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Surface acidity over vanadia/titania catalyst in the selective catalytic reduction for NO removal—in situ DRIFTS study

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Abstract

An in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) study of the selective catalytic reduction (SCR) of NO with NH_3 in the presence of O_2 was carried out over vanadia-based catalysts. Vanadia-based catalysts were prepared by impregnation method. The results indicated that the strength of Bronsted acidity positively increased with V_2O_5 loading, whereas Lewis acidity remained almost constant at a typical SCR operating temperature. Water vapor does not affect the adsorption of Lewis ammonia, but the formation of Bronsted acidity has to be accompanied by water vapor adsorption. Bronsted acidity is decreased with increasing temperature and disappeared at a temperature of around 500 °C for all testing catalysts, while Lewis acidity slightly decreased with increasing temperature. The disappearance of Bronsted acidity at a high temperature was related to the loss of adsorbed water vapor.

Keywords: Vanadia; Lewis acid; Bronsted acid; SCR; DRIFTS; FTIR

1. Introduction

Technology for the selective catalytic reduction (SCR) of nitric oxide (NO) by ammonia injection has been widely used to control NO_x emissions from stationary sources. Vanadium (V)/titanium (Ti)-based catalysts are the most active and commercially favored catalysts in field applications. In recent years, many in situ IR spectroscopy studies of the SCR reaction over vanadia (V_2O_5)-based catalysts have been carried out [1–15]. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) is one of the most frequently used and powerful tools of obtaining information concerning reactions at the surface of catalyst. These studies seem to agree on the reaction pathway on the vanadia-based catalyst. The SCR reaction is considered to involve the formation of adsorbed ammonia species on dual vanadium sites (V=O, V–OH or both) followed by reacting with gaseous or weakly adsorbed NO, according to an Eley–Rideal mechanism, as firstly proposed by Inomata et al. [16].

Relationships between catalytic activity and surface acidity have also been proposed [5,7,8,10,11,14]. Almost all authors agree that SCR activity is positively related to the surface acidity of catalysts. However, Busca et al. [17] indicated that the debate is still open concerning the nature of the active sites and of the active ammonia species. Topsoe and co-workers

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[4,7] proposed the adsorption of NH_3 onto Bronsted acid site as protonated ammonium (NH_4^+) ion dominated the SCR deNO$_x$ reaction. And it was confirmed by the IR studies of Schneider et al. [5], Centeno et al. [10], Amirids et al. [11] and Kamata et al. [14] that NH_4^+ ion species were evident and active on vanadia-based catalysts. Schneider et al. [5] prepared V-Ti catalysts that contained 5, 10, and 20% vanadia loadings. Distinct adsorption of NH_4^+ at Bronsted sites was observed on 10 and 20% V_2O_5 catalyst, but not clear on 5% V_2O_5 catalyst. The SCR activity increased with V_2O_5 loading at 200 °C and was proportional to the strength of the Bronsted-bound NH_4^+.

However, these results were different from the view of Belokopytov et al. [1] and Ramis and co-workers [2,3,8,9]. Ramis and co-workers prepared V-Ti catalysts that contained 1–5% vanadium loadings, and found that the amide adsorbed due to coordinated ammonia was much obvious and thermally stable than ammonium ions between room temperature and 350 °C. Ramis and co-workers [3,8,9] proposed that the SCR reaction was engaged by ammonia adsorbed onto Lewis acid sites as coordinated ammonia over vanadia-based catalysts, but not ammonium ions bonded to Bronsted acid centers, while Lewis acidity and Bronsted acidity both occurred on vanadia-based catalysts.

The effect of water on the SCR reaction is also an interesting topic. According to the results of Chen and Yang [18], water accelerates the formation of Bronsted acidity and enhances the SCR reaction on vanadia-based catalyst. In contrast, Turco et al. [19] reported that water inhibited the SCR reaction due to a competition with ammonia on the Lewis sites. However, no corresponding IR spectra were found in their study.

The debate about the active sites in the SCR reaction may be continuing because of the different V_2O_5 loadings, moisture content and working temperature used by researchers. However, complete IR spectra of ammonia adsorption on variously V_2O_5-loaded V-Ti catalysts, and information on the effect of water vapor and working temperature in the SCR reaction are yet to be provided. This study systematically investigates the influence of V_2O_5 loading, moisture content and working temperature on the development of surface acidity on V-Ti catalysts by in situ FTIR.

