SO_2 oxidation over the V_2O_5/TiO_2 SCR catalyst

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The effects of V_2O_5 loading of the V_2O_5/TiO_2 SCR catalyst on SO_2 oxidation activity were examined by infrared spectroscopy (DRIFT) and SO_2 oxidation measurement. Vanadium oxide added to the catalyst was found to be well dispersed over the TiO_2 carrier until covered with monolayer V_2O_5. The rate of SO_2 oxidation increased almost linearly with V_2O_5 loading below the monolayer capacity and attained saturation with further increase. The hydroxyl groups bonded to vanadium atoms, V–OH, might be altered by SO_2 oxidation. Both V=O and V–OH groups are likely involved in the adsorption and desorption of SO_2 and SO_3.

KEY WORDS: V_2O_5/TiO_2; SO_2 oxidation; DRIFT; SCR; $DeNO_x$

1. Introduction

Selective catalytic reduction (SCR) of nitrogen oxides (NO_x) with ammonia (NH_3) as a reductant has been found quite useful for treating exhaust gas [1,2]. In this reduction, V_2O_5/TiO_2-based catalysts with WO_3 are commonly used in consideration of high catalytic activity and thermal stability [3].

In SCR, sulfur in fossil fuel undergoes oxidation over the V_2O_5/TiO_2 catalyst as an undesirable side reaction. Sulfur trioxide produced readily reacts with NH_3 and water producing ammonium bisulfate or ammonium sulfate which may cause corrosion of materials downstream the SCR reactor. Deactivation of the catalyst due to plugging is also a problem. To minimize the side reaction, modification of the catalyst surface [4,5] and optimization of SCR operation conditions [6,7] have been carried out. The effects of conditions such as temperature and gas feed composition on SO_2 oxidation over the V_2O_5–WO_3/TiO_2 catalyst have been extensively studied by Svachula et al. [7], who established a kinetic expression for the effects of NO, NH_3, and other gas components and showed the side reaction to occur through surface sulfate species created by adsorption and desorption equilibrium of SO_2 and SO_3 [7]. Morikawa et al. [4] reported the catalytic activity of SO_2 oxidation of the ternary catalyst, $V_2O_5/M_xO_y/TiO_2$ (M is Ge, Zn, Mo, or W). Dunn et al. [5], in their study on SO_2 oxidation activity of binary and ternary catalysts, found the redox sites of oxides on the catalyst surface to possibly function independently with no synergistic interaction.

The demand for fossil fuel with higher sulfur and vanadium content compounds is increasing. Compounds containing vanadium in fuel are oxidized by combustion and conveyed with flue gas toward the SCR reactor. Vanadium species in flue gas gradually deposited onto the catalyst surface during long term SCR operation. V_2O_5 in the SCR catalyst is usually only several weight percents so as to prevent undesired SO_2 oxidation. Vanadium species accumulation results in greater V_2O_5 content on the catalyst surface, with consequently greater catalytic activity in SO_2 oxidation. To obtain an SCR catalyst whose use would not increase SO_2 oxidation activity, the relationship between amount and structure of V_2O_5 in the catalyst and catalytic activity of SO_2 oxidation should be clarified.

Attention in this study was directed to the manner in which V_2O_5 deposited on the catalyst surface increases the activity of SO_2 oxidation. Various V_2O_5/TiO_2 catalysts differing in V_2O_5 loadings were prepared. V_2O_5 on the TiO_2 carrier was varied from 1.5 to 15.3 wt% to clarify the effects of its amount. The reaction rate of SO_2 oxidation was measured and characterization of the preparations was made.

2. Experimental

2.1. Catalysts

Catalysts were prepared by impregnation of TiO_2 powder (Aerogil, P-25) with aqueous solution of NH_4VO_3 in oxalic acid. Excess water was evaporated while stirring, and the solid thus obtained was dried at 343 K and calcined at 723 K for 3 h in air. Five samples differing in V_2O_5 loading from 1.5 to 15.3 wt% were crushed and sieved into particles 150–250 μm in diameter.

