The influence of sulfur dioxide on propane oxidation activity over supported platinum and palladium

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Earlier studies have shown that sulfur dioxide and metal–support interaction can strongly influence propane oxidation over platinum. In particular, oxidation activity is enhanced when platinum is supported on sulfated γ-alumina or zirconia compared to γ-alumina. Therefore, it is of interest to compare the performance of palladium under the same experimental conditions. Four model catalysts were examined: Pt/γ-alumina, Pt/zirconia, Pd/γ-alumina and Pd/zirconia. The metal loading was kept at or below 0.05 wt% to emphasize changes in activity attributable to metal–support interaction. Reaction rates were measured with and without sulfur dioxide. Surface sulfation was analyzed by measuring acid strength and evaluating spectra obtained by Fourier-transform infrared spectroscopy. In contrast to platinum, sulfation does not promote propane oxidation on Pd/γ-alumina, and Pd/zirconia is less active than Pd/γ-alumina.

Keywords: propane; oxidation; platinum; palladium; sulfur dioxide; alumina; zirconia; activity; acidity; kinetics

1. Introduction

The oxidation of alkanes, as compared to other hydrocarbons (HC's), such as alkenes, is relatively slow [1]. Thus, as exhaust passes through a catalytic converter, the total HC concentration decreases, while the fraction of less reactive low molecular-weight alkanes increases. For example, Sigsby et al. [2] observed that the alkane concentration at a catalyst outlet exceeded the inlet concentration by 30%.

It has been reported that the propane oxidation rate over Pt/γ-Al_2O_3 can be substantially enhanced by sulfation of the alumina surface [3]. The increase in activity is presumably gained by additional reaction sites, generated by surface sulfate [4].

Other material properties that are known to influence propane oxidation over platinum are metal particle size [5] and support characteristics [6]. Thus, replacement of γ-alumina by zirconia as a support for platinum increased the propane oxidation activity by up to two orders of magnitude [6]. The support influence dominates for small particles, where a majority of the metal atoms are in direct contact with the support material.

Palladium is a more desirable precious metal component of three-way catalysts compared to platinum because of cost and availability. With the increased application of palladium in catalytic converters it is of interest to compare the catalytic alkane oxidation on palladium and platinum with respect to support material and sulfur exposure. The primary objective of this study is to examine whether the beneficial effects of alumina sulfation and alumina substitution by zirconia regarding alkane oxidation over platinum can also be observed over palladium.

2. Experimental

2.1. CATALYSTS

The catalysts were prepared by multiple impregnation of γ-alumina (Degussa, aluminum oxide C) and zirconia (Aldrich) with chloroplatinic acid (Johnson Matthey) or palladium(II) nitrate (Johnson Matthey). The support was well-stirred for 2 h in an aqueous solution which contained one-half the desired noble metal concentration. The samples were dried at 120°C in air for 2 h. The remaining solution was added and the catalysts were again dried at 120°C and finally calcined at 600°C for 20 h. Sample pretreatment consisted of reduction in hydrogen at 400°C for 2 h, followed by exposure to oxygen at 500°C for 20 h. The metal loadings were kept at or below 0.05 wt% to emphasize the effects of metal–support interaction. The nominal values are: 0.05 wt% Pt/γ-alumina, 0.04 wt% Pt/zirconia, 0.05 wt% Pd/γ-alumina and 0.02 wt% Pd/zirconia. At such low metal concentrations the catalysts are fully dispersed and each metal atom is essentially a surface atom [7–9]. No attempt was made to measure the fraction of Pd atoms exposed in the support surface at the extremely low metal concentration employed. Standard palladium dispersion, measured by routine chemisorption of CO or hydrogen, can be misleading because of CO dissociation [7], formation of bulk hydride, or loss of chemisorption capacity due to metal–support interaction. At the purposely low metal loadings selected for this study, most of the metal atoms should be exposed in the surface. Full metal dispersion [5] can be achieved up to a saturation limit of 2.2 $\mu mol/m^2$. The actual loadings were 0.03 and 0.4 $\mu mol/m^2$ for Pt on γ-alumina and zirconia, and 0.05 and 0.3 $\mu mol/m^2$ for Pd on γ-alumina and zirconia, well below this limit.

