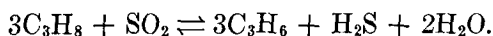


## Catalytic Oxidative Dehydrogenation of Propane to Propylene

The present work is an investigation of the system propane-sulfur dioxide over Pd/Al<sub>2</sub>O<sub>3</sub> catalyst in the reduced and sulfided states.

Pd/Al<sub>2</sub>O<sub>3</sub> was chosen because of the remarkable high yield and selectivity to propylene formation resulting from the dehydrogenation of propane (1).

The overall reaction for the dehydrogenation of propane to propylene with SO<sub>2</sub> can be written as



Previous studies (2) have shown that the above reaction is endothermic and that  $K_P$  increases with temperature.

Propane, hydrogen, nitrogen, oxygen, sulfur dioxide and hydrogen sulfide were high purity products. Catalyst, containing 0.5% wt Pd/Al<sub>2</sub>O<sub>3</sub> was supplied by Engelhard (UK) with fairly uniform particles of about  $\frac{1}{16}$  in. in size and surface area of about 250 m<sup>2</sup>/g.

The reaction was studied in a conventional fixed bed flow reactor and operated at atmospheric pressure. The products were analyzed by gas chromatography (Tables 1 and 2).

After the weighed quantity of catalyst has been introduced into the reactor, the latter was flushed with N<sub>2</sub> at a flow rate of 100 ml/min to eliminate oxygen. During this flushing, the reactor temperature was raised to 450°C over a period of 3 hr, hydrogen was then passed at a rate of 150 ml/min for 4 hr at the same temperature.

When sulfided catalyst was used, the sulfiding process was carried out by passing a mixture of H<sub>2</sub> + H<sub>2</sub>S (1:1 by volume, total volume 150 ml/min) for 4 hr at 350°C.

In order to maintain the catalyst in the sulfided state during the experiment, hydrogen sulfide was added to the propane feed at the rate of 20 ml/min during the heat-up period and during the first hour of the process.

Since the catalyst loses activity during operation due to deposition of carbon on the surface it was necessary to regenerate the catalyst. This was done by heating the catalyst in a stream of 80% O<sub>2</sub> and 20% N<sub>2</sub> at 450-500°C for several hours, this was followed by subjecting the catalyst to hydrogen treatment (or H<sub>2</sub> + H<sub>2</sub>S) for 4-6 hr at 550°C before it was ready for further dehydrogenation runs. The catalyst activity was completely restored after this regeneration process.

The dehydrogenation of propane to propylene was first investigated on the reduced and sulfided 0.5% Pd/Al<sub>2</sub>O<sub>3</sub> catalysts.

Results given in Table 1 show the performance of both catalysts at different temperatures using propane feed at 1 atm pressure and space velocity of 600 hr<sup>-1</sup>.

The reduced Pd/Al<sub>2</sub>O<sub>3</sub> is clearly superior to the sulfided catalyst. It shows a moderate activity as can be seen from conversion data, and high selectivity to propylene at temperatures as high as 611°C. On the other hand, sulfided Pd/Al<sub>2</sub>O<sub>3</sub> catalyst shows poor activity although its selectivity was fairly high (71%). Sulfiding Pd/Al<sub>2</sub>O<sub>3</sub> did not, therefore, improve activity and/or selectivity over the reduced catalyst.

Table 2 summarizes the results of added SO<sub>2</sub> on conversion and selectivity at different temperatures and C<sub>3</sub>H<sub>8</sub>/SO<sub>2</sub> ratios. The addition of SO<sub>2</sub> to the feed increases

TABLE 2  
Effect of SO<sub>2</sub> on the Dehydrogenation of Propane (Reduced Catalyst)

Temp (°C)	C <sub>3</sub> H <sub>8</sub> (ml/min)	SO <sub>2</sub> (ml/min)	N <sub>2</sub> (ml/min)	Conversion (%)	Selectivity (%)
562	60	10	30	18.3	22.3
562	60	20	20	24.8	16.7
582	60	10	30	26.5	18.4
582	60	20	20	41.4	14.8
618	60	10	30	40.6	22.7
618	60	20	20	52.2	20.3

the conversion of propane; however, the selectivities to propylene are far below those obtained with pure propane feed (see Table 1).

The conclusions which could be drawn from this study are: First, sulfiding palladium catalyst did not improve activity or selectivity. Second, the reduced Pd/Al<sub>2</sub>O<sub>3</sub> catalyst offers some advantages over the conventional Cr<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>-K<sub>2</sub>O dehydrogenation catalyst (3), especially in high temperature operations in which appreciable increase in selectivity per pass is noticed (see bottom of Table 1).

TABLE 1  
Dehydrogenation of Propane on Pd/Al<sub>2</sub>O<sub>3</sub><sup>a</sup>

Catalyst	Temp (°C)	Conver- sion	Selec- tivity
Pd/Al <sub>2</sub> O <sub>3</sub> (reduced)	552	5.52	94.2
	567	7.07	93.6
	590	11.18	93.1
	611	18.00	92.2
Pd/Al <sub>2</sub> O <sub>3</sub> (sulfided)	552	2.50	82.7
	567	0.71	75.8
	590	1.35	73.6
	611	3.40	71.0
16.8% Cr <sub>2</sub> O <sub>3</sub> -Al <sub>2</sub> O <sub>3</sub> -K <sub>2</sub> O (reduced)	590	28.7	85.9
	611	37.0	84.0

<sup>a</sup> Reduced and sulfided catalysts; space velocity, 600 hr<sup>-1</sup>; no SO<sub>2</sub> added.

In a few experiments coke deposited on chroma-alumina was measured and it averaged 2-4% of the propane converted compared with less than 1% for Pd/Al<sub>2</sub>O<sub>3</sub> catalyst.

The third conclusion is that oxidative dehydrogenation using SO<sub>2</sub> offers another alternative to overcome the equilibrium limitation of the reaction; Pd/Al<sub>2</sub>O<sub>3</sub> offers some hope in this respect.

Although it is premature at this stage to give some insight into the mechanisms of these reactions, however, SO<sub>2</sub> seems to abstract hydrogen from the alkane with the result that hydrogen sulfide and water are formed. These were detected by glc analysis.

On the other hand, the relatively low selectivity of Pd/Al<sub>2</sub>O<sub>3</sub> to propylene could result from the latter being oxidized by SO<sub>2</sub> to water and carbon dioxide. The presence of CO<sub>2</sub> among the reaction products seems to support this view.

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