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Oxidative Dehydrogenation of Butane over Orthovanadates

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The oxidative dehydrogenation of butane was studied over $NdVO_4$, $SmVO_4$, $EuVO_4$, and $Ba_3(VO_4)_2$ at 500 and 540°C. It was found that $NdVO_4$ and $SmVO_4$ were both quite active and selective for dehydrogenation, but $EuVO_4$ was less selective although very active. The products were butenes, butadiene, carbon oxides, and small amounts of C_2 and C_3 hydrocarbons. The selectivities for butenes over $NdVO_4$, $SmVO_4$, mixed V–Mg–oxide, and $Mg_3(VO_4)_2$ were found to be the same, but V–Mg–O was much more selective for butadiene than the other catalysts were. $Ba_3(VO_4)_2$ was selective, but both its activity and selectivity declined with time on stream due to the formation of $BaCO_3$. These oxides also showed different behaviors in temperature-programmed reduction and reoxidation. These observations can be explained by a model that relates the redox behavior of a catalyst to the availability of oxygen at the active site and thus to the catalytic behavior.

INTRODUCTION

It has long been of interest to understand how the properties of a catalyst influence its selectivities in the oxidation of alkanes for the production of unsaturated hydrocarbons such as alkenes, dienes, and aromatics, or of oxygenated products such as alcohols, ketones, and acids, and carbon oxides. Since the production of these different types of products involves different reactions that require different catalytic functions, which in turn depend on the bonding of the various components in the catalyst, it is important to understand how the nature of the bonding affects the catalytic behavior.

In our previous study of the oxidative dehydrogenation of propane and butane, it was discovered that magnesium orthovanadate, $Mg_3(VO_4)_2$, was a rather selective catalyst for the production of unsaturated hydrocarbons (*1–4*). However, magnesium pyrovanadate, $Mg_2V_2O_7$, or magnesium metavanadate, MgV_2O_6, was much less selective. The differences among these oxides were attributed to the fact that both pyrovanadate and metavanadate possess bridging lattice oxygen ions between two vanadium ions (V–O–V), whereas such groups are absent in orthovanadate. Since V^{5+} ions are readily reduced to lower oxidation states, such bridging oxygen ions can be easily removed from the catalyst, resulting in a high combustion activity of the catalyst.

In order to test this hypothesis, other orthovanadates were studied in which the Mg ions were replaced with Ba, Sm, Nd, or Eu ions. These orthovanadates have a common feature in that they consist of isolated VO_4 units. Every oxygen ion in these units bridges a V^{5+} ion and an alkali earth or a lanthanide ion. Thus the reducibility of these ions should affect the ease of removal of the oxygen ions. Since Ba^{2+} and Mg^{2+} are difficult to reduce, $Ba_3(VO_4)_2$ was expected to possess similar properties as $Mg_3(VO_4)_2$. Neither Sm^{3+} nor Nd^{3+} is easily reducible. A comparison of their orthovanadates with Mg would show whether orthovanadates of +2 and +3 ions behave similarly. Eu^{3+} is much more reducible than the others. Its orthovanadate would show the

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effect of reducibility. In this paper, the results of the reaction and reducibility study of these orthovanadates are reported and compared with those of a mixed V–Mg–O catalyst.

EXPERIMENTAL

Materials

Preparation of various oxides has been described in detail (*4*). $NdVO_4$ was prepared by first dissolving 10 g Nd_2O_3 (Aldrich Chemicals, 99.9%) in dilute nitric acid (15 ml conc. HNO_3 in 100 ml water). The solution was then heated, and a slurry was formed when 200 ml of NH_4OH (made from 30 ml conc. NH_4OH in 470 ml water) was added slowly and with constant stirring to the hot solution. Then 6.96 g of NH_4VO_3 was added to the slurry, and another 300 ml of NH_4OH was added. The final slurry was pale blue. It was suction filtered, washed, air dried at 80°C overnight, and calcined in air at 700°C for 1 h. X-ray diffraction of the final solid showed only diffraction lines of $NdVO_4$ (see Appendix). The surface area was 18 m^2/g.

$SmVO_4$ was prepared by dissolving 10 g Sm_2O_3 (Aldrich Chemicals, 99.9%) in dilute nitric acid. Five hundred milliliters of NH_4OH (made by diluting 15 ml of conc. NH_4OH to 500 ml) was added slowly with constant stirring to the hot solution to form a slurry. Then 6.71 g of NH_4VO_3 was added to the mixture, followed by another 500 ml of NH_4OH. The mixture was evaporated to dryness. During evaporation, another 11 ml of conc. NH_4OH was added to prevent segregation of the vanadium compound. The resulting solid was calcined at 700°C for 1 h. X-ray diffraction of the solid showed only $SmVO_4$. The surface area was 24 m^2/g.

