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Molecular structure–reactivity relationships for the oxidation of sulfur dioxide over supported metal oxide catalysts

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Abstract

The catalytic oxidation of sulfur dioxide to sulfur trioxide over several binary (M_xO_y/TiO_2) and ternary ($V_2O_5/M_XO_Y/TiO_2$) supported metal oxide catalysts was systematically investigated. The supported metal oxide components were essentially 100% dispersed as surface metal oxide species, as confirmed by Raman spectroscopy characterization. The sulfur dioxide oxidation turnover frequencies of the binary catalysts were all within an order of magnitude ($V_2O_5/TiO_2 > Fe_2O_3/TiO_2 > Re_2O_7/TiO_2 \sim CrO_3/TiO_2 \sim Nb_2O_5/TiO_2 > MoO_3/TiO_2 \sim WO_3/TiO_2$). An exception was the K_2O/TiO_2 catalysts, which is essentially inactive for sulfur dioxide oxidation. With the exception of K_2O, all of the surface metal oxide species present in the ternary catalysts (i.e., oxides of V, Fe, Re, Cr, Nb, Mo and W) can undergo redox cycles and oxidize SO_2 to SO_3. The turnover frequency for sulfur dioxide oxidation over all of these catalysts is approximately the same at both low and high surface coverages. This indicates that the mechanism of sulfur dioxide oxidation is not sensitive to the coordination of the surface metal oxide species. A comparison of the activities of the ternary catalysts with the corresponding binary catalysts suggests that the surface vanadium oxide and the additive surface metal oxide redox sites act independently without synergistic interactions. The $V_2O_5/K_2O/TiO_2$ catalyst showed a dramatic reduction in the catalytic activity in comparison to the unpromoted V_2O_5/TiO_2 catalyst. The ability of K_2O to significantly retard the redox potential of the surface vanadia species is primarily responsible for the lower catalytic activity of the ternary catalytic system. The fundamental insights generated from this research can potentially assist in the molecular design of the air pollution control catalysts: (1) the development of catalysts for low temperature oxidation of SO_2 to SO_3 during sulfuric acid manufacture (2) the design of efficient SCR $DeNO_x$ catalysts with minimal SO_2 oxidation activity and (3) improvements in additives for the simultaneous oxidation/sorption of sulfur oxides in petroleum refinery operations. ©1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Sulfur dioxide, SO_2, is formed from both the oxidation of sulfur contained in fossil fuels and industrial processes that treat and produce sulfur-containing compounds. The catalytic oxidation of sulfur dioxide appears in numerous industrial processes and has a significant environmental impact because of the associated sulfur oxide, SO_x, emissions. Approximately two-thirds of the 50 billion pounds of sulfur oxides released annually in the United States are emitted from coal fired power plants [1]. Industrial fuel combustion and industrial processes (primarily sulfuric acid manufacture, petroleum refining and smelting of non-ferrous metals) account for the remainder of the emissions.

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Sulfuric acid is the largest volume chemical currently produced in the world, ≈95 billion pounds per year [2], and is manufactured by the contact process, which involves the high temperature catalytic oxidation of sulfur dioxide to sulfur trioxide over a unique supported liquid phase catalyst (silica supported vanadium pyrosulfate with alkali promoters). Under reaction conditions, 450–610°C, the active vanadia component of the catalyst exists as a molten salt forming a very thin liquid layer on the surface of the silica support (only 100–1000 Å thick). Sulfur dioxide oxidation to sulfur trioxide proceeds on both the active sites located in the interior of the liquid film and on the boundary between the film and the surface of the silica support [3–5]. Thermodynamically controlled equilibrium limitations exist at the temperatures necessary for the catalyst to activate, $T > 420°\mathrm{C}$, and the conversion of the sulfur dioxide feed is incomplete with the unreacted portion typically being directly emitted into the environment. A catalyst that is active at temperatures below 400°C could completely convert all the unreacted sulfur dioxide and eliminate the emission of sulfur oxides from sulfuric acid plants.

In contrast to the sulfuric acid contact process, the oxidation of SO_2 to SO_3 is undesirable during the selective catalytic reduction (SCR) of nitrogen oxides (NO_x) found in the flue gas of power plants. SCR removes NO_x in the flue gas by reacting the nitrogen oxides with ammonia and oxygen to form nitrogen and water at ≈370°C over titania supported vanadia catalysts (e.g., $V_2O_5/WO_3–MoO_3/TiO_2$). Under typical SCR design and operating conditions, NO_x reduction efficiency is directly proportional to the $NH_3 : NO_x$ ratio up to NO_x reduction levels of ca. 80%. Operating with too high of a $NH_3 : NO_x$ ratio can lead to unreacted ammonia bypassing the reactor, ammonia slip, where it readily combines with SO_3 at temperatures below 250°C to form ammonium sulfates, which can block the catalyst's pores and foul downstream heat exchangers [6]. This problem is so serious that industrial specifications for SCR processes include upper limits for the outlet concentration of sulfur trioxide corresponding to ≈1–2% sulfur dioxide conversion. Several studies have investigated the development of catalysts capable of simultaneously suppressing the oxidation of sulfur dioxide to sulfur trioxide while efficiently promoting the selective catalytic reduction of nitric oxide [7–11]. The advantages of such catalysts would be: (1) the ability to install more intrinsically active SCR catalysts (e.g., higher vanadia loadings) without the fear of simultaneously increasing SO_3 production; and (2) savings in operating costs generated by lowering SCR temperatures, without the worry of ammonium sulfate production and deposition.

Two new NO_x/SO_x removal techniques, SNO$_x$ (Haldor Topsoe) and DeSONO$_x$ (Degussa), combine SCR technology with sulfuric acid production [12,13]. Flue gas is heated to 380°C and nitrogen oxides are removed via conventional SCR technology. The products are further heated to 420°C and the SO_2 is oxidized to SO_3 over a sulfuric acid contact catalyst. The sulfur trioxide is then contacted with water producing concentrated sulfuric acid. Any unreacted ammonia from the SCR reactor is oxidized to NO_x over the second catalyst bed, consequently, avoiding the formation of ammonium sulfates.

Sulfur oxide emissions from fluid catalytic cracking (FCC) units account for a sizable fraction of annual SO_x emissions and are increasingly being targeted by the Environmental Protection Agency (EPA). The amount of SO_x emitted from a FCC unit regenerator is a function of the quantity of sulfur in the feed, coke yield and conversion [14]. Typically, 45–55% of feed sulfur is converted to hydrogen sulfide in the FCC reactor, 35–45% remains in the liquid products, and ca. 5–10% is deposited on the catalyst in the coke [14,15]. The sulfur in the coke is oxidized to SO_2 (90%) and SO_3 (10%) in the FCC regenerator. Traditional techniques of SO_x control such as flue gas scrubbing and feedstock hydrodesulfurization are effective, but are labor and cost intensive. The least costly alternative is the use of a SO_x-reduction catalyst as an additive to the FCC catalyst inventory. The catalyst must be able to (1) oxidize SO_2 to SO_3 in the FCC regenerator, (2) chemisorb the SO_3 in the FCC regenerator, and then (3) release it as hydrogen sulfide in the reducing FCC reactor. Supported vanadia catalysts, such as Amoco's DeSO$_x$ catalyst ($V_2O_5/CeO_2/Mg_2Al_2O_5$), have demonstrated high activity towards these reactions.

