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Sulfur deactivation and regeneration of mono- and bimetallic Pd-Pt methane oxidation catalysts

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A B S T R A C T

Complete CH_4 oxidation (combustion) studies were conducted with Pt/Pd mono- and bimetallic, $\gamma\text{-}Al_2O_3$ supported catalysts before and after exposure to SO_2. CO and SO_2 adsorption DRIFTS studies were used to identify sites that adsorbed SO_2 and evaluate the Pd:Pt mole ratio effect on sulfur surface species formation. Temperature-programmed oxidation, desorption, and reduction as models for possible catalyst regeneration were evaluated in terms of sulfur release and CH_4 oxidation performance recovery. At low temperatures, Pd-rich catalysts, i.e. with little to no Pt substitution, tended to form aluminum sulfate species, which could be removed at high temperatures to recover catalytic activity. In contrast, catalysts with higher Pt content were less effective at sulfate formation at low temperatures. In this case, molecular SO_2 and aluminum surface sulfite species inhibited the CH_4 oxidation reaction over a broader temperature range. In general, for the bimetallic samples the effectiveness of SO_2 regeneration methods decreased with increasing Pt content. Also, for bimetallic catalysts with higher Pt content, the associated sintering effects from the temperature programmed regeneration methods were more significant.

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1. Introduction

Natural gas contains methane, other hydrocarbons, such as ethane and propane [1–3], and trace level species including sulfur species [4]. In comparison with diesel engines, natural gas engine combustion produces lower CO_2, CO, NO_x, and soot emissions. One concern is of course the associated methane emissions and methane's greenhouse gas potential. A typical approach to mitigate such emissions would be the installation of an exhaust stream oxidation catalyst. Over such, under lean-burn conditions heavier hydrocarbons can be completely oxidized at low temperatures [3] but high temperatures are necessary for complete methane conversion [4]. However, lean-burn natural gas engine exhaust temperatures are relatively low (i.e. 300–500 °C) [1,5], resulting in methane slip. Furthermore, those trace sulfur species deactivate methane oxidation catalysts resulting in reduced catalytic activity with time-on-stream and thus increased levels of unconverted methane in natural gas engine exhaust [6].

There has been a substantial amount of CH_4 oxidation research published, with a comprehensive review of these by Gélin and Primet [4]. Specific challenges discussed in their review arti-cle include thermal sintering due to the required CH_4 oxidation temperature, the low CH_4 concentrations in the exhaust, H_2O inhibition, and degradation via sulfur poisoning. Studies have shown that for $O_2{:}CH_4$ molar ratios exceeding 2, i.e. lean-burn operation conditions, PdO-based catalysts are significantly more active than Pt-based catalysts [4]. Interestingly, under rich conditions, i.e. when there are stoichiometric or sub-stoichiometric amounts of O_2 relative to CH_4, Pt has been found to be more active [7]. The literature shows that substituting Pt for Pd, i.e bimetallics, results in catalysts with improved resilience with time on stream [8–15], and even small substitutions (7–10% Pt for Pd) provides some sintering resistance and increased catalytic activity [11,14,] in comparison to monometallic Pd catalysts. Thus there are known benefits of bimetallic systems for CH_4 oxidation.

In terms of sulfur poisoning/deactivation, it is well known that Pd-based catalysts are quite susceptible to sulfur. In one example, CH_4 oxidation on fresh and hydrothermally aged Pd/Al_2O_3 catalysts was evaluated. When 1 ppm SO_2 was added to the feed, the activity declined similarly for both catalysts [16]. In contrast to the abrupt decay in Pd-based catalyst activity upon SO_2 exposure [16], Lapisardi et al. found that CH_4 oxidation activity gradually declined for Pt/Al_2O_3 catalysts when exposed to H_2S [6].

Ottinger and coworkers studied sulfur regeneration of a Pd-based CH_4 oxidation catalyst via high temperature exposure as well as via a reductive treatment. They found that for the thermal regen-

eration, temperatures greater than $500\,°C$ were required to regain some activity, whereas the reductive treatment provided better regeneration efficiency [17]. Similarly, Arosio et al. [18] showed that, for Pd-based catalysts, higher temperatures (>750 °C) were required for sulfur regeneration in the presence of simulated lean-CH_4 oxidation conditions, but switching from this lean atmosphere to one which was CH_4 rich resulted in much lower temperatures required to recover activity.

Although bimetallic Pt/Pd catalysts show resistance to sintering and improved activity, researchers found that the bimetallic activity benefit only held true in the absence of sulfur [6]. Interestingly, SO_2 poisoning of a Pt/Pd bimetallic sample resulted in decreased activity, but a pre-reduction prior to SO_2 exposure had significantly less impact [15]. Since aluminum surface and bulk sulfates are stable up to $650\,°C$ [19] and $800–920\,°C$ [20] respectively, it is likely that sulfur species will compromise activity to some extent until these species can be decomposed at high temperatures. Although some researchers reported that aluminum sulfates are quite resistant to reduction [20], others found that aluminum sulfates, which thermally decompose above $800\,°C$, can be reduced in H_2 at $600\,°C$ [19].

In this study three approaches based on gas environment were evaluated for CH_4 oxidation activity regeneration, which should correlate to sulfur species decomposition. Here we focused on evaluating model sulfur regeneration methods as a function of Pd:Pt mole ratio.

