



# SO<sub>2</sub> adsorption and desorption characteristics of Pd and Pt catalysts: Precious metal crystallite size dependence

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## ABSTRACT

SO<sub>2</sub> adsorption and desorption on Pt/Pd mono- and bimetallic,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supported catalysts were characterized. There are dependencies on both particle size and Pd:Pt ratio, and here particle size effects on the adsorption and desorption trends and surface species formed were evaluated using DRIFTS and TPD studies. Catalysts with a smaller particle size tended to form a greater amount of aluminum sulfate species, which decomposed at high-temperature. In contrast, catalysts with larger particle sizes tended to form a greater amount of low-temperature decomposing and desorbing species, such as molecular SO<sub>2</sub> and surface aluminum sulfite. In general, it was found that the amount of SO<sub>2</sub> adsorbed and later desorbed during TPD decreased with increasing particle size.

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## 1. Introduction

Natural gas, which primarily consists of methane, is commonly viewed as a lower emission producing fuel in comparison to gasoline and diesel [1]. Any methane that is not combusted in the engine needs to be managed to mitigate methane emissions. This methane can be combusted over an oxidation catalyst placed in the exhaust stream [2–5]. Natural gas vehicle exhaust temperatures can be as low as 300 °C [1,6], making complete conversion challenging. The exhaust can also contain sulfur, a poison to many oxidation catalysts. Even trace sulfur can result in deactivating the catalyst and reducing the extent of methane conversion [7].

Researchers found that alumina-supported bimetallic Pt/Pd catalysts resulted in higher activity with time on stream in comparison to monometallic Pt and Pd catalysts [7,8]. This improvement was maintained when exposed to sulfur [7] and water [7,8]. Electron micrographs of fresh Pd<sub>0.65</sub>Pt<sub>0.35</sub>/Al<sub>2</sub>O<sub>3</sub> samples displayed evidence of very small particles in Pt-rich regions and large particles in Pd-rich regions. After these catalyst samples were aged in steam at 600 °C, only large particles were observed. The authors concluded that the Pt-containing catalysts sintered when exposed to steam at high temperatures [8]. Researchers also found that smaller Pd particles are more easily oxidized to form PdO in comparison to larger Pd

particles [9], and for Pt-based catalysts, oxygen adsorbed on larger Pt particles is more reactive than oxygen on smaller Pt particles [10]. For these reasons, sintered Pt particles can be more active for complete methane oxidation [10] whereas the PdO activity decays upon sintering [11] resulting in less methane conversion. In high-Pd content bimetallic catalysts, the interaction between PdO and Pt weakens the Pd-O bond such that PdO forms at higher temperatures and decomposes at lower temperatures in comparison to the PdO in monometallic Pd catalysts. This feature also affects how easily the PdO surface forms oxygen vacancies, which are known to promote PdO activity in the methane oxidation reaction. Lapisardi et al. postulated that bimetallic catalysts are more resistant to sintering because these oxygen vacancies are made with greater ease for bimetallics than those for monometallic Pd [8]. These results form some basis in evaluating thermal degradation effects. However, the relationship between sulfur poisoning impact and particle size has not been studied.

The work discussed in this paper focuses on what species are formed during Pd and Pt catalyst exposure to SO<sub>2</sub> and their stability as a function of temperature. Initial experiments demonstrated that in order to understand why sulfur release characteristics varied with precious metal (PM) particle size, it was imperative that the Pd:Pt mole ratio contribution be decoupled. For this reason, the sulfur release characteristics due to particle size effects were studied independently by conducting SO<sub>2</sub> adsorption and temperature-programmed desorption (TPD) studies on catalysts with the same Pd:Pt mole ratios.

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## 2. Experimental methods

### 2.1. Catalyst preparation and experimental set-up

The 40% Pd-basis Pd(NO<sub>3</sub>)<sub>2</sub> and 99.995% trace metals basis Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> precursors as well as the Puralox  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> TH 100/150 were purchased from Sigma-Aldrich. The incipient wetness impregnation method was used for powder catalysts synthesis. The total number of precious metal moles was kept constant for all catalysts using a 1 wt.% Pd/Al<sub>2</sub>O<sub>3</sub> catalyst as a basis of reference for precious metal content. All samples were dried overnight and calcined in air at 550 °C. A bimetallic sample, Pd<sub>0.5</sub>Pt<sub>0.5</sub>/Al<sub>2</sub>O<sub>3</sub>, was also prepared, using co-impregnation with the same precursors and procedure.

Each catalyst bed consisted of active catalyst and inert beads. To achieve an equivalent monolith space velocity of 50,000 h<sup>-1</sup> while assuming a 2 g/in<sup>3</sup> washcoat loading, 200 ml/min total flowrate and 29.3 mg of active catalyst sample was used. The active and inert catalyst particles were sieved to achieve a mesh size range of 250–420  $\mu$ m. Each catalyst sample was placed in a 4 mm diameter quartz tube. Quartz wool was placed at each end of the catalyst bed in order to secure the bed particles, maintain the catalyst bed position in the quartz tube, and maintain the catalyst bed length of 20 mm. The quartz tube was installed in a tubular furnace within the powder reactor system as shown in Supplementary Information Schematic 1. Bronkhorst and MKS mass flow controllers were used to control the feed gas flowrates. A ThermoScientific Linderg/Blue tube furnace was used to set the temperature and control the heat supplied to the catalyst bed.