In addition, petroleum refining operations such as FCC and hydrodesulfurization (HDS) yield hydrogen sulfide as an undesired product. The hydrogen sulfide is typically concentrated and fed to a Claus plant to produce elemental sulfur. However, due to equilibrium limitations only 97% of the sulfur is recovered in the Claus plant and the tail gas, therefore, needs to be treated before being released to the atmosphere. The mobil oil SO_x treatment (MOST) process involves combusting the Claus tail gas with air, converting all of the sulfur species to SO_2 and SO_3. The SO_x is sorbed onto a $V_2O_5/CeO_2/Mg_2Al_2O_5$ spinel where it is later regenerated to produce concentrated H_2S and SO_2, which is recycled to the Claus plant for further processing [16].

In spite of the industrial importance and environmental consequences of the above catalytic oxidation processes involving sulfur dioxide, few fundamental studies have been performed on the kinetics and mechanism of sulfur dioxide oxidation with the exception of the unique sulfuric acid contact catalyst [3–5]. However, the studies on commercial sulfuric acid catalysts are not applicable to the environmental oxidation reactions over conventional solid metal oxide catalysts since the contact catalyst contains the active vanadia/alkali/sulfate component as a molten salt on the silica support.

The objective of this research is to establish the fundamental kinetics and molecular structure–reactivity relationships for the oxidation of sulfur dioxide to sulfur trioxide over oxide catalysts that contain the oxide phase in the solid state. The oxide catalysts investigated consist of supported metal oxide catalysts since these are excellent model catalyst systems that also find wide application as commercial catalysts. Combining in situ molecular characterization studies with the corresponding kinetic studies have resulted in a fundamental understanding of the sulfur dioxide oxidation reaction. It is hoped that the insights generated from these studies will assist in (1) the development of catalysts for low temperature (200–300°C) oxidation of SO_2 to SO_3 during sulfuric acid manufacture, (2) the design of SCR $DeNO_x$ catalysts with minimal SO_2 oxidation activity, and (3) improvements in additives for the simultaneous oxidation/sorption of sulfur oxides in petroleum refinery operations.

2. Experimental

2.1. Catalyst synthesis

The oxidation catalysts used in this research program were supported metal oxide catalysts possessing two-dimensional metal oxide overlayers on high surface area oxide supports. Supported vanadium oxide catalysts (V_2O_5/M_xO_y where $M_xO_y = CeO_2$, ZrO_2, TiO_2, Al_2O_3 or SiO_2) received special attention due to their wide application in environmental catalytic processes. In addition, several other binary supported metal oxide catalysts (Fe_2O_3/TiO_2, Re_2O_7/TiO_2, CrO_3/TiO_2, Nb_2O_5/TiO_2, MoO_3/TiO_2, WO_3/TiO_2, K_2O/TiO_2) and ternary supported metal oxide catalysts ($V_2O_5/Re_2O_7/TiO_2$, $V_2O_5/CrO_3/TiO_2$, $V_2O_5/Fe_2O_3/TiO_2$, $V_2O_5/Nb_2O_5/TiO_2$, $V_2O_5/MoO_3/TiO_2$, $V_2O_5/WO_3/TiO_2$ and $V_2O_5/K_2O/TiO_2$) were examined. The supported metal oxide catalysts were prepared by incipient wetness impregnation. Details of catalyst preparation are given elsewhere [17,18]. Table 1 summarizes all of the catalysts employed in this study.

2.2. Raman spectrometer

Raman spectra were obtained for all the catalysts in order to obtain molecular structural information about the surface metal oxide phases on the high surface area metal oxide support. An Ar^+ laser (Spectra Physics, Model 2020-50) tuned to 514.5 nm delivered 10–30 mW of power measured at the sample. The scattered radiation from the sample was directed into a Spex Triplemate spectrometer (Model 1877) coupled to a Princeton Applied Research (Model 1463) OMA III optical multichannel photodiode array detector. The detector was thermoelectrically cooled to $-35°C$ to decrease the thermal noise. Twenty 30 s scans with a resolution of $<2\,cm^{-1}$ were averaged to produce the final composite spectra. Approximately 100–200 mg of the pure catalysts were made into self-supporting wafers and placed in the in situ Raman cell. The in situ Raman cell consists of a stationary holder, which has been described elsewhere [19]. The in situ cell was heated to 300°C for 1/2 h and then cooled to room temperature in order to dehydrate the samples before the Raman spectra were obtained. The entire procedure was performed in a stream of flowing oxygen (Linde, 99.99% pure) over the catalyst sample to ensure complete oxidation of the catalysts.

2.3. Reaction system

Kinetic studies of sulfur dioxide oxidation were performed in a heat-traced quartz reactor system

Table 1
Composition of catalysts studied

Catalyst	V (atoms nm^{-2})	V (surface coverage)	M (atoms nm^{-2})	M (surface coverage)
TiO_2	–	–	–	–
1% V_2O_5/TiO_2	1.3	0.17	–	–
2% V_2O_5/TiO_2	2.6	0.34	–	–
3% V_2O_5/TiO_2	3.9	0.50	–	–
4% V_2O_5/TiO_2	5.2	0.67	–	–
5% V_2O_5/TiO_2	6.5	0.83	–	–
6% V_2O_5/TiO_2	7.8	~1	–	–
1% Fe_2O_3/TiO_2	–	–	0.6	0.2
1% Re_2O_7/TiO_2	–	–	0.4	0.2
1% CrO_3/TiO_2	–	–	1.0	0.2
1% Nb_2O_5/TiO_2	–	–	0.8	0.1
1% MoO_3/TiO_2	–	–	0.7	0.1
1% WO_3/TiO_2	–	–	0.5	0.1
1% K_2O/TiO_2	–	–	2.4	~1
5% Fe_2O_3/TiO_2	–	–	3.0	0.8
5% Re_2O_7/TiO_2	–	–	2.0	0.8
5% CrO_3/TiO_2	–	–	5.3	0.8
5% Nb_2O_5/TiO_2	–	–	4.1	0.7
5% MoO_3/TiO_2	–	–	3.3	0.7
7% WO_3/TiO_2	–	–	3.3	0.8
1% V_2O_5/5% Fe_2O_3/TiO_2	1.3	0.17	3.0	0.8
1% V_2O_5/5% Re_2O_7/TiO_2	1.3	0.17	2.0	0.8
1% V_2O_5/5% CrO_3/TiO_2	1.3	0.17	5.3	0.8
1% V_2O_5/5% Nb_2O_5/TiO_2	1.3	0.17	4.1	0.7
1% V_2O_5/5% MoO_3/TiO_2	1.3	0.17	3.3	0.7
1% V_2O_5/7% WO_3/TiO_2	1.3	0.17	3.3	0.8
1% V_2O_5/1% K_2O/TiO_2	1.3	0.17	2.4	~1
1% V_2O_5/CeO_2	1.8	0.25	–	–
4% V_2O_5/CeO_2	7.0	~1	–	–
1% V_2O_5/ZrO_2	1.7	0.25	–	–
4% V_2O_5/ZrO_2	6.8	~1	–	–
1% V_2O_5/Al_2O_3	0.36	~0.05	–	–
20% V_2O_5/Al_2O_3	7.3	~1	–	–
1% V_2O_5/SiO_2	0.25	0.25	–	–
4% V_2O_5/SiO_2	1.0	~1	–	–