$EuVO_4$ was prepared in a manner similar to $SmVO_4$ except that 30 ml of conc. NH_4OH was added to the mixture during evaporation to dryness. X-ray diffraction showed only $EuVO_4$. The surface area was 31 m^2/g.

$Ba_3(VO_4)_2$ was prepared by dissolving 24.7 g of $Ba(NO_3)_2$ (Alfa, Puratronic grade) in 100 ml of hot water. Five hundred milliliters of 0.5 *M* NH_4OH was then added slowly. With constant stirring, an aqueous NH_4OH solution was added to this slurry, which was slowly evaporated to dryness. The amount of NH_4VO_3 added was such that the final solid would have about 10% excess Ba. The dried solid was calcined at 620°C for 4 h. X-ray diffraction showed only $Ba_3(VO_4)_2$. No BaO peaks were detected.

$Mg_3(VO_4)_2$ was the same as that used before (*1*). Its surface area was 1.7 m^2/g. The 40V-Mg-O was also the same as that used before (*3*). Its composition was 40 wt% V_2O_5 and 60 wt% MgO. X-ray diffraction showed that it contained $Mg_3(VO_4)_2$ and MgO. Its surface area was 31 m^3/g.

Reaction Studies

The oxidation of butane was carried out in a quartz microreactor. The reaction conditions were chosen such that in the absence of a catalyst, there were negligible reactions (*2*). Unless noted, the catalysts were diluted with twice the weight of silica (<70 mesh, Davision 62, acid washed), which was found to be inactive under the reaction conditions.

The feed consisted of 4% butane, 8% oxygen, and the balance He. The standard flow rate was 100 ml/min, and the conversions were varied by changing either the weight of the catalyst or the flow rate. The products were analyzed by gas chromatography as before (*2, 4*). The butane conversions were calculated from the relative amounts of reactants and products in the reactor exit stream. The oxygen conversions were calculated assuming that any hydrogen unaccounted for in the products formed water.

Reduction and Reoxidation Studies

These were carried out in a 135-ml recirculation system. Reduction and reoxidation were monitored with a Tian-Calvet heat flow-type differential scanning calorimeter (SETARAM DSC 111) by following the heat released during reduction and reoxidation. Typically, 50–100 mg of catalyst was supported with quartz wool inside a 7-mm-o.d.

TABLE 1
Product Distributions in the Oxidation of Butane on $NdVO_4$[a]

Wt.[b] (g)	Conversion (%)		Selectivity (%) (C_4 basis)								
	O_2	C_4H_{10}	CO	CO_2	C_2	C_3	1-C_4H_8	2-*t*-C_4H_8	2-*c*-C_4H_8	C_4H_6	Dehyd.[c]
							540°C				
0.04	16	11.1	19.4	22.2	0	2.6	20.9	11.5	13.0	10.5	55.9
0.06	31	18.2	23.3	28.7	1.5	1.5	16.9	8.6	10.0	9.3	44.8
0.08	42	22.5	28.4	33.6	2.1	1.0	12.7	6.8	7.4	7.9	34.8
0.08[d]	39	23.0	26.5	31.5	2.2	1.1	14.4	8.3	7.2	8.8	38.7
0.16	70	30.7	30.6	37.9	1.6	1.0	9.7	5.6	6.5	7.2	29.0
0.16	62	30.8	30.0	37.2	1.7	1.2	10.3	5.8	6.6	7.2	29.9
							500°C				
0.08	11	8.5	17.4	20.8	0	0	22.6	14.0	14.8	10.4	61.8
0.12	29	16.8	22.8	28.5	0	1.5	16.7	10.7	11.0	8.8	47.2
0.16	38	21.4	27.9	32.9	0	1.1	13.0	8.5	8.9	7.9	38.3
0.32	87	38.4	35.1	43.9	0.7	0.7	5.5	4.2	4.9	5.0	19.6

[a] Feed: 4% butane, 8% O_2, and 88% He.

[b] Catalysts were diluted with twice the weight of SiO_2.

[c] Total selectivity to butenes and butadiene.

[d] The reactor volume after the catalyst bed was filled with quartz chips.

quartz tube. The quartz tube fit snugly in the sample cell of the DSC, and another quartz tube filled with only quartz wool was used in the reference cell.

