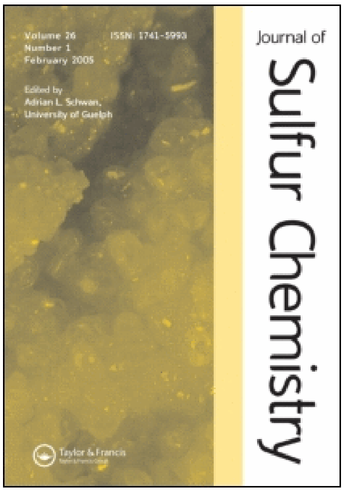

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## COMMUNICATION

# Oxidative dehydrogenation of propane to propene in the presence of $H_2S$ at short contact times

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The oxidative dehydrogenation of propane to propene at short contact times over $V_2O_5/A1_2O_3$ was remarkably enhanced by the introduction of $H_2S$ in the feed mixture. Overall conversion of propane over this catalyst at 700 °C and 5 ms contact time was 53.7% with selectivity to propene of 56.5%, providing a net propene yield of 30.4%.

*Keywords*: Oxidative dehydrogenation; Propane; $H_2S$

## 1. Introduction

The selective oxidative dehydrogenation (ODH) of short-chain alkanes into their corresponding olefins has been of great interest in recent years. This process provides an attractive alternate route for the production of alkenes from alkanes compared with the conventional cracking and dehydrogenation processes. This is because ODH is thermodynamically favored at lower temperatures, and the presence of $O_2$ inhibits the formation of coke prevalent in non-oxidative routes. Vanadia- and molybdena-based oxide catalyst systems have been found to be effective for this reaction, but the unselective combustion reactions limit alkene selectivities [1, 2]. Especially for the oxidative dehydrogenation of propane to propene, the selectivity losses with increasing conversion are extensive and reported to be due to propene re-adsorption, and subsequent oxidation to carbon oxides (CO and $CO_2$), which leads to propene yields lower than 30% [3–6]. Therefore, it is still very challenging to be able to carry out the oxidative dehydrogenation of propane with a high propene yield.

Many efforts have been made to gain high yields of propene in the oxidative dehydrogenation of propane. Recently, short-contact-time oxidative dehydrogenation of light alkanes at high temperatures has been shown to be a promising route for the selective production of short-chain olefins. Schmidt and co-workers performed much of the pioneering work [7]. For the propane ODH, up to 60% selectivity to total olefins (propene selectivity below 30%) at

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nearly 100% conversion of propane has been achieved with a catalyst contact time of 5 ms at 800–1000 °C [8]. However, most of these studies are based on noble metal Pt catalyst systems, with little work having been done on vanadium- or molybdate-based oxide catalysts [9]. In addition, it has been shown that the addition of some mild oxidants, such as $CO_2$ and $N_2O$, can effectively promote the selectivity for propene [10, 11].

While the use of gas-phase promoters has been considered in the oxidative dehydrogenation of propane, addition of $H_2S$ to the feed gas has not been investigated to our knowledge. Gaseous doping with hydrogen sulfide was, however, investigated in the presence of a $Pt/Al_2O_3$ catalyst as to its effect on catalyst activity and selectivity for propane dehydrogenation without $O_2$, but no apparent enhancement of propene formation was found [12]. Claims of selectivity benefits can, however, be found within the patent literature from incorporation of $H_2S$ in the thermal dehydrogenation of propane to propene for uncatalyzed systems [13, 14]. In this paper we report on the study of the oxidative dehydrogenation of propane to propene in the presence of $H_2S$ at short contact times. This study shows that the yield of propene can be significantly enhanced by the introduction of $H_2S$ in the feed gas and suitable optimization of the reaction conditions.

