

**Effects of Pretreatment Conditions on the Activity of a Pt/Al<sub>2</sub>O<sub>3</sub>  
Catalyst for the Oxidation of Di(n-)propyl Sulfide**

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**Introduction:**

Organic sulfur compounds are known to poison noble metal catalysts and are often present in stream of air which must be purified. Sulfur compounds may poison platinum oxidation catalysts by adsorbing onto active sites. When the concentration of the organic sulfur compound is high enough to saturate the catalyst surface, oxidation of the more reactive organic molecules will not occur until temperatures sufficient to destroy the sulfur compounds are reached (1,2,3). Because of this, it is important to gain an understanding of the behavior of different chemical states of supported platinum when exposed to known catalytic poisons.

The temperature at which a Pt/Al<sub>2</sub>O<sub>3</sub> catalyst is calcined in air has been shown to influence both the dispersion and chemical state of platinum (4-11). Platinum dispersion increases following air calcination up to 550-600°C. Calcination above this temperature has been shown to severely decrease dispersion (5,6,8,11). Pt/Al<sub>2</sub>O<sub>3</sub> catalyst, prepared from H<sub>2</sub>PtCl<sub>6</sub> will form platinum(IV) complexes when calcined between 300-600°C, while metallic platinum crystallites are formed following calcination at higher temperatures (5-7). Platinum is reported to be more active as a metal, onto which oxygen is chemisorbed, for oxidation reactions involving organics (1,7,12). Volter et al. (7) studied the n-heptane oxidation activity of these complexes between 150 and 300°C. The activity of the catalyst (prepared from H<sub>2</sub>PtCl<sub>6</sub>) was shown to increase with an increase in calcination temperature (between 500°C and 900°C). From this work they concluded that reduced platinum is more reactive than oxidized platinum for complete oxidation of n-heptane.

This work investigates the activity and poison resistance of a supported platinum catalyst as a function of the catalyst oxidation state resulting from different pretreatments.

**Experimental:**

*Materials:* The Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst used in this study was obtained from Houdry. It contained 1% platinum by weight and was prepared from H<sub>2</sub>PtCl<sub>6</sub>. The nominal BET surface area is reported to be 200 m<sup>2</sup>/g.

**Apparatus:** Reaction studies were performed using a fixed-bed reactor. Pre-purified air was further purified by passing through a drierite/13X filter in order to remove any traces of water. Air flow to the reactor was controlled by a 0-2.0 Nl/min (Nl defined as a liter at 0°C, 1 atmosphere) mass flow controller. Di(n-)propyl sulfide was injected into the air stream using a syringe pump. This produced a near constant concentration of 100 ppm (v/v) di(n-)propyl sulfide in air stream. The reactor consisted of a 0.75 cm id 316 stainless steel tube, approximately 5 cm in length. Three type K thermocouples were evenly distributed along the reactor and extended into the catalyst bed. A preheater was located just above the catalyst bed. Both the reactor and preheater were surrounded by an aluminum block which served as the furnace. Reactor temperature was controlled to  $\pm 0.5^\circ\text{C}$  by controlling the temperature of the block. The temperature differential along the catalyst bed did not exceed  $2^\circ\text{C}$  during any of the runs. The concentration of sulfur containing compounds present in the reactor effluent was analyzed using a Hewlett-Packard 5790 GC equipped with a flame photometric detector (FPD) and modified for automatic sampling.

