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The Effect of Potassium in the Preparation of Magnesium Orthovanadate and Pyrovanadate on the Oxidative Dehydrogenation of Propane and Butane

MAYFAIR C. KUNG AND HAROLD H. KUNG

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

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The catalytic properties of magnesium orthovanadate, magnesium pyrovanadate, and mixed oxides of vanadium and magnesium in the oxidative dehydrogenation of propane and butane were studied. The mixed oxides prepared by two different methods, with or without the use of K, were compared. For samples without K, Mg orthovanadate was quite selective for the oxidative dehydrogenation of both propane and butane, whereas Mg pyrovanadate was selective only for propane. However, samples that contained residual K showed decreased selectivity. The mixed oxides were selective for both hydrocarbons, although those prepared without K contained only orthovanadate as the vanadate phase, whereas those prepared with K contained both orthovanadate and pyrovanadate phases. However, judging from the CO/CO_2 ratios, all mixed oxides behaved as if they contained only Mg orthovanadate on the surface. Upon heating the samples, the concentration of potassium on the surface increased. Finally, interesting correlations between the rates of consumption of oxygen and of different alkanes were observed. © 1992 Academic Press, Inc.

INTRODUCTION

Recently, it has been reported that mixed vanadium–magnesium oxides were selective oxidative dehydrogenation catalysts for butane, propane, 2-methylpropane, and cyclohexane (*1–6*). However, the particular phase of magnesium vanadate present depended on the preparation method. A mixed oxide prepared from $MgCO_3$ that was precipitated from $Mg(NO_3)_2$ and $(NH_4)_2CO_3$ contained MgO and Mg orthovanadate ($Mg_3(VO_4)_2$) (*1*), whereas that prepared from $Mg(OH)_2$ that was precipitated from $MgCl_2$ and KOH contained MgO, Mg orthovanadate, and Mg pyrovanadate ($Mg_2V_2O_7$) (*6*). Their catalytic properties also differ. Mg orthovanadate from the carbonate preparation was selective for the oxidative dehydrogenation of butane and propane (*1–3, 5*), whereas Mg pyrovanadate and Mg metavanadate from similar preparations were nonselective for the butane reaction (*3*). On the other hand, the Mg orthovanadate from the hydroxide preparation was nonselective for the butane reaction, whereas Mg pyrovanadate was selective for the propane reaction (*6*).

In view of the differences among the catalysts prepared by the two methods, it became interesting to investigate in greater detail the reasons behind the differences. In particular, the possible effect of the residual potassium in the catalyst from the hydroxide method was investigated. The oxidative dehydrogenation of both butane and propane was compared on the same catalysts with respect to the effect of the nature of the hydrocarbon. This paper reports the results of such an investigation.

EXPERIMENTAL

Catalyst Preparation

The catalysts were prepared by two methods. The first method is referred to as the KOH method, and the resulting catalysts are designated -K. In this method (*6*), $Mg(OH)_2$ was first precipitated from a mag-

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nesium chloride solution ($MgCl_2 \cdot 6H_2O$, Aldrich Chemicals, ACS Reagent grade) using KOH (Mallinckrodt, analytical reagent). The precipitate was separated from the solution by centrifugation at 22,000 G using a Sorvall RC-5B centrifuge (Dupont Instrument), and then washed and centrifuged repeatedly for five times before drying at 90°C *in vacuo* for 6 h. Catalysts of various Mg/V ratios were then prepared using appropriate amounts of this $Mg(OH)_2$ and a solution of NH_4VO_3 (Johnson Matthey, 99%) in 1 wt% ammonium hydroxide. The suspension was evaporated to dryness while being stirred, and the dried solid was heated at 550°C for 6 h. These mixed oxide catalysts were labeled V–Mg–O, and the numbers in front indicate the weight% of V_2O_5 in the solid. Stoichiometric compounds of Mg orthovanadate and Mg pyrovanadate were prepared by heating mixed oxides of the appropriate compositions (60V–Mg–O and 69V–Mg–O, respectively) at 625, 640, 750, and 800°C for 23, 17, 9, and 12 h at each temperature.

A 39V–Mg–O was separately prepared as described above except that a table-top centrifuge was used in the preparation of $Mg(OH)_2$. Thus in this preparation, the separation of the solid from the mother liquor was much less efficient, and, as is shown later, this sample contained a high concentration of residual K.