The samples were sulfated by the oxidation of sulfur dioxide ($O_2/SO_2 = 3$) at 500°C for 5 h. The suffix -SO_2 is used here to denote a catalyst that has undergone sulfation. To emphasize the effect of support material on catalyst activity the two supports chosen have significant differences. Hence, γ-alumina is an essentially amorphous material with a specific surface area of 85.5 m^2/g, while zirconia is highly crystalline and possesses a much lower surface area of 5.5 m^2/g. The BET surface areas were derived from nitrogen adsorption isotherms at liquid nitrogen temperature.

2.2. ACTIVITY STUDIES

Propane oxidation was used as a probe reaction to compare changes in catalytic activity. In excess oxygen, the kinetic rate of propane oxidation can be described as first order in propane concentration [5,6]. An integral flow system, operated at atmospheric pressure, was used for the activity measurements. The powdered samples were placed on a fritted quartz-glass disk in a vertical reactor. The flow components consisted of 5 cm^3/min propane, 70 cm^3/min oxygen and 1300 cm^3/min argon. The propane consumption in the gas phase was measured as a function of temperature by a mass spectrometer (VG Quadrupoles). The peaks monitored were m/e 29 (propane; fragmentation peak), m/e 32 (oxygen; parent peak), m/e 40 (argon; parent peak) and m/e 44 (carbon dioxide; parent peak). The contribution of propane to m/e 44 was calibrated and subtracted. The analyses were based on the known concentration of argon. It was calculated, from the carbon balance and the amount of propane and oxygen reacted, that 95% of the propane was oxidized to carbon dioxide and water.

Each sample contained the same amount of platinum or palladium (5 μmol). The charge was increased to 2.5 g by admixing blank powders of γ-alumina or zirconia to provide the same flow resistance through the sample. The oxidation activity of the blank supports was measured and found to be negligible, unless otherwise stated. Catalyst temperature was measured with a thin exposed thermocouple wire placed in contact with the sample. Data reproducibility was very good and there was no evidence of hysteresis between conversions measured upon heating and cooling.

2.3. FOURIER-TRANSFORM INFRARED (FTIR) STUDIES

Diffuse reflectance spectroscopy was employed in this study. This technique is an effective method for investigating opaque powders [10]. The infrared beam was aligned by four planar and two ellipsoidal mirrors of the cell assembly (Harrick Scientific). The planar mirrors and sample holder height were adjusted to achieve maximum intensity. The cell was equipped with CaF_2 windows and could be operated under vacuum or atmospheric flow conditions. Under our flow conditions the maximum temperature attainable in the cell was 300°C.

Infrared spectra were obtained with a Nicolet 740 spectrometer coupled with a Nicolet 680 data system. Radiation was monitored by a liquid-nitrogen cooled, wide band mercury–cadmium–telluride (MCT) detector (4000–400 cm^{-1}). The nominal resolution was 4 cm^{-1}, the number of scans 500. All spectra were ratioed against an open-beam nitrogen background without the cell.

Platinum supported on γ-alumina or zirconia was used to study the reaction of sulfur with the supports. The samples were thoroughly mixed with potassium bromide (catalyst : KBr = 1 : 10) for improved radiation scattering. In situ sample pretreatment, carried out at 300°C and 25 cm^3/min for 1 h, consisted of reduction in hydrogen, followed by exposure to oxygen, and finally, treatment in helium. The spectra of unsulfated samples were subtracted from those obtained after sulfation under matching conditions to identify adsorption bands generated by the sulfur treatment.

2.4. ACID STRENGTH MEASUREMENTS

The surface acid strength was qualitatively measured with Hammett indicators [11]. This method employs indicators of known pKa for which the neutral base and conjugate acid differ in color. The Hammett function, Ho, is defined as the inverse logarithm of the indicator dissociation constant, Ka. The indicators ranged in acidity over 20 orders of magnitude from bromothymol blue, Ho = +7.2, to 2,4-dinitrofluorobenzene, Ho = −14.52.

A few drops of the indicator solution (0.1% in benzene) were added to the powdered catalyst (100 mg) after drying in air at 400°C for 2 h. Based on color it was determined whether the catalyst surface acidity was of sufficient strength to convert the indicator into its conjugate acid. Indicators of increasing pKa were used until the adsorbed indicator remained in its basic form, and thus, the maximum surface acid strength was determined.