2.2. Characterization

Catalyst textural properties were determined by N_2 adsorption at 77 K (Fisons instruments, Sorptomatic 1990), subsequent to degassing at 593 K for 3 h.

DRIFT spectra were taken with a Jeol JIR-7000 spectrometer having a diffuse reflectance attachment (Spectra-Tech). Adsorption was measured in a heatable reaction cell at 4 cm^{-1}.

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Catalyst powder was preheated in the reaction cell at 593 K for 1 h under a stream of oxygen prior to NH_3 adsorption measurement. At room temperature, the catalyst was exposed to a 1.5% NH_3 and nitrogen gas mixture for 30 min. To examine NH_3 adsorbed on the catalyst following heat treatment, the catalyst was heated from 373 to 573 K under a stream of nitrogen in the IR cell, where spectra were taken.

The changes in catalyst surface structure under SO_2 oxidation were examined by DRIFT. After being preheated in a stream of oxygen at 573 or 673 K and purged by nitrogen for 30 min, the catalyst was exposed to a 500 ppm SO_2 and 7500 ppm O_2 (nitrogen balance) or a 1% SO_2 and 50% oxygen (nitrogen balance) mixture at specified temperatures. Spectra were taken at activated temperatures.

2.3. Activity measurement

SO_2 oxidation activity was measured under steady-state conditions a plug-flow type microreactor (6 mm in diameter) at total flow rate (STP) 150 ml/min, catalyst weight 0.2 g, nearly atmospheric pressure, and reaction temperature 573–733 K. Reactant concentrations were 500 ppm SO_2, 7500 ppm O_2, and N_2 balance. SO_2 in the reactant and product streams were determined by NDIR (Horiba). SO_2 to SO_3 conversion was formed by

$$X_{SO_2} = \frac{C^{in}_{SO_2} - C^{out}_{SO_2}}{C^{in}_{SO_2}}, \tag{1}$$

where $C^{in}_{SO_2}$ and $C^{out}_{SO_2}$ are SO_2 concentrations in the inlet and outlet streams, respectively. SO_2 concentration in outlet stream was measured by varying the catalyst bed temperature from 573 to 733 K. In most cases, conversions reached steady values in 1 h except for lower temperatures where it took several hours before steady values. Preliminary experiments, with variously sized catalyst particles, showed the effects of limited diffusion in particle pores to be negligible under the present experimental conditions. At different flow rates of reactants, with the proportion of catalyst weight to the flow rate kept the same, the external diffusion effect was found not significant. The reaction rate, r_{SO_2}, was calculated as follows for a differential reactor:

$$r_{SO_2} = \frac{F^0_{SO_2}}{WS} X_{SO_2}, \tag{2}$$

where $F^0_{SO_2}$, W, and S are molar flow of SO_2 in inlet, catalyst weight, and specific surface area of the catalyst, respectively. The conversion of SO_2, X_{SO_2}, was less than 0.15 throughout the study.

3. Results and discussion

3.1. Infrared study on preparations

Specific surface areas of the catalysts remained essentially constant at 50.5 ± 0.6 $m^2\,g^{-1}$ for 0–2.9 wt% V_2O_5 loading. Above 5.7 wt% V_2O_5 loading, the surface area decreased gradually. The surface areas at 10.7 and 15.3 wt% V_2O_5 loadings were 46.9 and 39.5 $m^2\,g^{-1}$, respectively.

