



## Experimental and kinetic study of SO<sub>2</sub> oxidation on a Pt/γ-Al<sub>2</sub>O<sub>3</sub> catalyst



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### ABSTRACT

An SO<sub>2</sub> oxidation experimental study was performed and a kinetic model was developed to describe SO<sub>2</sub> oxidation over a Pt/γ-Al<sub>2</sub>O<sub>3</sub> oxidation catalyst. An apparent activation energy of 98.8 kJ mol<sup>-1</sup> was measured when SO<sub>3</sub> was present in the feed. Reaction orders of 0.88 and -0.24 were obtained for SO<sub>2</sub> and O<sub>2</sub>, respectively, and the SO<sub>3</sub> reaction order was found to be -0.42. A microkinetic model based on a Langmuir-Hinshelwood mechanism was proposed and a one dimensional steady-state model was developed. A plug flow reactor model was assumed and the set of algebraic differential equations was solved at various temperatures to predict the SO<sub>2</sub> conversion as a function of temperature. The relative importance of each step in the reaction mechanism was studied at different temperatures to identify the rate determining step (RDS). According to the model, at temperatures below 300 °C, O<sub>2</sub> adsorption/desorption and the surface reaction between the adsorbed SO<sub>2</sub> and oxygen control the overall rate, whereas at higher temperatures the surface reaction is the RDS. The model predictions imply that, at low temperatures, SO<sub>3</sub> inhibits SO<sub>2</sub> oxidation through occupation of the active sites required for oxygen adsorption, verifying the higher activation energy observed in the presence of SO<sub>3</sub> in the feed. The modeling results revealed that the relative importance of the individual rates in the mechanism as well as the surface coverages were strongly temperature dependent.

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### 1. Introduction

Sulfur is a common poison for automotive catalysts. For example, sulfur oxides in diesel engine exhaust interact with the diesel oxidation catalyst (DOC) as well as other aftertreatment catalysts leading to performance loss over time [1]. A number of studies have focused on sulfur interactions with DOCs [1–3] and its effect on NO oxidation activity [4–6] and oxidation of other emissions [7,8]. In those investigations, sulfur interactions with the metal, metal oxides, as well as the catalyst support have been studied using experimental and computational methods. However, few studies have focused on the SO<sub>2</sub> oxidation reaction itself. DOC SO<sub>2</sub> oxidation kinetics would of course enable prediction of residual SO<sub>2</sub> and product SO<sub>3</sub> concentrations exiting the catalyst, which in turn could be used to determine deactivation rates of downstream catalyst systems.

Modeling of SO<sub>2</sub> interactions with Pt-based catalysts has been studied, however, mostly for lean NO<sub>x</sub> trap (LNT, or NO<sub>x</sub> storage/reduction (NSR)) catalysis in terms of diesel automotive

applications. Olsson et al. [9] studied sulfur poisoning and regeneration of a Pt-containing LNT. They developed a kinetic model that included sulfur deactivation of the LNT, which accounted for sulfur poisoning, regeneration of the catalyst for NO<sub>x</sub> trapping and sulfur release. Their sulfur sub-model contained steps for SO<sub>2</sub> adsorption on two sites, barium and alumina, and the subsequent oxidation to form sulfates. It was suggested that sulfur poisoning might occur on both Ba and alumina, with the poisoned Ba sites leading to NO<sub>x</sub> storage loss [9]. Dawody et al. [10] studied the effect of SO<sub>2</sub> exposure conditions on sulfur accumulation on Pt/SiO<sub>2</sub> as well as its impact on the NO<sub>x</sub> storage/reduction performance of a Pt/BaO/Al<sub>2</sub>O<sub>3</sub> LNT and BaO/Al<sub>2</sub>O<sub>3</sub>. It was found that both SO<sub>2</sub> exposure in combination with O<sub>2</sub> or H<sub>2</sub> caused deactivation of the NO<sub>x</sub> storage capacity of the NSR samples, but they noted that exposure to SO<sub>2</sub> with H<sub>2</sub> increased the formation of sulfur-containing species on the samples. Moreover, it was shown that the presence of Pt enhanced the adsorption of SO<sub>2</sub> under all exposure conditions [10]. In another study performed by Dawody et al. [11], a kinetic model was developed that included SO<sub>2</sub> interactions with a NSR catalyst. The model consisted of six sub-models: (i) NO<sub>x</sub> storage under sulfur-free conditions; (ii) SO<sub>2</sub> storage on NO<sub>x</sub> storage sites; (iii) SO<sub>2</sub> oxidation over platinum sites; (iv) SO<sub>3</sub> storage as bulk sulfates on both barium and alumina bulk sites; (v) SO<sub>2</sub> interaction