3. Results and discussion

3.1. ACTIVITY STUDIES ON UNSULFATED SAMPLES

Fig. 1 is a graph of propane conversion versus temperature for 0.05 wt% Pt/γ-Al_2O_3 (open circles) and 0.04 wt% Pt/ZrO_2 (open squares). A temperature of 390°C is required for 50% propane conversion over Pt/γ-Al_2O_3. This same conversion is accomplished for Pt/ZrO_2 at a lower temperature of 285°C. Thus, for an equivalent amount of platinum, the oxidation is favored over Pt/ZrO_2 compared to Pt/γ-Al_2O_3. These results are in agreement with earlier activity studies conducted in a recirculation batch reactor [6]. Evidence obtained by different techniques indicates that small platinum clusters have a strong interaction with γ-alumina. These techniques include temperature-programmed reduction [12], X-ray photoelectron spectroscopy (XPS) [13], Fourier-transform infrared spectroscopy (FTIR) [14] and Raman spectroscopy [15]. It is thought that this noble metal–alumina interaction

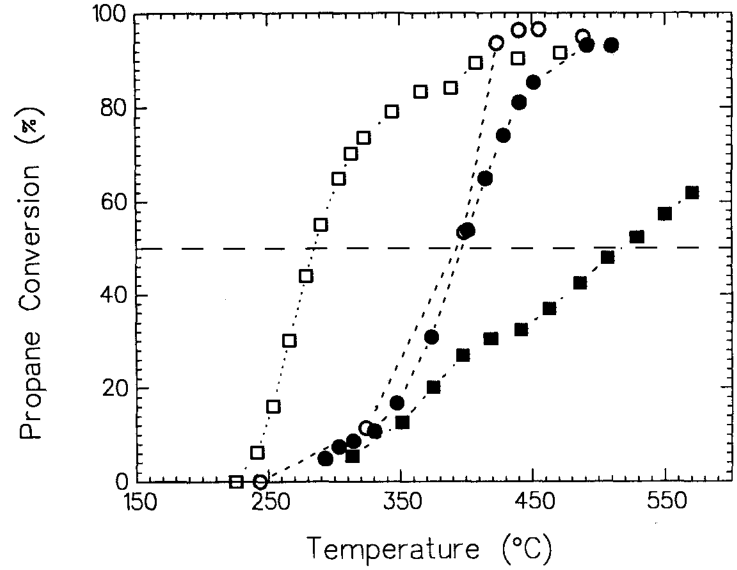

Fig. 1. Support effect on propane oxidation activity for 0.05 wt% Pt/γ-Al_2O_3 (○), 0.04 wt% Pt/ZrO_2 (□), 0.05 wt% Pd/γ-Al_2O_3 (●) and 0.02 wt% Pd/ZrO_2 (■).

deactivates some of the sites active for propane oxidation [6]. Zirconia, on the other hand, is less reactive compared to γ-alumina [16] and hence, does not suppress propane oxidation rates over platinum.

Also shown in fig. 1 are activity data for 0.05 wt% Pd/γ-Al_2O_3 (filled circles) and 0.02 wt% Pd/ZrO_2 (filled squares). The temperature for 50% propane conversion over Pd/γ-Al_2O_3 is 390°C, the same as over Pt/γ-Al_2O_3. However, in contrast to platinum, palladium supported on zirconia is much less active. To achieve 50% propane conversion over Pd/ZrO_2, a temperature of 530°C is required, 140°C higher than that of palladium on γ-alumina. Thus, while substitution of γ-alumina with zirconia causes a substantial increase in propane oxidation activity over Pt, a decrease results over Pd.

The reasons for this striking dissimilarity remain unclear at this point. It is expected that, similar to Pt/ZrO_2, palladium does not interact strongly with zirconia [17]. The palladium surface environment could be probed by X-ray photoelectron spectroscopy, however, the low metal loadings employed in this study make it difficult to obtain meaningful results, especially since zirconium lines interfere with the XPS features of palladium [18].

3.2. ACTIVITY STUDIES ON SULFATED SAMPLES

In fig. 2 the propane oxidation activity is plotted for 0.05 wt% Pt/γ-Al_2O_3 untreated (open circles) and after exposure to a SO_2/O_2 mixture (filled circles). After sulfation, the temperature for 50% conversion is reduced by 140°C to 250°C. Thus, exposure to sulfur increases propane oxidation activity over Pt/γ-Al_2O_3.