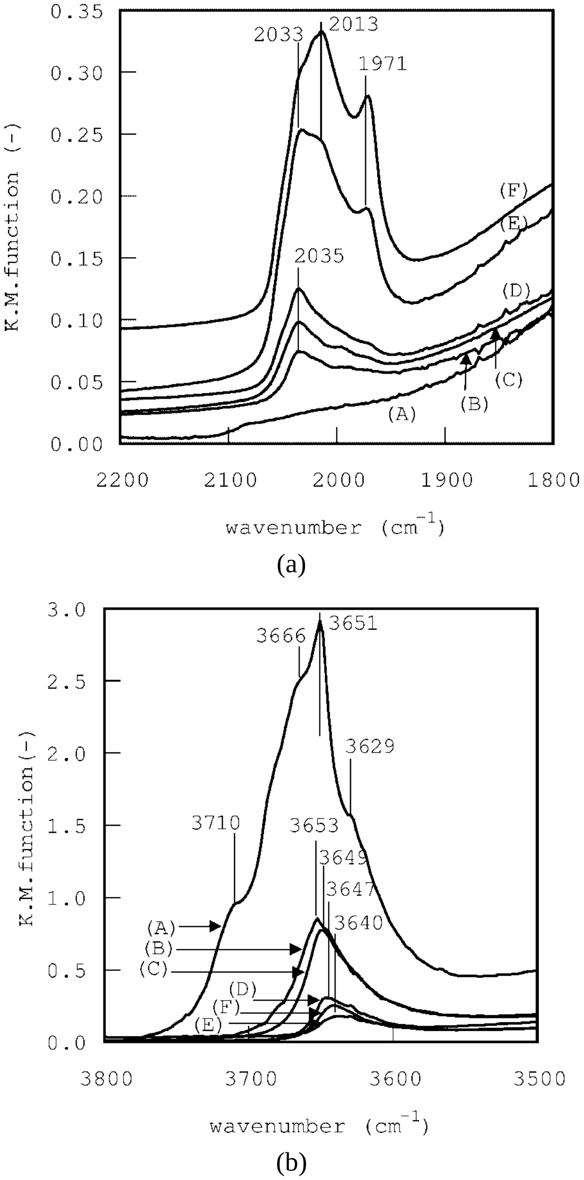


Figure 1. DRIFT spectra of V_2O_5/TiO_2 catalysts with different V_2O_5 loadings after being heated at 573 K under a stream of oxygen. Spectral regions, 1800–2200 and 3500–3800 cm^{-1}, are shown in (a) and (b), respectively. (A) 0, (B) 1.5, (C) 2.9, (D) 5.7, (E) 10.7, and (F) 15.3 wt% V_2O_5.

Figure 1 shows infrared spectra of catalysts with different V_2O_5 loadings. At V_2O_5 loadings of 1.5–5.7 wt%, the first overtone of the V=O stretching mode was apparent at 2035 cm^{-1}. This band intensity increased with V_2O_5 loading up to 5.7 wt%. Above 10.7 wt%, intense bands could be seen at 2033, 2013, and 1971 cm^{-1} suggesting bulk-like V_2O_5 structure formation on the surface. No band in this spectral region was observed for the TiO_2 surface. From the structure of V_2O_5 [8], the average loading corresponding to a complete monolayer was found to be 1.2 mg V_2O_5 per m^2 of the support surface area, with (100), (010), and (001) planes considered [9]. The catalyst with 5.7 wt% V_2O_5 load-

