The effect of oxide structure and cation reduction potential of vanadates on the selective oxidative dehydrogenation of butane and propane

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The oxidative dehydrogenation of butane over a series of orthovanadates of cations of different reduction potentials showed a correlation that the selectivity for dehydrogenation decreased with increasing ease of reduction of the cation. The highest selectivity was observed on Mg orthovanadate. Mg pyrovanadate was nonselective for butane oxidation, but was as selective as Mg orthovanadate in propane oxidation. These results were interpreted by the different structures of the two Mg vanadates.

Keywords: Propane; butane; alkane; oxidation; dehydrogenation; vanadates; cation reduction potential; oxide structure

1. Introduction

The oxidative dehydrogenation of alkanes to unsaturated hydrocarbons has been a challenging problem. For a mixture of alkane and oxygen, the most thermodynamically favored products are carbon oxides and water, whereas the desired alkenes are often the least thermodynamically favored. Thus far, only a few catalysts have been reported to show reasonable selectivities for this reaction, particularly under conditions of high alkane conversions, low temperatures, and high O_2/alkane ratios. Therefore, it is of interest to identify catalytic properties that affect the selectivity.

Magnesium vanadates have been studied as oxidative dehydrogenation catalysts. It was found that magnesium orthovanadate is a rather selective catalyst for the oxidative dehydrogenation of butane [1,2], propane [3] and cyclohexane [4]. Upon comparison with the low selectivities observed on V_2O_5 in these reactions, it was suggested that the high selectivities demonstrated by Mg orthovanadate could be a result of the nonreducible Mg^{2+} ion in the Mg-O-V

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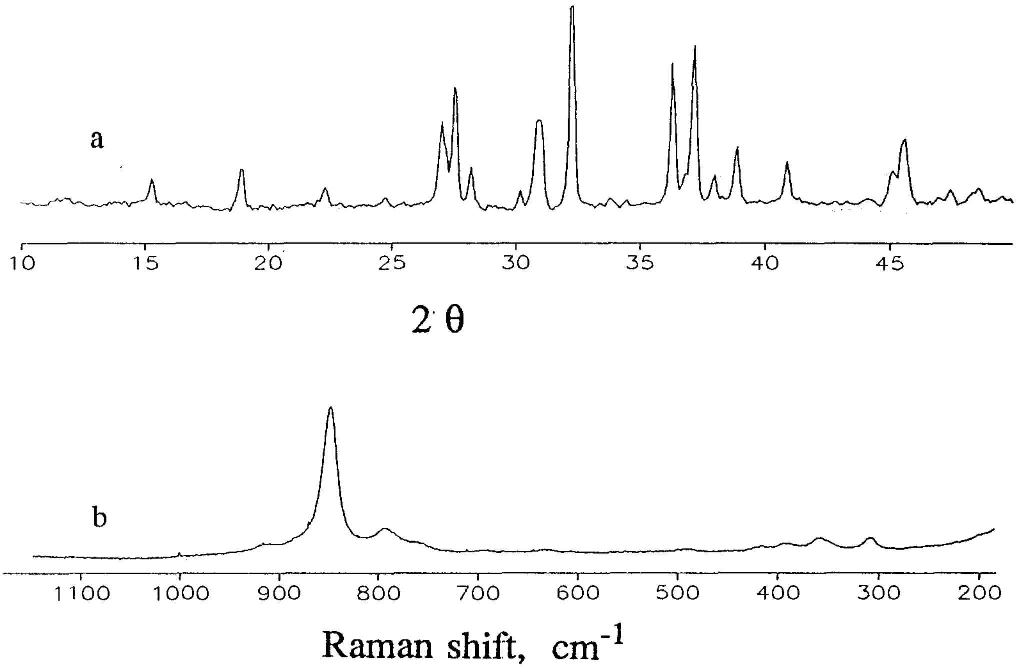

Fig. 1. X-ray diffraction pattern (curve a) and laser Raman spectrum (curve b) of $Cu_3(VO_4)_2$.

bond and its lower acidity as compared to V_2O_5 [1]. The importance of the low reducibility of the M ion in the M-O-V bond was later used to explain the differences among Nd, Sm, Mg, and Eu orthovanadates [5].

