APPLIED CHEMISTRY

Adsorption Behavior of Moisture over a Vanadia/Titania Catalyst: A Study for the Selective Catalytic Reduction Process

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A study of the inter-relationship between moisture, vanadia content, operation temperature, and surface acidity for a selective catalytic reduction (SCR) process for nitric oxide (NO) removal was conducted. The effects of operating parameters on the roles of Brønsted and Lewis acids acting in the SCR reaction were specified by the observed NO removal and the spectra of in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). The results indicated that H_2O competed with NH_3 molecules to be adsorbed on the pure titania catalyst that contained only Lewis acid sites. However, the competition did not occur over a vanadia-based catalyst on which both Brønsted and Lewis acid sites appeared in the presence of H_2O. As compared to that under dry conditions where only Lewis acid sites were found, the catalytic activity was lower under moisturized conditions even though both acids existed and there are fewer reaction sites available. It is concluded that surface acid sites are varied according to different operation conditions. Lewis acidity was dominant under the condition of low vanadia content and in the absence of H_2O molecules. It is also less sensitive to temperature. In contrast, Brønsted acidity was dominant under the condition of high vanadia content and in the presence of H_2O molecules, and it is highly affected by temperature.

1. Introduction

The selective catalytic reduction (SCR) process for the removal of nitric oxide (NO) by ammonia (NH_3) was first developed in Japan in the 1970s.[1] This technology is now widely used to control NO_x emission from stationary sources. Bosch and Janssen[2] first made an extensive survey of catalysts that are active in this process. The major active catalysts include metal oxides, zeolites, and noble metal deposited on alumina or ceramic monoliths. Among metal oxides, vanadia (V_2O_5) supported on oxides such as alumina, silica, and titania (TiO_2), especially V_2O_5/TiO_2, was active and commonly used in field application because of its thermal stability and resistance toward sulfur poisoning.

The reactivity of V_2O_5-based catalysts has been examined abundantly;[3−16] however, some were conducted at temperatures relatively lower than those in field application and/or in the absence of H_2O and SO_2. The mechanism on the V_2O_5-based catalysts has also been frequently discussed in the literature.[1,2,4,8,9,12−14,17,24] However, Busca et al.[1] indicated that only a few studies can fully satisfy the requirements such as closing a catalytic cycle with the correct stoichiometry or clarifying the nature, bonds, and charge of chemical species. Moreover, the proposed surface intermediates usually lack spectroscopic evidence.[1]

In recent years, many in situ technologies such as in situ Fourier transform infrared, Raman, and X-ray photoelectron spectroscopies, etc., were developed to measure the "real" reaction and the true status of the reactive site over the surface of the catalyst. Some adsorbed surface reactants, intermediates, and reaction mechanisms were reinforced by in situ infrared (IR) and Raman spectra. Busca et al.[1] summarized active sites and reactant species involved in the most popular reaction schemes on V_2O_5-based catalysts and other transition-metal-based catalysts. Although there are a few exceptions[21,24−27] indicating that NO was also adsorbed on the surface of catalyst and the Langmuir−Hinshelwood mechanism could not be ruled out, most researchers agree that the reaction between the reactants, adsorbed NH_3, and gaseous NO follows an Eley−Rideal mechanism.

On the other hand, it has been widely accepted that Brønsted acid sites are present together with Lewis acid sites on the V_2O_5-based catalysts, which means that two or more reaction schemes were taking place on the surface of the V_2O_5-based catalyst at the same time. Our previous DRIFTS study[28] also confirmed this result. However, there is still limited information available on the relationship between the operation parameters and catalyst's surface acidity and catalytic reactivity.

This study comprehensively investigated the influences of water vapor, V_2O_5 content, and temperature windows on the surface acidity and catalytic reactivity of the V_2O_5/TiO_2 catalyst. By combination of the analysis on in situ DRIFTS spectra and observed NO removal, the role of Brønsted and Lewis acid sites acting in the SCR reaction was specified.