The second method used is referred to as the $(NH_4)_2CO_3$ method, and the resulting catalysts are designated -N (*1*). $MgCO_3$ was first prepared by adding $(NH_4)_2CO_3$ (Alfa Products, ACS reagent) to a solution of $Mg(NO_3)_2$ (Aldrich Chemicals, ACS reagent). The carbonate was then decomposed at 700°C to yield MgO. An appropriate amount of this oxide was added to an aqueous solution containing 0.5 wt% ammonium vanadate and 1 wt% NH_4OH at 70°C. With stirring, the suspension was evaporated to dryness. The resulting solid was dried at 100°C and then calcined at 550°C for 6 h to form the mixed V–Mg–O catalyst. A stoichiometric $Mg_3(VO_4)_2$ was prepared by heating a mixed 60V–Mg–O to 550, 660, and 650°C for 48, 62, and 115 h, respectively, and a stoichiometric $Mg_2V_2O_7$ by heating a mixed 69V–Mg–O to 550°C for 6 h.

Catalyst Characterization

Surface areas were determined by the nitrogen BET method. The surface areas of the catalysts were: $Mg_3(VO_4)_2$-N = 1 m^2/g, $Mg_3(VO_4)_2$-K < 1 m^2/g, $Mg_2V_2O_7$-N = 6 m^2/g, 39V–Mg–O-K = 22 m^2/g, 60V–Mg–O-K = 15 m^2/g. X-ray diffraction was performed on a Rigaku (Denke Ltd.) diffractometer with Cu radiation in a step scan mode of 0.1° per step and 20 s counting time per step. The oxide powders were supported on adhesive tapes which gave a gentle sloping background at low angles. This background has been subtracted from the spectra shown. XPS was performed in a VG Scientific Spectrometer system using Al radiation (1486 eV). The samples were pretreated by heating in air at 550°C for 1 h immediately before being mounted into the XPS chamber. The sensitivity factors used were 0.15 for the Mg 2*s* peak, 1.2 for V 2*p*3/2, 0.85 for K 2*p*3/2, and 0.2 for C 1*s*. These values were supplied by the manufacturer for the particular instrument used. The potassium contents were analyzed by induction-coupled plasma using a Thermo Jerrell–Ash instrument.

Catalytic Reaction

Reactions were carried out in a quartz U-tube reactor. The precatalytic region, which ranged from 1.3 to 3 cm^3 in volume depending on the amount of catalyst used, was filled with fine quartz chips to minimize contributions due to gas phase reaction. The postcatalytic region was a capillary tube of 2 mm i.d. and had a volume of 0.7 cm^3. It was shown earlier that under these conditions, there were little gas phase reactions in the absence of a catalyst (*7*). The catalyst powder was supported by quartz wool. A thermocouple was placed in the center of the catalyst bed. The tubings after the reactor

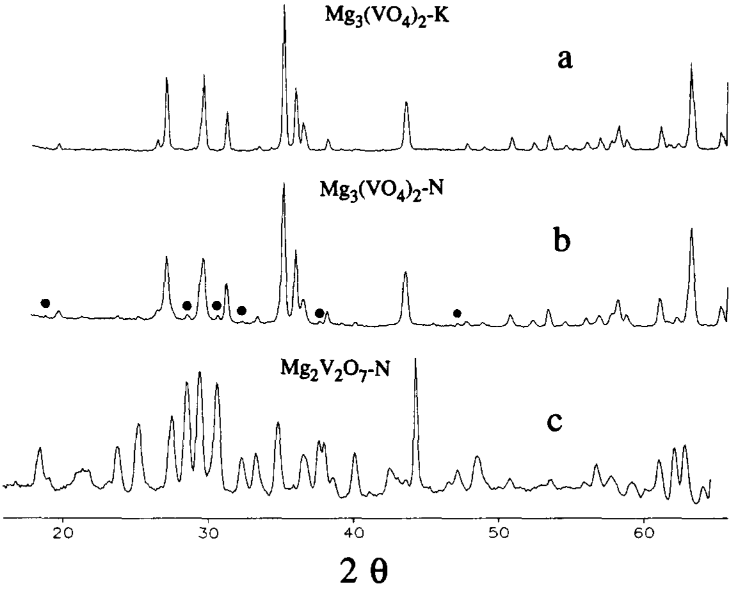

FIG. 1. X-ray diffraction patterns of: (a) $Mg_3(VO_4)_2$ prepared by the KOH method; (b) $Mg_3(VO_4)_2$ prepared by the $(NH_4)_2CO_3$ method, peaks marked by ● were assigned to pyrovanadate; (c) $Mg_2V_2O_7$ prepared by the $(NH_4)_2CO_3$ method.

were heated to prevent condensation of products.

