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Pd catalysts for total oxidation of methane: Support effects

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ABSTRACT

We prepared a series of Pd catalysts for total oxidation of methane on different supports: Al_2O_3, ZrO_2–CeO_2 and CeO_2. We characterized the catalysts' structures by XRD and their surface chemistries by temperature programmed reduction (TPR) and oxidation (TPO); and measured their activities for methane oxidation in temperature programmed reaction experiments (TPRx). By fitting a kinetic model to the TPRx results, we extracted apparent activation barriers (E_{app}) and pre-exponents (A_{app}) for methane oxidation over each of the catalysts. Activity correlates strongly with A_{app}, which we interpret as a relative measure of the density of PdO–Pd* (* is an O-vacancy) site pairs. TPR results support this view: PdO in low activity (low A_{app}) catalysts, such as Pd/CeO_2, is relatively resistant to reduction, meaning that formation of the Pd* partner of the site pair is difficult—and the number of site pairs that can form is low.

1. Introduction

Supported palladium catalysts for total hydrocarbon oxidation have important applications in power generation, where they enable methane combustion at relatively low temperature for avoiding formation of thermal NO_x; in emissions control, including automotive catalysts; and as the active elements of sensors that detect combustible gasses. A number of reviews have been published on supported Pd catalysts for methane oxidation [1–5]. At a mechanistic level, the catalytic chemistry of methane oxidation on Pd catalysts is complex. Oxidation is usually described as a Mars–van Krevelen cycle [6], in which a *pair* of sites—PdO and Pd* (where * is an 'O-vacancy')—act in concert to activate the stable C—H bond. The activity of the catalyst depends on a number of factors, but the density and activity of site pairs are among the most important [6,7]. These characteristics are functions of the size, morphology and surface chemistry of PdO crystallites that reside on the support surface, which in turn depend on the details of catalyst preparation [6,8–11], operating conditions [10] and, significantly, the interactions of PdO with its support [7,12–15]. Different supports can stabilize PdO crystallites in different sizes and morphologies [16]. The support can even be an active participant in the catalytic chemistry through exchange of its O atoms with PdO [17,18]. In this work, we compare Pd catalysts prepared on three different supports, Al_2O_3, ZrO_2–CeO_2, and CeO_2. Microkinetic analyses of the temperature-programmed methane oxidation data show that activity correlates strongly with A_{app}, the apparent reaction pre-exponent, which we interpret as a measure of the relative density of site pairs on the catalyst surface. Results of temperature-programmed reduction experiments support this view.

2. Methods

2.1. Catalyst preparation

Table 1 lists the catalysts studied in this work. They were prepared by impregnating Al_2O_3 (Strem 13-2525, 'Al'), ZrO_2–CeO_2 (Alfa Aesar 39216, 'ZrCe') or CeO_2 (Alfa Aesar 12925, 'Ce') oxides with solutions of $Pd(NO_3)_2$ (10 wt% in 10% HNO_3, Aldrich 380040, 'NO_3') or $Pd(NH_3)_4(NO_3)_2$ (tetraamine palladium nitrate, 10 wt%, Aldrich 377384, 'TAPN') precursors. For each preparation, approximately 1 g of oxide was first dried at 400 K for 30 min in a vacuum oven. Then, precursor solution was stirred into the dried powder in 20 μL increments until the powder started to become sticky. The precursor was decomposed by calcination in a box furnace at 773 K for 1 h; the heating rate of the furnace is approximately 40 K/min. Table 1 summarizes the Pd contents of the catalysts calculated from the amount of precursor solution added to their supports. The 1.0 $Pd(NO_3)$/Ce sample was prepared by two impregnations, with an intermediate calcination at 773 K. We also evaluated a commercially available 1% Pd/Al_2O_3 (Alfa Aesar, '1.0 Pd/Al(AA)') as a reference material.

2.2. X-ray diffraction

X-ray diffraction patterns were acquired for the supports and the calcined catalysts using a Pananalytical X'pert Pro X-ray

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Table 1
Supported Pd catalysts studied in this work. Except for 1.0 Pd/Al(AA), Pd contents are calculated from preparation. Pd dispersion and crystallite size are estimated from the results of pulse CO chemisorption experiments.

	Calculated Pd (wt%)	Dispersion	Crystallite size (nm)
1.0 Pd/Al(AA)	1.02*	0.23	4.8
1.4 Pd(NO_3)/Al	1.35	0.21	5.3
1.4 Pd(TAPN)/Al	1.44	0.32	3.6
1.1 Pd(NO_3)/ZrCe	1.13	0.20	5.7
0.5 Pd(TAPN)/ZrCe	0.54	0.41	2.7
0.5 Pd(NO_3)/Ce	0.52	0.10	11.1
1.0 Pd(NO_3)/Ce	0.95	–	–

* From manufacturer's certification.

diffractometer in theta–2theta (θ–2θ) configuration. X-rays with 1.54 Å wavelength were generated from a Cu source operated at 35 kV and 10 mA. Diffraction patterns were recorded over a 2θ range from 10° to 90° with 0.0525° step size.

2.3. CO pulse chemisorption

Pd dispersion was characterized by pulse CO chemisorption using a Micromeretics 2920 instrument. The instrument is configured as a flow-through, fixed-bed quartz U-tube reactor enclosed in a high-temperature furnace. Samples are held in place within the reactor by a small quartz wool plug. For the chemisorption experiment, 0.10–0.15 g of catalyst was first pre-treated in 50 ccm 10% H_2/Ar (Airgas) for 2 h at 523 K and then cooled to 323 K in 50 ccm He (Airgas). A series CO pulses (9.991% CO/He, Airgas) were injected into the He flow; a thermal conductivity detector (TCD) monitored relative CO content of the reactor effluent during each pulse. Injections were terminated when the size of the detected pulses no longer changed. Dispersion (fraction of Pd atoms at the surfaces of crystallites) and crystallite size were estimated from CO uptake assuming adsorption stoichiometry of 1:1 CO:Pd.

