Effects of sulfate species on V_2O_5/TiO_2 SCR catalysts in coal and biomass-fired systems

Xiaoyu Guo, Calvin Bartholomew, William Hecker, Larry L. Baxter *

Department of Chemical Engineering, Brigham Young University, 350 Clyde Building, Provo, UT 84602, USA

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ABSTRACT

Sulfation occurs when commercial vanadia SCR catalysts are exposed to SO_2-laden coal combustion flue gases. Effects of sulfation on the surface chemistry of vanadia/titania catalysts and SCR activity have not been adequately addressed in previously published work. In this work, *in situ* FTIR spectroscopy and *post situ* XPS investigations were performed during vanadia/titania catalyst sulfation under simulated coal combustion flue gas conditions. *In situ* FTIR spectroscopy combined with XPS analyses on fresh and sulfated TiO_2, 2% and 5% V_2O_5/TiO_2 indicate that sulfate does not form on vanadia sites but rather on titania sites. FTIR spectroscopy data show that sulfation inhibits NO adsorption in the presence of oxygen, but greatly enhances NH_3 adsorption by generating additional Brønsted acid sites while reducing the concentration of Lewis acid sites. Observed increases in the intrinsic NO reduction activity of sulfated vanadia/titania catalysts (relative to fresh catalysts) are consistent with spectroscopy data showing that the sulfation enhances NO reduction activity by increasing the number of active sites without changing the activation energy or site acid strength.

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1. Introduction

Selective catalytic reduction (SCR) of NO_x with NH_3 over vanadia/titania catalysts represents the most widely used and efficient post-combustion technique for reducing NO_x emissions from stationary combustion sources sufficient to meet stringent emission regulations. In most stationary combustion processes, SO_2 forms by oxidation of sulfur present in the fuel. SO_2 is the equilibrium sulfur species at high-temperature, oxidizing conditions. At flue gas temperatures, SO_3 is more stable than SO_2 but its formation is strongly kinetically limited. SCR catalysts designed to promote NO_x reduction to N_2 commonly also promote SO_3 formation. In a typical SCR process, SO_3 can react with the ammonia reducing agent, leading to the formation of ammonia sulfate and bisulfate. Ammonia bisulfate is an undesirable product because it forms small acidic and corrosive particles that can plug small passages in the air heater, cause fouling of the catalyst surface, and plug catalyst pores.

Surface sulfate species also form when gas-phase SO_3 interacts with SCR catalyst surface species, including vanadium and titanium oxide, or other catalyst components. Previous investigations indicate that sulfur species either enhance or reduce catalyst activity [1,2]. Brønsted acid sites, the suggested active centers, are

reportedly strengthened with the formation of surface sulfates, which in turn increase and stabilize catalyst activity [3]. On the other hand, calcium sulfate, formed when sulfur oxides react with free CaO present in flyash of coal combustion processes, reportedly masks the catalyst surface and thereby deactivates the catalyst by limiting reactant gas access to the catalyst interior surface [4].

Previous investigations of SO_2 interactions with vanadia/titania catalysts have been limited in scope and accordingly fail to provide a consistent picture of the chemistry of surface sulfur species and their effects on catalytic activity. For example, there is no consensus regarding the mechanisms of formation, location, and chemical structure of SO_x (SO_2, SO_3, sulfate species) adsorbed on vanadia/titania catalysts, and how sulfate species influence active sites and catalyst activity [5,6]. Orsenigo et al. [5] compared effects of sulfation on NO_x reduction and SO_2 oxidation activities, suggesting that sulfation occurs first on vanadia sites and later on titania and tungsta sites. However, these conclusions were drawn in the absence of confirming experimental evidence from surface science methods. Dunn et al. [6], Choo et al. [7], and Amiridis et al. [8] investigated the correlation between sulfation and vanadia/titania catalyst performance; and Chen and Yang [9] investigated SCR activity on sulfated TiO_2. However, these investigations were performed either on vanadia catalysts with artificially introduced sulfate species by impregnation [6–8]; or on *in situ* sulfated TiO_2 but not vanadia catalysts [9]. It is questionable if impregnated sulfate species in the catalyst are representative of sulfate species formed during the SCR reaction in the presence of

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* Corresponding author. Tel.: +1 801 422 8616; fax: +1 801 422 0151.
E-mail address: larry_baxter@byu.edu (L.L. Baxter).

SO_2. It was also unclear from those works if surface species monitored *ex situ* are the same as those formed under *in situ* conditions.

To address the above issues, we designed and completed a systematic *in situ* experimental investigation of sulfation on vanadia/titania SCR catalyst performance. *Operando* FTIR spectroscopy was applied for monitoring surface species during sulfation, while *ex situ* XPS analyses determined elemental composition and the oxidation states on both non- and sulfated vanadia catalysts. The combination of *in situ* FTIR and *ex situ* XPS techniques reveals (1) details regarding the chemical speciation of the catalyst surface, (2) a better understanding of the effects of surface sulfate species on SCR catalyst performance, and (3) further insights into the reaction and deactivation mechanisms. Effects of catalyst sulfation on BET surface area and porosity, NH_3 and NO adsorption capacities, NO_x reduction activity, and concentration and temperature dependencies of SCR catalysts were also investigated. The results of these experiments shed new light on (1) the chemical nature of surface sulfate sites, (2) the mechanism and extent of sulfate activity enhancement of catalyst NO_x reduction activity, and (3) the SCR reaction mechanism.

2. Experimental

2.1. Catalyst preparation

Titanium dioxide (P25, Degussa) was densified by mixing with distilled water at 1:1.75 weight ratio and dried at 120 °C for 24 h followed by calcination at 600 °C for 4 h. The densified titanium dioxide was then ground with an agate mortar and pestle into a fine powder.

