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NOTE

Selective Oxidative Dehydrogenation of Propane over V–Mg–O Catalysts

Vanadium–magnesium oxides were found to be active and selective catalysts for the oxidative dehydrogenation of propane to propene. A selectivity of up to 65% was obtained at 10% conversion, but decreased with increasing conversion. No oxygenates were detected. The reaction rate was 0.6 ± 0.15 order in propane and zeroth order in oxygen. For comparison, the rate for butane oxidative dehydrogenation was 0.85 ± 0.15 in butane and zeroth order in oxygen. Both reactions were believed to proceed primarily with the breaking of a methylene C–H bond to form an adsorbed alkyl radical species. © 1988 Academic Press, Inc.

INTRODUCTION

Selective conversion of alkanes to unsaturated hydrocarbons is a potentially important process to utilize alkanes. The current commercial process makes use of a chromia–alumina catalyst (*1*) in which alkanes are converted to unsaturated hydrocarbons and hydrogen. For small hydrocarbons ($<C_6$), the reaction temperature is high, usually above 600°C, since the yield is limited by thermodynamic equilibrium at low temperatures. At such a high temperature, undesirable reactions such as cracking of the hydrocarbons and coking of the catalyst occur. In practice, the chromia–alumina catalysts require regeneration every several minutes.

Oxidative dehydrogenation in which water is formed as a by-product instead of hydrogen does not have the limitation by thermodynamic equilibrium, and catalyst deactivation is usually not a problem since coke and its precursors can be efficiently removed by oxygen. To date, however, there are only a few reports on selective oxidative dehydrogenation of alkanes (*2–5*). Lunsford and co-workers have used N_2O as an oxidant for the selective oxidation of ethane to ethene (*3*). Selective dehydrogenation using oxygen has also been reported on Mo–Mg–O, Ni–Mg–O (*4*), and Co–Mg–O (*5*) catalysts. A selectivity for a mixture of butenes and butadiene from butane as high as 58% has been claimed (*6*).

Recently, we reported that a V–Mg–O catalyst is a selective oxidative dehydrogenation catalyst for butane to butenes and butadiene using oxygen as the oxidant (*7*). The conclusion from characterization of the catalysts with X-ray diffraction, IR spectroscopy, Auger electron spectroscopy, and scanning electron microscopy was that the active phase is magnesium orthovanadate. We report here the results for the oxidation of propane on these catalysts and the comparison of them with those of butane.

EXPERIMENTAL

The preparation of the catalysts was described previously (*7*). Briefly, MgO was prepared by precipitation from a magnesium nitrate (Fisher Scientific) solution with ammonium carbonate (Alfa Products), followed by calcination in air at 700°C. An aqueous solution containing 0.5 wt% ammonium vanadate and 1 wt% ammonium hydroxide at 70°C was added to MgO powder. The suspension was dried with stirring to a paste. This step was repeated until the appropriate amount of vanadium was added. Then the suspension was dried overnight at 80°C. The resulting solid was calcined at 550°C for 6 h. The BET surface areas and the actual compositions as deter-

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TABLE 1

Surface Areas and Compositions of the Catalysts

Catalyst	Surface area (m^2/g)	wt% MgO	wt% V_2O_5
MgO	28	100	0
V_2O_5	3.5	0	100
19V–Mg–O	46	81.1	18.9
24V–Mg–O	74	76.3	23.7
40V–Mg–O	31	60.1	39.8
60V–Mg–O	7	40.7	59.3

mined by atomic absorption spectroscopy are listed in Table 1.

Reactions were run in a conventional flow system with a quartz U-tube reactor at close to atmospheric pressure. The conversion of propane for an empty reactor increased with increasing temperature, but was negligible (<0.5%) even at 540°C. Under the same conditions, a reactor with quartz wool and silica gel showed lower conversion than an empty reactor.

The catalysts were supported by quartz wool. Except for MgO, the catalysts were diluted with twice the weight of silica gel. Under the standard conditions, the feed was 4 vol% propane (Linde, CP grade), 8% oxygen (Linde, hydrocarbon free), and the balance He (Linde, high purity). The flow rate was 100 ml/min at room temperature. Products were analyzed by gas chromatography. The experimental details were similar to those reported earlier (7).