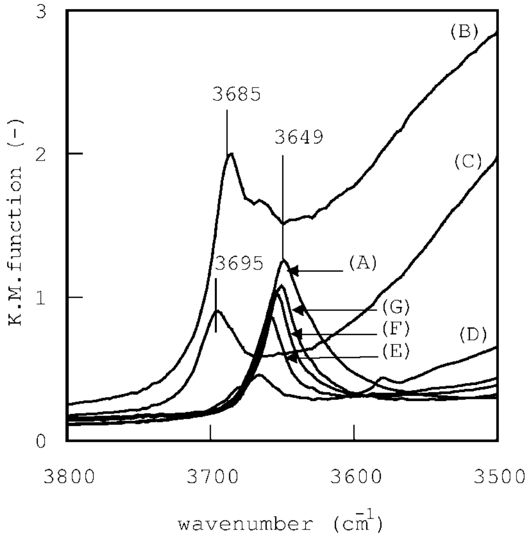
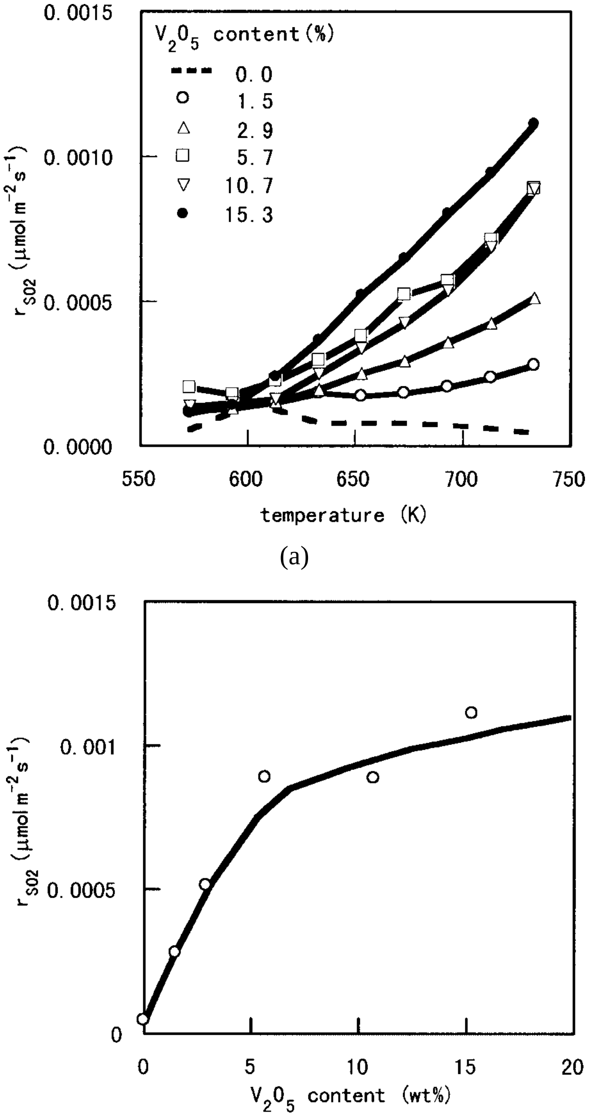


Figure 2. DRIFT spectra of V_2O_5/TiO_2 catalysts with 2.9 wt% V_2O_5 loading. (A) After being heated at 593 K under flowing oxygen, (B) after being cooled to RT, (C) after being exposed to 1.5% NH_3 and purged by nitrogen, (D)–(G) after being heated at 373 (D), 473 (E), 523 (F), and 573 K (G) under flowing nitrogen.

ing would thus appear to be covered with a monolayer of V_2O_5, a possibility supported by the spectra taken. Below 5.7 wt% V_2O_5 loading, the surface vanadyl species may be dispersed in monomeric and polymeric forms on the TiO_2 surface [10].

In the OH stretching region, an intense band centered at 3651 cm^{-1} with its shoulders at 3710, 3666, and 3629 cm^{-1} was observed for the TiO_2 surface, as shown in figure 1(b). The shoulder at 3710 cm^{-1} may possibly have been due to a contamination, while other bands would have resulted from Ti–OH groups with different coordination situations [11]. With V_2O_5 loading, the ν_{OH} band intensity decreased greatly and at greater V_2O_5 loading, the ν_{OH} band shifted somewhat toward lower wavenumbers. Above 10.7 wt% V_2O_5 loading, the band could be seen at 3640 cm^{-1}. Bands for V_2O_5 loading have been assigned to OH groups bonded to vanadium, V–OH [12,13].

SCR reaction occurs between NH_3 adsorbed at acid sites of the catalyst and gaseous or weakly adsorbed NO [14–20] and thus the V_2O_5/TiO_2 catalyst acidity should be a significant factor of its performance in NO reduction. The results of infrared study (DRIFT) on adsorption of NH_3 on the catalysts are thus discussed briefly. Subsequent to gaseous NH_3 exposure, ammonium ions, NH_4^+, and coordinatively adsorbed NH_3 on the surface were observed in all cases at room temperature [12,13]. After being heated in a stream of nitrogen, NH_4^+ and NH_3 desorption was noted to occur. For the TiO_2 carrier, only a weak band of NH_4^+ was observed which disappeared even at 373 K. NH_4^+ on TiO_2 may have been due to trace contamination, since pure TiO_2 has no Brønsted acidity [13]. Figure 2 shows infrared spectra of the OH stretching region of the 2.9 wt% V_2O_5 catalyst subsequent to NH_3 adsorption from RT to 573 K. The ν_{OH} band decreased in intensity with adsorption of NH_3 at room temperature. Further decrease was observed after heat treatment at 373 K. The intensity was somewhat restored with increase in temperature. The change in the ν_{OH} band by adsorption and desorption of NH_3 is consistent with the NH_4^+ bands observed. V–OH groups may thus be considered responsible for the Brønsted acidity of the V_2O_5/TiO_2 catalyst, as suggested previously [12,13].