In a typical run, the catalyst was first treated in flowing O_2 (5 ml/min STP, 53.3 kPa) at 500°C for 1 h. The sample was then cooled to 30°C. After evacuation, the system was filled with 79 kPa of Ar which was recirculated over the catalyst at 10 ml/min STP. The output of the calorimeter was recorded as the baseline when the catalyst was heated at 5°C/min to 800°C. For the reduction study, the catalyst was treated with O_2 at 500°C as described above. Then the catalyst was reduced in a mixture of 13.3 kPa of CO and 66 kPa of Ar flowing over the catalyst at 10 ml/min STP, while the temperature was raised at 5°C/min to 800°C.

Reoxidation of a reduced catalyst was accomplished using a mixture of 13.3 kPa of O_2 and 66 kPa of Ar flowing over the catalyst at 5 ml/min STP and heating the catalyst at 5°C/min to 800°C. The amount of oxygen consumed was determined from the pressure drop in the system after the catalyst was cooled to 30°C at the end of the experiment.

In some experiments, reduction was performed in 79 kPa of CO and reoxidation in 53 kPa of O_2, and the heating rate was 10°C/min.

RESULTS

Butane Oxidation

On both $NdVO_4$ and $SmVO_4$, butane oxidation was studied at 500 and 540°C. The products were primarily the three isomers of butene, butadiene, and carbon oxides. Small amounts of cracked products were also observed, especially at higher temperatures, consisting of ethane or ethene (which were not separated), and propene. The carbon balance was always satisfied to within ±3%, which was the experimental uncertainty.

Table 1 shows the reaction data for $NdVO_4$. Butenes were the major products over the range of conversions studied. Among the butenes, 1-butene was predomi-

TABLE 2
Product Distributions in the Oxidation of Butane on $SmVO_4$[a]

Wt.[b] (g)	Conversion (%)		Selectivity (%) (C_4 basis)								
	O_2	C_4H_{10}	CO	CO_2	C_2	C_3	1-C_4H_8	2-*t*-C_4H_8	2-*c*-C_4H_8	C_4H_6	Dehyd.[c]
								540°C			
0.025	5	4.8	12.8	12.8	0	6.4	29.7	12.8	19.2	6.4	68.1
0.025[d]	13	7.9	21.1	22.6	0	3.7	22.6	11.3	11.3	7.5	52.7
0.05	15	11.3	15.6	19.5	5.2	5.2	23.5	10.5	13.0	7.8	54.8
0.05[d]	26	14.1	25.9	29.6	1.8	1.8	16.7	7.5	9.2	7.4	40.8
0.06	34	18.5	28.0	31.5	2.1	1.4	15.0	6.7	8.1	7.5	37.3
0.12	56	26.3	32.2	36.6	1.5	1.5	10.4	5.2	5.9	6.3	27.8
0.16	78	34.1	35.7	40.4	1.5	1.1	7.6	3.9	4.3	5.5	21.3
								500°C			
0.06	12	7.9	19.0	22.1	0	0	22.9	12.9	15.2	7.7	58.7
0.08	20	11.8	19.9	24.8	0	0	20.7	12.4	12.7	9.8	55.3
0.12	27	14.6	25.3	28.6	0	1.7	16.1	9.2	10.7	8.3	44.3
0.16	44	21.1	28.7	34.4	0	1	12.6	7.4	8.5	7.4	35.9

[a] Feed: 4% butane, 8% O_2, and 88% He.
[b] Catalysts were diluted with twice the weight of SiO_2.
[c] Total selectivity to butenes and butadiene.
[d] Total flow rate was 50 ml/min.

nant. The selectivity for the C_4 hydrocarbon products decreased with increasing conversion, whereas that for the combustion products increased. The selectivity at a certain conversion was nearly independent of temperature over the range studied. Unlike on the V–Mg–O catalysts (*2*), butadiene was not a major product on $NdVO_4$ even at high conversions. The yields of butadiene were always lower than those of butenes.

Table 2 shows the reaction data for $SmVO_4$. These data were very similar to those for $NdVO_4$ and showed similar trends. Thus 1-butene was the primary C_4 product. The selectivity for dehydrogenation was a weak function of temperature, and decreased with increasing conversion. The seectivity for butadiene was low even at high conversions.

The activities of $NdVO_4$ and $SmVO_4$ were comparable. However, on the basis of per unit weight of catalyst, they were slightly ess active than the V–Mg–O catalysts (*2*). The behavior of these catalysts reached a steady state within 1 h of reaction and showed no evidence of deactivation.