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## Nomenclature

$a_j$	active site density for reaction $j$ (mol site $m^{-3}$ )
$A$	face area ( $m^2$ )
$\vec{c}_s$	vector of molar concentrations of trace species at catalyst surface (mol $m^{-3}$ )
$F$	function to specify surface coverages ( $s^{-1}$ )
$k_{m,i}$	mass transfer coefficient for species $i$ (mol $m^{-2} s^{-1}$ )
$r_j$	rate of production of reaction $j$ (mol mol site $^{-1} s^{-1}$ )
$S_{ij}$	stoichiometric coefficient of species $i$ in reaction $j$
$S$	surface area per reactor volume ( $m^{-1}$ )
$t$	time (s)
$T_g$	temperature of bulk gas phase (K)
$T_s$	temperature of solid phase (K)
$w$	molar flow rate (mol $s^{-1}$ )
$x_{g,i}$	mole fraction of species $i$ in bulk gas phase
$x_{s,i}$	mole fraction of species $i$ in gas at catalyst surface
$X_{SO_2}$	outlet $SO_2$ conversion (%)
$z$	axial position (m)
$\vec{\theta}$	vector of surface coverages

with platinum in the presence of  $H_2$ ; and (vi) oxidation of accumulated sulfur compounds on platinum by  $NO_2$ . Their model was able to describe the main features in the experiments such as the decrease in the  $NO_x$  storage performance after exposure to sulfur.

Many research groups have studied  $SO_2$  oxidation over vanadium-based catalysts [12–16], with fewer evaluating Pt-based catalysts, however, these investigations mainly focus on  $SO_2$  oxidation under conditions applicable to sulfuric acid production, i.e. with high concentrations of  $SO_2$  (percent levels), and not those relevant to automotive emissions (ppm levels). For example, Benzinger et al. [17] investigated  $SO_2$  oxidation kinetics over Pt in a micro-structured reactor. They performed a detailed mechanistic study and numerically simulated  $SO_3$  formation in a single channel configuration. Good agreement was observed between their simulation results and the experimental data. A rate determining step sensitivity analysis on the reaction steps showed that the adsorption/desorption of  $SO_2$  and the surface reaction between the adsorbed species were similar under their experimental conditions. Therefore, they suggested that the rate determining step could change depending on the experimental conditions. In work performed by Sharma et al. [18], a microkinetic model for  $SO_2$  oxidation on Pt was proposed with an ultimate goal of understanding the DOC– $SO_x$  interactions. They considered 12 reversible catalytic reactions and five surface species ( $S^*$ ,  $O^*$ ,  $SO^*$ ,  $SO_2^*$  and  $SO_3^*$ ) with some kinetic parameters taken from the literature and some calculated using semi-empirical methods. Steady-state isothermal PFR simulations were performed and the model predictions were compared to the experimental data of a Pt/SiO<sub>2</sub> coated monolith. Two kinetic parameters were adjusted in their model and a further validation was carried out against  $SO_2$  conversion experimental data with a Pt/TiO<sub>2</sub> catalyst. Fair agreement between the model predictions and experimental data was observed. The reversible surface reaction between the adsorbed species was identified as the most important reaction step based on their sensitivity analysis. However,  $SO_3$  adsorption/desorption showed the largest sensitivity at low temperatures (250 °C) [18].