2. Experimental

2.1. Preparation and physicochemical analysis of the catalysts

Impregnation method was used to prepare vanadia-based catalysts. Pure TiO_2 powder (99.9% anatase, 17.35 m^2/g BET surface area) was impregnated with stoichiometric NH_4VO_3 dissolved in oxalic acid. The product was dried at 120 °C for 24 h and calcined at 550 °C for 4 h.

The surface areas of the catalysts were measured by nitrogen adsorption at 77 K using a surface area analyzer (Micromeritics, ASAP 2000), according to the Brunauer–Emmett–Teller (BET) equation. The surface chemical elemental analysis was conducted using a scanning electron microscope (SEM, HITACHI S-4700) coupled with an energy dispersive X-ray analyzer (EDX). X-ray powder diffraction analyses were conducted using a diffractometer (Shimadzu XD-5) and Cu Kα radiation as an X-ray source. The chemical state of vanadium atom was identified by X-ray photoelectron spectroscopy (Physical Electronics, ESCA PHI1600), coupled with a spherical capacitor analyzer and Mg Kα as the radiation source.

Table 1 lists the physical and chemical properties of catalysts prepared in this study. One can see that catalysts prepared by the impregnation method have almost the same BET surface area of 10–11 m^2/g, slightly less than that of pure TiO_2. This was caused by the deposition of V_xO_y on the surface of TiO_2. The XRD analysis indicated that TiO_2 in catalyst powder was in the form of anatase TiO_2, and no rutile crystallization was detected. However, the vanadium oxide content was limited and XRD cannot detect catalysts

Table 1
Physical and chemical properties of catalysts used in this study

Catalyst	V:Ti[a]	Calculated V_2O_5 weight fraction (%)	BET surface area (m^2/g)
Pure TiO_2	0:100	0	12.7
1%	1:99	1.1	11.2
2%	1.1:98.8	1.26	10.8
5%	2.8:97.2	3.2	10.7
10%	8.9:91	11.1	10
20%	15.8:84.2	21.3	10.7

[a] Surface atomic fraction (%) by SEM/EDS analysis.

with a low vanadium oxide content (such as 1 or 2%). According to the identification of XPS experiments, almost all vanadium was in the +5 oxidation state. Therefore, vanadium oxide was existed primarily as the form of V_2O_5 on the surface of the catalyst.

2.2. DRIFTS experiments

NO and NH_3 were supplied from cylinders at concentrations of 1% in N_2. Clean air with a relative humidity of 35% was obtained by passing compressed air through a silica gel air dryer and a Gelman-TDC filtration system. The clean air and N_2 were used to for dilution and controlled by mass flow controllers (MKS, Andover, MA). The concentrations of NO gas were measured by a NO_x–SO_x analyzer (SIEMENS ULTRAMAT 23, Nuremberg, Germany). The moisture content was controlled by passing carrier gases through an impinger at different flow rates. The impinger was kept in a water (or ice) bath.

DRIFTS spectra were obtained using a temperature-controlled DRIFTS chamber (Spectra-Tech 0030-01) with ZnSe windows coupled to a Bruker Vector 22 infrared spectrometer with KBr optics and a DTGS detector. The samples were ground into powder and placed on a disk inside the chamber without packing or dilution. The original reflectance IR intensity from the sample was controlled under a baseline with a variation of around 10%. Before the SCR reaction proceeded, the samples were activated in flowing clean air at 550 °C for 1 h to oxidize and remove impurities on the surface of the catalyst. The samples were then cooled down to the reaction temperature and the reflectance spectra were collected as background reference spectra. All spectra were obtained by coadding 200 scans at a resolution of 4 cm^{-1}.

3. Results and discussion

3.1. Surface acidity versus V_2O_5 loading

In situ DRIFTS spectra of SCR reaction over catalysts with various V_2O_5 loadings are shown in Fig. 1 with an arbitrary unit of absorbance. The operating conditions were set at 2000 ppm of NO, 2000 ppm of NH_3, 25% relative humidity, a flow rate of 250 ml/min in the chamber (with air as the diluting and carrier gas) and a temperature of 300 °C. Positive bands at 3350 and 1610 cm^{-1} are clearly seen in all the spectra, indicating that NH_3 is adsorbed onto Lewis acid sites as coordinated ammonia [2,3,10]. The strength of the Lewis acidity on the V_2O_5-based catalysts was almost constant like that of pure TiO_2. According to the report of Ramis et al. [2,3], Lewis ammonia can be adsorbed onto a titanium or vanadium center, but it is difficult to distinguish these two cases from the IR spectra. Hence, Lewis acid sites were mainly on the TiO_2 support, since V_2O_5-based catalysts and pure TiO_2 powder yielded almost the same intensity of Lewis acidity.