The results for $EuVO_4$ are shown in Table 3. This catalyst was much more active than the other two rare earth vanadates. For example, at 500°C, the use of 0.08 g of $NdVO_4$ or $SmVO_4$ resulted in 8 to 12% conversion, whereas this conversion could be obtained with 0.009 g of $EuVO_4$. This difference in activity was more than could be accounted for by the difference in surface areas. Compared to the other two catalysts, $EuVO_4$ was less selective for dehydrogenation, but the decrease in selectivity with increase in conversion was less prominent. The selectivity for butadiene was particularly low, whereas the selectivities for carbon oxides were high. The catalyst deactivated slowly, and the data in Table 3 are those obtained after 4 h of time on stream. The catalyst turned dark gray after use, probably due to carbon deposits and reduction of the catalyst. The

TABLE 3

Effect of Conversion on the Product Selectivity in the Oxidation of Butane on $EuVO_4$[a]

T(°C)	Wt.[b] (g)	Conversion (%)		Selectivity (%) (C_4 basis)								
		O_2	C_4H_{10}	CO	CO_2	C_2	C_3	1-C_4H_8	2-t-C_4H_8	2-c-C_4H_8	C_4H_6	Dehyd.[c]
403	0.1	3.4	0.8	0	100	0	0	0	0	0	0	0
425	0.1	8.1	3.5	10	60	0	0	10	10	10	0	30.0
441	0.1	85	43.6	13.3	57.2	5.8	1.6	10.3	4.2	4.0	3.6	22.1
451	0.1	89	46.5	13.1	56.7	6.5	1.9	10.1	4.1	3.8	3.8	21.8
497	0.01	18	8.9	10.3	48	0.6	3.4	18.3	10.3	9.1	0	37.7
503	0.01	29	15.7	10.9	49	3.6	1.8	18.1	7.3	7.3	1.8	34.5
505	0.01	31	17.3	10.8	47.7	4.6	1.6	17.0	7.7	7.7	3.0	32.4
500	0.004[d]	9.5	4.2	15.4	46.2	0	0	23.1	7.7	7.7	0	38.5
500	0.009[d]	19.7	8.9	9.6	48.4	0	0	19.4	9.6	9.6	0	38.6
500	0.013	16	7.8	11.1	48.2	0	3.7	18.5	11.1	7.4	0	37.0

[a] Feed: 4% butane, 8% O_2, and 88% He; total flow rate: 200 ml/min.

[b] Catalysts were diluted with twice the weight of SiO_2.

[c] Total selectivity to butenes and butadiene.

[d] Total flow rate: 100 ml/min.

original color and activity could be restored by treating the catalyst in flowing O_2 at 400°C for 20 min.

The catalytic activity of a batch of barium orthovanadate was studied by first bringing the catalyst to 500°C and then increasing the temperature to 540°C over a 2-h period. When the catalyst was first brought to 500°C, a butene conversion of about 6% was observed, and the products were about 60% dehydrogenation products and about 25% cracking products. When the temperature was raised to 520°C after 45 min, the conversion was increased initially to about 16%, but declined gradually to less than 5%. In the mean time, the selectivity for dehydrogenation calculated from the gas-phase products declined from about 60 to 38%, while the selectivity for combustion increased correspondingly. At 16% conversion, the products detected could only account for 89% of the carbon in the feed. Further increase in temperature to 540°C did not result in significant changes in conversion or product selectivities. X-ray diffraction of a used catalyst showed the presence of barium carbonate, which was not found in a fresh catalyst.

Reduction and Reoxidation

The temperature-programmed reduction and reoxidation profiles of various vanadates performed using a heating rate of 5°C/min are shown in Fig. 1. The baselines determined when the samples were in an Ar atmosphere have been subtracted from these data. In the reduction cycle, Mg, Nd, and Eu orthovanadates showed broad peaks that

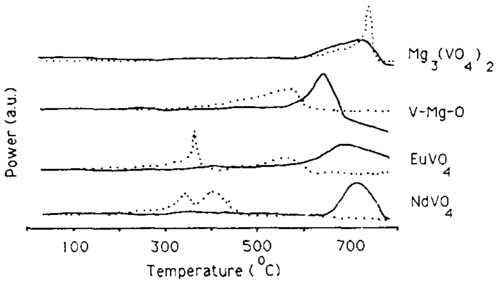

FIG. 1. Temperature-programmed reduction (—) and reoxidation (···) profiles of various vanadates. Heating rate = 5°C/min.

began at temperatures above 500°C. For Eu orthovanadate, the peak began with a broad shoulder. The reduction was close to completion at about 800°C. The reduction profile of 40V–Mg–O showed a much sharper peak than the orthovanadates, and the reduction was complete at 700°C.