## 2. Results and discussion

The test results for homogeneous oxidative dehydrogenation of propane at 800 °C with and without $H_2S$ in the feed gas at various residence times are compared in table 1. The data in the first five rows show the results of the gas-phase reaction of propane + $O_2$ ($C_3H_8$: $O_2$ = 4:1) without $H_2S$. Both $C_3H_8$ and $O_2$ conversions declined with a decrease in the residence time from 1.5 to 0.005. Ethylene was the predominant product although $C_3H_6$ selectivity increased significantly with decreasing residence time. The large amount of $CH_4$ and $C_2H_4$ in the product mixture suggests that $C_3H_8$ cracking instead of dehydrogenation is the key reaction in the homogeneous $C_3H_8 + O_2$ reaction at 800 °C.

Table 1. Effect of $H_2S$ as a promoter and residence time on the homogeneous oxidative dehydrogenation of propane.[a]

| Feed gas | Residence Time ($t$/s) | Conversion/% $C_3H_8$ | $O_2$ | $H_2S$ | Selectivity[b]/% $C_3H_6$ | $C_2H_4$ | $CO_x$ | $CH_4$ | $C_2H_6$ | Yield of $C_3H_6$/% |
|---|---|---|---|---|---|---|---|---|---|---|
| $C_3H_8/O_2$[c] | 1.5 | 96.3 | 100 | – | 8.7 | 43.1 | 5.9 | 26.1 | 3.4 | 8.3 |
| | 0.5 | 69.6 | 100 | – | 20.6 | 37.4 | 9.8 | 18.7 | 2.8 | 14.3 |
| | 0.1 | 68.4 | 98.5 | – | 27.3 | 40.8 | 6.2 | 18.0 | 2.4 | 18.7 |
| | 0.01 | 63.2 | 85.4 | – | 29.0 | 39.9 | 5.6 | 17.7 | 2.2 | 18.3 |
| | 0.005 | 58.1 | 75.0 | – | 31.1 | 39.6 | 4.8 | 17.0 | 2.6 | 18.1 |
| $C_3H_8/O_2/H_2S$[d] | 1.5 | 100 | 100 | 19.6 | 17.0 | 28.4 | 4.3 | 18.6 | 2.9 | 17.0 |
| | 0.5 | 96.0 | 100 | 15.6 | 27.9 | 25.9 | 5.9 | 14.9 | 2.4 | 26.8 |
| | 0.1 | 82.5 | 100 | 24.3 | 43.9 | 35.5 | 1.1 | 14.5 | 2.6 | 36.2 |
| | 0.01 | 75.6 | 94.4 | 19.4 | 49.8 | 28.5 | 1.2 | 15.8 | 2.0 | 37.6 |
| | 0.005 | 64.3 | 90.2 | 16.2 | 50.9 | 29.0 | 1.3 | 16.1 | 1.7 | 32.7 |

[a] Reaction conditions: $T$ = 800 °C, $P$ = 1 atm.
[b] Small amounts of $C_2H_2$, $CS_2$, and COS were also detected, but are not shown here.
[c] $C_3H_8$:$O_2$ = 4:1.
[d] $C_3H_8$:$H_2S$:$O_2$ = 4:2:1.

The introduction of $H_2S$ to the feed gas was found to have a noticeable effect (bottom five rows of data in table 1) in that the amounts of $CO_x$, $C_2H_4$, and $CH_4$ were reduced significantly.

Most importantly, propene selectivity increased and propene became the major product, especially at residence times below 0.5 s. Although the conversions of $C_3H_8$ and $O_2$ also declined with decreasing residence times in the presence of $H_2S$, it is of interest to note that both $C_3H_8$ and $O_2$ conversions were markedly enhanced relative to the results without $H_2S$. This leads to a higher yield of propene in the presence of $H_2S$ as a gas-phase promoter by achieving higher propene selectivity while maintaining a high conversion of $C_3H_8$ at the same time. As can be seen from table 1, nearly 50% selectivity to propene with 75.6% conversion of propane was obtained at 0.01s residence time, giving the highest propene yield of 37.6%. In comparison, the yield of propene at the same residence time without $H_2S$ being present was only one-half of this value. Therefore, it can be concluded that the presence of $H_2S$ in the feed mixture has a very significant promoting effect on the activity and selectivity to propene in this study. In general, the results also show that short residence times can improve the selectivity and yield of propene by effectively suppressing side reactions to some extent.