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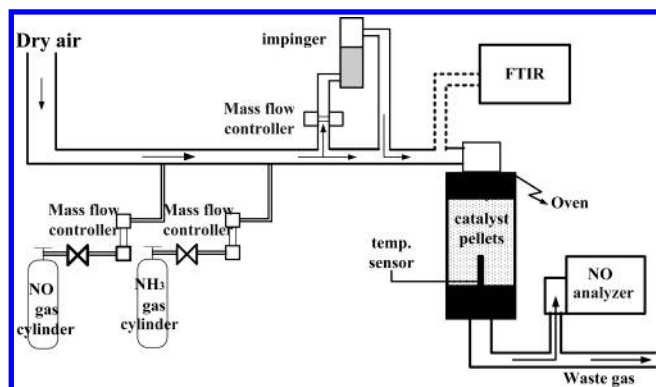
Figure 1. Schematic diagram of the SCR apparatus.

2. Experimental Section

For the preparation of V_2O_5/TiO_2 catalysts in this study, refer to the authors' previous study.[28] Briefly, V_2O_5/TiO_2 catalysts were prepared by the impregnation method. The V_2O_5 loadings on TiO_2 were 2, 5, 10, and 20 wt %. All catalysts used in this study have almost the same Brunauer−Emmett−Teller (BET) surface area of around 11 m²/g.

In situ DRIFTS spectra were obtained using a temperature-controlled DRIFTS chamber (Spectra-Tech 0030-01) with ZnSe windows coupled to a Bruker Vector 22 IR spectrometer with KBr optics and a DTGS detector. Prior to tests, all catalyst samples were activated in dry air at 500 °C for 1 h to oxidize and remove impurities on the surface of the catalysts and then cooled to 400 °C to correct the background spectrum. All spectra were obtained by coadding 200 scans at a resolution of 4 cm⁻¹.

The catalyst activities were tested by a tubular flow reactor with operation conditions corresponding to those of the DRIFTS tests. Figure 1 showed the schematic diagram of the SCR apparatus used in this study. The reactor consisted of a quartz tube with 2 cm i.d. and 40 cm length, and it was installed vertically in an oven. The catalyst pellets were supported with a fitted glass mesh located in the center of the reactor. The catalyst temperature was measured by a thermocouple at the center of the catalyst bed. Mass flow controllers (MKS, Andover, MA) controlled the flow rates of all gaseous streams. The sources of NO and NH_3 were supplied by cylinders, and the clean dry air from the cylinder was introduced for dilution purposes to obtain the NO and NH_3 concentrations of both at 2000 ppmv for the DRIFTS and activity tests. The inlet and outlet concentrations of NO were measured by a NO_x analyzer (Siemens ULTRAMAT 23).

The catalytic activities were tested under two moisture contents (dry and wet conditions) and were determined by the integral data of the conversion of NO through a packed-bed reactor. A water vapor concentration of 11 000 ppmv under wet conditions was obtained by passing dry air through an impinger containing deionized water. The impinger was kept in a constant-temperature-controlled water bath. In a typical run, the total flow rate over the catalyst bed was set at 2000 cm³/min corresponding to a space velocity of 19 100 h⁻¹. The Reynolds number was on the order of 10⁴ to ensure a plug-flow pattern.

3. Results and Discussion

3.1. H_2O Adsorption. Figures 2−4 demonstrated the adsorption of H_2O with increasing temperature on pure
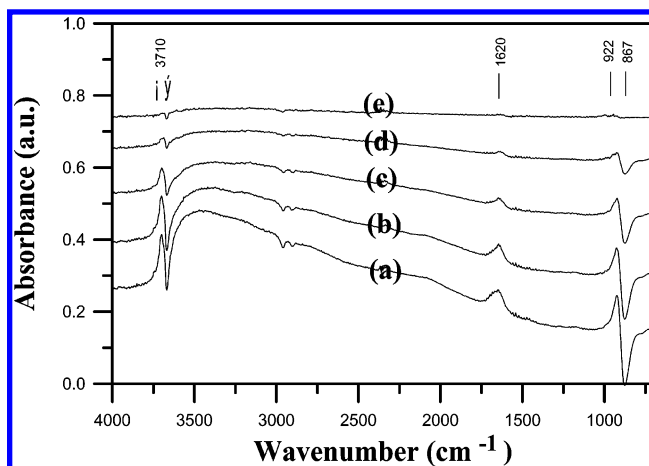