The reoxidation profiles were quite different for the different orthovanadates as shown in Fig. 1. The profile for $Mg_3(VO_4)_2$ showed a sharp peak at about 720°C with a long tail on the low-temperature side, ending at about 600°C. The reoxidation was complete at about 760°C. The profiles for Nd and Eu orthovanadates showed two distinct peaks. For both compounds, the lower temperature peak began at about 250°C. The higher temperature peak for $NdVO_4$ overlapped slightly with the lower temperature peak, whereas for $EuVO_4$, the two peaks were well separated.

The reoxidation profile of 40V–Mg–O showed two overlapping peaks that began at about 350°C and ended at about 620°C.

An attempt was made to obtain a reduction profile for V_2O_5. However, using the conditions associated with a heating rate of 5°/min, the sample of 10 wt% V_2O_5/SiO_2 exhibited a large endotherm, possibly due to the onset of the high mobility of lattice ions preceding melting, that began at about 550°C before any detectable exotherm due to reduction appeared. Under the conditions associated with a heating rate of 10°/min, it was possible to detect the onset of reduction of unsupported V_2O_5 which occurred at about 500°C, as is shown in Fig. 2. However, the reduction was not yet complete at about 640°C. The temperature was held at 640°C until no more heat was generated. The profile for reoxidation of the reduced sample is shown in Fig. 2. Reoxidation was complete at about 560°C.

For comparison, the reduction and reoxidation profiles of Mg and Nd orthovanadate obtained under the conditions used for V_2O_5 are also shown in Fig. 2.

In the reoxidation cycle for all these samples, it was observed that small amounts of heat were released from the reduced samples when they were first exposed to oxygen at room temperature, probably due to the heat of adsorption of oxygen or oxidation of the surface. This is not shown in the profiles in Figs. 1 or 2.

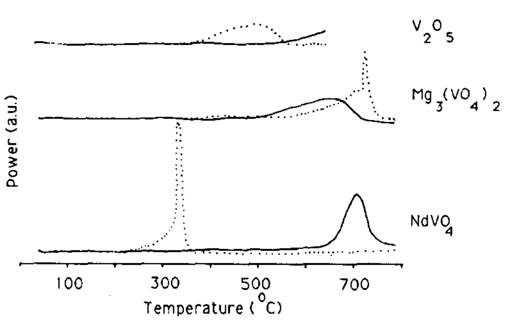

FIG. 2. Temperature-programmed reduction (—) and reoxidation (···) profiles for various vanadates. Heating rate = 10°C/min.

The amounts of oxygen consumed in the reoxidation of the various samples, including the amounts consumed at room temperature, are listed in Table 4. In most cases, about 0.75 to 0.83 oxygen atoms were consumed per V ion in the samples. This corresponded to an average vanadium oxidation state between 3.5 and 3.33 in the reduced sample. For V_2O_5, reduction to V_2O_3 was essentially complete.

DISCUSSION

The results in Tables 1 and 2 show that both $NdVO_4$ and $SmVO_4$ are relatively ac-

TABLE 4

Stoichiometry of Oxygen Consumption in the Reoxidation of Various Vanadate Samples

Sample	Wt. (g)	V in sample (10^{-4} mol)	O consumed/V
$NdVO_4$	0.0880	3.40	0.758
$EuVO_4$	0.0934	3.50	0.829
$Mg_3(VO_4)_2$	0.0532	3.51	0.820
40V-Mg-O	0.0761	3.33	0.757
V_2O_5	0.0988	5.43	0.970

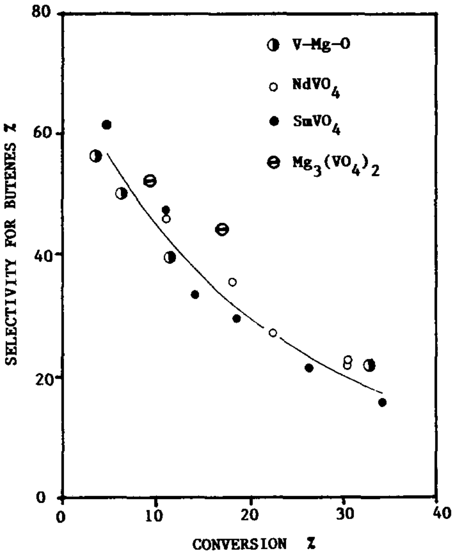

FIG. 3. Selectivity for butene formation as a function of conversion at 540°C.

tive and selective catalysts for the oxidative dehydrogenation of butane. The results for $Ba_3(VO_4)_2$ also show that this oxide could be a rather selective catalyst, but the formation of $BaCO_3$ degrades its performance. These observations are consistent with the conjecture that orthovanadates of nonreducible cations that possess isolated VO_4 groups are selective catalysts for oxidative dehydrogenation of alkanes.