Meanwhile, strong positive bands at 3100, 3032, 2800 and 1415 cm^{-1} that related to ionic ammonium on Bronsted acid sites [5–7,10] were detected for 20% V_2O_5 catalyst. The strength of Bronsted acidity

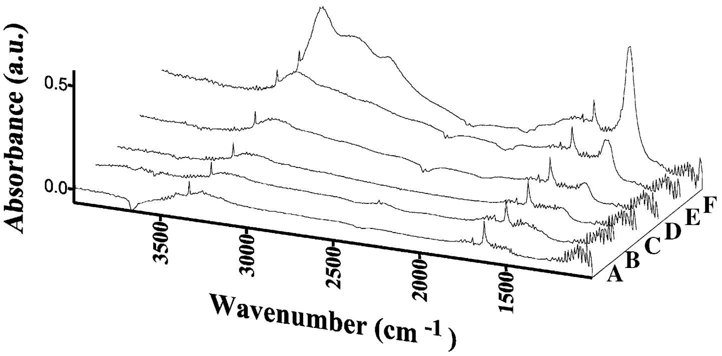

Fig. 1. In situ DRIFTS spectra of SCR reactions over different V_2O_5 contents at 300 °C: (A) pure TiO_2; (B) 1% V_2O_5; (C) 2% V_2O_5; (D) 5% V_2O_5; (E) 10% V_2O_5; (F) 20% V_2O_5.

declined as the V_2O_5 content fell, and disappeared over pure TiO_2. The negative band at 2050 cm^{-1} was observed for catalysts with V_2O_5 contents that exceeded 5%, and is associated with the disappearance of the first overtone of the stretching vibration, V=O group [7,10]. The disappearance of V=O, when coupled with a strong Bronsted acidity, indicated that ammonium was adsorbed onto V_2O_5. These results indicate that both Lewis acid sites and Bronsted acid sites coexisted on V_2O_5-based catalysts at the typical SCR operating temperature. Lewis acidity occurred mainly on TiO_2 support, and additives of V_2O_5 on the catalyst surface contributed to Bronsted acidity such that this acidity increased with V_2O_5 loading.

3.2. *SCR reaction mechanism*

Fig. 2 shows the in situ DRIFTS spectra of SCR reaction for 20% V_2O_5 at 300 °C in sequence of (A) NO/Air/NH_3, (B) NO/Air followed by (C) turn on of NH_3 steam again. As the flow of NH_3 was suppressed in the SCR feed for 30 min, the resulting spectra (middle spectra) was decreased in strength. This is because the originally adsorbed ammonia and ammonium were either desorbed or reacted with nitric oxide. And because no other NH_3 was supplied to the stream, so no new derivant nitric oxide species adsorbed on catalyst surface and resulted in flatter spectra. If NH_3 flow was restored, the same DRIFTS spectra as in the steady state of SCR reaction was obtained again (upper spectra). The same tendencies were also observed on other catalysts prepared in this study. These results indicated that gaseous NO reacts with adsorbed NH_3 species, following an Eley–Rideal type mechanism [16].

3.3. *Formation of surface acidity*

Experiments were conducted using N_2 as the carrier gas to further understand the formation of surface acidity. Fig. 3 shows the results. The operating conditions were the same as those in Fig. 1 except that the carrier gas was changed from air to N_2. The moisture content was much higher in air as a carrier gas than in N_2. One can see that only coordinated ammonia (3350, 3253 and 1610 cm^{-1}) adsorbed onto Lewis