Table 2 shows the results for the catalytic performance of $A1_2O_3$ and $V_2O_5/A1_2O_3$ catalysts in the oxidative dehydrogenation of propane at 700 °C and 0.005 s contact time. For comparison, the results of gas-phase oxidative dehydrogenation of propane at 0.005 s residence time are also presented. It can be seen that much lower conversions of $C_3H_8$ and $O_2$, along with higher selectivities to propene, were obtained in the homogeneous reaction at 700 °C both with and without $H_2S$ compared with the data in table 1 conducted at 800 °C. With $H_2S$ in the feed mixture, up to 70% selectivity to propene could be achieved with a conversion of 28.1% propane at 700 °C. No apparent differences in the activity and selectivity of products were observed between $A1_2O_3$ as a catalyst and the homogeneous reactions both with and without $H_2S$. In contrast, $V_2O_5/A1_2O_3$ catalyst was found to be selective for the formation of $CO_x$, but not propene, in the oxidative dehydrogenation of propane without $H_2S$ at 700 °C. This same catalyst, however, turned out to be an effective catalyst for the ODH of propane when $H_2S$ was added to the feed gas. As can be seen from table 2, up to 56.5% propene selectivity with 53.7% conversion of propane was obtained, providing a yield of propene of 30.4%. This value, to the best of our knowledge, is higher than those reported in the literature for the catalytic oxidative dehydrogenation of propane in the absence of $H_2S$. Indeed, when ethylene is taken into account with propene, it is notable that the $V_2O_5/A1_2O_3$ catalyst offers an olefin selectivity of up to 81% at a high propane conversion. It should be noted that the propene yield was only 19.7% in the homogeneous reaction under the same conditions, so that the excellent performance of $V_2O_5/A1_2O_3$ catalyst in the presence of $H_2S$ must be attributed to some feature of the catalyst in the current investigation.

Table 2. Catalytic oxidative dehydrogenation of propane in the presence of $H_2S$ at short contact time.[a]

| | | Residence | Conversion/% | | | Selectivity[c]/% | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Catalyst | Feed gas | or Contact Time[b] ($t$/s) | $C_3H_8$ | $O_2$ | $H_2S$ | $C_3H_6$ | $C_2H_4$ | $CO_x$ | $CH_4$ | $C_2H_6$ | Yield of $C_3H_6$/% |
| | $C_3H_8/O_2/H_2S$ | 0.005 | 28.1 | 79.3 | 13.2 | 70.3 | 16.9 | 1.8 | 8.9 | 0.4 | 19.7 |
| | $C_3H_8/O_2$[d] | 0.005 | 31.3 | 56.6 | – | 43.0 | 36.0 | 3.3 | 13.5 | 1.7 | 13.5 |
| $Al_2O_3$ | $C_3H_8/O_2/H_2S$ | 0.005 | 24.2 | 89.6 | 9.7 | 71.3 | 13.9 | 5.7 | 5.6 | 0.3 | 17.2 |
| | $C_3H_8/O_2$[d] | 0.005 | 26.8 | 56.3 | – | 44.5 | 34.8 | 3.1 | 12.7 | 2.2 | 11.9 |
| $V/Al_2O_3$ | $C_3H_8/O_2/H_2S$ | 0.005 | 53.7 | 100 | 8.7 | 56.5 | 25.1 | 1.0 | 12.9 | 1.4 | 30.4 |
| | $C_3H_8/O_2$[d] | 0.005 | 22.8 | 99.0 | – | 25.0 | 29.9 | 22.3 | 13.6 | 2.1 | 5.7 |

[a] Reaction conditions: $T = 700\,°C$, $P = 1$ atm, $C_3H_8$:$H_2S$:$O_2$ = 4:2:1.