Product analyses were performed by online gas chromatography using a total of three columns: a 3.65-m × 6.4-mm column containing tetraglyme coated on chromosorb P used at room temperature to separate O_2 + CO, CO_2, alkanes, alkenes, and butadiene; a 2-m × 3.2-mm Carbosphere (Alltech) column used at room temperature to separate O_2 and CO; and a 1.5-m × 3.2-mm Porapak Q (Alltech) column operated between 140 and 180°C to separate the hydrocarbons and the oxygenates. The first two columns were connected to a TCD detector, and the third to a FID detector.

In a typical reaction run, the feed composition was adjusted to the desired value with the catalyst kept at room temperature. The temperature was then raised to the desired value in about 20 min. The system was then allowed to stabilize, which usually took about 30 min, before the steady state data were collected. The feed composition was analyzed before each product analysis. A typical run lasted 4 to 6 h.

RESULTS AND DISCUSSION

The data for the stoichiometric compounds are presented and discussed first so as to elucidate the effect of residual potassium in the oxide. This is then followed by the data for the mixed oxides, and finally, a brief discussion of new observations made in these studies.

Mg Orthovanadate and Pyrovanadate

The X-ray diffraction patterns of stoichiometric Mg orthovanadate and α-Mg pyrovanadate prepared in this study are shown in Fig. 1. The patterns for Mg orthovanadate prepared by the KOH method (Fig. 1a) and for Mg pyrovanadate by the $(NH_4)_2CO_3$ method (Fig. 1c), except for the sharp peak at 44.5° in the pyrovanadate pattern, agreed very well with those in a published report (*6*) and in the reference files (*8*). This 44.5° peak was also present in some mixed V–Mg–O samples, but it disappeared rapidly under reaction conditions. It corresponded to a diffraction peak from a carbonate compound of magnesium. Since this peak was not present in the working cata-

TABLE 1

The XPS Surface Mg/V Ratios of Different Oxides

Catalyst	Mg/V
$Mg_3(VO_4)_2$ ($(NH_4)_2CO_3$ method)	1.3 +/− 0.2
$Mg_3(VO_4)_2$ (KOH method)	1.5 +/− 0.2
$Mg_2V_2O_7$ ($(NH_4)_2CO_3$ method)	1.1 +/− 0.2
39V–Mg–O (KOH method)	6.1 +/− 0.2
60V–Mg–O (KOH method)	
As prepared	1.6 +/− 0.1
After 2.5 h reaction	1.6 +/− 0.2
After 10 h at 625°C	1.7 +/− 0.2
After 10 h at 625°C, 17 h at 640°C, and 8 h at 750°C	1.5 +/− 0.2

lyst, no further investigations were conducted. Mg orthovanadate prepared by the $(NH_4)_2CO_3$ method (Fig. 1b) showed the presence of small amounts of Mg pyrovanadate. The presence of the pyrovanadate impurities could be a result of $MgCO_3$ contamination in the MgO used in the preparation, since the MgO used in this preparation was obtained by decomposing $MgCO_3$. The presence of undetected $MgCO_3$ in MgO would result in a Mg/V ratio in the final compound that was lower than expected.

Table 1 shows the surface Mg/V ratios of these compounds as determined by XPS. The surfaces of all these samples were partially covered with carbon. To investigate if the carbon contamination affected the surface Mg/V ratios, a Mg orthovanadate-N sample was heated in an atmosphere of O_2 at 550°C in the pretreatment chamber of the XPS spectrometer. It was then moved into the analysis chamber without exposure to air. Its surface C/Mg ratio was a factor of two smaller than that of the sample without this *in situ* pretreatment but the Mg/V ratio was unchanged. Thus it was assumed that surface carbon did not affect the surface Mg/V ratios.

The data in Table 1 show that the surface Mg/V ratios of Mg orthovanadate prepared by either method were the same within experimental error. The ratio for Mg pyrovanadate was lower, as one would expect because of the stoichiometry. These were comparable to the bulk ratios, suggesting that there was no significant surface enrichment of either cation. They were somewhat different from those reported previously (*6*, *9*). This might be due to different instrumental factors used in the calculations.

The catalytic properties of the stoichiometric compounds are shown in Table 2. A comparison of the data for propane oxidation over Mg pyrovanadate using a high O_2/C_3 ratio of 11/1 and a low O_2/C_3 ratio of 2/1 showed that the feed composition had only a small effect on the selectivities. The difference between the runs of different feed compositions can be readily attributed to the different conversions. (This can be seen readily when the data are compared with others in Fig. 4 below). For this reaction over Mg orthovanadate, the samples prepared by the $(NH_4)_2CO_3$ method were somewhat more selective for the dehydrogenation products than the one prepared by the KOH method. The high selectivities on Mg orthovanadate-N confirmed the result of Ross and co-workers (*5*). Mg pyrovanadate prepared by the $(NH_4)_2CO_3$ method also showed a high selectivity for dehydrogenation, which was in general agreement with Ref. (*6*). However, the selectivity for oxygenates on this catalyst was much lower than in that report.