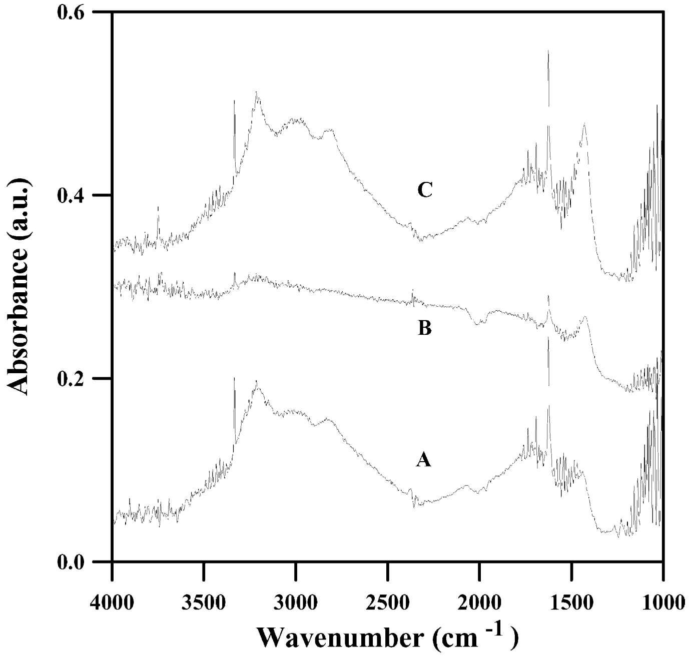

Fig. 2. In situ DRIFTS spectra over 20% V_2O_5 catalyst at 300 °C: (A) NO/NH_3/Air SCR reaction; (B) NO/Air for 30 min; (C) NO/NH_3/Air SCR reaction.

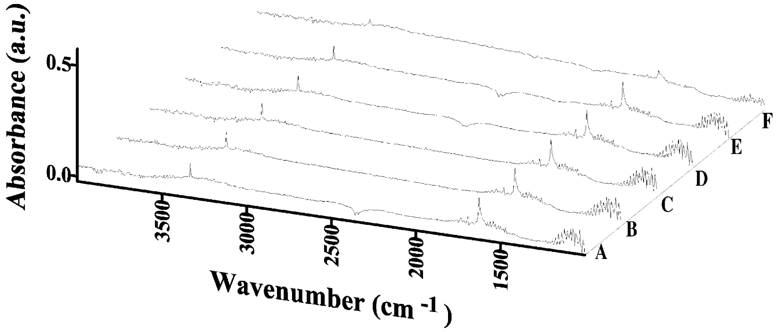

Fig. 3. In situ DRIFTS spectra of ammonia adsorption in N_2 at 300 °C: (A) pure TiO_2; (B) 1% V_2O_5; (C) 2% V_2O_5; (D) 5% V_2O_5; (E) 10% V_2O_5; (F) 20% V_2O_5. The moisture contents were negligible during the experiments.

acid sites were detected in all spectra. The Bronsted acidity disappeared for all tested V_2O_5 catalysts, but the strength of Lewis acidity was almost the same as that in Fig. 1. This result indicates that water vapor has no effect on the adsorption of Lewis ammonia, but the formation of Bronsted acidity may be related to the existence of water vapor.

It is noticed that no competition occurred between Lewis ammonia and water vapor, this is different from the result of Turco et al. [19]. But as referred to the catalyst they engaged has 33% V(IV) in the total vanadium content and a side reaction might occur by water produced from ammonia oxidation. The vanadium investigated in this study was almost all in a +5 oxidation state, and Lewis ammonia here preferred to adsorb on the TiO_2 support as seen in Fig. 3. This diversity may be due to difference in surface structure. Therefore, a more through investigation is required

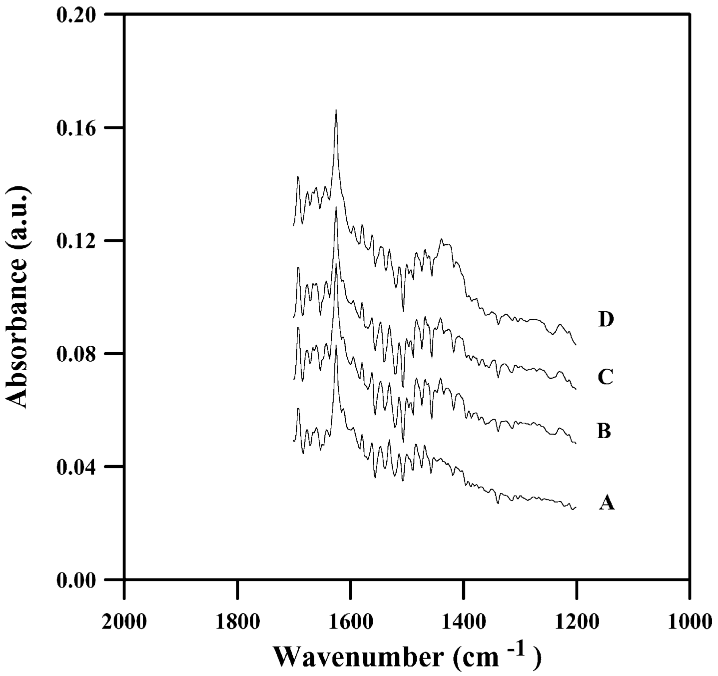

Fig. 4. In situ DRIFTS spectra of ammonia adsorption over 20% V_2O_5 catalyst and 300 °C to study the effect of moisture content: (A) dry N_2; (B) 400 ppm H_2O/N_2; (C) 600 ppm H_2O/N_2; (D) 6000 ppm H_2O/N_2.

to determine the adsorbed species on V_xO_y and its support.

