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NOTE

Oxidative Dehydrogenation of Cyclohexane over Vanadate Catalysts

The oxidative dehydrogenation of cyclohexane was studied at 440 and 484°C over $NdVO_4$, $Mg_3(VO_4)_2$, and a mixed V–Mg–O catalyst. Cyclohexene was the major initial product. Benzene, carbon oxides, and a trace of cyclohexadiene were also observed. The catalytic behavior of the mixed V–Mg–O catalyst in this reaction was very similar to its behavior in the oxidation of butane. However, the behaviors of $NdVO_4$ in the two reactions were different. The difference between the two catalysts was attributed to their different rates of reoxidation.

INTRODUCTION

It has been observed that mixed V–Mg–O catalysts containing 19 to 40 wt% V_2O_5 were quite active and selective catalysts for the oxidative dehydrogenation (OXD) of butane (*1*). On these catalysts, the selectivities for dehydrogenation products (butenes and butadiene) did not vary much with vanadium contents, and were about 50% at a butane conversion of 50%. A correlation was found between the high yields of dehydrogenation products and the appearance of magnesium orthovanadate. Thus it was concluded that $Mg_3(VO_4)_2$ was the active component. In addition to butane, OXD of ethane, propane, and 2-methylpropane had been carried out over mixed V–Mg–O (*2, 3*). The dehydrogenation selectivities differed substantially among these compounds.

A subsequent study showed that indeed stoichiometric $Mg_3(VO_4)_2$ was a selective OXD catalyst for butane (*2*). However, when compared with the mixed V–Mg–O catalysts, it was less selective for butadiene, although the selectivity for butenes was comparable. The difference was not due to different surface areas, although the exact reason is not known. Later it was found that Nd and Sm orthovanadates showed very similar selectivities for OXD of butane as Mg orthovanadate (*4*).

This paper reports the results of the oxidative dehydrogenation of cyclohexane over a mixed V–Mg–O, a stoichiometric Mg orthovanadate, and Nd orthovanadate. The purposes of the study are: (1) to further understand the differences in selectivities in the OXD of different alkanes; (2) to see if the difference found in the butane reaction between Mg orthovanadate and mixed V–Mg–O is also observed for other alkanes; and (3) to see if the similarities between V–Mg–O and $NdVO_4$ are also found for other alkanes.

EXPERIMENTAL

The catalysts used included a 40V–Mg–O catalyst (40 wt% V_2O_5 and 60% MgO, 31 m^2/g) which was a mixture of $Mg_3(VO_4)_2$ and MgO (*1, 5*), a 60V–Mg–O catalyst (60 wt% V_2O_5 and 40% MgO, 7 m^3/g) that was predominantly $Mg_3(VO_4)_2$ with very small amounts of MgO and V_2O_5, and $NdVO_4$ (18 m^2/g) that was the same as the one used previously (*4, 5*). Reactions were run at 400 to 484°C in a conventional flow system using a quartz U-tube microreactor filled with quartz chips. The powder catalyst was diluted with twice the weight of silica and supported by quartz wool. In the absence of a catalyst, no reaction was detected up to 520°C.

The products were analyzed by gas chromatography. The various C_6 products were analyzed with a BX10 column (Altech Associates), and O_2, CO, and CO_2 were analyzed with a Carbosphere column (Altech Associates).

The feed was a mixture of He, O_2, and

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cyclohexane usually at a ratio of 89 : 7.5 : 3.75 that was determined by gas chromatography. The total flow rate was either 50 or 100 ml/min. Cyclohexane was introduced by passing a portion of the helium stream through a saturator.

In a typical reaction run, the catalyst was first heated in a stream of 50 ml/min O_2 at 540°C for 1 h. Then the temperature was lowered to the reaction temperature, and the oxygen flow rate was reduced to the desired value for reaction. He was introduced, and then cyclohexane. The system was allowed to stabilize for about 50 min before the first product sample was taken for analysis. The carbon balance was always satisfied to within ±3%, and oxygen balance was within ±5%, if we assumed that all the undetected hydrogen appeared as water which was not detected.

It was unlikely that the nonoxidative dehydrogenation pathway contributed to the observed results. At these temperatures, the nonoxidative dehydrogenation of cyclohexane to cyclohexene is thermodynamically unfavorable (*6*). Similarly, the nonoxidative dehydrogenation of cyclohexene to cyclohexadiene is expected to be unfavorable. Although the nonoxidative formation of benzene is favorable (*6*), there was no evidence of hydrogen in the product stream. However, the possibility that any hydrogen formed was quickly oxidized to water could not be excluded.

RESULTS AND DISCUSSION

Cyclohexene, benzene, and CO_x were the products detected. The product yields reached a steady state within 50 min of reaction, except that of benzene on both V–Mg–O catalysts. On 40V–Mg–O, the benzene yield decreased with increasing time on stream, and reached a steady state only after 2 h at 440°C. The approach to steady state was faster at a higher temperature and also faster for 60V–Mg–O.