Contrary to propane oxidation, the behavior of these compounds showed much larger differences in the oxidation of butane. As shown in Table 2, Mg orthovanadate prepared by either method was quite selective. However, Mg pyrovanadate was much less selective. The samples prepared by the $(NH_4)_2CO_3$ method behaved similarly to the one reported by us earlier (*3*).

These results showed that catalysts prepared by the two methods showed some differences. In general, the catalysts prepared by the KOH method are slightly less selective for dehydrogenation than those prepared by the $(NH_4)_2CO_3$ method. The difference is more apparent if the literature results are considered together. We attribute the

TABLE 2

Product Selectivities and Conversions for Mg Orthovanadate and Mg Pyrovanadate Prepared by Different Methods

Catalyst	Wt. (g)	Total flow (cc/min)	T (°C)	Feed O_2/HC/He	Conv. (%)	Product select. (%)[j]			
						CO	CO_2	Alkenes	Diene
			Oxidation of propane						
$Mg_3(VO_4)_2$									
ex $(NH_4)_2CO_3$	2.0	100	541	10/1/39	6.7	10.1	26.3	63.6	
ex KOH	3.18	50	539	2/1/22	3.5	14.8	31.6	53.6	
ex KOH (Ref. (*6*))	1.0	50	550	10/1/39	8.3	0	94.0	6.0	
$Mg_2V_2O_7$									
ex $(NH_4)_2CO_3$[a]	0.77	50	502	11/1/88	7.9	20.9	17.7	61.4	
	0.77	50	510	2/1/22	12.0	27.2	18.4	54.4	
	1.06	50	500	2/1/22	15.5	33.3	20.7	46.0	
ex KOH (Ref. (*6*))[b]	0.2	50	550	10/1/39	6.9	10.4	18.8	53.5	
			Oxidation of Butane						
$Mg_3(VO_4)_2$									
ex KOH	3.18	50	505	2/1/22	7.2	11.4	32.3	49.7[c]	6.6
ex $(NH_4)_2CO_3$	1.38	200	540	2/1/22	8.5	13.0	14.0	53.2[d]	12.7
	1.38	100	540	2/1/22	17.0	16.0	20.0	43.3[e]	12.7
$Mg_2V_2O_7$									
ex $(NH_4)_2CO_3$	0.60	100	500	2/1/22	6.8	33.3	33.4	31.4[f]	0.4
	0.77	50	503	2/1/22	17.7	44.2	38.7	15.2[g]	1.9
	0.60	100	540	2/1/22	11.1	40.0	33.9	24.5[h]	1.5
ex $(NH_4)_2CO_3$ (Ref. (*3*))	1.20	200	540	2/1/22	20.0	50.0	33.0	14.6[i]	1.5

[a] Less than 0.5% of the products were oxygenates.
[b] 17.3% of the products were oxygenates.
[c] Distribution was: 1-butene 23.3%, t-2-butene 13.1%, and c-2-butene 13.3%.
[d] Distribution was: 1-butene 24.8%, t-2-butene 14.2%, and c-2-butene 14.2%.
[e] Distribution was: 1-butene 20.9%, t-2-butene 10.7%, and c-2-butene 11.7%.
[f] Distribution was: 1-butene 19.3%, t-2-butene 5.9%, and c-2-butene 6.2%.
[g] Distribution was: 1-butene 9.2%, t-2-butene 3.1%, and c-2-butene 2.9%.
[h] Distribution was: 1-butene 15.2%, t-2-butene 4.7%, and c-2-butene 4.6%.
[i] Distribution was: 1-butene 10.6%, t-2-butene 2.0%, and c-2-butene 2.0%.
[j] The balance was C_2 and C_3 hydrocarbons.

difference to the residual potassium in the sample by the KOH method. These will be discussed further later.

Table 3 shows the relative reactivities of different alkane molecules on magnesium pyrovanadate. These rates followed the order that $C_2 < C_3 < C_4 \sim$ i-C_4, which parallels the order of decreasing C–H strength of the weakest bond in the molecule and is consistent with the proposal that the rate-limiting step is the breaking of the first C–H bond, like that on V–Mg–O. The rates per unit surface area of these molecules on Mg pyrovanadate are less than half of that reported for the V–Mg–O catalyst (*3*), suggesting that either there are fewer active sites on the oxide or the sites are less active.