Figure 2. In situ DRIFTS spectra of H_2O adsorption on pure TiO_2 at various temperatures under wet conditions: (a) room temperature; (b) 100 °C; (c) 200 °C; (d) 300 °C; (e) 400 °C.
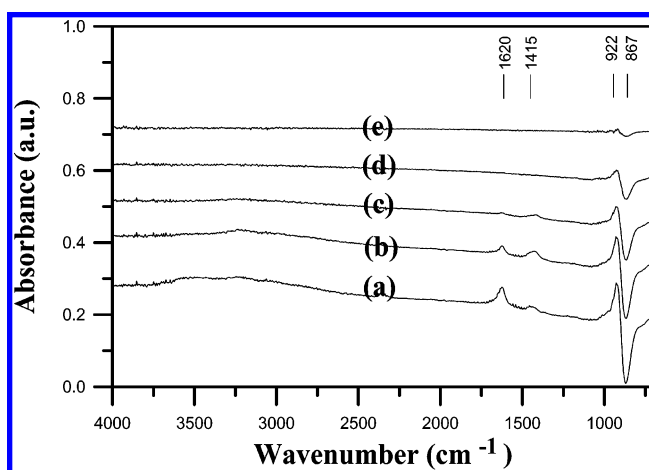

Figure 3. In situ DRIFTS spectra of H_2O adsorption on 5% V_2O_5/TiO_2 at various temperatures under wet conditions: (a) room temperature; (b) 100 °C; (c) 200 °C; (d) 300 °C; (e) 400 °C.

TiO_2, 5% V_2O_5/TiO_2, and 20% V_2O_5/TiO_2 catalysts, respectively. In Figure 2 for the test of pure TiO_2, an obvious positive broad band at 3000−3650 cm⁻¹ is assigned as the hydroxyl group from H_2O and sharp peaks at 3710, 1620, and 922 cm⁻¹ are characteristic of a tetrahedral coordinated vacancy, designated as Ti−OH.[24,25,29] Meanwhile, a negative band at 867 cm⁻¹ is assigned as the disappearance of the vibration of Ti−O in TiO_2.[29] These results indicated that H_2O is preferably adsorbed on TiO_2. The spectrum gained at room temperature showed the strongest intensity, but it is decreased with increasing temperature and disappeared at temperatures higher than 400 °C. This suggests that H_2O was chemisorbed on TiO_2.

On the contrary, the adsorption of H_2O on V_2O_5-based catalysts was not the same as that on TiO_2. The strong positive broad band at 3000−3650 cm⁻¹ on TiO_2 as observed in Figure 2 was no longer seen for 5% V_2O_5/TiO_2 and 20% V_2O_5/TiO_2 catalysts as shown in Figures 3 and 4. The results indicated that H_2O weakly or physically adsorbed on V_2O_5; in other words, the surface was not saturated with water on V_2O_5-based catalysts. Schneider et al.[21] indicated that the surface hydroxyl group preferably existed on TiO_2 or V_2O_5 at low temperatures, and H_2O could be continually desorbed up to 300 °C. Topsoe[19] also showed that a clean oxidative V_2O_5 could be obtained after exposure of O_2 flow at 400 °C for 2 h. Therefore, an environment of no water vapor