$SO_2$  adsorption on a Pt(111) surface and reactivity of the adsorbed sulfur species has been widely studied using different spectroscopic techniques [6,19–24]. First principles density functional study regarding  $SO_2$  binding and oxidation on Pt has also been performed [25–27]. Lin et al. [25] performed DFT calculations and predicted that on an O precovered Pt(111) surface, the

activation barrier for an assumed Eley-Rideal mechanism was less than that for the Langmuir-Hinshelwood reaction. However, they suggested that the actual mechanism of sulfur oxidation might be highly sensitive to environmental conditions due to the large sensitivity of the surface thermodynamics to oxygen coverage on Pt as well as the stability of surface-bound  $SO_4$  under highly oxidizing conditions [25].

In the present work, a  $SO_2$  oxidation model was built using data obtained from experiments with a monolithic Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst. As a starting point in developing the kinetic model, the kinetic scheme presented in Dawody et al. [11] was assumed. A systematic optimization methodology, previously reported in the literature [28], was used to estimate the rate coefficients using experimental data. A separate set of experimental data was used to verify the accuracy of the model. The relative importance of each step in the reaction mechanism was evaluated at different temperatures to identify the rate determining step (RDS).

## 2. Experimental methodology

### 2.1. Catalyst and reactor descriptions

The Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst used in this study was provided by Johnson Matthey in monolithic form. The monolith had a platinum loading of 50 g/ft<sup>3</sup>, an Al<sub>2</sub>O<sub>3</sub> loading of  $\sim 1.6$  g/in<sup>3</sup>, and a cell density of 325 channels/in<sup>2</sup>. A monolithic core of 1.96 cm diameter and 3.68 cm length with a cross section of 130 cells was used in the bench reactor experiments. High temperature insulation was wrapped around the sample in order to block the space between the monolith and the wall of the reactor to minimize the gas flow bypassing the catalyst. The catalyst sample was inserted into a quartz tube reactor and small glass tubes, 2.5 mm i.d. and 3 mm o.d., were placed upstream of the sample to ensure mixing and uniformity of the gas flow. The reactor assembly was placed in a temperature controlled furnace. For temperature measurements, three thermocouples were inserted at different locations inside the reactor. One thermocouple was located upstream of the catalyst, the two others were placed inside the sample, one close to the inlet face and the other close to the outlet face, all radially centered. MKS mass flow controllers were used to meter the gas flow rates and to set the desired gas concentrations. The inlet and outlet gas lines were heated to 150–200 °C in order to enhance temperature uniformity of the monolith and to prevent deposition of sulfur species in the lines. For experiments that required  $SO_3$  in the feed,  $SO_2$  and  $O_2$ , were metered into an upstream reactor which consisted of another monolith core of Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. This catalyst was loaded in a 1 in diameter stainless steel tube reactor which was placed in a ceramic heater. A low flow rate, 300 ml/min with a space velocity of 3700 h<sup>-1</sup> along with a relatively high temperature, i.e. in the range of 350–400 °C, were used such that complete conversion of  $SO_2$  to  $SO_3$  was achieved. An appropriate concentration of  $SO_2$ , balanced in  $O_2$ , was selected according to the desired  $SO_3$  concentration in the main reactor, and metered through the catalyst core. This upstream reactor outlet was then added to the main feed stream and fed to the quartz tube reactor.

A MKS MultiGas MG-2030 FT-IR analyzer was used for the gas phase concentration measurements. The instrument was set to measure a data point every 0.5 s at a resolution of 0.5 cm<sup>-1</sup>. Due to the interfering peaks of  $SO_2$  and  $SO_3$  in the IR absorption spectra, an accurate calibration method needed to be used for the  $SO_2$  and  $SO_3$  measurements. This calibration method was created by removing the overlapping regions of the  $SO_2$  and  $SO_3$  IR absorption spectra from the analysis band which is used for their quantification. Frequency ranges of 1294–1363 cm<sup>-1</sup> and 1389–1426 cm<sup>-1</sup> were selected as analysis bands in the  $SO_2$  and  $SO_3$  calibration meth-

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