TABLE 3

Relative Rates of Reaction of Alkanes on Mg Pyrovanadate ex $(NH_4)_2CO_3$

Temperature (°C)	i-C_4:C_4:C_3:C_2
540	0.91 : 1 : 0.70 : 0.16
500	0.89 : 1 : 0.64

Mixed V–Mg–O

Two mixed V–Mg–O catalysts, 60V–Mg–O-K and 39V–Mg–O-K, were prepared that differed in the centrifugation step. In the preparation of 60V–Mg–O-K, a much more powerful centrifuge was used, thus there was a much better separation of the solid from the mother liquor. Indeed, the residual potassium content in this sample

TABLE 4

The Potassium Contents in Different Oxides

Catalyst	Bulk K (wt%)	Surface K/V[a]
$Mg_3(VO_4)_2$-N	0.004	Nondetectable
60V–Mg–O-K	0.019	
As prepared		0.002
After heated to 750°C 23 h and 800°C 2 h		0.04
39V–Mg–O-K	0.50	0.05

[a] The surface Mg/V ratios are shown in Table 1.

was twenty five times lower than that in 39V–Mg–O-K (Table 4).

The X-ray diffraction patterns of these two samples are shown in Figs. 2b and 2c. They are similar to those in Ref. (*6*) for comparable samples. The pattern for 60V–Mg–O-K (Fig. 2b) showed the presence of both Mg orthovanadate and pyrovanadate and a trace of MgO. The unidentified peak at about 44.5° was also present. In contrast, 60V–Mg–O-N prepared by the $(NH_4)_2CO_3$ method showed only the presence of Mg orthovanadate (Fig. 2a). The pattern for 39V–Mg–O-K (Fig. 2c) showed the diffractions of orthovanadate and MgO. Catalysts of this composition prepared by the $(NH_4)_2CO_3$ method have been shown to display only Mg orthovanadate as the vanadate phase (*1*).

Thus it appears that in mixed oxide samples, the relative amounts of orthovanadate and pyrovanadate phases depended on both the composition and the method of preparation. For samples prepared by the KOH method, substantial amounts of pyrovanadate were found, even though according to the overall composition, orthovanadate should be the only vanadate phase present. Since the transformation of a mixture of MgO and V_2O_5 proceeds via first the formation of metavanadate, then pyrovanadate, and then orthovanadate (*10*), the result shows that residual K in the sample facilitates the formation of Mg pyrovanadate and increases its stability.

This stability of the $Mg_2V_2O_7$ phase in 60V–Mg–O-K was examined. Figure 3a shows the X-ray pattern of a sample after

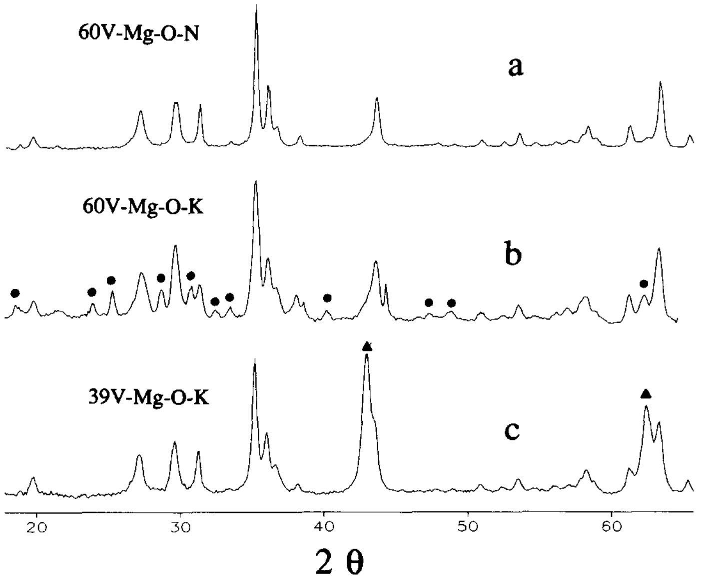

FIG. 2. X-ray diffraction patterns of mixed V–Mg–O: (a) 60V–Mg–O-N; (b) 60V–Mg–O-K; and (c) 39V–Mg–O-K. Peaks marked by ● and ▲ were assigned to pyrovanadate and MgO, respectively.