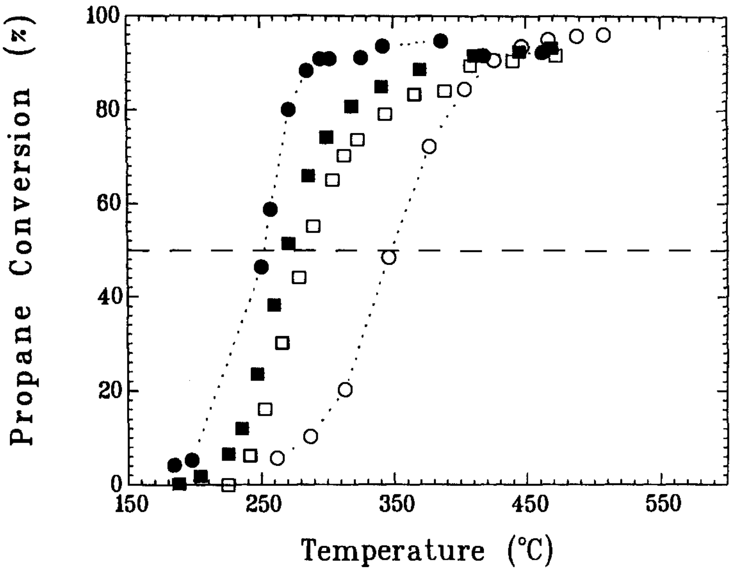

Fig. 2. Sulfation effect on propane oxidation activity on supported platinum for 0.05 wt% Pt/γ-Al_2O_3 (○), 0.05 wt% Pt/γ-Al_2O_3-SO_2 (●), 0.04 wt% Pt/ZrO_2 (□) and 0.04 wt% Pt/ZrO_2-SO_2 (■).

This result confirms previous observations [3,19] and is believed to reflect new active sites generated by surface sulfate [4].

Also depicted in fig. 2 are activity data for 0.04 wt% Pt/ZrO_2 before (open squares) and after sulfation (filled squares). In contrast to Pt/γ-Al_2O_3, exposure to sulfur dioxide does not change the catalytic activity of Pt/ZrO_2 within the experimental error, although a surface sulfate is formed under these conditions [20]. The uncertainty of the 50% conversion temperature is empirically taken to be ±5°C, and could approach ±10°C. Thus, sulfation increases propane oxidation activity of platinum on γ-alumina, but has essentially no effect when zirconia is used as a support.

The dependence of propane oxidation activity on support material and catalyst sulfation for the palladium series is shown in fig. 3, with circles again indicating γ-alumina and squares zirconia. After sulfation, propane oxidation activity over palladium decreases on either support. For Pd/γ-Al_2O_3, the temperature for 50% propane conversion increases by 140°C from 390°C for the untreated sample (open circles) to 530°C for the sulfated sample (filled circles). The decrease in activity after sulfation is much more pronounced for Pd/ZrO_2 (filled squares). In fact, at the maximum experimental temperature, 600°C, the activity was only about 30% for Pd/ZrO_2-SO_2. The dotted line near the data points of Pd/ZrO_2-SO_2 is the activity measured for blank ZrO_2-SO_2. Hence, after sulfur treatment, palladium supported on zirconia is totally inactive for propane oxidation. Attempts to restore the activity through reduction in hydrogen at 400°C did not succeed. Reduction at higher temperatures was avoided since palladium sintering would complicate data analysis.

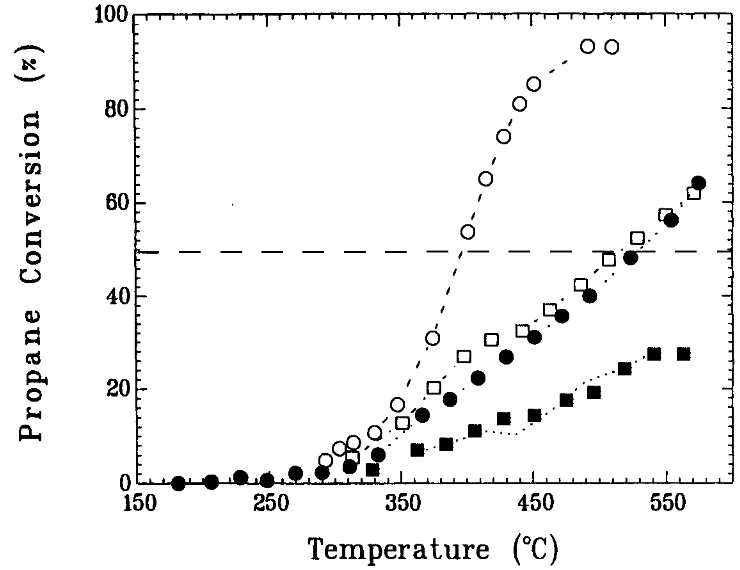

Fig. 3. Sulfation effect on propane oxidation activity on supported palladium for 0.05 wt% Pd/γ-Al_2O_3 (○), 0.05 wt% Pd/γ-Al_2O_3-SO_2 (●), 0.02 wt% Pd/ZrO_2 (□) and 0.02 wt% Pd/ZrO_2-SO_2 (■).