connected to either an on-line gas chromatograph or an on-line gas-phase FTIR [17,18]. Reaction temperature was generally varied between 200° and 400°C. Varying the catalyst charge to the microreactor allowed space velocities to range from 10 000 to 40 000 h^{-1}, while maintaining a constant feed flowrate of 160 sm^{-1}. Sulfur dioxide and oxygen concentrations in the feed gas were varied between 50 and 2000 ppm and 0.1% and 18%, respectively. Conversion calculations in most instances are based on the differences between inlet and effluent sulfur dioxide concentration. Each catalyst/support system was checked for variations in steady-state activity over a 120 h period. The standard operating conditions for the sulfur dioxide oxidation kinetic experiments that were performed are summarized in Table 2. Assuming standard operating conditions, SO_2/He and O_2/He gas diffusivities were calculated. Effectiveness factors, based on these diffusivities, were calculated to be between 0.99 and 1.00 for the catalyst particle sizes tested, i.e., 80–200 μm, indicating that heat and mass transfer limitations were not present during these studies [20].

The on-line gas chromatograph (HP 5890 A) was equipped with two sulfur oxide sensitive detectors: thermal conductivity (TCD) and sulfur chemilumines-

Table 2
Standard operating conditions for kinetic studies

	Range tested	Standard condition
Reactor temperature (°C)	200–400	320
Gas hourly space velocity (h^{-1})	10000–40000	10000
Feed flowrate (s/m^{-1})	160	160
Feed SO_2 partial pressure (ppm)	40–2000	1000
Feed O_2 partial pressure (%)	0.1–18	18
SO_2 Conversion (%)	0.1–99	<10
Catalyst particle size range (μm)	80–200	80–200
Catalyst charge (mg)	100–1000	1000

cence (SCD–Sievers 355). Ultra high purity helium (Linde, 99.999% pure), which has been passed through water (Alltech), hydrocarbon (Alltech) and oxygen traps (Alltech), is used as the carrier gas. Product and feed gases are sampled by a 10-port valve (Valco) constructed of a sulfur resistant material (Nitronic 50) and equipped with two 100 ml sampling loops. Two identical packed columns (6′ × 1/4″ OD glass column packed with Chromosorb 107) running in parallel are installed prior to the detectors. Separation is accomplished in 5 min using an isothermal chromatograph oven temperature of 200°C. All of the GCs external lines and the injection valve are heated to at least 200°C to prevent the adsorption of sulfur oxides. Data acquisition from the detectors and control of the chromatograph's operation is handled by a desktop computer running a dedicated program (HP Chemstation V 4.0).

The gas-phase FTIR (Midac) is equipped with a 10 m path gas cell with KBr windows (Infrared Analysis, Model 10-PA-RC-Ag), which has a volume of 3.1 l and is operated at a pressure of 150 torr and 25°C. In order to quantify sulfur dioxide, spectra are obtained by averaging 16 scans with a resolution of 0.5 cm^{-1}. Dilute sulfur dioxide (1000 ppm SO_2, balance He) has major IR adsorption bands in the 1300–1400 cm^{-1} range (1344, 1350, 1360 and 1372 cm^{-1}), 1100–1200 cm^{-1} range (1133 and 1164 cm^{-1}), and 480–560 cm^{-1} range (507 and 539 cm^{-1}), while sulfur trioxide has several additional and characteristic bands at 816, 1034, 1093 and 1266 cm^{-1} [17]. Calibration procedures are given elsewhere [21].

3. Molecular structure of supported metal oxide catalysts

To fully understand the molecular structure–reactivity relationships for the oxidation of sulfur dioxide over supported metal oxide catalysts a detailed knowledge of the molecular structures of the surface metal oxide species is required. Several studies have shown that Raman spectroscopy can readily discriminate between different surface metal oxide structures with different coordinations and bond lengths [22,23]. Raman spectroscopy is an optical technique and, therefore, can be applied to study the structural changes of the surface metal oxide species under in situ conditions where the environment around the catalyst is controlled (temperature, pressure and gas composition). The present paper will only focus on experimental results obtained under well-defined conditions with monolayer and sub-monolayer loaded supported metal oxide catalysts. During acquisition of Raman spectra the supported metal oxide catalyst samples were maintained under dehydrated conditions. Dehydrated conditions are created by heating the catalyst to elevated temperatures, 300–500°C, in a flowing oxygen-containing stream for at least 30 min. Such treatment desorbs adsorbed moisture from the catalyst surface and maintains the surface metal oxide species in the fully oxidized state [24].

3.1. Binary supported metal oxide catalysts (M_xO_y/TiO_2)

The dehydrated Raman spectra of the low and high surface coverage titania supported metal oxide catalysts have recently been published [17]. A weak Raman band at ≈790 cm^{-1} is due to the TiO_2 (anatase) component of the support. Raman bands between 980 and 1030 cm^{-1} are assigned to the terminal M=O vibration (where M = V, Re, Cr, Nb, Mo or W) of the surface metal oxide species [24]. Raman bands characteristic of bridging M–O–M bonds, 860–940 cm^{-1}, associated with polymerized surface species are also found in the spectra of the high surface coverage vanadium, chromium, niobium and molybdenum oxide supported catalysts. Titania supported iron oxide catalysts do not posses Raman active vibrations in the 800–1200 cm^{-1} spectral region because of the absence of terminal Fe=O bonds and are overshadowed by the strong TiO_2 (anatase) bands below 800 cm^{-1}. However, surface iron oxide species on an Al_2O_3 support exhibited a broad Raman band at $\approx$750 cm^{-1} [25].