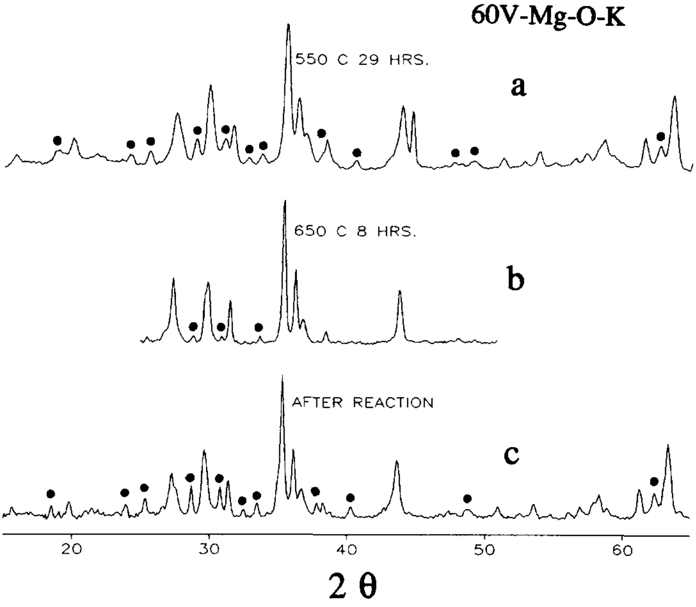

FIG. 3. X-ray diffraction patterns of 60V–Mg–O-K after various treatments: (a) 550°C for 29 h; (b) an additional 650°C for 8 h; (c) after being used in reaction. Peaks marked by ● were assigned to pyrovanadate.

being heated at 550°C for a total of 29 h. When it was compared to Fig. 2b, only minor changes were found. The conversion to Mg orthovanadate was much more effective by heating to a higher temperature, as is shown in Fig. 3b, which is the pattern of a sample that had been heated to 650°C. The X-ray pattern of a 60V–Mg–O-K sample after being used in a reaction at 540°C is shown in Fig. 3c. Upon comparison with Fig. 3a, it can be seen that there were no significant changes due to reaction, except for the disappearance of the unidentified peak at 44.5°.

The catalytic properties of 60V–Mg–O-K and 39V–Mg–O-K are shown in Table 5. The behavior of 60V–Mg–O-K in both propane and butane oxidation was comparable to those reported in Ref. (*2*) and Ref. (*6*) prepared using either method. This is illustrated in Fig. 4 for the oxidation of propane, which shows that these catalysts all possessed a very similar dependence of selectivity on conversion. The behaviors of the stoichiometric Mg orthovanadate and Mg pyrovanadate prepared in this study are also shown for comparison.

The behavior of 39V–Mg–O was different. Its activity per unit surface area was slightly lower than 60V–Mg–O. It was slightly less selective than 60V–Mg–O in propane oxidation and considerably less selective in butane oxidation.

The fact that high selectivities in propane dehydrogenation were observed on 60V–Mg–O-K is not surprising in view of the fact that both Mg orthovanadate and Mg pyrovanadate are quite selective for this reaction (Table 2). However, it is surprising to observe high selectivities in butane dehydrogenation on this sample, since Mg pyrovanadate is quite nonselective. One possibility is that the Mg pyrovanadate in the catalyst transforms during reaction to orthovanadate. However, this is not supported by results of X-ray diffraction of a used catalyst, which showed only a small extent of transformation (Fig. 3c).

Our model to explain this is that the surface of the 60V–Mg–O-K catalyst is more

TABLE 5

Catalytic Behavior of Mixed V–Mg–O (KOH method)

Feed[a]	T (°C)	Conv. (%)	Product select. (%)			
			CO	CO_2	Alkenes	Diene
	Catalyst: 60V–Mg–O (KOH prep)					
Propane/O_2/He[b] 1/11/38	515	7.0	12.9	25.5	61.6	
	540	11.0	16.0	27.0	57.0	
Butane/O_2/He[c] 1/11/38	540	12.0	12.7	23.7	48.6[d]	15.0
	Catalyst: 39V–Mg–O (KOH prep)[e]					
Propane/O_2/He 1/11/38	540	13.5	7.8	43.8	47.4[f]	
Butane/O_2/He 1/11/38	500	12.4	11.1	44.0	30.5[g]	14.4

[a] Total flow rate was 100 ml min^{-1}.

[b] 0.3 g of catalyst used.

[c] 0.2 g of catalyst used.

[d] Butene distribution was, %: 1-butene, 23.3; c-2-butene, 13.5; t-2-butene, 11.8.

[e] 0.31 g of catalyst used.

[f] Balance was oxygenates.