Vanadia/titania catalysts were prepared by incipient impregnation using ammonium metavanadate (>99.5%, Fisher Scientific) as the active component precursor to achieve nominal metal loading of 1, 2, and 5 wt.%, all of which are below monolayer coverage since monolayer coverage is reached at 6 wt.% [8]. The precursor was added in a stoichiometric ratio into a warm (50 °C) oxalic acid solution, resulting in a deep blue solution. After the precursor solution cooled down, titania powder was added to it. The slurry thus formed was dried at 120 °C for 8 h while stirring to evaporate most of the water, followed by calcination at 550 °C for 6 h. After calcination, the catalyst was ground with an agate mortar and pestle to a fine powder.

2.2. A In situ FTIR spectroscopy

Infrared spectra were obtained using a Nicolet 730 FTIR spectrometer with an MCT detector. Circular, self-supported, thin catalyst wafers with 1.5 cm diameter were prepared by pressing 80 mg of sample. The catalyst wafer was mounted in a reactor cell depicted in Fig. 1. The reactor cell allowed reactant gases to pass across both wafer surfaces. Prior to collecting spectra, samples were pretreated in a high-purity flow of 5 wt.% O_2/He at 380 °C for 2 h. The background spectrum was recorded in flowing helium and was subtracted from the sample spectrum. In the experiment, the *in situ* IR spectra were recorded by accumulating 75 scans at a spectral resolution of 2 cm^{-1}.

2.3. Surface sulfation

The sulfation was conducted on TiO_2, 2 and 5 wt.% V_2O_5/TiO_2 with a gas composition of 2700 ppm SO_2, 5% O_2, 0 or 4% water vapor, and helium. Moisture was introduced by passing purified helium through a bubbler. Sulfation was carried out at 1 atm and 380 °C. *In situ* FTIR spectra were collected during sulfation with CaF$_2$ and KCl windows to prevent the flowing gases from diffusing
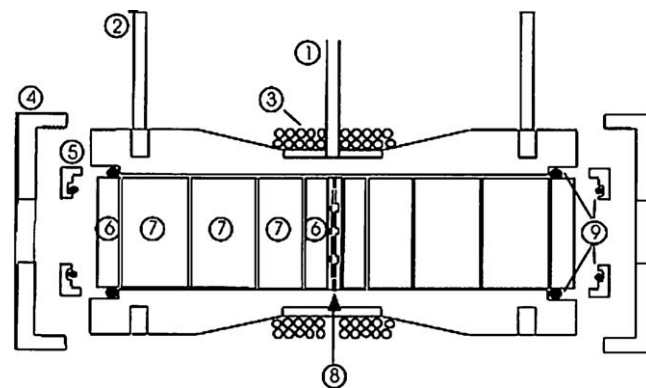

Fig. 1. Schematic diagram of the *in situ* IR reactor cell: (1) thermocouple port; (2) water cooling ports; (3) thermocoax heating cable; (4) end caps; (5) Teflon window holders; (6) CaF$_2$ windows; (7) KCl windows; (8) aluminum wafer holder; (9) Nitrile (large) and Kalrez (small) O-rings. Not shown are the gas inlet and outlet ports, located on either side of the reactor near (6) coming out of the page.

into the rest of the cell. CaF$_2$ was placed next to the catalyst pellet since it is inert to SO_2 and SO_3 containing gases. Additional KCl or NaCl windows also provided thermal insulation for the heated cell. CaF$_2$ windows were chosen for *in situ* FTIR monitoring due to their inertness to sulfation. Since, however, CaF$_2$ blocks IR radiation below 1100 cm^{-1}, a NaCl window was used for already-sulfated samples, since NaCl transmits IR below 1100 cm^{-1} (but above 625 cm^{-1}).

2.4. NH_3 and NO adsorption

Ammonia or NO adsorptions on the catalyst wafer were monitored by *in situ* FTIR spectroscopy. After pretreatment (Section 2.2), the temperature was decreased to 50 °C and room temperature for ammonia and NO adsorptions, respectively.

During NH_3 or NO adsorption, 1000 ppm NH_3 in helium (50 ml/min) or 1000 ppm NO in argon (95 ml/min) was introduced continuously for 1.0 h to ensure complete saturation of the sample. NH_3 or NO was then replaced by helium (50 ml/min) to purge the system for another hour to eliminate effects from physically adsorbed species. Subsequently, FTIR spectra were recorded. It was found that the amounts of NH_3 and NO adsorbed on the catalyst changed little before and after purging with helium.

2.5. X-ray photoelectron spectroscopy (XPS)

XPS is a surface sensitive analytical technique providing compositional data and elemental oxidation states in the outer 1–20 nm of a surface, with a minimum detection limit of 0.5 atomic %. XPS spectra were collected using an SSX-100 ESCA from an area 800 μm × 800 μm in size, using a monochromatised Al Kα (1486.7 eV) X-ray beam. All spectra were collected at a pressure of 5×10^{-9} Torr and a power consumption of 200 W. The instrument was regularly calibrated to the Au 4f$_{7/2}$ peak at 84.0 eV. Spectra are charge corrected to the main line of the C 1s spectrum set to 285.0 eV. Surface elemental composition and oxidation state were calculated using XPS instrument software.

2.6. Activity measurements

Activity data were collected in the intrinsic reaction regime and are thus truly represent surface reaction kinetics with negligible impacts from film and pore diffusion. In this investigation, catalyst activity measurements were carried out on 1 wt.% V_2O_5/TiO_2 in a temperature range of 250–300 °C to ensure intrinsic kinetics. These conditions correspond to Thiele modulus (M_T) of about 0.25