Raman spectroscopy is very sensitive to the appearance of microcrystalline metal oxide particles since their Raman cross sections are usually orders of magnitude greater than those of the corresponding surface metal oxide species. The major vibrations of the corresponding metal oxide microcrystals (e.g., V_2O_5, 994 cm^{-1}; α-Fe_2O_3, 410 cm^{-1}; T-Nb_2O_5, 680 cm^{-1}; α-MoO_3, 815 cm^{-1}; and WO_3, 808 cm^{-1}) usually occur at different frequencies than the strongest vibrations of the surface metal oxide species (typically $\sim$1000 cm^{-1} due to the presence of terminal M=O bonds) [24,25]. The absence of Raman bands characteristic of metal oxide microcrystals in the published spectra of these catalysts confirm the presence of only two-dimensional surface metal oxide overlayers on the titania support. It was not possible to rule out the existence of α-Fe_2O_3 and T-Nb_2O_5 microcrystals due to their overlap with the Raman vibrations of the TiO_2 support. Previous Raman and IR studies have shown that monolayer loadings of the titania supported catalysts correspond to 6% V_2O_5/TiO_2 ($\sim$7.9 V atoms nm^{-2}) [24], 6% CrO_3/TiO_2 ($\sim$6.4 Cr atoms nm^{-2}) [24], 7% Nb_2O_5/TiO_2 ($\sim$5.8 Nb atoms nm^{-2}) [24], 7% MoO_3/TiO_2 ($\sim$4.6 Mo atoms nm^{-2}) [24], 9% WO_3/TiO_2 ($\sim$4.2 W atoms nm^{-2}) [24], 6% Fe_2O_3/TiO_2 ($\sim$3.9 Fe atoms nm^{-2}) [24] and 1% K_2O/TiO_2 ($\sim$2.5 K atoms nm^{-2}) [26]. However, it is not possible to create a complete monolayer of surface rhenium oxide species on the titania support due to Re_2O_7 volatilization and the highest rhenium oxide surface coverages achieved to date correspond to 6% Re_2O_7/TiO_2 ($\sim$2.4 Re atoms nm^{-2}) [27]. Thus, the supported metal oxide catalysts employed in the present study possessed less than monolayer coverage and were essentially 100% dispersed as surface metal oxide species.

At low surface coverages (<0.2 monolayer), solid-state ^{51}V NMR [28,29], XANES [30–32] and UV-vis DRS studies [33,34] have shown that the dehydrated surface vanadium, chromium, rhenium, niobium, molybdenum and tungsten oxide species supported on titania generally tend to possess four-fold coordination. The absence of strong M–O–M Raman vibrations indicate that the surface species are predominately isolated. Raman [35–40], IR [39,39] and oxygen-18 exchange [38] experiments have suggested a mono-oxo structure for the isolated four-coordinated surface oxides of vanadium, chromium, niobium, molybdenum and tungsten. In contrast, Raman and IR studies have suggested that the surface ReO_4 species possess three terminal Re=O bonds and one bridging Re–O–Ti bond [27]. Mossbauer spectroscopy [41] has demonstrated that for low surface coverages (<0.5 Fe atoms nm^{-2}, corresponds to <0.13 monolayer) of iron oxide on a titania support, the dehydrated surface iron oxide species are primarily six-fold coordinated. Surface potassium oxide species preferentially titrate Lewis acid sites on the titania support to form Ti–O–K species, which increase the surface basicity [42].

At high surface coverages (>0.6 monolayer), the coordination of the dehydrated surface metal oxide species depends on the specific metal oxide and strong Raman signals due to polymerized surface species are also usually present (surface vanadia, chromia, molybdena, tungsta and niobia) [24]. However, the surface rhenium oxide species on titania do not possess Raman vibrations due to polymerized surface species and remain isolated at all coverages. Four-fold coordination is preferred for surface rhenium oxide, chromium oxide and vanadium oxide species, while six-fold coordination is preferred for surface molybdenum oxide, tungsten oxide and niobium oxide species. Mossbauer spectroscopy has determined that the dehydrated surface iron oxide species present on the titania support remain six-fold coordinated at surface coverages approaching monolayer coverage [41], but little information is currently available about the extent of polymerization of surface iron oxide species.

3.2. Ternary supported metal oxide catalysts ($V_2O_5/M_xO_y/TiO_2$)

The dehydrated molecular structures of catalysts impregnated with both vanadium oxide (0.17 monolayer) and a secondary metal oxide additive (0.7–0.9 monolayer of iron oxide, rhenium oxide, chromium oxide, niobium oxide, molybdenum oxide, tungsten oxide or potassium oxide) were also recently investigated with Raman spectroscopy [17]. There appears to be only minor structural interactions between the surface vanadium oxide species and the surface iron, rhenium, chromium, niobium, molybdenum and tungsten oxide species since the Raman band positions of the ternary catalysts are not shifted significantly relative to the respective binary catalysts. There does seem to be a slight increase in the intensity of the 880 to 930 cm^{-1} bands of the surface vanadia species, which can be attributed to an increase in the ratio of polymerized to isolated surface species caused by lateral interactions between the surface metal oxide additives and the surface vanadia species. There is no indication of metal oxide microcrystal formation in the spectra of the ternary catalysts, which confirms the submonolayer coverages of the ternary catalysts and 100% dispersion of the surface metal oxide species.

The addition of potassium oxide to the supported vanadia catalyst has a more pronounced effect on the surface vanadium oxide species as is evident from the Raman spectra of the 1% V_2O_5/1% K_2O/TiO_2 system [17]. The addition of approximately one monolayer of potassium oxide shifts the Raman band associated with the terminal V=O bond to 980–1000 cm^{-1}, which corresponds to an increase in the bond length of the V=O bond of ≈0.02 Å [43]. Previous solid state ^{51}V NMR [44] studies indicated that the surface vanadia species retains its four-fold coordination upon addition of K_2O. Furthermore, Raman dehydration studies found no evidence of crystalline vanadium–potassium oxide compound formation in the 1% V_2O_5/1% K_2O/TiO_2 sample.

3.3. *Binary supported vanadium oxide catalysts (V_2O_5/M_xO_y)*

Raman [24,35], IR [24,45] and solid state ^{51}V NMR [22] spectra of dehydrated vanadium oxide catalysts reveal that the structures of the surface vanadium oxide species are essentially identical on ceria, zirconia, titania and alumina and possess a combination of isolated and polymerized mono-oxo VO_4 surface groups with similar ratios of the species at any given vanadium oxide surface coverage. Monolayer surface coverages for catalysts comprising vanadium oxide supported on various high surface area metal oxide supports correspond to ≈6% V_2O_5/TiO_2, 4% V_2O_5/CeO_2, 4% V_2O_5/ZrO_2, and 20% V_2O_5/Al_2O_3. A complete vanadia monolayer could not be formed on SiO_2 due to the weak interaction between the surface vanadia species and the silica support. The highest loading attained on the silica support without microcrystalline vanadium pentoxide particle formation was 4% V_2O_5/SiO_2 (≈1 V atom nm^{-2}). Furthermore, the V_2O_5/SiO_2 system is unique in possessing only isolated $(Si–O)_3V=O$ species [22].