TABLE 2

Conversion and Selectivity in Propane Oxidation over V–Mg–O Catalysts

Catalyst	Weight (g)	Conversion %		Selectivity %			
		C_3H_8	O_2	CO	CO_2	C_2	C_3H_6
MgO	0.5	7.7	8.0	25.6	26.5	14.9	33
19V–Mg–O	0.3	35.8	52.9	18.9	36.4	2.3	42.4
24V–Mg–O	0.1	28.9	46.6	19.0	37.2	1.4	42.4
40V–Mg–O	0.2	33.4	54.9	23.1	33.7	1.3	41.9
V_2O_5	0.4	22.0	41.3	64.8	17.2	0	18.0

Note. 540°C, propane/oxygen = 2.

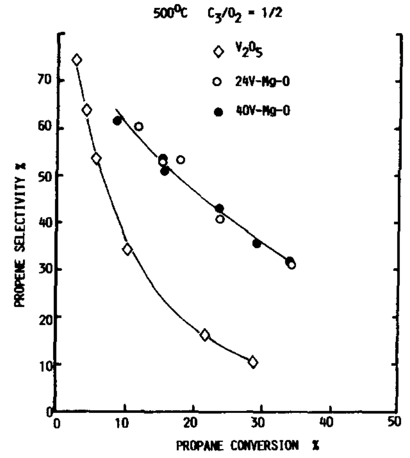

FIG. 1. Effect of conversion on propene selectivity in the oxidation of propane at 500°C.

RESULTS AND DISCUSSION

Table 2 shows some typical results of the oxidative dehydrogenation of propane on V_2O_5, MgO, and V–Mg–O catalysts. The major products were propene, CO, and CO_2. Small amounts of ethane and ethene (which were not separated) were also produced, especially on MgO. The carbon balance in all the reaction runs was within 5%. Thus little or no oxygenates were formed.

Results in this table show that V–Mg–O catalysts were active and selective for the dehydrogenation of propane. Significantly higher selectivity for propane was obtained than that on MgO or V_2O_5. This observation was similar to that for the oxidative dehydrogenation of butane (7).

Figures 1 and 2 show the dependence of selectivity on conversion for two V–Mg–O catalysts and vanadium oxide at 500 and 540°C, respectively. It can be seen that the selectivity decreased with increasing conversion on all catalysts. However, the decrease was much more rapid on V_2O_5 than on V–Mg–O. Except at very low conversions, the V–Mg–O catalysts were superior to V_2O_5. Comparison of the two figures showed that the selectivity increased slightly when the temperature was increased from 500 to 540°C.

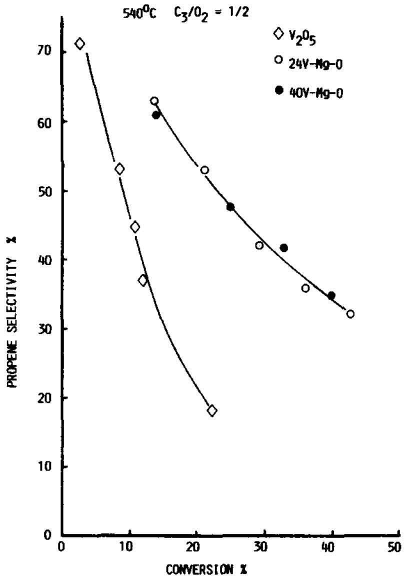

FIG. 2. Effect of conversion on propene selectivity in the oxidation of propane at 540°C.

The effect of changing the propane-to-oxygen ratio in the feed was investigated using the 24V–Mg–O catalyst at 540°C. Decreasing this ratio from 1/2 to 1/1 resulted in a decrease in propane conversion from 32.9 to 22.8%. The selectivity for propene increased from 42.9 to 52.8%. However, this increase could be accounted for almost totally by the decrease in the propane conversion.