3.3. FTIR STUDY OF SULFATED SAMPLES

FTIR spectroscopy was employed to confirm the existence of retained sulfur species after exposure to a SO_2/O_2 mixture at 500°C. Platinum is a catalyst for sulfate formation [3]. Thus, the samples chosen for the infrared study were 0.05 wt% Pt/γ-Al_2O_3 and 0.04 wt% Pt/ZrO_2. The reaction between sulfur and support metal oxides was monitored by the development of the spectral band at 1290 cm^{-1} which is assigned to asymmetric (ν_3) stretching of surface sulfate groups [3,20,21]. Surface sulfate is also formed on γ-alumina and zirconia without a catalytic metal [3,20–22].

The spectrum of 0.05 wt% Pt/γ-Al_2O_3-SO_2, displayed in fig. 4a, exhibits a broad absorbance, approximately 150 cm^{-1} wide, centered at 1280 cm^{-1}. This peak has been previously observed on Pt/γ-Al_2O_3 [3] and γ-Al_2O_3 [20–22] after sulfur exposure and is assigned to ν_3 stretching of sulfate groups. Fig. 4b represents 0.04 wt% Pt/ZrO_2 after sulfation. This spectrum displays features similar to that of 0.05 wt% Pt/γ-Al_2O_3-SO_2 with a broad absorbance centered approximately at 1280 cm^{-1}. Analogous to 0.05 wt% Pt/γ-Al_2O_3-SO_2, this peak is assigned to ν_3 stretching of surface sulfate.

A small absorbance in the 1560–1480 cm^{-1} region is observed on γ-alumina, but not on zirconia. This absorbance is possibly a manifestation of an interaction between platinum, sulfate and γ-alumina, producing additional reaction sites responsible for rate enhancement. The absence of a corresponding feature on zirco-

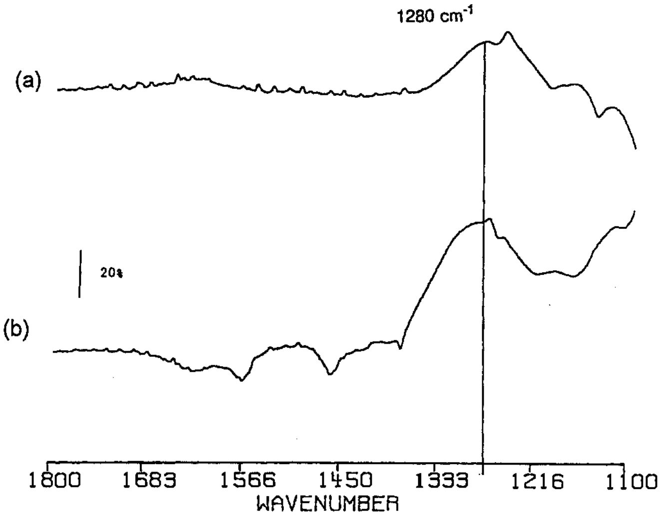

Fig. 4. Spectra of (a) 0.05 wt% Pt/γ-Al_2O_3-SO_2 and (b) 0.04 wt% Pt/ZrO_2-SO_2

nia could be explained by a weaker interaction between platinum and zirconia [12–16]. However, additional FTIR studies would be required to turn this conjecture into a more convincing argument.

It should be mentioned that we did not observe a peak at 1400 cm^{-1} which was expected according to an assignment by Chang [22]. Dr. R.O. Charter of Ford Research Laboratory has pointed out that sulfate invariably results in a very strong peak at 1100 cm^{-1}. Spectra of the bulk sulfates of copper, sodium, cobalt and zirconium [23,24] are good examples in support of these conclusions. Our results indicate that a shift to higher frequency occurs for sulfate species generated on the surface compared to bulk sulfate compounds.

