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Catalytic Oxidative Dehydrogenation of Propane to Propylene

The present work is an investigation of the system propane–sulfur dioxide over Pd/Al_2O_3 catalyst in the reduced and sulfided states.

Pd/Al_2O_3 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 deyhdrogenation of propane to propylene with SO_2 can be written as

$$3C_3H_8 + SO_2 \rightleftharpoons 3C_3H_6 + H_2S + 2H_2O.$$

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_2O_3 was supplied by Engelhard (UK) with fairly uniform particles of about $\frac{1}{16}$ in. in size and surface area of about 250 m^2/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_2 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 $H_2 + H_2S$ (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_2 and 20% N_2 at 450–500°C for several hours, this was followed by subjecting the catalyst to hydrogen treatment (or $H_2 + H_2S$) 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_2O_3 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^{-1}.

The reduced Pd/Al_2O_3 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_2O_3 catalyst shows poor activity although its selectivity was fairly high (71%). Sulfiding Pd/Al_2O_3 did not, therefore, improve activity and/or selectivity over the reduced catalyst.

Table 2 summarizes the results of added SO_2 on conversion and selectivity at different temperatures and C_3H_8/SO_2 ratios. The addition of SO_2 to the feed increases

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TABLE 2

Effect of SO_2 on the Dehydrogenation of Propane (Reduced Catalyst)

Temp (°C)	C_3H_8 (ml/min)	SO_2 (ml/min)	N_2 (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_2O_3 catalyst offers some advantages over the conventional Cr_2O_3–Al_2O_3–K_3O 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_2O_3[a]

Catalyst	Temp (°C)	Conversion	Selectivity
Pd/Al_2O_3 (reduced)	552	5.52	94.2
	567	7.07	93.6
	590	11.16	93.1
	611	18.00	92.2
Pd/Al_2O_3 (sulfided)	552	2.50	82.7
	567	0.71	75.8
	590	1.35	73.6
	611	3.40	71.0
16.8% Cr_2O_3–Al_2O_3–K_2O (reduced)	590	28.7	85.9
	611	37.0	84.0

[a] Reduced and sulfided catalysts; space velocity, 600 hr^{-1}; no SO_2 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_2O_3 catalyst.

The third conclusion is that oxidative dehydrogenation using SO_2 offers another alternative to overcome the equilibrium limitation of the reaction; Pd/Al_2O_3 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_2 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_2O_3 to propylene could result from the latter being oxidized by SO_2 to water and carbon dioxide. The presence of CO_2 among the reaction products seems to support this view.

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