[b] Residence time and contact time are defined to describe the non-catalytic and catalytic reaction, respectively.

[c] Small amount of $C_2H_2$, $CS_2$, and COS were also detected, but are not shown here.

[d] $C_3H_8$:$O_2$ = 4:1.

The effects of temperature on the catalytic ODH performance of $V_2O_5/Al_2O_3$ catalyst in the presence of $H_2S$ with a 0.005 s contact time are shown in figure 1. This figure shows that the conversion of $C_3H_8$ increased with reaction temperature, whereas that of $H_2S$ appeared to decrease (figure 1A), while nearly all $O_2$ was consumed at the studied temperatures ranging from 500–700 °C. These observations can be interpreted in terms of the mechanism of $H_2S$-assisted ODH shown in scheme 1 that leads to re-formation of $H_2S$, thus giving rise to an apparently lower $H_2S$ conversion with increasing conversion of propane.

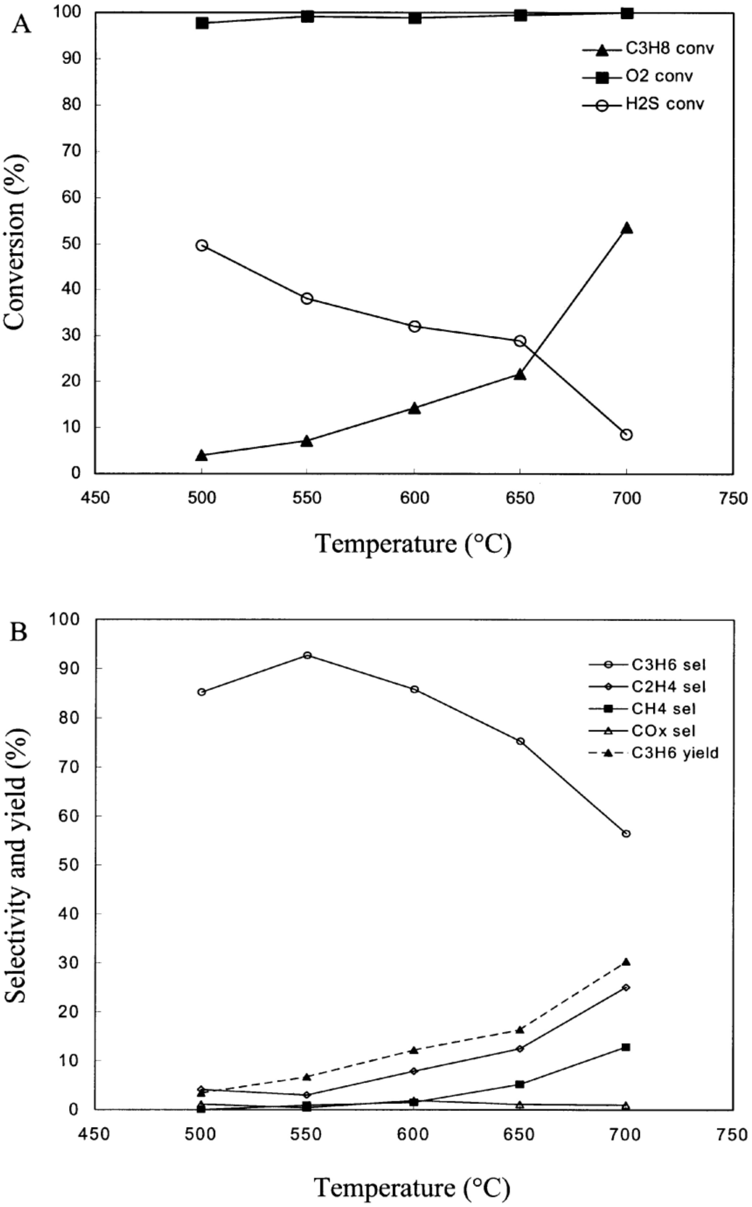

Figure 1. Effect of temperature on conversion (A) and selectivity and yield of $C_3H_6$ (B) for oxidative dehydrogenation of propane over $V_2O_5/Al_2O_3$ catalyst. (Reaction conditions: $C_3H_8$:$H_2S$:$O_2$ = 4:2:1, contact time = 0.005 s).