(a)

(b)

Figure 3. Dependence of oxidation rate, r_{SO_2}, on temperature (a) and V_2O_5 loading (b) at 733 K.

3.2. Rate of SO_2 oxidation

Figure 3(a) shows the rate of SO_2 oxidation, r_{SO_2}, as a function of temperature at various V_2O_5 loadings with which it increased, attaining saturation at high values. The apparent activation energy of r_{SO_2} was found to be 40–50 kJ/mol, this being several times that reported for SCR of NO with NH_3, which is strongly inhibited by gas diffusion [21]. For clarification of the relationship between r_{SO_2}

and V_2O_5 loading, the dependence of r_{SO_2} on the latter at 733 K and the results are shown in figure 3(b). The oxidation rate increased linearly for the most part with V_2O_5 loading up to 5.7 wt% and attained saturation with further increase. For the monolayer V_2O_5/TiO_2 catalyst with 5.7 wt% V_2O_5 loading, the rate was approximately $1 \times 10^{-3}\ \mu\text{mol}\,\text{m}^{-2}\,\text{s}^{-1}$ at 733 K, thus hundred or thousand times less than for SCR. In the case of SO_2 oxidation, surface reaction would appear possibly rate determining in contrast to SCR.

Below V_2O_5 monolayer capacity, the predominant structure of surface vanadium species may change from monomeric to polymeric form, with increase in V_2O_5 [10], and hence polymeric vanadyl species contribute mostly to the increase in oxidation rate.

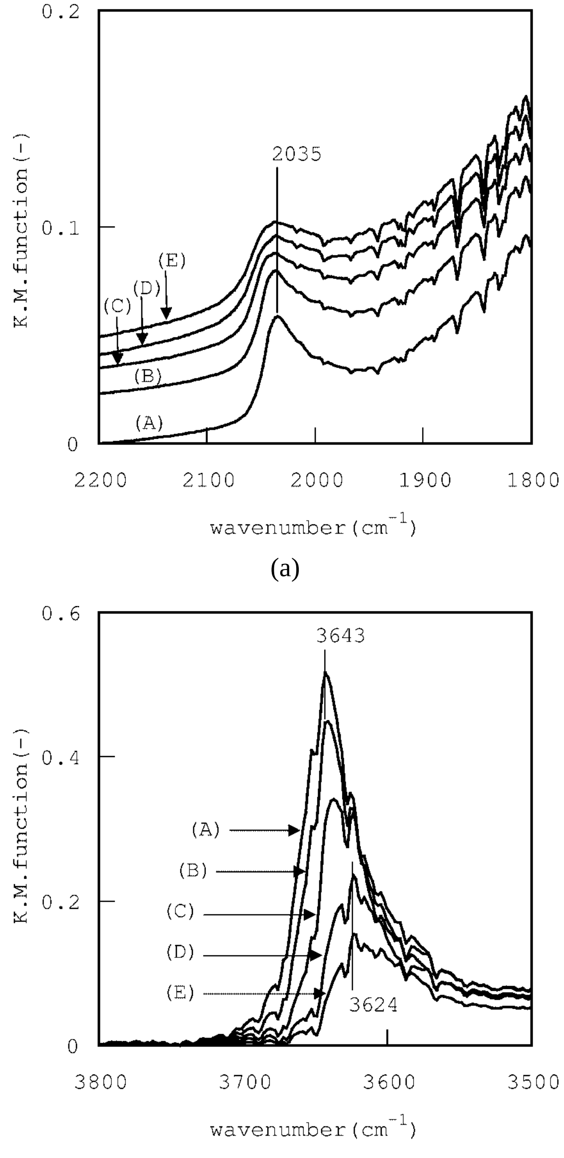
Under practical SCR conditions provided vanadium-containing compounds are present in the fuel, vanadium species in flue gas may be deposited on the catalyst surface directly from the gas phase and/or via liquid phase. SO_2 oxidation may increase with greater vanadium density on the catalyst surface. Once a bulk-like structure is formed, however, the rate of SO_2 oxidation attains saturation with further increase in V_2O_5 loading. It follows then that a catalyst such as would ensure bulk-like structure formation should be used so as to prevent increase in SO_2 oxidation activity. Support and additive for the catalyst should accordingly be optimized.