[g] Butene distribution was, %: 1-butene, 15.1; c-2-butene, 8.2; t-2-butene, 7.2.

representative of Mg orthovanadate than a mixture of orthovanadate and pyrovanadate. Thus the catalyst can be viewed as being made up of a mixture of particles, some of which are orthovanadate, some are MgO, and some are particles consisting of a core of pyrovanadate covered by a shell of orthovanadate. Alternatively, it is made up of two types of particles: one type being that of orthovanadate and another being that of pyrovanadate whose surface is partially covered with catalytically quite inactive MgO that suppresses the activity of the pyrovanadate.

These models are supported by the following observation. An examination of the data in Table 2 showed that in the oxidation of both butane and propane, Mg orthovanadate produced more CO_2 than CO, whereas the situation was reversed for Mg pyrovanadate. On 60V–Mg–O-K, more CO_2 was produced than CO (Table 5), which indicated that its catalytic behavior was typical of that of orthovanadate but not pyrovanadate. The surface Mg/V ratio shown in Table 1 is also consistent with this models.

The lower selectivities obtained with 39V–Mg–O-K in butane oxidation is attributed to the presence of a higher concentration of potassium in this catalyst than in 60V–Mg–O because of the less efficient centrifugation (Table 3). In fact, potassium tends to segregate to the surface such that the surface concentration of K on 39V–Mg–O-K was much higher than that on 60V–Mg–O-K (Table 3). This explanation was consistent with the results of the experiment that compared two 40V–Mg–O catalysts (($(NH_4)_2CO_3$ method): one, with 1 wt% K added as KNO_3 during preparation, and the other with no K added. Both samples showed X-ray diffraction patterns of only Mg orthovanadate and small amounts of MgO. The sample without K showed a butane dehydrogenation selectivity of 61% at 27% conversion, versus 53% selectivity at 20% conversion for the sample with K (*11*). The activity of the catalyst was also decreased by the addition of K.

The presence of Cl on the surface of these samples was also looked for by XPS. No

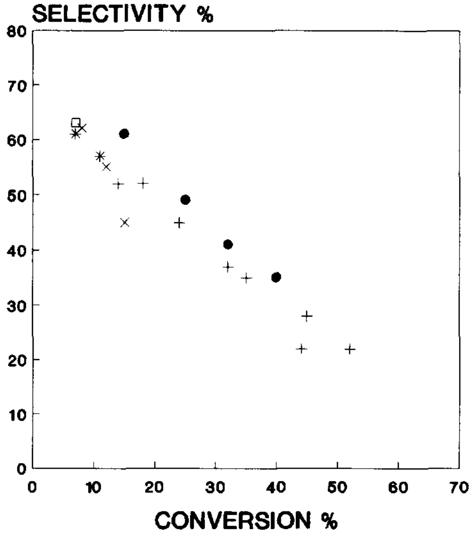

FIG. 4. The dependence of selectivity for dehydrogenation on conversion in propane oxidation on mixed V–Mg–O catalysts: ● V–Mg–O (($(NH_4)_2CO_3$ method, from Ref. (*2*)); + V–Mg–O (KOH method, Ref. (*6*); ✳ 60V–Mg–O-K, this work; □ Mg orthovanadate-N, this work; × Mg pyrovanadate-N, this work.

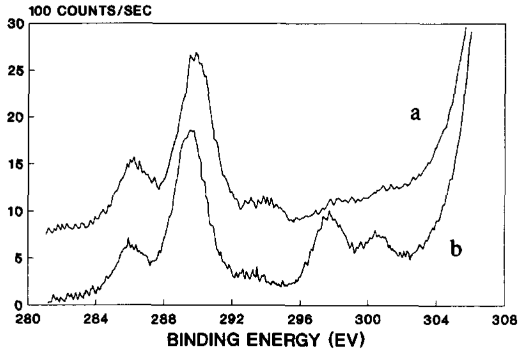

FIG. 5. XPS spectra of 60V–Mg–O-K: (a) as prepared; (b) after being heated further to 750°C for 23 h and 800°C for 2 h.

Cl was detected on either 60V–Mg–O-K as prepared or after prolonged heating to convert it to Mg orthovanadate. A trace of Cl was sometimes detected on 39V–Mg–O-K. Since K was present in much higher concentrations than Cl, it is likely that it has a much larger effect on the catalytic properties than Cl.

Surface segregation of K upon heat treatment of 60V–Mg–O-K was investigated by comparing the XPS spectra of a sample as prepared and one after heating to 750°C for 23 h and at 800°C for 2 h. Figure 5 shows the XPS spectra. There was electrical charging of about 4.9 eV for these spectra. The peaks between 286 and 295 eV (or 281 to 290 eV after correction for charging) were assigned to C 1*s*, and the peaks at 297.7 and 300.3 eV (292.8 and 295.6 eV after correction for charging) were assigned to K 2*p*3/2 and 2*p*1/2, respectively. The spectra showed that the K peaks became much more intense after heating. The increase was about twentyfold (Table 4). Since potassium affects the catalysts negatively, such thermal treatment on samples with residual K would degrade the catalytic performance. This may account for the observation in Ref. (*6*).