$$H_2S + \tfrac{1}{2}O_2 \longrightarrow \tfrac{1}{2}S_2 + H_2O$$

$$C_3H_8 + \tfrac{1}{2}S_2 \longrightarrow C_3H_6 + H_2S$$

$$\overline{\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad}$$

$$C_3H_8 + \tfrac{1}{2}O_2 \longrightarrow C_3H_6 + H_2O$$

SCHEME 1

Figure 1 further shows that lower temperatures favored the selective formation of $C_3H_6$ (figure 1B) with up to 92% selectivity to propene being obtained at a temperature of 550 °C. The conversion of propane under this condition was, however, lower than 10%. Increasing the temperature resulted in a decline in the selectivity to propene, but with apparently increased selectivity to $C_2H_4$ and $CH_4$. Interestingly, the selectivity to $CO_x$ always stayed at a very low level in the presence of the $V_2O_5/Al_2O_3$ catalyst, indicating that the over-oxidation of hydrocarbons in the reaction was being suppressed. This can be attributed to the presence of $H_2S$ in the reaction system, since much more $CO_x$ was produced without $H_2S$ over the same $V_2O_5/Al_2O_3$ catalyst at 700 °C, as shown in table 2. Overall the yield of propene was noted to increase (dashed line in figure 1B) with an increase in the temperature, although the selectivity to propene declined significantly.

In recent years attempts to produce both hydrogen and sulfur from hydrogen sulfide have received considerable attention [15]. Work in our laboratory has further successfully demonstrated that $H_2S$ can be effectively converted in to a mixture of sulfur, $H_2O$ and $H_2$ by catalytic partial oxidation at a 4:l $H_2S/O_2$ ratio using either $\alpha$- or $\gamma$- alumina catalysts at short contact times [16]. Indeed, considerable amounts of $S_2$ have been observed in the product mixture in the present study, which would indicate that the rate of reaction of $O_2$ with $H_2S$ is much greater than with hydrocarbon. In particular over the $V_2O_5/Al_2O_3$ catalyst, it can be seen that the selectivity to $CO_x$ when $H_2S$ is present in the feed gas was much lower than without $H_2S$ (table 2). The result, therefore, that nearly all $O_2$ is consumed by the $H_2S$ (figure 1) would suggest that the $S_2$ product can act as an active species similar to $O_2$ to carry out the selective oxidative dehydrogenation of propane to propene as suggested in scheme 1, in which $H_2S$ is recovered and the $CO_x$ products are significantly suppressed.

## 3. Conclusions

In conclusion, it has been demonstrated that the oxidative dehydrogenation of propane to propene in the presence of $H_2S$ at short contact time is a highly promising route for improving propene yield. The obtained results show the importance of both of these parameters in the reaction conditions used for the present study. Thus, an appropriate combination of both $H_2S$ in the feed and a short contact time can afford high yields of propene. Accordingly, the best propene yield achieved in this work was 30.4% over $V_2O_5/Al_2O_3$ catalyst in the presence of $H_2S$ in the feed at 0.005 s contact time and 700 °C. Further work is currently in progress to identify more active and selective catalysts, and also to elucidate the active role of $H_2S$ in the oxidative dehydrogenation of propane.