The effect of moisture content on the formation of Bronsted acidity was examined using a 20% V_2O_5 catalyst because Bronsted acidity was observed mainly on the catalysts with higher V_2O_5 content, as stated previously. The variation in the strength of Bronsted acid under different concentrations of water vapor was focused at 1415 cm^{-1} as seen in Fig. 4. Bronsted acidity increased with the concentration of water vapor at 300 °C. The positive relationship indicates that the formation of Bronsted acid has to be accompanied with the adsorption of water vapor by reducing V=O (negative band at 2050 cm^{-1}) to V–OH which is then connected to gaseous NH_3 to form ionic ammonium species.

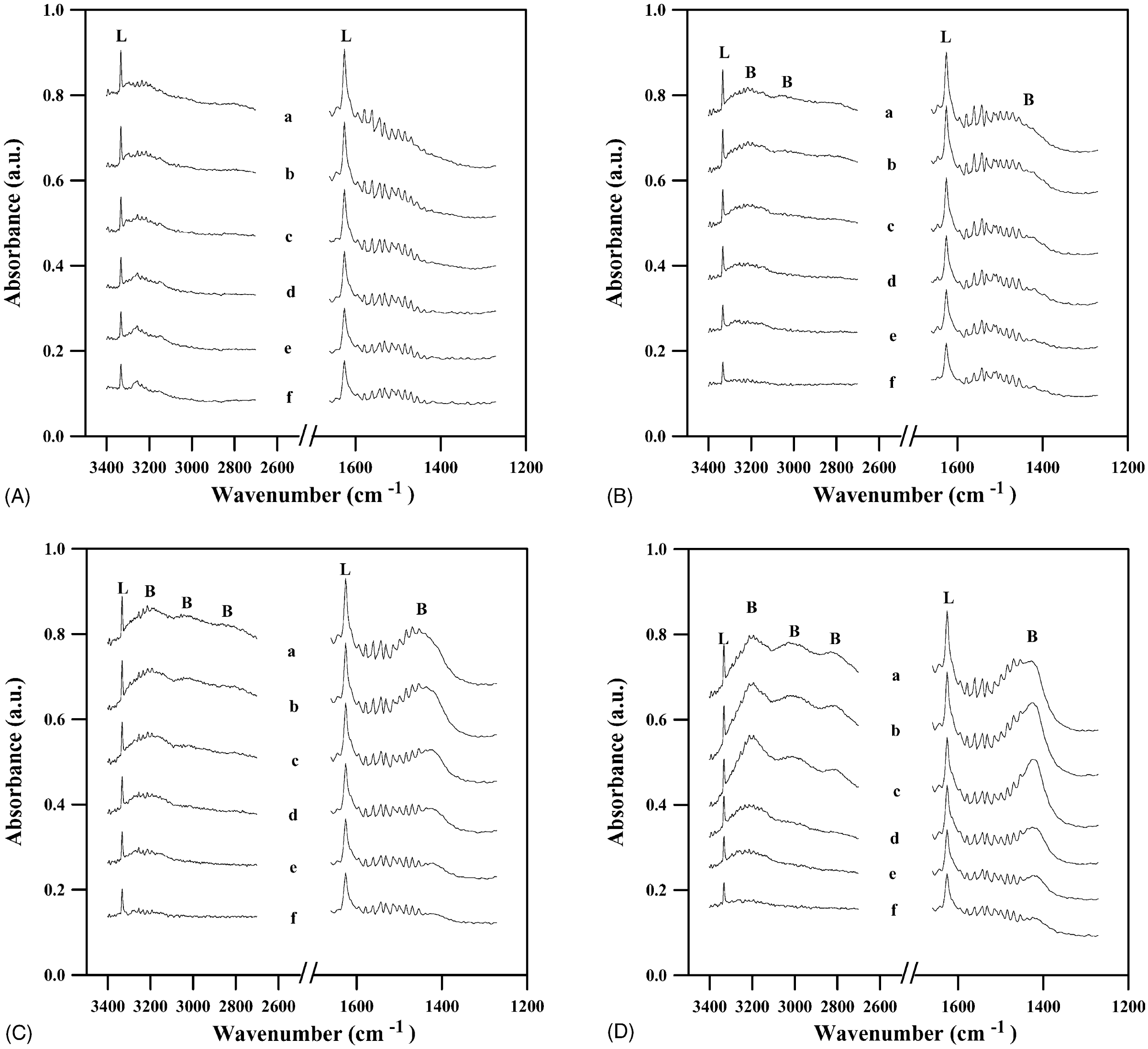

Fig. 5. Evolution of Bronsted acid and Lewis acid over (A) pure TiO_2 catalyst; (B) 1% V_2O_5 catalyst; (C) 2% V_2O_5 catalyst; (D) 5% V_2O_5 catalyst; (E) 10% V_2O_5 catalyst; (F) 20% V_2O_5 catalyst as a function of temperature: (a) room temp; (b) 100 °C; (c) 200 °C; (d) 300 °C; (e) 400 °C; (f) 500 °C (B and L represent NH_3 adsorbed on Bronsted and Lewis acid sites, respectively).