2.4. Temperature-programmed oxidation, reduction and reaction

Supports and catalysts were characterized by temperature-programmed reaction (TPRx), oxidation (TPO) and reduction (TPR) using a Micromeretics 2950HP instrument. This instrument is also configured as a flow-through, fixed-bed quartz U-tube reactor enclosed in a high-temperature furnace. Samples are held in place within the reactor by a small quartz wool plug. A thermocouple is located at the top (inlet) of the catalyst bed. Mass flow controllers regulate the flow of reaction and treatment gases. An integrated TCD reports a signal proportional to the difference between the thermal conductivities of the reactor inlet and outlet streams. Before entering the TCD, TPRx product gas flows through a cold trap to remove water produced during the oxidation reaction.

For the TPRx experiment, a ~0.1–0.2 g sample was first pre-treated in 50 ccm air (zero grade, Valley National) at 873 K for 15 min. After cooling to 323 K, the flow was changed to 50 ccm 2% CH_4 in air (Matheson). The catalyst temperature was increased at 10 K/min to 873 K, where it was held for 15 min; we refer to this as the 1up portion of the experiment. To complete the first reaction cycle, the catalyst was cooled at 10 K/min to 323 K in the CH_4/air mixture (1dn). A second cycle was started immediately without changing flow from the CH_4/air mixture (2up and 2dn). For supported Pd samples, a third cycle, preceded by a new air pre-treatment, was also performed (3up and 3dn).

For TPO characterization, a ~0.1 g sample was first cooled to 278 K flowing Ar. At 278 K, the flow was changed to 50 ccm of 10.0% O_2/He (Valley National). The sample was heated to 873 K at 10 K/min and then held at 873 K for 15 min before cooling at 20 K/min to 300 K in O_2/He flow. The reactor was purged with He and the sample was cooled to 233 K before changing the flow to 50ccm 10.8%H_2/Ar (Valley National) for TPR. The sample was heated to 873 K at 10 K/min and then held at 873 for 15 min. Next, the sample was cooled in 10.8% H_2/Ar at 20 K/min to 423 K and 10 K/min to 288 K. Flow was changed to Ar and a second TPO was conducted. We report results of the TPR and the second TPO only; the first TPO served as a pre-treatment to deliver a baseline, oxidized state for the TPR experiment.

3. Results

3.1. X-ray diffraction

Figures A1, A2 and A3 display diffraction patterns for Al_2O_3-supported catalysts, ZrO_2–CeO_2 supported catalysts and CeO_2 supported catalysts. No diffraction features that could be indexed to either Pd or PdO were identified in any of the Pd-catalysts. This result reflects small primary crystallite size, or perhaps simply relatively low Pd loadings [19]. Furthermore, Pd addition did not change the structure of any of the of the parent oxides. Al_2O_3 and Pd/Al catalysts all displayed diffraction patterns characteristic of γ-Al_2O_3. ZrO_2–CeO_2 and Pd/ZrCe catalysts' diffraction patterns reflect a mixture of monoclinic and tetragonal ZrO_2. No features that could be indexed to CeO_2 were identified in the patterns of ZrO_2–CeO_2 or the Pd/ZrCe catalysts. CeO_2 and Pd/Ce catalysts all displayed patterns characteristic of a highly crystalline CeO_2.

3.2. CO pulse chemisorption

Pd dispersions and crystallite sizes of the catalysts are reported in Table 1. Dispersions ranged from 0.10 and 0.41, corresponding to crystallite sizes between 2.7 and 11 nm. Dispersions in this range are typical of supported Pd catalysts made by solution impregnation of Pd salts [9,19–22]. For both the Al_2O_3 and ZrO_2–CeO_2 supports, catalysts prepared from the TAPN precursor display higher dispersion then those prepared from the NO_3 precursor. Others have reported dependencies of dispersion on precursor choice in incipient wetness preparation of supported Pd catalysts [9,22]; while beyond the scope of this work, we note that the differences likely reflect differences in the decomposition kinetics of the precursors. We measured the dispersion of only one of our two ceria-supported catalysts; it displayed the lowest dispersion within the sample set. Others have observed a dependence of Pd dispersion on support composition [12,20]. Even within cerias, Pd dispersion has been observed to depend on the details of support morphology and chemistry. For example, Satsuma et al. report that high surface area cerias interact strongly with Pd to keep Pd crystallites small [15]. On the other hand, the interaction between Pd and highly crystalline (like ours), low surface area, deeply reduced cerias is weaker, allowing larger Pd structures to form.

3.3. TPRx

Figure 1 shows the TPRx results for 1.0 Pd/Al(AA) as a plot of TCD signal vs. reaction temperature. The 0.0 to ~0.05 TCD signal scale corresponds to fractional CH_4 conversions, *x*, of 0.0–1.0. Results for the first reaction cycle (1up and 1dn) are plotted in blue, with a solid line for the increasing temperature portion of the cycle (1up) and a dotted line for the decreasing temperature portion (1dn). The second cycle is plotted in red (2up and 2dn) and the third cycle in green (3up and 3dn). For this catalyst, complete conversion is achieved across all three cycles. The catalyst exhibits highest activity—conversion at any reactor temperature is highest—during