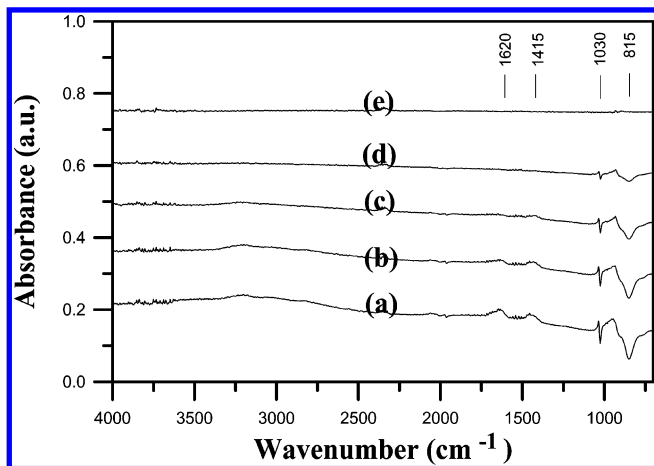**Figure 4.** In situ DRIFTS spectra of H_2O adsorption on 20% V_2O_5/ TiO_2 at various temperatures under wet conditions: (a) room temperature; (b) 100 °C; (c) 200 °C; (d) 300 °C; (e) 400 °C.

adsorption should be maintained at a temperature region of 300−400 °C or higher.

One can also see that the solid vibration of the 5% V_2O_5/TiO_2 catalyst differs from that of the 20% V_2O_5/ TiO_2 catalyst in the lower wavenumber region of 800− 1100 cm^{-1}. The bands at 1030 and 815 cm^{-1} shown in Figure 4 have been respectively assigned as the vibrations of V=O and V−O−V.[30] The negative ones at such frequencies coupled with a positive band at 1415 cm^{-1} indicated that Brønsted sites of V_2O_5 appear in the presence of H_2O.[19,21−23] However, no such solid vibration was seen on the 5% V_2O_5/TiO_2 catalyst. This may be due to the relatively low V_2O_5 content in the catalyst. No obvious broad band at 3000−3600 cm^{-1} was detected, but the same solid vibration position as that of TiO_2 indicated that V_2O_5 has a good dispersion on the 5% V_2O_5/TiO_2 catalyst.

3.2. Effect of H_2O on the Catalytic Activity. Figure 5 shows the moisture effect on the removal efficiency of NO as a function of temperature. Catalytic activity experiments were conducted under both dry and wet conditions, and their results in terms of NO removal efficiency were compared. One can see that the NO removal efficiency under dry conditions is obviously higher than that under wet conditions (H_2O = 11 000

ppmv) at a low-temperature region on both pure TiO_2 and V_2O_5-based catalysts. This result agrees with the view of most researchers.[5,11,12,16] For example, Amirids et al.[11] indicated that the additives of 8% H_2O in the influent resulted in a decrease in the SCR turnover frequency of 40−50% as compared to that tested in dry conditions at 350 °C. Also, 10−20% of NO conversion was declined when operated in a water vapor partial pressure of 50 Pa at 250−350 °C.[12] Amirids et al.[11] attributed this decrease to the competitive adsorption of H_2O and NH_3 on the V_2O_5 sites.

However, the removal efficiencies operated under both dry and wet conditions have almost the same values on all V_2O_5-based catalysts at a temperature of around 300 °C, but an obvious difference was found on the TiO_2 catalyst as seen in Figure 5. Table 1 lists the temperature needed to reach the highest removal efficiency of NO (denoted as T_{max}). The values of T_{max} on V_2O_5-based catalysts were at around 275−325 °C; these are in contrast to the values of 350−375 °C on the TiO_2 catalyst. This result may be related to the different H_2O adsorption abilities on the Lewis acid sites. The H_2O adsorption at 1620 cm^{-1} as shown previously in Figure 2 was obvious on the TiO_2 that contains Lewis acid sites only. The stronger adsorption of H_2O on the Lewis acid site only resulted in an obvious decline of activity from dry to wet conditions at T_{max}. This suggests that Lewis acid sites of TiO_2 or V_2O_5 were the reaction centers.