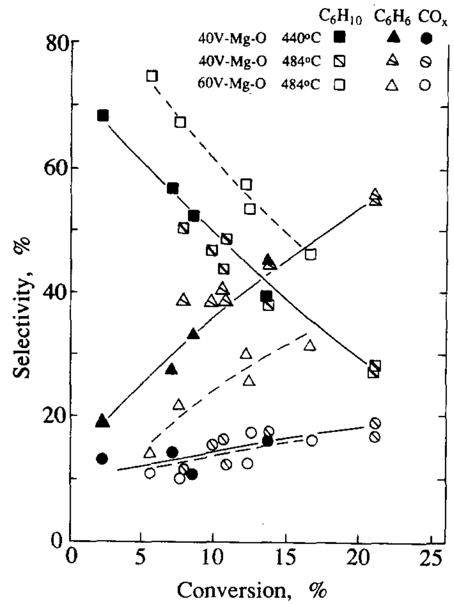

FIG. 1. Steady-state product selectivities as a function of conversion of cyclohexane over 40V–Mg–O and 60V–Mg–O. Feed composition: He/O_2/cyclohexane = 89/7.5/3.75.

The steady-state product distributions on 40V–Mg–O and 60V–Mg–O at 440 and 484°C are shown in Fig. 1. At 440°C, trace amounts of cyclohexadiene were also detected. Carbon dioxide was the predominant combustion product, being three to four times more than CO. Within experimental error, the product distributions were the same at the two temperatures. Likewise they were independent of the O_2 or cyclohexane partial pressures over the range studied (3.7–7.5%). The cyclohexene selectivity on 60V–Mg–O was higher than that on 40V–Mg–O, whereas the selectivities for benzene and carbon oxides were lower.

This difference persisted even when the 60V–Mg–O was physically mixed with MgO (1 : 2 wt ratio). Thus it is due to the very intimate mixing of MgO and $Mg_3(VO_4)_2$, such as the interface of these two phases that is present in the mixed oxide 40V–Mg–O but not in the nearly stoichiometric 60V–Mg–O. This higher selectivity for benzene parallels the higher selectivity for butadiene in the OXD of butane on the mixed V–Mg–O than the stoichiometric orthovanadate (*2*).

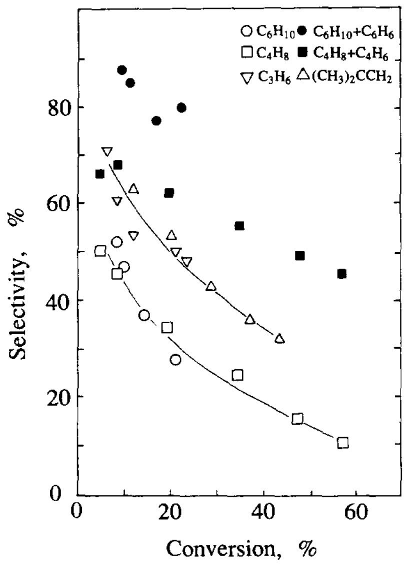

FIG. 2. Selectivities to dehydrogenation products as a function of conversion in the oxidation of various alkanes over mixed V–Mg–O catalysts. O_2/alkane ratio in the feed was 2/1. Reaction temperatures in °C were: propane and butane, 540; 2-methylpropane, 500; and cyclohexane, 484.

The manner with which the selectivities change with conversion on V–Mg–O catalysts is indicative of a sequential reaction. Cyclohexene is the initial product, which is further dehydrogenated to benzene. Carbon oxides may be formed by the oxidation of both cyclohexene and benzene. Such sequential dehydrogenation has also been observed in the reaction of butane (*1*, *2*).

It is interesting to compare the selectivities for alkenes in the OXD of various alkanes on mixed V–Mg–O catalysts. Figure 2 shows the data for propane, 2-methylpropane, butane, and cyclohexane. It is apparent that these four alkanes show a common trend, that the selectivity for alkenes decreases with increasing conversion. This behavior is consistent with the picture that alkenes are the primary initial products, and their selectivities decline at higher conversions because of their subsequent reactions. At a given conversion, the selectivities for alkenes from propane and 2-methylpropane are similar, and are higher than those from butane and cyclohexane. This may be explained as follows. The first step in the dominant pathway for further reaction of alkenes is the loss of an allylic hydrogen to form a surface allylic species. In the case of butene or cyclohexene, loss of another hydrogen from the surface allyl to form butadiene or cyclohexadiene is rapid. Thus their further reaction is facile and it competes with the desorption of the alkenes, and small amounts of butadiene and benzene appear as initial products. However, this route is not available to propene or 2-methylpropene; thus the selectivities for these two alkenes are higher.