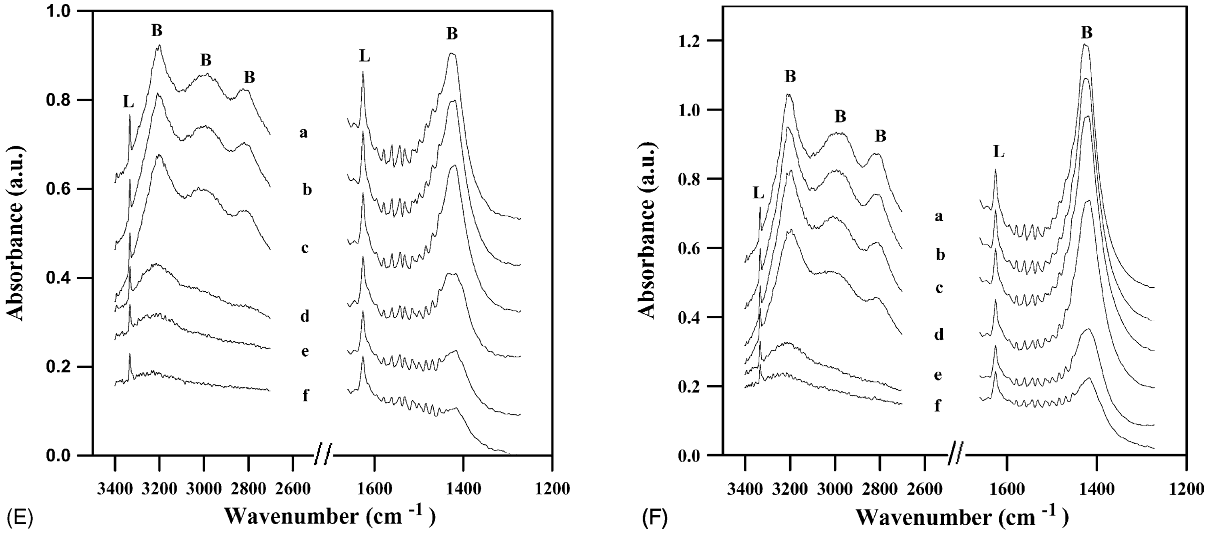

Fig. 5. (*Continued*).

3.4. *Temperature effect*

Typical SCR operating temperature was usually set at a limited range of −350 °C [20]. A broad temperature window is needed to evaluate the effect of temperature on surface acidity during SCR reaction.

Because ammonia was adsorbed at bands around 1200–1700 and 2700–3400 cm^{-1}, the following experiments focused on these two ranges. Fig. 5(A)-(F) present the IR spectra of ammonia adsorption over pure TiO$_2$, 1, 2, 5, 10, and 20% V$_2$O$_5$ catalyst, respectively, under different working temperatures. Fig. 5(A) indicates that only distinct adsorbed bands at 3350 and 1622 cm^{-1}, corresponding to the existence of Lewis acid sites, were observed on pure TiO$_2$. The strength of Lewis acidity seemed to be constant at temperatures from room temperature to 500 °C. The same tendencies were also seen over 1–20% V$_2$O$_5$ catalysts, as in Fig. 5(B)-(F). This result further demonstrates that ammonia was adsorbed onto Lewis sites at the TiO$_2$ support and it is almost independent of temperature.