Each catalyst sample was aged under the following flow conditions: 1.8 vol.% H<sub>2</sub>O and 10 vol.% O<sub>2</sub> in N<sub>2</sub>. To achieve the target PM particle size for a given experiment, the aging duration and temperature was varied from 8 to 90 h and 700 °C to 750 °C respectively. After the aging period, the reactor was kept at the aging temperature for an additional 30 min while the reactor was purged with N<sub>2</sub> to minimize the residual H<sub>2</sub>O and O<sub>2</sub> content within the catalyst bed and reactor system lines. The reactor system lines were kept at 150 °C to 180 °C in order to prevent water and sulfur species deposition on the lines.

### 2.2. Particle size measurements

After aging, all samples were reduced at 400 °C under a 5 vol.% H<sub>2</sub> in N<sub>2</sub> flow stream. Following reduction, the reactor was cooled to 35 °C. Using a Valco pulse injection valve, 10  $\mu$ l doses of CO were injected into the reactor at regular intervals. The CO injection pulse was measured using an MKS FTIR 2030. When the injection pulse-signature ceased to change with each additional CO pulse injection, the sample was considered saturated. After saturation was achieved, the total volume of CO adsorbed was used to determine the sample PM dispersion, surface area, and corresponding particle size. The dispersion values for fresh monometallic samples agreed with those obtained during validation with a Micromeritics ASAP 2020 Chemisorption system. The PM particle size was then determined using the Micromeritics particle size calculation, which relates the precious metal particle size to 6/(precious metal density\*metallic surface area), with the metallic surface area calculated from the CO uptake amount.

### 2.3. Temperature programmed desorption (TPD)

The aged catalysts were exposed to 30 ppm SO<sub>2</sub> in N<sub>2</sub> at 150 °C until saturation. After saturation, which typically took ~1 h, the reactor was purged with N<sub>2</sub> at 150 °C for an additional 15 min to minimize the residual SO<sub>2</sub> content within the reactor system lines and detach weakly adsorbed SO<sub>2</sub> from the catalyst surface. TPD

was then performed, with a ramp rate of 10 °C/minute to 900 °C followed by a hold at 900 °C for an additional 15 min. Gas concentration measurements were made with an MKS FTIR 2030.

### 2.4. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) characterization

Background spectra were gathered in 50 ml/min of He only at 35 °C, 150 °C, 250 °C, and 400 °C. The background spectra were subtracted from their corresponding spectra obtained at each temperature in the following experiments.

After aging in the reactor, catalysts were then transferred to the Harrick Scientific Praying Mantis DRIFTS cell and was exposed to an oxidation cleaning at 100 °C with 10 vol.% O<sub>2</sub> in He for 5 min. The catalyst then underwent a reduction pretreatment at 400 °C with 5 vol.% H<sub>2</sub> in He for 30 min. After the reduction pretreatment, the sample was maintained at the 400 °C for an additional 30 min while the cell was purged with He to minimize the residual H<sub>2</sub> content within the catalyst and DRIFTS system lines. The catalyst was then cooled to approximately 35 °C and exposed to 1 vol.% CO and 10 ol.% N<sub>2</sub> in He until CO saturation as determined by a lack of change in the collected DRIFTS spectra. The CO adsorption spectrum of each sample was analyzed and compared to that of a sample with the same catalyst composition but different particle size in an effort to assign peaks as well as confirm types of sites and relative PM particle sizes involved in adsorption.

Each catalyst was exposed to 100 ppm SO<sub>2</sub> and 10 vol.% N<sub>2</sub> in He at 150 °C until saturation, which typically took ~3 h. The same procedure was repeated but at 400 °C, chosen based on the TPD data to be reviewed below. Another set of samples was exposed to 100 ppm SO<sub>2</sub> and 10 vol.% N<sub>2</sub> in He at 150 °C until saturation. The system was then purged with He prior to increasing the sample temperature to 250 °C, where spectra were collected. The sample temperature was further increased to 400 °C where more spectra were collected. The desorption spectra were obtained after the DRIFTS spectra ceased to change at each temperature. The desorption temperatures, 250 °C and 400 °C, were selected based on sulfur release termination in the low-temperature range during TPD experiments, to be discussed below.

## 3. Results and discussion

### 3.1. Baseline sulfur desorption assessment

Table 1 lists example sulfur uptake and release amounts which were measured during the adsorption and subsequent TPD experiments for three of the samples examined. Regardless of catalyst Pd:Pt composition and PM particle size, mass balances were nearly closed. Residual sulfur remaining on the catalyst after the 900 °C TPD exposure could have resulted in the consistently smaller amount observed desorbing.

The SO<sub>2</sub> uptake amount varied for these three samples, each having a different metal content and particle size. In an effort to determine how particle size specifically affected the type of sulfur species formed and amount of release, adsorption and TPD profiles of catalysts with the same metal content but differing particle sizes were compared.

The SO<sub>2</sub> TPD profiles obtained when evaluating the 0.5 Pd–0.5 Pt sample with 3.6 nm, 15.2 nm, and 34.3 nm metal particle sizes are compared in Fig. 1. The 3.6 nm sample released the largest amount of high-temperature desorbing species while the 15.2 nm and 34.3 nm samples released the largest amounts of low-temperature desorbing species. In the high-temperature range, the desorption profile of the 15.2 nm sample began at a temperature similar to that of the 34.3 nm sample. On the other hand, the release amount

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