Figure 2 also shows the selectivities for total dehydrogenation in the case of butane and cyclohexane. The values for cyclohexane are much higher than butane, which reflects the fact that benzene is chemically more inert than butadiene.

That the activation of these alkanes proceeds via a similar mechanism involving cleavage of a C–H bond is supported by the comparison of their rates of reactions. It has been observed that the relative rates of reactions of ethane, propane, butane, and 2-methylpropane correlate with the strengths of the C–H bonds in the alkane molecules (*2*). In the case of propane and butane, butane reacts faster because it has more secondary carbons than propane. The rate of reaction of cyclohexane follows this trend. By extrapolating the rate data to the same temperature, cyclohexane is found to react 6.3 times faster than butane on 40V–Mg–O at 475°C, and 7 times faster on $NdVO_4$ at 500°C. This is consistent with the fact that cyclohexane has four more secondary carbons than butane.

It is interesting that the behavior of $NdVO_4$ is quite different from that of V–Mg–O catalysts in a number of aspects. First, its benzene yield reaches a steady state much faster than that on the V–Mg–O catalyst. Second, it shows a much higher selectivity for benzene and carbon oxides (see Fig. 3), and benzene is a substantial initial product. This is different from that in

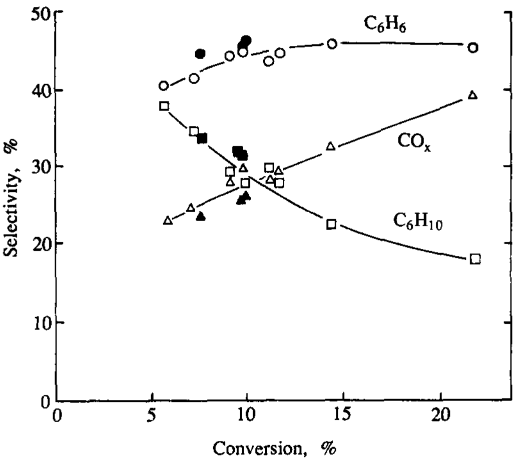

FIG. 3. Steady-state product selectivities as a function of conversion of cyclohexane over $NdVO_4$ at 484°C. Feed composition for open points was: He/O_2/cyclohexane = 89/7.5/3.75, and for filled points was: He/O_2/cyclohexane = 92.5/3.7/3.7.

the oxidation of butane where the selectivity for butenes on $NdVO_4$ is the same as on V–Mg–O, but the selectivity for butadiene is much lower on $NdVO_4$ than on V–Mg–O (*4*, *5*). Third, the reaction is nearly zeroth order in O_2 and first order in cyclohexane on V–Mg–O at 440°C over the range of 3.7 to 7.5% O_2 or cyclohexane, but it is 0.63 order in O_2 and 0.82 order in cyclohexane on $NdVO_4$.

The higher benzene and CO_x selectivities on $NdVO_4$ can be a result of the different degrees of oxidation of the catalysts at steady state and different surface residence times of the alkenes. It has been demonstrated by temperature-programmed reduction and reoxidation that $NdVO_4$ is slightly more difficult to be reduced, and a reduced $NdVO_4$ is much more rapidly reoxidized than V–Mg–O (*4*). Thus at steady state, the surface of $NdVO_4$ is less reduced than V–Mg–O. If all other factors are identical, $NdVO_4$ will have a higher tendency to oxidize cyclohexane beyond cyclohexene. This would be true for all molecules whose surface residence time is longer than the time constant for the oxidation of the surface species. In the case of butane oxidation, the higher temperature used and the higher volatility of the molecules involved result in a surface residence time that is comparable to or shorter than the time constant for oxidation such that butene desorbs rapidly after formation, and the difference in the butene selectivities between $NdVO_4$ and V–Mg–O becomes less noticeable. Such molecular specificity has also been observed over Mg pyrovanadate catalysts in the OXD of butane and propane (*1*, *7*).

The order dependence on the 40V–Mg–O catalyst is the same as those for the oxidation of propane and butane on this catalyst and in many other selective hydrocarbon oxidation reactions (*3*, *8–11*). However, the observed order dependence on $NdVO_4$ is unexpected.

In conclusion, cyclohexane can be selectively, oxidatively dehydrogenated to cyclohexene and benzene over orthovanadate catalysts. The reaction mechanism is similar to other alkanes studied in that the dehydrogenation reaction proceeds in a stepwise manner. On the V–Mg–O catalysts, the product distribution depends on the composition of the catalyst, which suggests that the interface of MgO and $Mg_3(VO_4)_2$ affects the properties of the catalyst. $NdVO_4$ and V–Mg–O catalysts show interesting differences, which could be related to their different rates of reduction and reoxidation.

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M. C. KUNG
H. H. KUNG[1]

Ipatieff Laboratory and Department of Chemical Engineering
Northwestern University
Evanston, Illinois 60208-3120

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[1] To whom correspondence should be addressed.