This may be figured out by Bai et al. [21] who used a theoretical model to obtain some kinetic parameters from a pilot experiment. They indicated that the ammonia adsorption rate constant was independent of the operating temperature. The catalyst they used had a stronger Lewis acidity than Bronsted acidity [22]. This phenomenon was due to the thermal stability of TiO$_2$ and explains why TiO$_2$ has been frequently used as a support for SCR catalysts.

Fig. 5(B)-(F) clearly show the dependence of Bronsted acid on different V$_2$O$_5$ contents and working temperatures. The adsorption bands (3200, 3100, 2800 and 1415 cm^{-1}) correspond to the ion form of ammonium adsorbed onto Bronsted acid sites. The adsorption strength is especially strong for 10 and 20% V$_2$O$_5$ catalysts at low temperatures. It was seen that the strength of the Bronsted acid was greatest at room temperature for all tested V$_2$O$_5$ catalysts. And it decreased as temperature increased such that the peaks at 3200, 3100, 2800 and 1415 cm^{-1} almost disappeared at around 400 °C, especially for catalysts with less than 5% V$_2$O$_5$.

Fig. 6(A) and (B) show the integrated intensities of Bronsted acid (1415 cm^{-1}) and Lewis acid (1622 cm^{-1}), respectively, obtained from the spectra in Fig. 5(A)-(F). One can see that the strength of Bronsted acid obviously decreased as V$_2$O$_5$ content decreased and temperature increased, whereas Lewis acidity only slightly decreased with increasing temperature. And the decline in Lewis acidity with increasing temperature may be within experimental errors.

These results indicate that working temperature has a great influence on the intensity of Bronsted acidity. As referred to the result of previous section that the

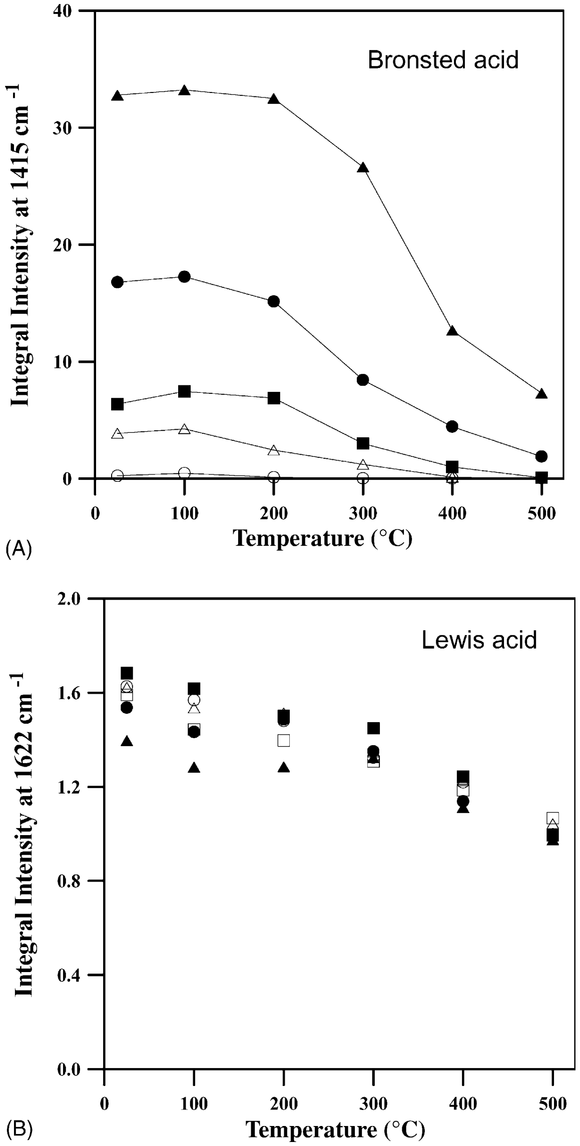

Fig. 6. Integrated intensity of (A) Bronsted acid ((○) 1%V_2O_5; (△) 2%V_2O_5; (■) 5% V_2O_5; (●) 10% V_2O_5; (▲) 20% V_2O_5) and (B) Lewis acid ((□) pure TiO_2; (○) 1%V_2O_5; (△) 2%V_2O_5; (■) 5% V_2O_5; (●) 10% V_2O_5; (▲) 20% V_2O_5) as functions of V_2O_5 content and temperature.