4. Molecular structure–reactivity relationships

4.1. *Binary supported vanadium oxide catalysts (V_2O_5/M_xO_y)*

4.1.1. *Role of bridging V–O–V bonds*

Several recent in situ Raman studies have demonstrated that the ratio of bridging V–O–V bonds to terminal V=O bonds increases with surface vanadia coverage on oxide supports, with the exception of V_2O_5/SiO_2 which only possesses isolated surface vanadia species and no bridging V–O–V bonds [35]. Consequently, the role of V–O–V bridging bonds in oxidation reactions can be chemically probed by examining the reaction turnover frequency, TOF — the number of SO_2 molecules oxidized per surface vanadia site per second, as a function of surface vanadia coverage. The sulfur dioxide oxidation activity of V_2O_5/TiO_2 catalysts of variable loading (1–6% V_2O_5, corresponding to 0.16–1.0 theoretical monolayers (∼1.5–8 V atoms nm^{-2}) for a 50 $m^2 g^{-1}$ Degussa P-25 TiO_2 support) was determined between 200° and 400°C [18]. The magnitude of the turnover frequency for 1% V_2O_5/TiO_2 varied from 3×10^{-6} s^{-1} at 200°C to 1×10^{-4} s^{-1} at 400°C. The results showed that the turnover frequency is approximately constant as the surface vanadia loading is varied up to monolayer coverage. Therefore, the reactivity of titania supported vanadia catalysts for the oxidation of sulfur dioxide to sulfur trioxide is independent of the surface density of bridging V–O–V bonds, which indicates that these bonds do not play a critical role in the overall SO_2 oxidation kinetics. In addition, a reaction requiring two or more surface vanadia sites to proceed would exhibit higher turnover frequencies at higher surface coverages due to the increasing number of polymerized surface vanadia species present at higher surface coverages. Thus, the observation that the SO_2 oxidation turnover frequency does not increase with increasing surface coverage by surface vanadia species indicates that only one surface vanadia site is necessary for the SO_2 oxidation to proceed. In summary, the bridging V–O–V bonds do not play a critical role in SO_2 oxidation kinetics and only one surface vanadia site appears to be required for this reaction. Similar trends in TOF versus surface vanadia coverages were shown to exist for ceria, zirconia, alumina and silica supported vanadia catalysts.

4.1.2. Role of the terminal V=O bond

The terminal V=O bonds can also be directly monitored with in situ Raman spectroscopy during oxidation reactions. The vibrational frequency of the terminal V=O is directly related to its bond strength (stronger or shorter bonds vibrate at higher cm^{-1} and weaker or longer bonds vibrate at lower cm^{-1}) [35]. Sulfur dioxide oxidation experiments over several well-characterized supported vanadia catalysts (V_2O_5/(Al_2O_3, TiO_2, ZrO_2 or CeO_2)) revealed that while the catalysts possessed essentially the same terminal V=O bond strength (1025–1031 cm^{-1}), the SO_2 oxidation TOFs varied by more than an order of magnitude: $V_2O_5/CeO_2 > V_2O_5/ZrO_2$, $V_2O_5/TiO_2 > V_2O_5/Al_2O_3$ [18]. Consequently, the SO_2 oxidation TOFs do not correlate with the characteristics of the terminal V=O bond and suggests that this bond does not play a critical role in this oxidation reaction. A similar lack of correlation between the terminal V=O bond characteristics and propane, butane and methanol oxidation TOFs was also previously found [46–48].

4.1.3. Role of bridging V–O–support bonds

The sulfur dioxide oxidation reactivity is apparently related to the bridging V–O–M bond since changing the specific oxide support ligand alters the turnover frequency by more than an order of magnitude (V/Ce > V/Zr, V/Ti > V/Al) [18]. The only significant differences between the surface vanadia species on the various oxide supports are the oxide support ligands (e.g., Ce, Zr, Ti, or Al). The electronegativity of the oxide support cation affects the electron density on the bridging V–O–M oxygen: a lower cation electronegativity will result in a slightly higher electron density (more basic V–O–M oxygen) and a higher cation electronegativity will result in a slightly lower electron density (less basic V–O–M oxygen). An inverse correlation between the Sanderson electronegativities [49] of the oxide support cations and the sulfur dioxide oxidation turnover frequencies appears to exist; the lower the oxide support cation electronegativity the higher the sulfur dioxide oxidation turnover frequency [18]. Therefore, the more basic the bridging V–O–M bond the higher the activity towards SO_2 adsorption and subsequent oxidation of the acidic sulfur dioxide molecule. Conversely, a less basic bridging oxygen depresses the adsorption of sulfur dioxide and its oxidation. Thus, it appears that the catalysts exhibiting higher turnover frequencies contain a higher percentage of surface vanadia sites adsorbing sulfur dioxide and, subsequently, undergoing redox cycles under reaction conditions.

The above analysis may also be applied to other catalytic oxidation reactions over supported vanadia catalysts. The mechanism and kinetics of methanol oxidation to formaldehyde over vanadia catalysts have been extensively examined in recent years [50]. It has been proposed that methanol adsorbs at a bridging vanadium–oxygen–support (V–O–M) bond via protonation of the bridging oxygen (H–O–M) and formation of a methoxy (V–OCH_3) intermediate. The rate determining step is the subsequent breaking of a methyl C–H bond to form formaldehyde. The trend in turnover frequencies for oxidation of the mildly acidic methanol molecule (V/Ce > V/Zr, V/Ti > V/Nb > V/Al ≫ V/Si) follows the same pattern as that observed for sulfur dioxide oxidation and inversely correlates with the Sanderson electronegativities of the support cations.

4.2. Binary supported metal oxide catalysts (M_xO_y/TiO_2)

The sulfur dioxide oxidation turnover frequencies at 400°C (i.e., the number of SO_2 molecules oxidized per surface metal oxide site per second) of the binary catalysts tested were all within an order of magnitude ($V_2O_5/TiO_2 > Fe_2O_3/TiO_2 > Re_2O_7/TiO_2 \sim CrO_3/TiO_2 \sim Nb_2O_5/TiO_2 > MoO_3/TiO_2 \sim WO_3/TiO_2$) with the exception of K_2O/TiO_2, which is apparently inactive for sulfur dioxide oxidation under the selected reaction conditions. As metal oxide overlayer surface coverage was increased from ~0.15 to ~1.0 monolayer, the sulfur dioxide oxidation turnover frequency was approximately constant.

