_2O_5/TiO_2)	10.0	183.0	900	900	1.8	0.70	[10]
90v17	12.2	87.0	900	900	1.8	1.64	[11]
190v4.5	7.7	197.0	900	900	1.8	0.52	[11]
TiV9	9.0	144.0	900	900	1.8	0.44	[12]

5, and 6 in Table 2 can be displayed as shown in Fig. 7. The activity comparison between the V_2O_5-TiO_2 catalysts examined in this work and those previously reported was made in Table 3. The most active catalyst, V_2O_5/TiO_2 (A3), prepared with a simple impregnation method from ammonium metavanadate and TiO_2 aerogel shows comparable activity with those prepared with a chemical vapor deposition method or the grafting method from vanadyl triisopropoxide and TiO_2 aerogel. The utilization of TiO_2 aerogel with a high surface area as a support does not seem to require special methods such as the grafting method to prepare the highly active V_2O_5/TiO_2 catalyst.

CONCLUSIONS

The selective catalytic reduction of NOx with ammonia in the presence of excess O_2 was investigated over various V_2O_5-TiO_2 aerogel catalysts prepared in different ways. The V_2O_5/TiO_2 (A3) catalyst prepared with an impregnation method from TiO_2 aerogel showed the highest NH_3-SCR activity at low temperatures. This catalyst also showed a wide temperature window exhibiting high NOx conversions. This superior catalytic activity is closely related to the large amounts of strong acidic sites as well as the surface vanadium species with characteristics such as easily reducible property and monomeric and polymeric vanadia surface species.

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