The dependence of the selectivity for butenes and for total dehydrogenation (butenes and butadiene) as a function of conversion for the various vanadates are shown in Figs. 3 and 4, respectively. It is interesting, as shown in Fig. 3, that the selectivities for butenes over $NdVO_4$, $SmVO_4$, $Mg_3(VO_4)_2$, and V–Mg–O are the same. This indicates that on all of these oxides, the first step of the dehydrogenation reaction—formation of alkene—is the same. The different total dehydrogenation selectivities shown in Fig. 4 are due to the different rates of formation of butadiene, which is the same for Mg, Nd, and Sm orthovanadates, but higher on the V–Mg–O catalyst. That a V–Mg–O catalyst, which is made of $Mg_3(VO_4)_2$ and MgO, behaves differently than $Mg_3(VO_4)_2$ has also been observed in the oxidation of cyclohexane (5). It is probably a result of synergistic interaction between the two phases, the nature of which requires further investigation.

The selectivity for dehydrogenation over $EuVO_4$ is notably lower than for the other orthovanadates, especially at low conversions. This is consistent with the conjecture stated at the beginning that the redox property of the cation in the *M*–O–V bridging unit should affect the selectivity of the catalyst. Of the cations studied here, Eu undergoes oxidation and reduction (between +2 and +3) more readily than Mg^{2+}, Nd^{3+}, and Sm^{3+}. As will be discussed later, this results in a higher combustion activity of this catalyst.

Results of the temperature-programmed reduction and reoxidation experiments provided interesting insight into the role of the redox properties in this reaction. An examination of Fig. 1 shows that the gross features of the reduction curves of the various vanadates and of V–Mg–O are similar. The reduction peaks begin at about 600°C and are over or almost over at 800°C. There are

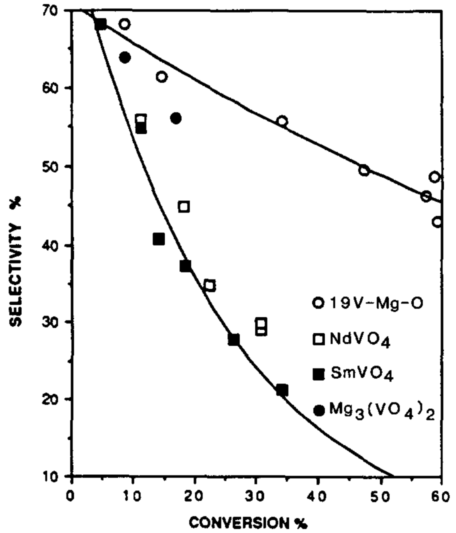

FIG. 4. Selectivity for total dehydrogenation (butenes and butadiene) as a function of conversion at 540°C.

some minor differences. The reduction peak of $EuVO_4$ shows a long and slow rise that begins at 500°C. The reduction of V–Mg–O is complete at about 680°C, which is the lowest temperature of all the samples. Comparing V–Mg–O and $Mg_3(VO_4)_2$, the reduction peak of the former sample is sharper and is about 100°C lower in temperature. This is probably due to the surface area effect. V–Mg–O has a much higher surface area than $Mg_3(VO_4)_2$, and it contains smaller crystallites. Since the rate of bulk reduction is limited by diffusion of lattice oxygen ions, smaller crystallites can be reduced more rapidly than larger crystallites. Finally, reduction of V_2O_5 takes place at a lower temperature than the vanadates, as is shown in Fig. 2. The sample begins to melt before reduction is complete.

The different orthovanadates are each reduced to about the same extent of 0.8 O ions per V ion (Table 4). Thus the reduced oxides contain a mixture of V^{3+} and V^{4+}, assuming that the other cations are not reduced. On the other hand, V_2O_5 is reduced to V_2O_3. It is interesting that although Eu is expected to be more easily reduced than the other cations except V, the extent of reduction of $EuVO_4$ was similar to the other samples. This indicates that the orthovanadate structure can only sustain a certain degree of reduction. Any further reduction would require more severe conditions.

The reoxidation behaviors of the vanadates are quite different. Both $NdVO_4$ and $EuVO_4$ show two reoxidation peaks. For both oxides, there is a low temperature peak at 320–340°C. For $NdVO_4$, a second peak appears at 480°, whereas for $EuVO_4$, it appears at 520°C. The appearance of two well-separated peaks suggests that reoxidation of these two samples occurs in stages, probably due to the structural changes associated with reoxidation. However, more detailed investigations are needed to identify definitively the reasons for the two peaks.