formation of Bronsted acid has to be accompanied with the adsorption of water vapor. At high temperature, water may be desorbed from the surface of the catalyst. The release of water vapors leads to an oxidized surface (V–OH to V=O) and gaseous ammonia can be alternately and partially adsorbed onto V=O group or titanic center to form an amide species. This confirms the discussions of Busca and co-workers [9,17] and Ramis and co-workers [9] that Bronsted acid site can desorb a water molecule to form Lewis site. Therefore, a conclusion could be obtained that Bronsted acid sites prefer to exist over catalysts with a higher V_2O_5 content and at a lower temperature, whereas the presence of Lewis acid sites was irrelevant to temperature and was mainly contributed by TiO_2 support during the SCR reaction.

4. Conclusions

In this study the influences of V_2O_5 content, water vapor and working temperature window on surface acidity of vanadia-based catalysts were systematically investigated. This study has explained the causes of the ongoing debate on adsorption sites during SCR reactions. Bronsted acidity increases with V_2O_5 loadings, but decreases with increasing temperature. Bronsted acidity disappearance at a high temperature is related to the loss of water vapor adsorption. Water vapor, however, does not effect the formation of Lewis acidity, which is observed mainly on the TiO_2 support.

This work has provided further insight into surface acidity. However, a more complete investigation of the effect of catalyst preparation, physicochemical properties of the catalyst, the composition of the inlet gases and relative reactivity on surface acidity is needed to elucidate fully the role of these factors in the SCR reaction.

Acknowledgements

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References

[1] Y.V. Belokopytov, K.M. Kholyavenko, S.V. Gerei, J. Catal. 60 (1979) 1.
[2] G. Ramis, G. Busca, V. Lorenzelli, P. Forzatti, Appl. Catal. 64 (1990) 243.

[3] G. Ramis, G. Busca, F. Bregani, P. Forzatti, Appl. Catal. 64 (1990) 259.
[4] N.Y. Topsoe, J. Catal. 128 (1991) 499.
[5] H. Schneider, S. Tschudin, M. Schneider, A. Wokaun, A. Baiker, J. Catal. 147 (1994) 5.
[6] N.Y. Topsoe, H. Topsoe, J.A. Dumesic, J. Catal. 151 (1995) 226.
[7] N.Y. Topsoe, J.A. Dumesic, H. Topsoe, J. Catal. 151 (1995) 241.
[8] G. Ramis, L. Yi, G. Busca, Catal. Today 28 (1996) 373.
[9] J.M.G. Amores, V.S. Escribano, G. Ramis, G. Busca, Appl. Catal. B 13 (1997) 45.
[10] M.A. Centeno, I. Carrizosa, J.A. Odriozola, Appl. Catal. B 19 (1998) 67.
[11] M.D. Amirids, R.V. Duevel, I.E. Wachs, Appl. Catal. B 20 (1999) 111.
[12] M.A. Centeno, I. Carrizosa, J.A. Odriozola, Appl. Catal. B 29 (2001) 307.
[13] M.A. Larrubia, G. Ramis, G. Busca, Appl. Catal. B 30 (2001) 101.
[14] H. Kamata, K. Takahashi, C.U.I. Odenbrand, J. Mol. Catal. A 139 (1999) 189.
[15] M.D. Amirids, I.E. Wachs, G. Deo, J.M. Jehng, D.S. Kim, J. Catal. 161 (1996) 247.
[16] M. Inomata, A. Miymoto, Y. Murakami, J. Catal. 62 (1980) 140.
[17] G. Busca, L. Lietti, G. Ramis, F. Berti, Appl. Catal. B 18 (1998) 1.
[18] J.P. Chen, R.T. Yang, J. Catal. 125 (1990) 411.
[19] M. Turco, L. Lisi, R. Pirone, P. Ciambelli, Appl. Catal. B 3 (1994) 133.
[20] F.P. Boer, L.L. Hegedus, T.R. Gouker, K.P. Zak, CHEMTECH 20 (1990) 312.
[21] H. Bai, S.H. Lee, C.-H. Lin, J.F. Hwang, C.L. Hsieh, J. Environ. Eng., ASCE 127 (8) (2001) 735.
[22] R.Y. Weng, J.F. Lee, Appl. Catal. A 105 (1993) 41.