**Procedure:** Approximately 0.145g of 35-65 mesh (U.S. series) catalyst particles were diluted with crushed glass of a similar size so as to achieve a bed volume of  $2\text{ cm}^3$ . The catalyst was pretreated by first drying for 4 h at  $125^\circ\text{C}$  in pretreatment gas (air or 8%  $\text{H}_2$  in He), after which, the catalyst bed was raised to the pretreatment temperature at approximately  $4^\circ\text{C}/\text{min}$ . Pretreatment temperatures of  $300^\circ\text{C}$ ,  $410^\circ\text{C}$ ,  $600^\circ\text{C}$  and  $800^\circ\text{C}$  were employed using a gas flow rate of 1.0 Nl/min. The final pretreatment temperature was maintained for 16 hours. At pretreatment temperatures of  $410^\circ\text{C}$  and below, pretreatment was carried out *in-situ*. When employing higher temperatures, the catalyst was placed inside a quartz tube furnace and heated to the desired temperature, which was maintained for 16 h. The catalyst was then cooled in flowing helium, weighed, diluted with glass and introduced to the reactor.

Following pretreatment, the reactor was adjusted to  $230^\circ\text{C}$ , which was the temperature employed for all runs. The reactor was sealed and di(n-)propyl sulfide flow was established (100 ppm in 1.7 Nl/min air) through the reactor by-pass. When the concentration of sulfide remained constant (about 2 hours), feed gas was diverted to the reactor. All lines were heated electrically at  $125\text{-}150^\circ\text{C}$  in order to avoid condensation. Conversions were determined as a function of time-on-stream from the concentration of di(n-)propyl sulfide in the effluent stream. A blank run was performed prior to reaction studies. This run indicated that the reactor walls and glass diluent were inert at reaction conditions.

**XPS Analysis:** XPS spectra of fresh and spent catalyst were recorded using a Perkin-Elmer Phi 570 ESCA/SAM system employing MgK- $\alpha$  x-rays. The system was equipped with a reaction chamber which allowed for recording spectra of catalyst following pretreatment at temperatures below  $550^\circ\text{C}$  without exposure to atmosphere. Materials which were calcined at higher temperatures were analyzed following pretreatment in a quartz tube furnace. Spent catalyst were analyzed following removal from the reactor and separation from the glass diluent. Platinum

spectra were recorded following 100 to 200 scans of the 4d photoelectron region so as to reduce signal-to-noise. No shifting of peaks were observed during the scanning process indicating that the prolonged exposure of the sample to the x-ray source did not alter the platinum oxidation state. All binding energies are referenced to the aluminum 2p photoelectron peak at 74.0 eV. This was used as a reference since the position of this peak is invariant to the pretreatments employed here (4).

### Results and Discussion:

Figure 1 shows the platinum 4d photoelectron region of the catalyst following calcination at temperatures of 300°C, 410°C, 600°C and 800°C (spectra A through D, respectively) and exposure to hydrogen at 300°C (spectrum E). The platinum 4f region, which exhibits the strongest signal, could not be analyzed due to interference with the aluminum 2p photoelectron peak. The binding energy of the 4d<sub>5/2</sub> photoelectron peak for the catalyst calcined at 300°C and 410°C is 317.0±0.2 eV. This binding energy is consistent with studies performed elsewhere (4,13) and indicates platinum is in an oxidized environment. As the calcination temperature is increased from 410°C to 600°C, a strong shoulder at approximately 315.0 eV becomes evident. Further increasing the calcination temperature to 800°C results in a decrease of 2.0 eV in the binding energy of the platinum 4d<sub>5/2</sub> photoelectron peak. Similar changes in binding energies have been reported (4,13,14) and are indicative of reduced supported platinum. It is clear from this figure that increasing the calcination temperature from 410°C to 800°C results in increasing the extent of platinum reduction. The majority of the platinum is in the oxidized state following calcination at 300°C and 410°C, while the majority of the platinum is in a reduced state following calcination at 800°C. These results are consistent with those of Lieske and co-workers (5-7), who have extensively studied platinum species formed following calcination of Pt/γ-Al<sub>2</sub>O<sub>3</sub> catalysts prepared from H<sub>2</sub>PtCl<sub>6</sub>. Their results showed that calcination below 600°C yields platinum(IV) species, while calcination at higher temperatures leads to the formation of metallic platinum.