3.3. Catalyst surface change during SO_2 oxidation

SO_2 present in trace amount in the flue gas may alter the V_2O_5/TiO_2 catalyst during long term operation. To clarify the effects of SO_2 oxidation on the surface of the catalyst, an infrared study (DRIFT) of the V_2O_5/TiO_2 catalyst undergoing SO_2 oxidation was conducted.

Figure 4 shows infrared spectra of the 1.5 wt% V_2O_5/TiO_2 catalyst under a stream of a 750 ppm SO_2 and 1% O_2 gas mixture at 673 K. Prior to SO_2 exposure, V=O and V–OH bands were observed at 2035 and 3643 cm^{-1}, respectively. During exposure, the band at 1365 cm^{-1} was readily apparent and was assigned to the stretching frequency of S=O on the catalyst surface [22]. At greater contact time with the gas stream, band intensity increased and a shift toward higher wavenumber was apparent. $\nu_{V=O}$ and ν_{OH} bands showed decreased intensity with increase in gas stream contact time.

The effects of SO_2 oxidation on the surface of the V_2O_5/TiO_2 catalyst were examined using infrared spectra and a gas mixture containing 1% SO_2 with 50% oxygen. Such a study should indicate how a catalyst changes during long term SCR operation. Figure 5 shows infrared spectra of the V_2O_5/TiO_2 catalyst at various V_2O_5 loadings under 1% SO_2 stream with 50% O_2 at 573 K. The ν_{OH} band intensity was noted to decrease with SO_2 oxidation in all cases and particularly so at higher V_2O_5 loadings. For the catalyst with 1.5 wt% V_2O_5 loading, a ν_{OH} band shift from 3635 to 3626 cm^{-1} was noted. Only a trace ν_{OH} band was evident at 3624 cm^{-1} for the 3.0 wt% V_2O_5 loading. Above 5.7 wt%, the V–OH band almost completely disappeared during oxidation.



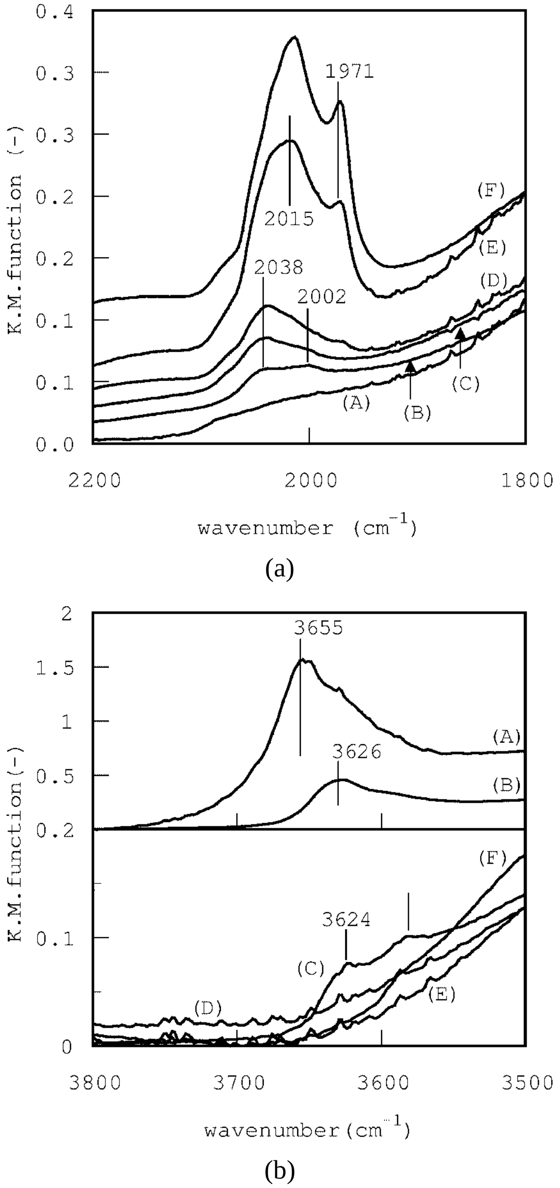
(a)