As discussed above, at low surface coverages (<0.2 monolayer) the dehydrated surface vanadium, chromium, rhenium, niobium, molybdenum and tungsten oxide species supported on titania generally tend to possess four-fold coordination and the absence of strong M–O–M Raman vibrations indicate that the surface species are predominately isolated. At high surface coverages (>0.6 monolayer), however, the coordination of the dehydrated surface metal oxide species depends on the specific metal oxide and strong Raman signals due to polymerized surface species are also usually present (surface vanadia, chromia, molybdena, tungsta and niobia). Four-fold coordination is preferred for surface rhenium oxide, chromium oxide and vanadium oxide species, while six-fold coordination is preferred for surface iron oxide, molybdenum oxide, tungsten oxide and niobium oxide species. The observation that the turnover frequency for SO_2 oxidation over all of these catalysts is approximately the same at both low and high surface coverages indicates that the mechanism of sulfur dioxide oxidation is not sensitive to the coordination of the surface metal oxide species. Furthermore, SO_2 oxidation occurs at similar rates over both isolated and polymerized surface metal oxide species, which is expected for a reaction requiring only one active site [18].

The redox properties of the titania supported metal oxide catalysts have also been probed with the partial oxidation of methanol to formaldehyde and followed a trend similar to that found for sulfur dioxide oxidation: $V_2O_5 \sim Re_2O_7 > CrO_3 \sim MoO_3 > Nb_2O_5 \sim WO_3 > K_2O$ [48,51–53]. The yield of selective oxidation products (e.g., formaldehyde, methyl formate, dimethoxy methane) for supported niobium oxide and tungsten oxide catalysts were approximately two orders of magnitude less than for supported vanadium oxide and rhenium oxide. Tungsten oxide was shown to increase the yield of acid products (e.g., dimethyl ether). In addition, a very similar trend was observed for methanol oxidation over niobia supported metal oxide catalysts ($V_2O_5 > CrO_3 > Re_2O_7 > MoO_3 > WO_3$) [37]. These trends indicate that V_2O_5/TiO_2, Re_2O_7/TiO_2, CrO_3/TiO_2, MoO_3/TiO_2 and to a lesser degree Nb_2O_5/TiO_2 and WO_3/TiO_2 possess surface redox sites which can efficiently catalyze sulfur dioxide oxidation to sulfur trioxide. The activities of the K_2O/TiO_2 catalysts ($<5 \times 10^{-7}\,s^{-1}$) are less than that exhibited by an unpromoted TiO_2 support ($\sim 2 \times 10^{-6}\,s^{-1}$) and indicate that the surface K_2O species do not undergo redox cycles at any appreciable rate under the chosen experimental conditions.

4.3. Ternary supported metal oxide catalysts ($V_2O_5/M_xO_y/TiO_2$)

The reactivity studies of the binary catalysts suggest that with the exception of K_2O, all of the surface species present in the ternary catalysts (i.e., oxides of V, Fe, Re, Cr, Nb, Mo and W) can undergo redox cycles and oxidize sulfur dioxide to sulfur trioxide to some extent. With the exception of $V_2O_5/K_2O/TiO_2$, a comparison of the activities of the ternary catalysts with the corresponding binary catalysts indicates that the vanadium oxide and the additive supported metal oxide surface redox sites are essentially acting independently without synergistic interactions, since the sum of the activities of the individual binary catalysts may be added to yield the activity of the corresponding ternary catalyst system [17]. The absence of synergistic interactions is expected for single-site reactions such as sulfur dioxide oxidation, whereas dual site reactions, e.g., SCR of NO_x with NH_3, will exhibit an increase in turnover frequency as surface coverage increases. The promotional effect for dual site reactions can be attributed to the increasing surface density of neighboring reaction sites as surface coverages approach monolayer. In contrast, the potassium promoted ternary catalyst deactivated the V_2O_5/TiO_2 catalyst by direct interaction of the K_2O with the surface vanadia species and reduction of its redox potential [26] caused by interaction of K^+ cations with the V–O–Ti bond [48].

The results found in this study concerning the sulfur dioxide oxidation activities of ternary ($V_2O_5/M_xO_y/TiO_2$) catalysts are in agreement with the observation of Morikawa et al. [7] that V_2O_5/TiO_2 catalysts promoted by WO_3 or MoO_3 exhibit higher rates of sulfur dioxide oxidation than unpromoted catalysts. Although the TOFs for WO_3/TiO_2 and MoO_3/TiO_2 are significantly lower than the TOF for V_2O_5/TiO_2. In the same study, Morikawa and coworkers found that vanadia catalysts promoted with either GeO_2

or ZnO exhibit a drastic decrease in SO_2 oxidation activity. Although no spectroscopic evidence was provided, the basic GeO_2 and ZnO molecules most likely complexed with the acidic vanadium oxide surface species and reduced their redox potentials as was seen to occur for the K_2O promoted V_2O_5/TiO_2 catalyst.

In contrast to the results found in the present study, Sazonova et al. [9] reported that the addition of high loadings of tungsten oxide to a V_2O_5/TiO_2 catalyst substantially suppresses sulfur dioxide oxidation activity. However, Sazonova et al. failed to recognize that for the loadings of surface vanadia (~3 monolayers) and tungsten oxide (~6 monolayers) species used in their study, the surface species are no longer molecularly dispersed and form WO_3 and V_2O_5 crystallites. Since no information about the structures or dispersions of the metal oxides was presented, it is not possible to clearly identify the reason for the decrease in oxidation activity, however, it is most likely due to the presence of the metal oxide crystalline phases, which are not much less active than the corresponding surface metal oxide species for redox reactions [18,35].

It has been proposed by Lietti et al. [54] that electronic interactions between neighboring surface vanadia and surface tungsten oxide sites on a titania support may lead to an increase in both SCR $DeNO_x$ and sulfur dioxide oxidation activities at temperatures below 230°C. This is based on the observation that the reactivity of a ternary (i.e., 1.4% V_2O_5/9% WO_3/TiO_2) catalyst in the SCR reaction is higher than that of the corresponding binary (i.e., 1.4% V_2O_5/TiO_2 and 9% WO_3/TiO_2) catalysts physically combined. Lietti et al. acknowledge that at temperatures above 230°C this synergism is due to both the increased Brönsted acidity and higher total surface coverage of the ternary catalyst relative to the binary catalysts, which allows the dual-site mechanism of the SCR reaction to proceed more efficiently. However, at temperatures below 230°C they propose that (1) the SCR rate determining step is the reoxidation of the reduced surface vanadia species and (2) the ternary catalyst possesses superior redox properties at these temperatures. The redox properties of the ternary $V_2O_5/WO_3/TiO_2$ catalysts at 200° and 230°C have been probed by the single-site sulfur dioxide oxidation [18] and selective oxidation of methanol to formaldehyde [35] reactions, respectively. However, neither study showed an increase in redox activity for the ternary catalyst with respect to the corresponding binary catalysts. Furthermore, the turnover frequency for the SCR $DeNO_x$ reaction (10^{-3} to $10^{-2}\,s^{-1}$) is intermediate between the turnover frequencies for sulfur dioxide oxidation ($10^{-6}\,s^{-1}$) and methanol oxidation ($10^{0}\,s^{-1}$) at 230°C over supported vanadia catalysts. Therefore, there does not appear to be any evidence for an electronic interaction between the surface vanadia and tungsten oxide species of the ternary catalyst, which allows redox reactions to proceed more efficiently.