Figures 6−8 show in situ DRIFT spectra of the SCR reaction under both dry and wet conditions on pure TiO_2, 5% V_2O_5/TiO_2, and 20% V_2O_5/TiO_2 catalysts, respectively, at T_{max}. In Figure 6, Lewis NH_3 was detected at bands of 3350 and 1620 cm^{-1} under both dry and wet conditions, but absorption bands at 3710 cm^{-1} and uprising peaks of around 3000−3600 cm^{-1} in the lower spectrum indicate that H_2O could still be partially adsorbed on the surface of TiO_2 at T_{max}. This results in an obvious decline of activity as seen in Figure 5a. The decrease of activity due to competitive adsorption between H_2O and NH_3 appears in the case of pure TiO_2 that contains only Lewis acid sites. Also, this is because H_2O is preferably adsorbed on the Lewis acid site of TiO_2, even at temperatures higher than 400 °C.

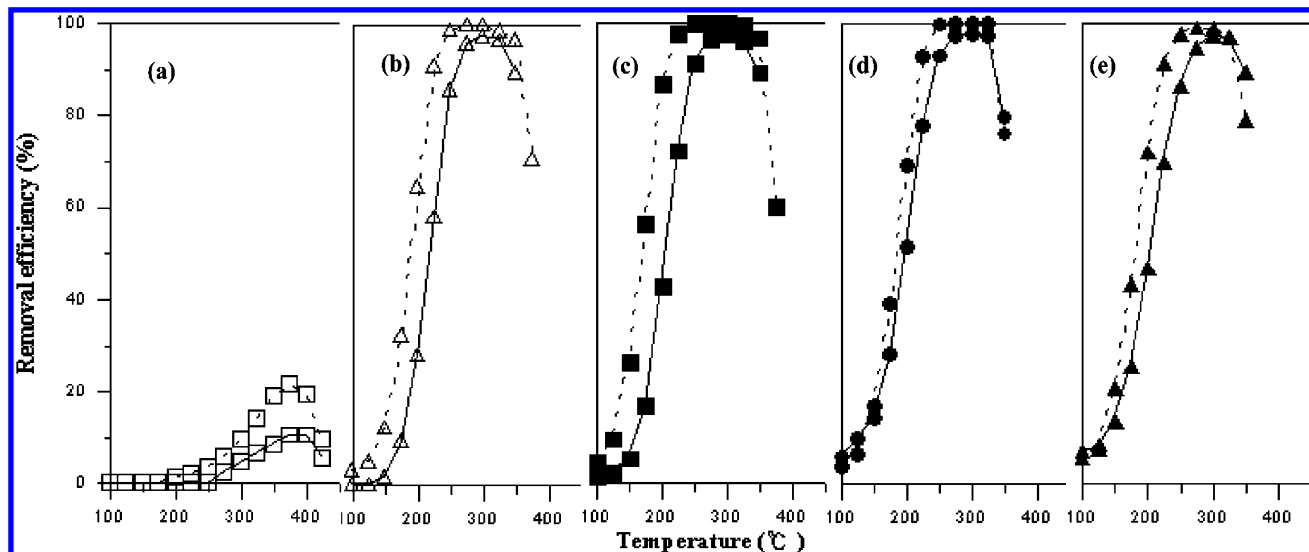On the other hand, Figures 7 and 8 show that only Lewis acid sites (3350 and 1620 cm^{-1}) were detected on

Figure 5. Effect of H_2O on the removal efficiency of NO as a function of temperature: (a, □) pure TiO_2; (b, △) 2% V_2O_5; (c, ■) 5% V_2O_5; (d, ●) 10% V_2O_5; (e, ▲) 20% V_2O_5 (- - -, in the absence of H_2O; −, in the presence of H_2O).