Figure 3 compares the dependence of selectivity on conversion for propane and butane at 540°C. For butane, oxidative dehydrogenation can produce either butenes or butadiene. It can be seen that the selectivity for butenes from butane was lower and decreased more rapidly with increasing conversion than that for propene from propane. However, the selectivity for total dehydrogenation (butenes and butadiene) was higher and decreased much more slowly than that for propene.

The partial pressure dependence of the reaction rate was investigated at 540°C by changing the pressure of either alkane or oxygen while keeping the other constant. The results are shown in Figs. 4 and 5. For the oxidation of both propane and butane, the rate was independent of oxygen partial pressure. Thus it was zeroth order in oxygen. However, the rate increased with increasing partial pressures of alkane. The orders were found to be 0.6 ± 0.15 for propane, and 0.85 ± 0.15 for butane. The rate constants were 0.012 mol/$g_{cat.}$ min–$atm^{0.85}$

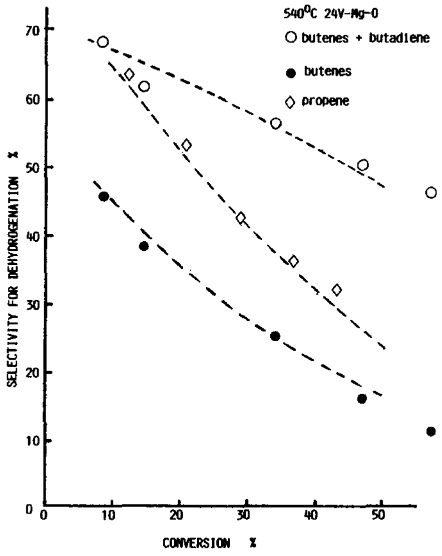

FIG. 3. Comparison of the effect of conversion on the selectivity for oxidative dehydrogenation of propane and butane. The dotted lines are from equations in the text. The butane data are for catalyst 19V–Mg–O, and propane data 24V–Mg–O.

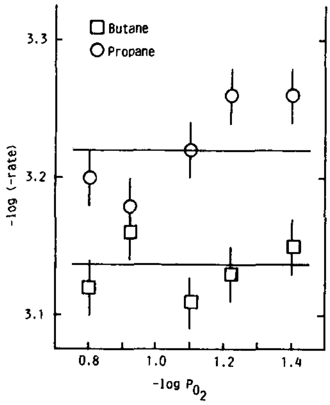

FIG. 4. Effect of oxygen partial pressure on the reaction rate at 540°C. Catalyst, 24V–Mg–O; P_{alkane} = 0.04 atm; and space velocity = 322 g–s/mol of feed.

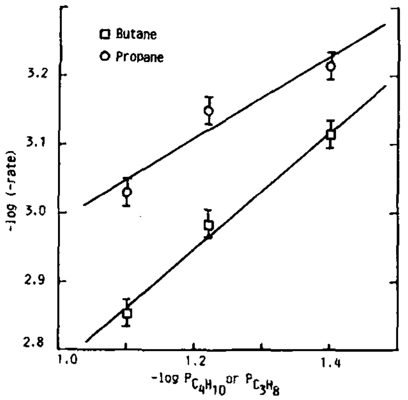

FIG. 5. Effect of alkane partial pressure on the reaction rate at 540°C. Catalyst, 24V–Mg–O; $P_{\text{oxygen}} = 0.08$ atm; and space velocity = 322 g-s/mol of feed.

and 0.004 mol/$g_{\text{cat.}}$ min–$\text{atm}^{0.6}$ for butane and propane, respectively.

The similarity between the results for propane and butane suggests that the two reactions proceed with a similar reaction mechanism. Following our earlier suggestion for butane, it appears that propane first reacts primarily by breaking a methylene C–H bond to form an adsorbed alkyl radical. Rapid breaking of a second C–H bond at an end carbon then forms propene. A methylene C–H bond is first broken instead of a methyl C–H bond because it is weaker by 15 kJ/mol. This suggestion is consistent with the fact that under similar reaction conditions and at low conversions, butane reacts about 1.5 times faster than propane. This can be interpreted by the fact that butane has more methylene C–H bonds than propane.