5. Kinetics of SO_2 oxidation over supported vanadia catalysts

5.1. Effect of low SO_2 adsorption probability on reaction rate

The reason for the extremely low sulfur dioxide oxidation turnover frequencies exhibited by monolayer supported vanadia catalysts ($3.7\times10^{-6}\,s^{-1}$ for V_2O_5/SiO_2 to $2.2\times10^{-4}\,s^{-1}$ for V_2O_5/CeO_2 at 400°C [18]) may be either that: (1) the quantity of vanadium oxide–sulfur oxide surface complexes formed under reaction conditions is very low, however, once formed the surface complexes readily decompose to produce sulfur trioxide (low adsorption probability and fast rate determining step); (2) large numbers of stable surface complexes are formed, which slowly react to produce sulfur trioxide (high adsorption probability and slow rate determining step); or (3) small numbers of stable surface complexes are formed (low adsorption probability and slow rate determining step). As long as the surface coverage of adsorbed SO_2 species is not so high as to be limited by steric factors, the number of vanadium oxide–sulfur oxide surface complexes formed at a certain temperature, as determined by adsorption experiments, can be viewed as the maximum number of surface vanadia sites capable of simultaneously undergoing redox cycles at that temperature. The observation that the adsorption and oxidative adsorption of SO_2 onto monolayer supported vanadia catalysts at temperatures between 80° and 150°C is negligible rules out option (2) [55,56]. Thus, consistent with options (1) and (3) above, it appears that the low SO_2 oxidation turnover frequencies of monolayer supported vanadia catalysts may be due to a lack of surface vanadia sites adsorbing sulfur dioxide and undergoing redox cycles under reaction conditions (low adsorption probability). Since no data regarding the fundamental rate of vanadium oxide–sulfur oxide surface complex decomposition to products is currently found in the literature, it is not possible to distinguish between the options of fast or slow rate determining step.

5.2. *Effect of reaction environment*

Qualitative data detailing the effects of complicated reaction environments on SO_2 oxidation kinetics over industrial-type catalysts can be found in the literature [57]. Unfortunately, limited information is presented in these studies as to the effects of the various reaction gases on the structure of the surface vanadia species. Therefore, in an effort to relate reaction kinetics with well-characterized catalytic systems, the effects of only oxygen and sulfur oxide partial pressures on SO_2 oxidation kinetics will be addressed in detail since the effects of these gases on the molecular structures of supported vanadia catalysts are well understood.

5.2.1. *Effect of oxygen*

Several studies using a reaction gas mixture containing ≈1000 ppm of SO_2 have confirmed that when oxygen partial pressures are varied above 1 vol%, the rate of SO_2 oxidation over dehydrated vanadia catalysts is nearly constant (i.e., the reaction rate is independent (zero order) of the gas-phase oxygen partial pressure) [8,18,57]. When the oxygen partial pressure is varied between 0.1 and 1 vol% oxygen, the dependence of the rate of oxidation on the gas-phase oxygen partial pressure was seen to be approximately half-order [18]. Thus, in the case of industrial conditions traditionally experienced by supported vanadia catalysts (e.g., 2–6 vol% oxygen), the catalyst surface is essentially saturated with adsorbed oxygen and the surface vanadia species are essentially present in the V^{5+} state possessing dehydrated isolated and polymerized VO_4 structures.

5.2.2. *Effect of sulfur oxides*

The influence of sulfur dioxide partial pressure on the rate of oxidation requires a more complex analysis due to the presence of the product sulfur trioxide, which may compete with sulfur dioxide for adsorption on the surface vanadia species. The basicity of the bridging oxygen in the V–O–M bond appears to be responsible for influencing the adsorption of acidic molecules on the surface vanadia species. The electronic structures of sulfur dioxide and sulfur trioxide molecules in the gas phase indicate the electron deficiency of the sulfur atom and, consequently, the acidity of the sulfur in the resonance hybrid structure for sulfur trioxide (+2) is higher than that for sulfur dioxide (+1). As a result, sulfur trioxide will experience a greater attraction to the electrons of the bridging oxygen of the V–O–M bond, resulting in a preferential adsorption of sulfur trioxide. This results in a stronger bonding of sulfur trioxide to the surface vanadia species and, consequently, competitive adsorption with sulfur dioxide [18].

When product inhibition by sulfur trioxide is not taken into account, the apparent reaction rate dependence on gas-phase sulfur dioxide concentration for vanadia supported catalysts can be crudely fitted to a half-order dependence. However, assuming competitive adsorption of sulfur trioxide the rate dependence on sulfur dioxide concentration was shown to be first-order with a negative first-order dependence on sulfur trioxide. Thus, the SO_2 oxidation reaction over supported vanadia catalysts exhibits a first-order dependence on SO_2 partial pressures and a negative first-order dependence on SO_3 partial pressures [18].

5.2.3. *Effect of reaction temperature*

The temperature dependence of the oxidation of SO_2 to SO_3 over a series of supported vanadia catalysts was investigated using a reactant mixture of 1000 ppm SO_2, 18% O_2 and balance He. In view of the results previously discussed, the data were analyzed by assuming a differential plug-flow reactor model and a rate equation first-order in SO_2, zero-order in O_2 and negative first-order in SO_3:

$$r_{SO_2} = \frac{k[SO_2][O_2]^0}{[SO_3]} \tag{1}$$

The apparent activation energy of 21 ± 2 Kcal/mol was approximately constant as surface vanadia coverage on a titania supported catalysts was varied between 0.16 and 1.0 theoretical monolayers (1.5–8 V atmos nm^{-2}) [18]. Essentially the same activation energy was found for SO_2 oxidation over ceria, zirconia, alumina and silica supported vanadia catalysts.

6. Mechanism of SO_2 oxidation over supported vanadia catalysts

Numerous mechanisms for the oxidation of SO_2 over supported V_2O_5/TiO_2 catalysts have been proposed [8,18,57]. Forzatti and coworkers proposed that the active site for the oxidation of sulfur dioxide over V_2O_5/TiO_2 catalysts involved a dimeric vanadia sulfate species [57], which is in disagreement with the findings of Wachs and coworkers that SO_2 oxidation requires only a single vanadia surface site [18]. The inability of the currently available spectroscopic techniques to elucidate the molecular structure of the vanadium oxide–sulfur oxide surface complexes, which must be formed under reaction conditions, prevents the validation of any one of these mechanisms. Furthermore, the failure of thermal techniques (e.g., TGA and TPD) to provide information regarding the rates of adsorption and desorption of SO_2 and SO_3 on the active vanadia sites prevents a clear determination of the rate determining step of the SO_2 oxidation reaction over these catalysts. It has been proposed that in situ spectroscopic studies of the SO_2 oxidation reaction over monolayer supported vanadia catalysts using isotope-exchanged reactants (e.g., $^{18}O_2$, $S^{18}O_2$, $S^{18}O_3$, etc.) may be able to clarify some of the issues that must be addressed before a sound proposal for a mechanism can be made [20].