(b)

Figure 4. DRIFT spectra of V_2O_5/TiO_2 catalysts with 1.5 wt% V_2O_5 loading after being heated at 673 K under a stream of 750 ppm SO_2 and 1% O_2 mixture. Before (A) and after (B)–(E) exposure to SO_2 and O_2 mixture. (B) 15, (C) 60, (D)120, and (E)180 min.

The change in the V=O stretching region with exposure to 1% SO_2 and 50% O_2 gas mixture is shown in figure 5(a). The V=O band originally at 2035 cm^{-1} decreased in intensity at V_2O_5 loadings from 1.5 to 6 wt%. For the same samples, a shoulder appeared at 2002 cm^{-1}. Surface vanadyl species would thus appear to change during SO_2 oxidation, especially so at lower V_2O_5 loadings. Under a nitrogen stream, no such change was noted.

By SO_2 oxidation, ν_{OH} and $\nu_{V=O}$ band intensities and positions were altered. Thus, not only V=O species but hydroxyl groups bonded to vanadium atoms are likely involved in the adsorption and desorption of SO_2 and SO_3. Svachula et al. [7] indicate the active sites for the SO_2 oxidation to be



(a)

(b)

Figure 5. DRIFT spectra of V_2O_5/TiO_2 catalysts with different V_2O_5 loadings after being heated at 573 K under a stream of 1% SO_2 and 50% O_2 (N_2 balance) mixture for 1 h. (A) 0, (B) 1.5, (C) 2.9, (D) 5.7, (E) 10.7, and (F) 15.3 wt% V_2O_5.

formed through an equilibrium among dimeric vanadyl sites, their sulfated forms, and SO_3 in gas phase. On the TiO_2 surface, the structure of the sulfur species is thought to depend on water [23,24]. Under dry conditions, the sulfate oxide is bound to three Ti atoms via oxygen whereas, under wet conditions, the structure takes on the bridged bidentate form with OH groups bound to sulfur atoms [23]. The structure may be proposed for sulfate oxide formed on V_2O_5 during SO_2 oxidation. Some V–OH groups may be converted to hydroxyl groups that bind to sulfate oxides.

In the case of industrial SCR, water concentration may vary from several to 10% depending on the fuel and plant. Accordingly, the hydroxyl groups bonded to metals should be abundantly present and possibly in equilibrium with other surface species and water in the gas phase [25,26]. To determine the effects of water and other gas components on the surface of the V_2O_5/TiO_2 catalyst during long term SCR operation, further study is required. V–OH groups are Brønsted acid sites through which SCR reaction may proceed, and thus catalytic activity in SCR reaction may change with modification of V–OH groups.

4. Conclusion

The rate of the SO_2 oxidation is shown by the present study to increase with V_2O_5 loading up to monolayer coverage of V_2O_5. To prevent increase in SO_2 oxidation due to V_2O_5 deposited on the catalyst surface, support and/or additives materials must be optimized. Infrared study suggested V–OH groups to be altered in SO_2 oxidation. Adsorption and desorption of SO_2 and SO_3 may come about over V=O and V–OH groups on the catalyst surface.

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