General Discussion

It is demonstrated in this study that, in the absence of effects due to potassium, Mg orthovanadate is a selective oxidative dehydrogenation catalyst for butane and propane. In fact, our earlier work has shown that the catalyst is also selective for 2-methylpropane and cyclohexane. However, it is not selective for ethane (*3*). On the other hand, it is surprising that Mg pyrovanadate is as selective in propane oxidation as orthovanadate, but is much worse for butane. Interestingly, in spite of the high selectivity in propane oxidation, Mg pyrovanadate is not selective in 2-methylpropane oxidation. At 6.8% conversion, the selectivity for dehydrogenation was only 25.5%.

When the steady state conversion and selectivity data for the C_3 and C_4 hydrocarbons were plotted as in Fig. 6 to show the rates of consumption of alkane versus the rates of consumption of gaseous oxygen, two correlations were obtained. One correlation (line a) showed that the rates of consumption of oxygen were about two times the rates of consumption of alkane for alkane conversions less than 15%. It contained data

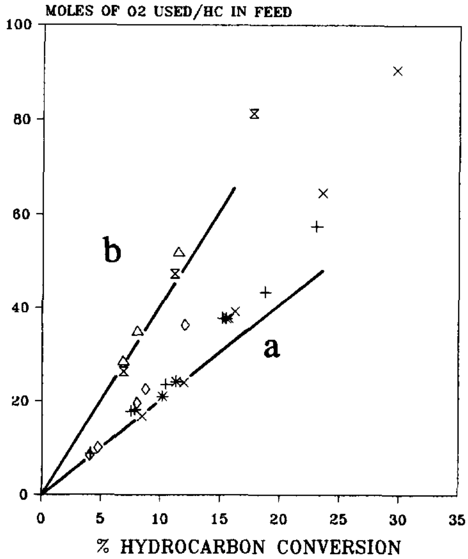

FIG. 6. The relationship between rates of hydrocarbon consumption and oxygen consumption in the oxidation of various alkanes on V–Mg–O mixed oxide prepared by the $(NH_4)_2CO_3$ method and Mg pyrovanadate. V–Mg–O-N: + C_3, × C_4, ◇ i-C_4; $Mg_2V_2O_7$: ✳ C_3, ⧗ C_4, △ i-C_4.

for both propane and butane on Mg orthovanadate and the data for propane on Mg pyrovanadate. The second correlation (line b) contained the data for butane and 2-methylpropane on Mg pyrovanadate and represented a rate of consumption of oxygen about four times that of alkane.

That these correlations exist is interesting and unexpected. Since most of the data were for low conversion experiments, one can assume that they have little complications due to secondary reactions (that is, further reactions of the products). Thus the initial slopes of the lines represent the average number of oxygen atoms consumed by each alkane molecule during its residence on the surface. For orthovanadate, this number is four. For pyrovanadate, it could be four or eight. This difference may lie in the different structures of the two vanadates. The orthovanadate consists of isolated VO_4 tetrahedra (*12*), which could limit the number of oxygen ions available to each adsorbed hydrocarbon molecule. The pyrovanadate consists of pyrovanadate groups which are corner-shared VO_4 tetrahedra (*13*). One may speculate that depending on the details in the interaction of a hydrocarbon molecule with the pyrovanadate group, different numbers of oxygen ions could be made available to the adsorbate. Further investigations are needed to better understand these correlations.

CONCLUSION

1. Differences were established in the catalytic behavior of V–Mg–O catalysts prepared by two different methods. They were explained by the effect of residual potassium in the preparation made from KOH. Magnesium orthovanadate, when free of potassium impurities, is a selective oxidative dehydrogenation catalyst for propane and butane. The presence of residual K in the oxide lowered the selectivity, especially in the butane reaction. Interestingly, magnesium pyrovanadate is quite selective for propane dehydrogenation but not for butane dehydrogenation.

2. The presence of potassium increased the thermal stability of Mg pyrovanadate against reaction with MgO to form Mg orthovanadate.

3. It was observed that the data at low conversions for the oxidative dehydrogenation of alkanes on Mg orthovanadate and Mg pyrovanadate followed correlations between the rates of consumption of gaseous oxygen and of alkane. The correlations may be a result of the number of oxygen ions available to react with each adsorbed species as determined by the structure of the solid.

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