However, based on the currently available kinetic information it is possible to theorize a general reaction pathway for SO_2 oxidation over supported vanadia catalysts [18]. Sulfur dioxide may adsorb and coordinate onto the vanadium–oxygen–support (V–O–M) bond of either isolated or polymerized surface $(M\text{–}O)_3V^{+5}{=}O$ sites resulting in either the $(V^{+5})\cdot SO_2$-ads or the $(V^{+3})\cdot SO_3$-ads state. This is followed by the cleavage of the $V^{+5}\text{–}O\text{–}SO_2$ or $M\text{–}O\text{–}SO_2$ bond and formation of $SO_{3(g)}$, which represents the rate determining step. The electron deficiency and, consequently, the acidity of the sulfur in the resonance hybrid structure for SO_3 (i.e., +2) is higher than that for SO_2 (i.e., +1). As a result, sulfur trioxide will experience a greater attraction to the electrons of the bridging oxygen of the V–O–M bond, resulting in a preferential adsorption of SO_3. This results in a stronger bonding of SO_3 to the surface vanadia species and, consequently, competitive adsorption on (V^{+5}) sites. The reduced vanadia site is then reoxidized by dissociatively adsorbed oxygen, thereby regenerating the active (V^{+5}) sites.

7. Molecular design of air pollution control catalysts

The insights generated from this research can potentially assist in (1) the development of catalysts for low temperature (200–300°C) oxidation of SO_2 to SO_3 during sulfuric acid manufacture, (2) the design of efficient SCR $DeNO_x$ catalysts with minimal SO_2 oxidation activity and (3) improvements in additives for the simultaneous oxidation/sorption of sulfur oxides in petroleum refinery operations.

7.1. Low-temperature sulfuric acid catalysts

As this research has shown, conventional supported vanadia catalysts are sulfur tolerant and can potentially operate efficiently in the 200–300°C temperature range, possibly offering an alternative to the current molten-salt sulfuric acid contact catalyst. Reactivity studies have shown that V_2O_5/CeO_2 catalysts exhibit high activity towards the oxidation of SO_2 to SO_3. Therefore, if regulatory pressures force a reduction in sulfur oxide emissions from sulfuric acid manufacturers, monolayer V_2O_5/CeO_2 catalysts will offer an alternative to the commercial $V_2O_5/K_2S_2O_7/SiO_2$ contact catalyst as a tail-end (clean-up) catalyst, however further optimization of the structural (e.g., abrasion resistance) and reactivity (e.g., enhanced oxidation rates through optimization of catalyst surface area and pore structure), characteristics of the V_2O_5/CeO_2 catalyst must be performed before this catalyst will show substantial advantages over the commercial sulfuric acid contact catalyst.

7.2. Low-temperature $DeNO_x$ catalysts

One of the primary impediments in the development of low-temperature (e.g., 200–300°C) SCR catalysts is the reaction between ammonia and sulfur trioxide to form ammonium sulfates, which readily deposit on the catalyst surface at temperatures below 250°C. In order to design low-temperature SCR catalysts, it is necessary to identify catalysts that can efficiently promote the SCR reaction without significantly increasing the oxidation of sulfur dioxide. Amiridis et al. [58] conducted a systematic investigation of the SCR activity of several of the ternary catalysts which were also evaluated above (e.g., $V_2O_5/Fe_2O_3/TiO_2$, $V_2O_5/Nb_2O_5/TiO_2$, $V_2O_5/MoO_3/TiO_2$ and $V_2O_5/WO_3/TiO_2$). Catalysts promoted with molybdenum oxide or tungsten oxide showed the highest SCR activities in the presence of nitric oxide, ammonia, oxygen, sulfur dioxide and water. Niobium oxide and iron oxide promoted catalysts only showed a slight increase in catalytic activity in relation to the binary V_2O_5/TiO_2 catalyst. Amiridis et al. concluded that the promotional effect on SCR activity induced by the surface tungsten oxide and surface molybdenum oxide additives may be due to the increased Brönsted acidity exhibited by these surface metal oxide species. These studies suggest that tungsten oxide is the most efficient additive for V_2O_5/TiO_2 catalysts at promoting the selective catalytic reduction of nitric oxide and simultaneously exhibiting low activity towards the oxidation of sulfur dioxide to sulfur trioxide.

Wachs et al. [59] recently found that the turnover frequency of 1% Re_2O_7/TiO_2 catalysts was approximately twice as that of a 1% V_2O_5/TiO_2 catalyst for the selective catalytic reduction of nitric oxide with ammonia ($3.2 \times 10^{-4}\,s^{-1}$ vs. $1.7 \times 10^{-4}\,s^{-1}$ at 200°C). However, the selectivity for N_2 formation was depressed for the Re_2O_7/TiO_2 catalyst relative to V_2O_5/TiO_2 ($\sim$70% vs. $\sim$100%). This observation, coupled with the present observation that the sulfur dioxide oxidation turnover frequency of Re_2O_7/TiO_2 is less than half that of V_2O_5/TiO_2, suggests that a catalyst containing low loadings (0.1–0.2 monolayer) of surface rhenium oxide and higher loadings (0.7–0.9 monolayer) of surface tungsten oxide may be an efficient low-temperature SCR catalyst.

7.3. Petroleum refinery SO_x-reduction additives

Reactivity studies have shown that V_2O_5/CeO_2 catalysts exhibit high activity towards the oxidation of SO_2 to SO_3. However, it was also observed that a monolayer V_2O_5/CeO_2 catalyst experiences a drastic (>95%) loss in SO_2 oxidation activity after several hours of exposure to a flowing SO_2 and oxygen containing stream at 400°C, due to the transformation of the highly-active surface vanadia monolayer and formation of less active bulk cerium sulfate and cerium vanadate compounds [18,60]. Although this would seemingly suggest that monolayer V_2O_5/CeO_2 is inappropriate for most air pollution control applications, it appears that V_2O_5/CeO_2 is well suited for application as a SO_x adsorbent in FCC applications. The short residence times of FCC regenerators (<5 s) should be insufficient to cause substantial reductions in catalytic activity. In addition, the ability of V_2O_5/CeO_2 catalysts to form bulk-like cerium-oxy-sulfur compounds is advantageous in SO_x transfer where the oxidation activity of the vanadia species is secondary to the catalyst's ability to adsorb quantities of sulfates larger than can be provided by monolayer surface coverage (40+ wt% SO_4 [61] vs. 3 wt% SO_4). These findings suggests that monolayer V_2O_5/CeO_2 catalysts may be effective components in SO_x transfer additives.

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