The reoxidation curves for V–Mg–O and V_2O_5 both show one broad peak made up of overlapping peaks, which may indicate that the reoxidation process and the associated lattice rearrangements of these samples occur gradually.

It is interesting that the reoxidation curves for the lower heating rate (Fig. 1) are much better resolved than those for the higher heating rate (Fig. 2). In particular, the peaks are much compressed for the higher heating rate. This is due to the more prominent autocatalytic effect when the high heats of oxidation are released over a shorter time period.

The following interpretation may be used to explain the catalytic results and the reduction–reoxidation behavior of the samples. Under the reaction condition of about 500°C, V_2O_5 is very active in combustion because of the high mobility of the atoms in the sample. The mobility is substantially suppressed by the formation of orthovanadates which have isolated VO_4 units. Consequently these compounds show much higher selectivities in the reaction.

The differences among the different orthovanadates can be correlated with their different redox behaviors. It has long been postulated that the activity and selectivity of an oxide in selective oxidation reactions are related to the rate of reduction of the oxide. An oxide that is too difficult to be reduced is too inactive, while one that is too easily reduced is active but nonselective. An active and selective catalyst should have an optimal rate of reduction. This concept is shown graphically in Fig. 5a.

It is also generally accepted that the rate of reduction of an oxide depends on the extent of reduction. The more reduced is an oxide, the slower is the rate of reduction. Combining these two factors, one arrives at a conclusion that the selectivity of a catalyst in oxidation depends on the degree of reduction of the oxide under reaction conditions, which would determine the rate of reduction of the oxide.

At steady state, a catalyst undergoes reduction and reoxidation. The extent of reduction of the oxide depends on the relative rates of these two processes, which in turn

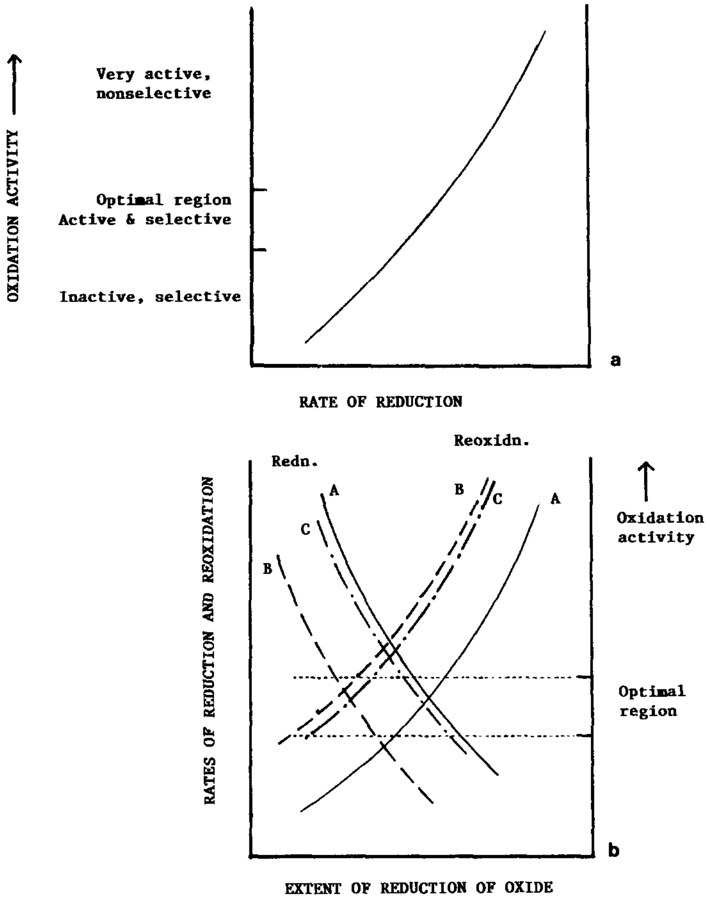

FIG. 5. Schematic illustrations showing the relationship among rates of reduction and reoxidation, the extent of reduction, and the catalytic behavior.

depends on the extent of reduction. This is shown in Fig. 5b. The steady state of the catalyst corresponds to the intersection of the reduction and reoxidation curves. If this intersection corresponds to a state of the catalyst that is in the optimal region, the catalyst will be active and selective, which is the case for the set of curves labeled A.