3.4. ACID STRENGTH MEASUREMENTS

The surface acid strength, which is influenced by surface sulfates [20], was measured qualitatively with Hammett indicators. The results are summarized in table 1. These experiments were conducted in an attempt to correlate observed platinum and palladium activity differences with support material and catalyst sulfation. The measured acid strength was found to be practically independent of the noble metal. Prior to sulfation, γ-alumina and zirconia exhibit the same surface acid strength, $Ho \geqslant +4.8$. However, after sulfation, γ-alumina shows a moderate increase in acid strength to $Ho \geqslant +1.1$, while zirconia displays a substantially greater increase to $Ho \geqslant -5.6$. A number of studies have reported the formation of a superacid, $Ho \leqslant -12$, upon sulfation of zirconia [20,21,25–27]. However, superacid sites are not generated upon sulfation of crystallized zirconia, but rather on the amorphous oxide which is initially sulfated and crystallized upon calcination [25–27]. The zirconium oxide used in this study was a highly crystalline material of

Table 1
Dependence of catalyst activity on acid strength

Catalysts	Ho	Ka	Temp (°C) at 50% propane conv.
γ-Al_2O_3	$\geqslant +4.8$	10^{-5}	550
γ-Al_2O_3-SO_2	$\geqslant +1.1$	10^{-2}	525
0.05 wt% Pt/γ-Al_2O_3	$\geqslant +4.8$	10^{-5}	390
0.05 wt% Pt/γ-Al_2O_3-SO_2	$\geqslant +1.1$	10^{-2}	250
0.05 wt% Pd/γ-Al_2O_3	$\geqslant +4.8$	10^{-5}	390
0.05 wt% Pd/γ-Al_2O_3-SO_2	$\geqslant +1.1$	10^{-2}	530
ZrO_2	$\geqslant +4.8$	10^{-5}	–
ZrO_2-SO_2	$\geqslant -5.6$	10^{5}	–
0.04 wt% Pt/ZrO_2	$\geqslant +4.8$	10^{-5}	285
0.04 wt% Pt/ZrO_2-SO_2	$\geqslant -5.6$	10^{5}	285
0.02 wt% Pd/ZrO_2	$\geqslant +4.8$	10^{-5}	530
0.02 wt% Pd/ZrO_2-SO_2	$\geqslant -5.6$	10^{5}	–

monoclinic structure [28] and thus, upon sulfation, the increase in acid strength was not to that of a superacid (table 1).

In addition to acidity data, table 1 also displays averaged activity data in terms of the temperature for 50% propane conversion before and after exposure to sulfur dioxide. For palladium, supported on either γ-alumina or zirconia, the acidity increases and the oxidation activity decreases after sulfation. Thus, an increase in surface acid strength is accompanied by a lower activity for the palladium catalysts. For platinum, however, a relationship between acid strength and activity is not as apparent. Platinum supported on γ-alumina exhibited an increase in both surface acid strength and activity upon sulfation. In contrast, sulfation of Pt/ZrO_2 results in a greater increase in acid strength compared to γ-alumina with no apparent increase in oxidation activity. Thus, at this point no distinct correlation exists between acidity and propane oxidation activity for supported platinum and palladium. Further research is needed to explain the differences of platinum and palladium with respect to support material and catalyst sulfation.

5. Conclusions

The beneficial effects of alumina sulfation [3], as well as the substitution of γ-alumina by zirconia [6] as a support, previously reported for propane oxidation on platinum, are not observed for palladium. Specific conclusions for this comparative study are:

(1) For highly dispersed platinum and palladium, propane oxidation activity decreases in order Pt/zirconia > Pt/γ-alumina = Pd/γ-alumina > Pd/zirconia. The series demonstrates a pronounced support influence on the catalytic activity of small metal clusters.

(2) After sulfation, via SO_2 oxidation, propane oxidation activity increases on Pt/γ-alumina and remains unchanged on Pt/zirconia. In contrast to platinum, sulfation causes a deactivation in activity for both Pd/γ-alumina and Pd/zirconia. The irreversible deactivation after sulfation suggests essentially complete chemical poisoning of surface sites active for propane oxidation on the less noble metal, palladium. The detrimental effect of SO_2 is especially bothersome for the desirable substitution of platinum and rhodium by palladium.

(3) Evidence of a surface sulfur species on Pt/γ-alumina and Pt/zirconia, generated by SO_2 oxidation, is observed as a broad absorbance centered at about 1280 cm^{-1} which is assigned to asymmetric (ν_3) stretching of sulfate groups.

(4) The acid strength of zirconia is significantly increased after sulfation, while that of γ-alumina is only slightly raised. No correlation was found between surface acid strength and changes in propane oxidation activity over supported platinum and palladium.

It should be stressed that the catalytic effects described here were studied only on simple model catalysts. Additional components in a fully formulated catalytic converter may result in other beneficial or detrimental modifications of catalyst performance. A full evaluation of these exploratory findings obviously requires further work in an automotive environment.

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