Extrapolation of the results in Fig. 3 to zero conversion shows that in butane dehydrogenation, the initial products consist of approximately 55–60% butenes, 15–20% butadiene, and the balance carbon oxides. At higher conversions, butadiene is also produced by subsequent dehydrogenation of butenes. If we assume that after the first step of the activation of the alkane, each subsequent step of the dehydrogenation reaction is first order in the reactant, and that for every molecule of butane reacted, 0.55 molecule of butene and 0.15 molecule of butadiene are formed, and for every butene molecule reacted, 0.7 molecule (the same fraction of selective dehydrogenation as for butane) of butadiene is formed, the rate expressions are

$$dP_{\text{butane}}/dt = -k_1(P_{\text{butane}})^{0.85}$$

$$dP_{\text{butenes}}/dt = 0.55k_1(P_{\text{butane}})^{0.85} - k_2P_{\text{butenes}}$$

$$dP_{\text{butadiene}}/dt = 0.7k_2P_{\text{butenes}} + 0.15k_1(P_{\text{butane}})^{0.85} - k_3P_{\text{butadiene}},$$

where k_1, k_2, and k_3 are the rate constants for the reaction of butane, butenes, and butadiene, respectively, and $k_1 = 0.012$. The data in Fig. 3 can be reasonably well fit by setting the ratio $k_1 : k_2 : k_3 = 1 : 4.7 : 1$.

The data for propane can be analyzed similarly. The initial products are 80% propene and 20% carbon oxides. Assuming that the rate expressions are

$$dP_{\text{propane}}/dt = -k_4(P_{\text{propane}})^{0.6}$$

$$dP_{\text{propene}}/dt = 0.8k_4(P_{\text{propane}})^{0.6} - k_5P_{\text{propene}},$$

where k_4 and k_5 are the rate constants for the reaction of propane and propene, respectively, and $k_4 = 0.004$, the data can be fit well if $k_4 : k_5 = 1 : 3.7$. The fact that the ratios k_1/k_2 and k_4/k_5 are roughly the same is consistent with the aforementioned conclusion that the oxidation of propane and butane proceed via a similar mechanism.

These results suggest that the oxidation reaction is initiated by a highly reactive surface oxygen species. This oxygen species reacts with alkane, alkene, or diene with similar reactivity and relatively indiscriminately. Thus the rate constants for each of the hydrocarbon species are comparable in magnitude. This also explains the very small temperature dependence of the selectivity versus conversion curves. The reaction of this species with propane or butane results in the formation of propene or butenes. Reaction of this species with propene would result in combustion. Reaction with butenes would form butadiene, which if it further reacts would result in combustion. This explains the decrease in selectivity with increasing conversion.

It is interesting to note that under similar conditions, a V–P–O catalyst produces acrylic acid and little propene in the oxidation of propane (*8*). We attribute this to the absence of V=O in the V–Mg–O catalysts in which the active component is magnesium orthovanadate (*7*), and to the fact that these catalysts are basic, which enhances the desorption of basic alkene molecules.

In conclusion, the V–Mg–O catalysts are active and selective for the oxidative dehydrogenation of propane to propene. The reaction probably proceeds by first breaking a methylene C–H bond to form an adsorbed alkyl radical. The absence of any oxygenate products is attributed to the absence of V=O bonds and to the basic properties of the catalysts.

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REFERENCES

1. Pines, H., "Catalytic Conversion of Hydrocarbons." Academic Press, 1980.
2. Hucknell, D. J., "Selective Oxidation of Hydrocarbons." Academic Press, New York, 1974.
3. Ward, M. B., Lin, M. J., and Lunsford, J. H. *J. Catal.* **50,** 306 (1977).
4. Stepanov, G. A., Tsailingol'd, A. L., Levin, V. A., and Pilipenko, F. S., *Stud. Surf. Sci. Catal. Part B* **7,** 1293 (1981).
5. Doroshenko, V. A., Shapovalova, L. P., and Tmenov, D. N., *Z. Prik. Khim.* **55,** 80 (1982).
6. Italian patent 845192 (1969).
7. Chaar, M. A., Patel, D., Kung, M. C., and Kung, H. H., *J. Catal.* **105,** 403 (1987).
8. Ai, M., *J. Catal.* **101,** 389 (1986).

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