Table 1. Temperature (T_{max}) Needed To Reach the Highest NO Removal Efficiency for Different V_2O_5/TiO_2-Based Catalysts

	catalyst				
	pure TiO_2	2% V_2O_5/TiO_2	5% V_2O_5/TiO_2	10% V_2O_5/TiO_2	20% V_2O_5/TiO_2
T_{max} (°C)	350−375	275−300	275−300	275−300	300−325

V_2O_5-based catalysts under dry conditions. However, an excellent catalytic activity was observed in Figure 2b−e that both Lewis and Brønsted sites were detected under wet conditions (positive bands at 3100, 3032, 2800, and 1415 cm^{-1} and a negative band at 2050 cm^{-1} that related to the disappearance of the first overtone of the stretching vibration, the V=O group).[10,19,22,23] This suggests that Lewis acid sites were the major reaction centers.
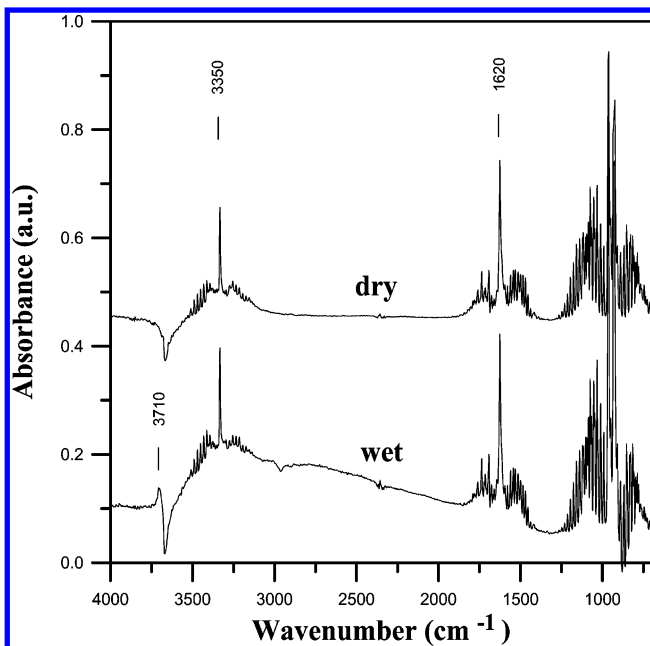

Figure 6. In situ DRIFTS spectra of SCR reaction on pure TiO_2 at T_{max} = 350 °C (dry, in the absence of H_2O; wet, in the presence of H_2O).

In conclusion, the existence of H_2O physically adsorbed on V_2O_5 or chemisorbed on TiO_2 leads to an apparent decrease of the catalytic activity.

3.3. Active Sites over Vanadia/Titania Catalysts. Table 2 lists the surface reactant species, proposed active sites, and corresponding operation parameters used in the literature.[1,4,10,17−19,21−23,31] Two representative active sites are classified. One is the Lewis site reacting with coordinative NH_3 or amide proposed by Ramis et al.[18] and Went et al.[10] The other is the binary Brønsted site (V=O, V−OH, or both) coupled with ammonium proposed by Inomata et al.[4] first and then Gasior et al.[31] and Topsoe and co-workers[19,22,23] subsequently. These two cases seem to be irrelevant at first sight, but a relationship can be found on the difference of the V_2O_5 content used in their tests. The Brønsted site was found mainly on the pure V_2O_5 or TiO_2/V_2O_5-based catalyst with a V_2O_5 content higher than 20%. Although only 6% of V_2O_5 was used by Topsoe et al.,[19] it corresponded to a small BET surface area of 7 m^2/g. In contrast, the Lewis site appeared on a catalyst with less than 10% of V_2O_5. The difference in operation temperatures is the second diversity being observed from literature to literature. Brønsted sites were usually observed at relatively lower operation temperatures as compared to those of observed Lewis sites. Therefore, an argument on the major active sites may be due to different test conditions in the literature.