## 4. Experimental

Two commercial catalysts, $\gamma$-$Al_2O_3$ (Almatis, DD-431) and $V_2O_5/Al_2O_3$ (Axens DN-115, $V_2O_5$ loading $= 13\%$), were used in this study. The oxidative dehydrogenation of propane was carried out in a fixed-bed horizontal-flow quartz tubular reactor at atmospheric pressure and high temperatures (600–800 °C). A larger, 10.7 mm i.d. quartz reactor was used for longer-contact-time (or residence time) experiments, while a smaller, 8.1 mm i.d. reactor was used for shorter-contact-time runs. In the case of gas-phase tests, an appropriate amount of quartz chips (4–10 mesh) was placed in the reactor within the hot zone. The unoccupied volume within this packed region was regarded as the main reaction zone, which was small enough to run homogeneous ODH reactions at short residence times down to 5 ms. For catalytic ODH experiments, the catalyst was packed at the beginning of the hot zone where the feed gases were introduced. The catalyst packing volume ranged from 0.4 to 4 mL, corresponding to contact times of 0.005 to 2 s.

Oxygen was premixed with nitrogen (used as an internal standard for analysis) and then introduced through an inner quartz tube (i.d. = 5 mm) directly to the catalyst bed while the mixture of propane/$H_2S$ or propane alone flowed onto the catalyst surface through the main reactor tube. Such a design avoids the generation of possible explosive mixtures due to the premixing of oxygen with flammable propane. Calculation of the contact time ($t_c$) or residence time ($t_{res}$) in the experiments was corrected to the actual reaction temperature using equations (1) and (2).

$$t_{res}(\mathrm{s}) = \frac{V_{\text{reaction zone}}\ (\text{mL}) \times 294\ (\text{K}) \times 60}{\text{Metered flow (294 K, mL/min)} \times \text{Furnace temperature (K)}} \tag{1}$$

$$t_c(\mathrm{s}) = \frac{V_{\text{catalyst}}\ (\text{mL}) \times 294\ (\text{K}) \times 60}{\text{Metered flow (294 K, mL/min)} \times \text{Furnace temperature (K)}} \tag{2}$$

Gas samples for analysis were withdrawn using a peristaltic pump connected to a capillary quartz tube, which was placed immediately downstream of the catalyst bed. For homogeneous gas-phase experiments, samples were retrieved with the same capillary system from the end of the reaction zone.

Analysis of the reactants and products was performed by gas chromatography using several SRI 8610 gas chromatographs equipped with TCD detectors. $N_2$, $O_2$ and CO were analyzed on a 5 Å molecular sieve column using He as carrier, and $H_2$ was analyzed separately also on a 5 Å molecular sieve column but using argon as the carrier gas. Hydrocarbons ($C_1$–$C_3$) and sulfur-containing compounds ($H_2S$, $SO_2$, COS and $CS_2$) as well as $CO_2$ were analyzed on a Poropak QS column using He as carrier and a temperature-programmed run. Analyses were performed in triplicate after the reactor had been allowed to stabilize at the new process conditions for 30 min. All experimental data presented here were shown to be reproducible.

Reported conversions, selectivities, and yields were calculated using equations (3)–(5) and $N_2$ as an internal standard:

$$\text{Conversion (i) \%} = \frac{\text{moles of reactant (i) in the feed} - \text{moles of reactant (i) after reaction}}{\text{moles of reactant (i) in the feed}} \times 100 \tag{3}$$

where i may refer to $C_3H_8$, $H_2S$ or $O_2$.

$$\text{Selectivity (j) \%} = \frac{\text{moles of reactant (i) converted in to product (j)}}{\text{moles of converted reactant (i)}} \times 100 \tag{4}$$

where i represents $C_3H_8$ while j refers to CO, $CO_2$ or one of $C_1$–$C_3$ hydrocarbons.

$$\text{Yield of product (j) \%} = \text{Conversion of reactant (i)} \times \text{Selectivity of product (j)} \tag{5}$$

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