2. Experimental methods

2.1. Catalyst preparation and reactor experimental set-up

The precursors, $Pd(NO_3)$ and $Pt(NH_3)_4(NO_3)_2$, and Puralox γ-Al_2O_3, were procured from Sigma-Aldrich. Using the incipient wetness impregnation method, the following Pd-Pt/Al_2O_3 powder catalysts were prepared: $Pd_{1.0}Pt_{0.0}/Al_2O_3$, $Pd_{0.9}Pt_{0.1}/Al_2O_3$, $Pd_{0.7}Pt_{0.3}/Al_2O_3$, $Pd_{0.3}Pt_{0.7}/Al_2O_3$, and $Pd_{0.0}Pt_{1.0}/Al_2O_3$. All catalysts contained the same total number of precious metal (PM) moles used to synthesize a 1 wt.% Pd/Al_2O_3 catalyst. After drying overnight, all samples were calcined in air at $550\,°C$.

For all reactor pretreatment and experimental conditions, 29.3 mg of active catalyst was used with a 200 mL/min flow, to achieve an equivalent monolith space velocity of $50,000\,h^{-1}$ assuming a 2 g/in³ loading. The active catalyst mass was diluted with silica beads to prevent dense packing and hot spots within the catalyst bed. Each sample was installed in a 4 mm diameter quartz tube. Quartz wool was placed at both catalyst bed ends to secure the bed particles, maintain the catalyst bed position in the quartz tube, and maintain the 20 mm catalyst bed length. Prior to experiments, all samples underwent an oxidation pretreatment at $100\,°C$ with 10 vol.% O_2 in N_2 for 5 min, and were then heated to $400\,°C$ and reduced under 5 vol.% H_2 in N_2 for 30 min. Following reduction, the reactor was purged with N_2 only for 30 min prior to being cooled to $35\,°C$. Using a Valco pulse injection valve, 10 μL doses of CO were injected into the reactor at regular intervals. When the CO injection pulse-signature ceased to change with each additional CO pulse injection, as measured by an MKS FTIR 2030, the sample was considered saturated. After saturation was achieved, the total CO uptake volume was used to determine the sample PM dispersion and corresponding particle size. The dispersion values for fresh monometallic samples were comparable to those obtained during validation with a Micromeritics ASAP 2020 Chemisorption system. Preliminary data demonstrate that sulfur interactions are influenced by particle size. To avoid this complexity in the data analysis, all samples for this study contained particles in the same particle size range.

Each catalyst sample was then pretreated with 2000 ppm CH_4 and 10 vol.% O_2 in N_2 until CH_4 conversion stabilized, assumed to be when the CH_4 conversion ceased to change while the gas temperature and feed gas concentration were kept constant. All catalyst samples containing any Pd were stabilized at ∼500 °C. The monometallic Pt sample was stabilized at ∼650 °C because methane combustion did not occur until higher temperatures were reached in this case. Catalysts having been prepared through this protocol are referred to as fresh catalyst samples.

Bronkhorst and MKS mass flow controllers were used to control the inlet gas flowrates. For all reactor experiments, the gas concentrations at the catalyst bed outlet were measured using an MKS MultiGas 2030 FTIR Spectrometer gas analyzer. A Thermoscientific Lindberg/Blue tube furnace was used to set and control the temperature of the catalyst bed. Type K thermocouples were placed at the catalyst bed inlet and outlet to measure the inlet and outlet gas temperatures.

All catalytic activity assessments used the same reference temperature-programmed oxidation (TPO) protocol: 2000 ppm CH_4 and 10 vol.% O_2 in N_2 with a 5 °C/min temperature ramp rate. Following the pretreatment under reactants, each sample underwent a reference TPO to obtain a baseline of its fresh catalytic activity. After each regeneration procedure, the reference TPO was performed again in an effort to compare the initial catalytic activity to that observed following regeneration.

Each sample was exposed to 30 ppm SO_2 and 10 vol.% O_2 in N_2 at $100\,°C$. After SO_2 saturation was achieved, the reactor was purged with N_2 at $100\,°C$ to reduce the residual SO_2 in the reactor system lines and remove weakly adsorbed SO_2 from the sample.

2.2. Sulfur regeneration

After the SO_2 exposure, each catalyst sample underwent one of the following regeneration methods.

1. Selected samples underwent the reference TPO protocol. CH_4 oxidation and SO_2 desorption were monitored during the temperature ramp. The SO_2 release characteristics helped define experimental conditions for SO_2 DRIFTS studies, to be discussed below.
2. Temperature-programmed desorption (TPD) was performed to determine at what temperatures under inert conditions sulfur species would decompose or desorb. The TPD was performed in a flow stream of N_2 only using the following protocol: a ramp rate of 10 °C/min to $900\,°C$ followed by a hold at $900\,°C$ for an additional 15 min.
3. Temperature-programmed reduction (TPR) was performed with selected samples up to $600\,°C$ in a 5 vol.% H_2 in N_2 flow stream, and held there for 30 min in an attempt to reduce and decompose sulfate species. Following reduction, the reactor was purged with N_2 prior to the reoxidizing the sample in 10 vol.% O_2 in N_2 at $600\,°C$ for 30 min.

2.3. Thermal degradation effects

After the catalyst CH_4 conversion stabilized, the sample temperature was increased in pure N_2 at a ramp rate of 10 °C/minute to $650\,°C$ followed by a hold at $650\,°C$ for an additional 15 min. After cooling the sample, a reference TPO was performed to assess changes in performance due to the $650\,°C$ exposure. The above protocol was repeated for a $900\,°C$ exposure.

Precious metal particle sizes were measured after these high temperature exposures. After the TPO reference protocol, the samples were reduced at $400\,°C$ under a 5 vol.% H_2 in N_2 flow. Following reduction, the reactor was cooled to $35\,°C$. Using a Valco pulse injection valve, 10 μL of CO were injected in regular intervals. When