Figure 2 illustrates conversion as a function of time on stream for catalysts pretreated at different calcination temperatures. No partial oxidation products were detected. Sulfur balances were performed on the effluent during all runs and were between 85 and 96% for the period of 3 hours into the run until the run was terminated. Discrepancies in the sulfur balances were attributed to formation of SO<sub>3</sub>, which could not be analyzed. Calcination at 300°C yields a catalyst which deactivates throughout the duration of the run. Increasing the calcination temperature to 410°C improves the catalyst performance. Following an initial rapid deactivation, the catalytic activity increases, achieving an ultimate conversion of 71%. Increases in activity of oxidation catalysts during start-up have been reported elsewhere (15). The cause of the initial sharp decrease in activity was not investigated. However, complexing of surface platinum with adsorbed sulfur or the presence of chlorine on the sample may be responsible for this behavior. Further increasing the calcination temperature to 600°C decreases the catalytic activity (relative to the sample calcined at 410°C). In this instance, the steady-state conversion was 40%. A further decrease in activity is observed upon increasing the

calcination temperature to 800°C.

Following an initial induction period, catalysts calcined at 410 and 600°C increased to a stable level of activity. However, the catalyst calcined at 300°C continued to deactivate throughout the duration of the run. Lieske and co-workers (5,6) have demonstrated that calcination at 300°C will yield a different oxidized platinum species than that produced following calcination at higher temperatures. Apparently, this species is somewhat susceptible to deactivation in the presence of sulfur compounds.

Figure 3 compares the activity of the catalyst calcined at 800°C to that of the catalyst reduced in hydrogen at 300°C. Catalysts were analyzed following the run by XPS. Results indicated that the reduced platinum was not oxidized during the reaction exposure. In both cases, a rapid loss of activity was followed by a steady, low level of conversion. Pretreatment in hydrogen at low temperatures is reported to yield a highly dispersed reduced platinum phase (14), while calcination at high temperatures is reported to yield a poorly dispersed reduced platinum phase (5,6,8,11). Note that in spite of the expected difference in platinum dispersion, the two materials possess similar catalytic properties. This suggests that the loss of catalytic activity observed upon increasing the calcination temperature from 410°C to 800°C cannot be attributed solely to decreased platinum dispersion.

The activity of the Pt/Al<sub>2</sub>O<sub>3</sub> catalyst studied here was found to be a strong function of the platinum oxidation state. As the extent of platinum reduction is increased, the catalytic activity for complete oxidation of di(n)-propyl sulfide decreases. Reduced platinum is believed to be more reactive than oxidized platinum for reactions involving complete oxidation of hydrocarbons (1,7,12). Volter et al. (7) has shown that while increasing the calcination temperature from 500°C to 900°C dispersion decreases, the activity of Pt/Al<sub>2</sub>O<sub>3</sub> for oxidation of n-heptane increases. Although platinum dispersion will be altered by the different pretreatments, it is not felt that differences in catalytic activities observed here is the sole result of dispersion. Note that while the extent of reduction is similar for catalysts pretreated in hydrogen at 300°C and calcined at 800°C, a different dispersion is expected but the catalytic behavior is similar. This indicates that the oxidation state is an important consideration in determining the activity of supported platinum catalysts. Chlorine is known to poison platinum oxidation catalysts (1,10). No chlorine could be detected from catalysts calcined at 600°C and above, based on wet chemical analysis, yet these materials possessed the lowest level of activity. Because of this, it was not felt that chlorine played a major role in determining catalytic activity. The differences in reaction behavior, as illustrated in Figure 2, are attributed to the relative amounts of reduced and oxidized platinum species, with the oxidized species being more efficient in sulfide oxidation.

The presence of sulfur compounds in mixed feed streams has been shown to severely reduce hydrocarbon oxidation activity through adsorption onto the catalyst surface (2,3,16). It is possible that while the reduced metal phase is more active in hydrocarbon oxidation, it is much more susceptible to sulfur poisoning in that sulfur

will adsorb onto the metal and effectively block the active site. The oxidized platinum species, while not as active towards hydrocarbon oxidation (7), apparently is more resistant to sulfur poisoning and hence more active than the reduced platinum phase.