However, the existence of Brønsted acid sites under wet conditions should not be taken as an unworkable functional group. Brønsted acidity existence on a V_2O_5-based catalyst was commonly accepted.[1,16,18,24,28] Our previous study[28] indicated that the formation of Brønsted acidity was accompanied by water vapor adsorption and was proportional to the V_2O_5 content. Chen and
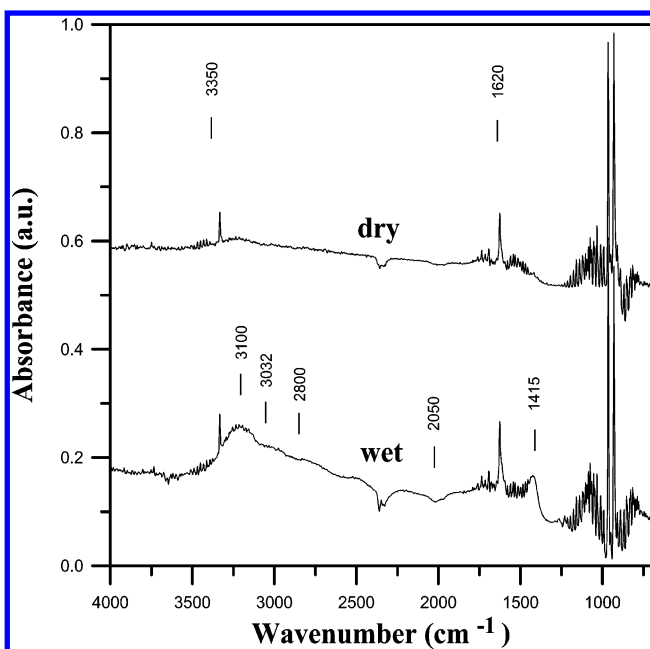

Figure 7. In situ DRIFTS spectra of SCR reaction on 5% V_2O_5/TiO_2 at T_{max} = 300 °C (dry, in the absence of H_2O; wet, in the presence of H_2O).
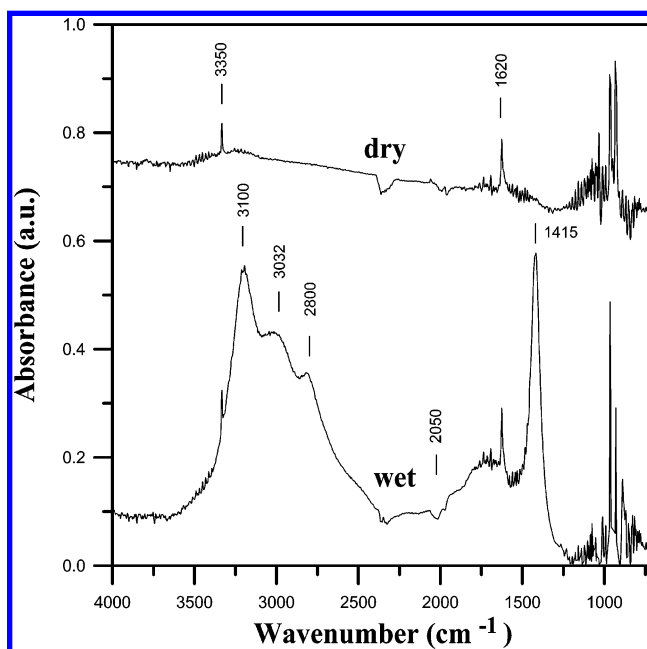

Figure 8. In situ DRIFTS spectra of SCR reaction on 20% V_2O_5/TiO_2 at T_{max} = 300 °C (dry, in the absence of H_2O; wet, in the presence of H_2O).

Table 2. Proposed Surface Reactant Species, Active Sites, and Corresponding Operation Parameters in the Literature for the SCR Reaction on V_2O_5-Based Catalysts

