

Effect of water on the deactivation of Pd-based catalysts during methane oxidation at low temperature

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Introduction

A significant barrier to the widespread use of natural gas vehicles (NGVs) is the unburned CH₄ emitted from the engine exhaust. CH₄ combustion of the exhaust gas is hindered by low concentrations of CH₄ (500-5000 ppmv) in the presence of water and relatively low exhaust gas temperatures (~500 °C) [1]. Although Pd catalysts show high initial CH₄ oxidation activity at low temperatures, they lose activity during reaction, in part due to the presence of water [2]. During CH₄ oxidation, O₂ molecules dissociate on Pd sites and exchange with oxygen on the support. Pd active sites are re-oxidized with oxygen from the support during the catalytic reaction [3]. Since water is thought to inhibit the O exchange between the Pd and the support, which reduces the CH₄ oxidation activity, the goal of this study was to examine the effect of water on the deactivation behavior of Pd-based catalysts.

Materials and Methods

A γ -alumina (224 m²/g and 0.53 cm³/g) was used as the catalyst support. Pd and Pd-Ce premixed solutions (7wt% Pd, 3wt% Ce) were prepared for incipient wetness impregnation of the support. Following impregnation the samples were dried and calcined by heating to 450 °C at 10 °C/min and holding the final temperature for 15 h. Catalyst activities were measured in a fixed-bed microreactor with a total inlet gas flow of 250 sccm consisting of 5000 ppmv CH₄, 20 vol.% O₂, balance He (dry feed) and a GHSV= 180,000 cm³.g⁻¹.h⁻¹. Catalyst stability was measured with (5 vol.%) and without water added to the feed gas. The reaction temperature was increased from ambient to the desired temperature at 5°C/min in the presence of the reactant, and then held constant as the reaction proceeded for 24 h. BET surface area was measured using a Micromeritics ASAP 2020 analyzer. XRD analysis was done with a D8 diffractometer using a Co source operating at 40 kV and 40 mA. A Micromeritics Autochem II 2920 was used for CO pulsed chemisorption uptake on the reduced Pd catalysts. A Leybold MAX200 XPS was used to determine the Pd/(Al+Ce) ratio on the catalyst surface.

Results and Discussion

Figure 1 shows the deactivation of both catalysts in the absence and presence of added water with time-on-stream. The 7wt%Pd/Al₂O₃ catalyst showed higher conversion both with and without water addition compared to the 7wt%Pd-3wt%Ce/Al₂O₃ catalyst over the entire 24 h period. Although both Pd and Pd-Ce catalysts showed deactivation in the absence of added water, a faster exponential decay in conversion was observed in the first 400 min, followed by a linear deactivation trend, with extra water added. After switching off the water, the conversion recovered to the level observed without added water, indicating reversible inhibition of the catalyst activity by water for both catalysts. The deactivation profiles for all catalysts over a range of temperatures were well described by a kinetic model that included inhibition of the reaction by water adsorption.

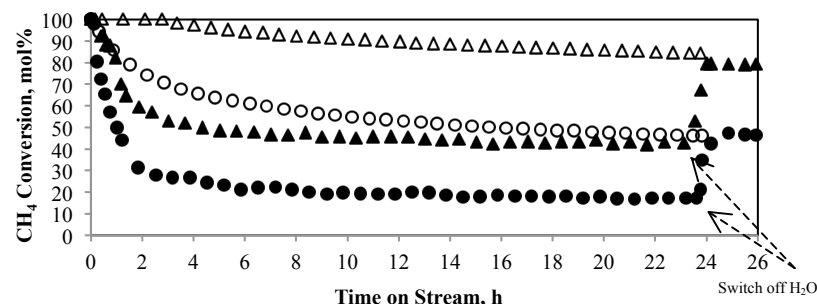


Figure 1. Time-on-stream activity for Pd/Al₂O₃ (▲), Pd-Ce/Al₂O₃ (●) catalysts without extra water (open symbol) and with extra water (closed symbol) feed stream for 24 h, T=350 °C, 250 sccm feed flow rate, 5000 ppmv CH₄, 5 vol.% H₂O.

Table 1 shows the properties of the Pd/Al₂O₃ and the Pd-Ce/Al₂O₃ catalysts before (fresh) and after (used) testing with added water. BET surface area and PdO crystallite size for both catalysts did not change significantly after 24 h reaction at 350 °C in the presence of water. This shows minimal impact of the reaction conditions on the morphology of the catalysts.

Table 1. Properties of fresh (a) and steam-aged (b) Pd/Al₂O₃ and Pd-Ce/Al₂O₃ catalysts.

Catalysts	BET	XRD	CO Uptake	XPS	
	SA (m ² /g)	d _{PdO} (nm)	cc/g	Pd/(Al+Ce) (%)	BE (eV)
^a 7%Pd/Al ₂ O ₃	218	5.7	4.58	2.3	337
^b 7%Pd/Al ₂ O ₃	185	5.0	3.81	2.3	337
^a 7%Pd-3%Ce/Al ₂ O ₃	189	4.5	3.44	6.3	337
^b 7%Pd-3%Ce/Al ₂ O ₃	152	4.5	3.35	5.2	337

(a) calcined catalysts at 450 °C for 15 h in 100 sccm air

(b) catalysts exposed to the feed gas for 24 h at 350 °C with 5 vol.% H₂O

Significance

Pd-based catalysts are active for the complete combustion of CH₄ but they deactivate rapidly in the presence of small amounts of water. The fast deactivation with added water is consistent with water adsorption on the surface of the catalyst that inhibits O transfer [3] from the support to PdO whereas the slower, linear deactivation may be due to sintering. The reversible adsorption of water results in no significant change in the physical properties of the catalysts.

References

- Gelin, P.; Primet, M. *Appl. Catal., B* **2002**, 39, 1.
- Ciuparu, D.; Perkins, E.; Pfefferle, L. *Appl. Catal., A* **2004**, 263, 145.
- Schwartz, W.R.; Pfefferle, L.D. *J. Phys. Chem. C* **2012**, 116, 8571.