#### Conclusions:

Increasing the calcination temperature of a Pt/Al<sub>2</sub>O<sub>3</sub> catalyst from 410°C to 800°C will result in decreased catalytic activity due to an increase in the extent of platinum reduction. The reduced metal phase is inferior in terms of activity and poison resistance to the oxidized metal phase in the complete oxidation of di(n-propyl) sulfide.

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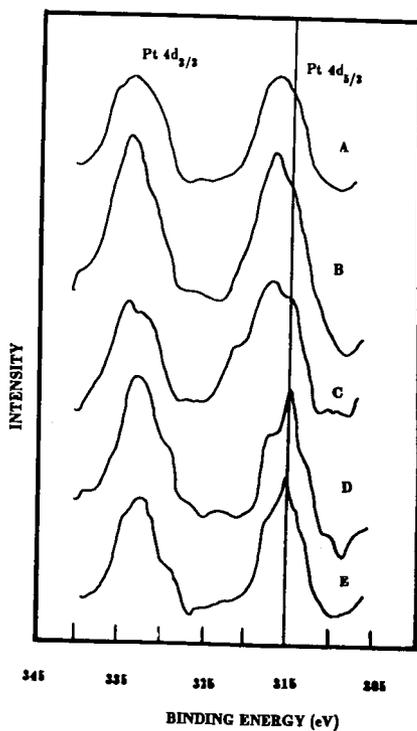


Figure 1: XPS spectra of the platinum 4d photoelectron region for a 1% Pt/Al<sub>2</sub>O<sub>3</sub> catalyst following 16 hours calcination in flowing air and 16 hours reduction in hydrogen at 300°C. A) calcination at 300°C, B) calcination at 410°C, C) calcination at 600°C, D) calcination at 800°C and E) reduction in hydrogen at 300°C.

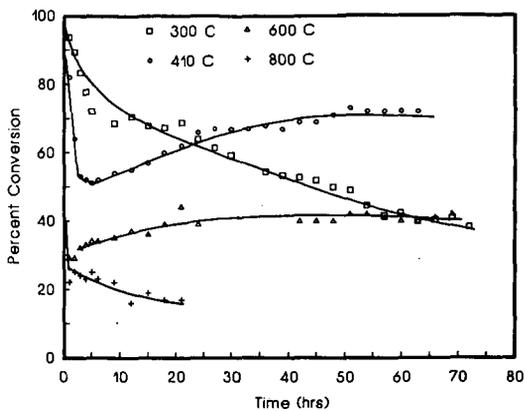


Figure 2: Conversion of di(n)-propyl sulfide (100 ppm in 1.70 Nl/min air) as a function of time on stream for catalysts calcined at different temperatures. ■ 300°C, ● 410°C, ▲ 600°C, + 800°C.

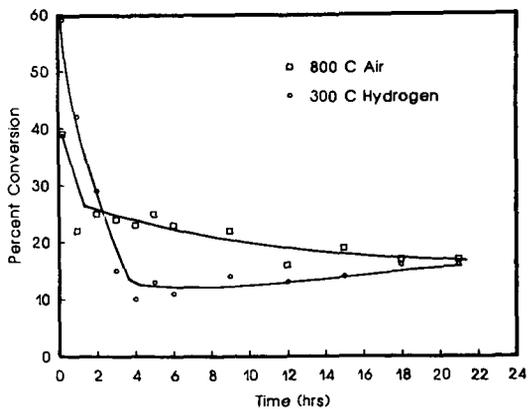


Figure 3: Conversion of di(n)-propyl sulfide (100 ppm in 1.70 Nl/min air) as a function of time on stream for catalysts pretreated in air at 800°C and in hydrogen at 300°C.