Reactant species	Proposed active site	V_2O_5 content by weight (%)	Temp. Range (°C)	Reference
NH_4^+	Bronsted site [a]	100	r.t. ~ 90	Takagi et al. [17]
NH_4^+	$\overset{\displaystyle O}{\underset{\displaystyle \parallel}{}}$ $\overset{\displaystyle OH}{\underset{\displaystyle \vert}{}}$ $-O-V-O-V-O-$	100	180 ~ 330	Inomata et al. [4]
NH_4^+	$\overset{\displaystyle OH}{\underset{\displaystyle \vert}{}}$ $V+V-O-V$	100	~ 250	Gasior et al. [31]
$O^-\ H_3N^+\ HO$ $\underset{V}{\vert}$ $\underset{V}{\vert}$	$\overset{O}{\underset{\parallel}{}}$ $\overset{HO}{\underset{\vert}{}}$ $-V-$ $-V-$	~ 6[b] ~ 100	250 ~ 350	Topsoe and co-workers [19,22,23]
NH_4^+	Bronsted site [a]	~ 20	100 ~ 200	Schneider et al. [21]
NH_3ads	Lewis site [a]	~ 9.8	150 ~ 450	Went et al. [10]
NH_2	$\overset{O}{\underset{\parallel}{V}}$	~ 5	~ 350	Ramis et al. [18]

[a] Chemical structure is unavailable. [b] BET surface area: 7 m^2/g.

Yang[9] also indicated that H_2O molecules enhanced the reaction rate because they provided the OH group required in the SCR reaction.

In reference to the proposed active sites listed in Table 2, although Brønsted sites are not entirely the same, it is ascertainable that they were all based on binary vanadium atoms. In the presence of oxygen, one single V=O group is needed in a reaction cycle on the Lewis acid site, but two vanadium atoms are needed on Brønsted acid sites.[1,18,23] Therefore, a decrease of the catalytic activity due to Brønsted acid sites appearing at T_{max} may be attributed to fewer Brønsted reaction sites available under wet conditions than Lewis reaction acid sites under dry conditions. Ramis and co-workers[18,24] indicated that the H_2O molecules could be adsorbed on the vanadium center of the Lewis site of the V_2O_5-based catalyst, but they did not remain on it because they changed to the Brønsted site subsequently. This result is especially obvious at temperatures below T_{max} because the formation of Brønsted acidity is more sensitive to temperature.[28]

However, it is difficult to quantify the relative activity of Brønsted and Lewis acid sites because H_2O molecules are also the reaction products. Furthermore, Went et al.[32] indicated that V_2O_5 is present as isolated, mono-meric vanadyl species or polymeric vanadate at low V_2O_5 loading in contrast to crystalline species at high V_2O_5 loading. Even on the catalyst with monolayer coverage of V_2O_5, a proportion of crystallites still exist on the surface of the catalyst. This result may lead to some challenges on the quantification of IR results (e.g., differences in density and solid geometry). Therefore, it is improper to demonstrate that only one active site exists on the V_2O_5-based catalyst under the conditions that cover broad ranges of V_2O_5 content, temperature, and moisture content.

4. Conclusions

This study provides results of IR spectra to clarify the argument on the competitive adsorption of H_2O and NH_3 and the relationship between Brønsted and Lewis sites on the V_2O_5/TiO_2 catalyst. Competition between H_2O and NH_3 molecules occurred on the TiO_2 catalyst that contains a Lewis site only and not on the V_2O_5-based catalyst where both Lewis and Brønsted acids exist. The H_2O molecules partially adsorbed on the vanadium center of the Lewis site of the V_2O_5-based catalyst and then changed to the Brønsted site subsequently. However, it results in a decrease of activity due to fewer reaction sites available.

It is not a conflict that Lewis and Brønsted sites coexist on the V_2O_5-based catalyst. However, the exist-

ence of Lewis or Brønsted acid sites depends on different operation conditions. Lewis acid sites were the major active sites under the condition of low V_2O_5 content in the absence of H_2O, and they are less sensitive to temperature. In contrast, Brønsted acid sites were the major ones under the condition of high V_2O_5 content with the presence of H_2O, and they are highly affected by temperature.

The relationship between Lewis and Brønsted sites was elucidated for the case of V_2O_5/TiO_2 catalysts in this study. However, other chemicals such as tungsten (W) oxide or molybdenum (Mo) oxide may also be additives for the commercial catalysts. This could lead to results different from those observed in this study. Therefore, further study may be needed to investigate the interaction between surface sites and the operation conditions to gain more information for field applications.

Acknowledgment

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