Since the V–Mg–O catalyst is quite active and selective, it may be assumed that its reduction–reoxidation behavior can be represented by this set of curves. For $NdVO_4$, the oxide reduces more slowly but oxidizes more rapidly. Its behavior corresponds to the set of curves labeled B. The oxide is also active and selective since the intersection falls within the region of optimal behavior. However, $EuVO_4$ reduces at about the same rate as V–Mg–O, but it oxidizes much more rapidly. Its behavior is represented by curves C. The argument presented would suggest that this oxide is more active but less selective than the $NdVO_4$ or V–Mg–O, as has been observed.

A consequence of this model is that, in general, an active and selective catalyst is partially reduced at steady state. The extent of reduction and the rate of reoxidation of the reduced active sites determine the availability of lattice oxygen for oxidation of surface intermediates. These in turn are determined by the structure and the composition of the catalyst. Therefore, it is possible that the function of some of the modifiers of selective oxidation catalysts is to change the rates of reduction and reoxidation of an oxide, which results in a different steady state of the catalyst and the corresponding different behavior.

Concepts similar to that presented in Fig. 5 have been suggested by other investigators. In their investigation of the V–P–O catalysts for oxidation of butane to maleic anhydride, Hodnett and Delmon found that the extents to which the catalyst could be oxidized and reduced was sensitive to the amount of excess phosphorus ($P/V > 1$) (*6*). They proposed that the most important effect of excess phosphorus in determining selectivity is to restrict the availability of lattice oxygen at the reaction site and the rate of replenishment of the lattice oxygen consumed. Along a similar line, Cavani *et al.* reported a correlation between the selectivity for maleic anhydride from butane on $(VO)_2P_2O_7$ catalysts with their different rates of oxidation of V(IV) to V(V) and thus different degrees of surface oxidation (*7*). They proposed that selectivity is determined by the degree of surface oxidation and thus the availability of oxidizing centers near the hydrocarbon adsorption centers, the rate of oxidation of the surface reaction intermediates to the desirable products of selective oxidation, and the stability of the desirable products with respect to further oxidation.

There are also studies that suggest the importance of the rate of reduction and/or oxidation of a sample. For example, it has been reported that oxides containing vanadium ions in multiple oxidation states are more selective in methanol oxidation (*8*) and propene oxidation (*9*) than are oxides of V^{5+}. The rapid interconversion of V^{5+} and V^{4+} in a V–P–O catalyst has been considered an important factor for its high selectivity in the oxidation of butane to maleic anhydride (*10*). Finally, by systematically replacing the cation *M* in the bridging Bi–O–*M* groups, it has been found that the reducibility of the cation *M* affects the activity and selectivity in the oxidative dimerization of propene to benzene (*11*, *12*).

In conclusion, it has been shown in this study that orthovanadates made from V_2O_5 and another oxide that is not easily reducible are quite selective catalysts in the oxidative dehydrogenation of alkanes. The selectivity depends on both the conversion and the nature of the other oxide. The catalytic data and the redox behavior of the orthovanadates can be explained using a model which suggests that the relative rates of reduction and reoxidation of the oxide under reaction conditions determines the catalytic behavior and the extent of reduction of the oxide at steady state. One possible role of a catalyst modifier is to change the rates of reduction and reoxidation, and the corresponding catalytic behavior.

APPENDIX

X-Ray Diffraction of Rare Earth Orthovanadate Samples (Cu*K*α Radiation)[a]

$SmVO_4$		$NdVO_4$		$EuVO_4$	
2θ	I^b	2θ	I	2θ	I
18.6	m	18.4	m	18.6	m
24.6	vs	24.4	vs	24.7	vs
31.0	w	30.6	w	31.1	w
33.2	s	32.8	s	33.2	s
35.1	w	34.7	w	35.2	w
37.6	vw	37.3	vw	37.8	vw
39.9	w	39.5	w	40.1	w
44.4	w	44.0	w	44.6	w
47.4	w	46.9	w	47.7	w
49.0	m	48.5	m	49.1	m
50.3	w	49.8	w	50.0	w
51.4	vw	50.9	vw	57.0	w
56.7	w	53.5	vw	58.0	vw
57.8	vw	56.2	w	61.8	w
61.6	w	57.3	w	64.0	w
63.7	w	60.9	w	66.3	vw
66.1	vw	63.2	w	69.6	w
69.3	w	65.3	vw	73.0	w
72.8	w	68.7	w		
79.3	vw	72.0	w		
		78.3	w		
		79.3	w		

[a] From spectra in Ref. (*4*).

[b] vs, very strong; s, strong; m, medium; w, weak; vw, very weak.

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