The objective of this work is to further test the importance of the reducibility of the cation. In particular, the catalytic properties of Mg orthovanadate were compared with those of orthovanadates of the general formulas $M_3^{2+}(VO_4)_2$ and $M^{3+}VO_4$ in which the cation M are of different reduction potentials, and with those of Mg pyrovanadate which contains pyrovanadate groups made up of corner-sharing VO_4 units. Results for the oxidation of butane and propane are reported. Since reduction potentials of cations in solids are not readily available, aqueous reduction potentials were used as the guideline.

2. Experimental

Catalysts were prepared generally by the decomposition of a mixture of the appropriate precursor compounds. Details of the preparation will be described in a later publication [7]. All solids were characterized with X-ray diffraction and, with the exception of Mg pyrovanadate, also with laser Raman spectroscopy. Fig. 1 shows the X-ray pattern and laser Raman spectrum of $Cu_3(VO_4)_2$. The spectra for the other orthovanadates were similar except for small shifts in the peak positions. From these data, it was concluded that the desired phase was formed. In the case of Zn and Ni orthovanadate, approximately 5 and 10%, respectively, of unreacted oxides were detected. The surface areas of these samples were of the order of 2 to 6 m^2/g.

Steady state reactions were run in a conventional flow microreactor. A thermocouple was placed in the center of the catalyst bed to ensure the absence of hot spots. The products were analyzed by on-line gas chromatography. The carbon balance was satisfied in all cases within experimental uncertainties ($\pm 2\%$). Unless noted, the feed composition was 4% (by volume) butane, 8% O_2, and 88% He, the total pressure was near atmospheric.

3. Results and discussion

Oxidation of butane proceeded readily at 500 °C on all samples. The observed carbon products were the isomers of butene, butadiene, CO and CO_2. Table 1 shows the product distributions on various orthovanadates at about the same conversion of 12%. As observed previously [1,2,4,6], Mg orthovanadate was a rather selective catalyst for oxidative dehydrogenation. Unlike mixed oxides of V-Mg-O that contained a mixture of MgO and $Mg_3(VO_4)_2$ [1], butenes were produced with much higher selectivities than butadiene on all orthovanadates tested in this study. These data showed that the selectivity for oxidative dehydrogenation on these compounds can be correlated with the aqueous reduction potential of the cation in the compound: the more easily reducible the cation, the lower the selectivity. On the other hand, no obvious correlation could be made between the activity and the reduction potential. However, the large uncertainties in the activities caused by the low surface areas of the samples made the comparison not quantitative.

Among the orthovanadates listed in table 1, $CrVO_4$ was less selective than expected based on the reduction potential. The reason for this has not been investigated, but we believe that it might be a result of the tendency for Cr^{6+} to be formed on the surface of the oxide in the presence of oxygen. Cr^{6+} is a very strongly oxidizing species.

This correlation between the selectivity and the reduction potential can be explained by the effect of the ease of removal of lattice oxygen on the selectivity. The structures of these orthovanadates are similar as evident by their similiar X-ray patterns and Raman spectra [7]. They contain only M-O-V bonds as a result of the isolated VO_4 units. In particular, no V-O-V bonds are present. When these compounds are reduced by the removal of lattice oxygen, the relative ease of reduction is determined by the reduction potentials of the M and the V ions. Assuming that the reduction potentials of the cations in the solid parallel those in aqueous solutions, $Cu_3(VO_4)_2$ would be thermodynamically the easiest to be reduced and Mg orthovanadate would be the most

Table 1
Product distribution for butane oxidation at 500 ° C [a]

Catalyst	Reduction potential, (volts) [g]	Total flow, (ml/min)	Catalyst wt (g)	Conv. (%)	Product selectivity (%) [b]						CO	CO_2	Total dehyd. (%) [c]
					C2/C2 =	C3/C3 =	1-butene	c-2-b	t-2-b	1, 3-BD			
$Mg_3(VO_4)_2$	−2.40	96	4.0	11.3	0.9	0.6	21.2	15.2	12.1	10.1	11.2	28.1	58.6
$NdVO_4$ [d,e]	−2.30	100	0.04	11.1	0.0	2.6	20.9	13.0	11.5	10.5	19.4	22.2	55.9
$SmVO_4$ [d]	−2.30	100	0.08	11.8	0.0	0.0	20.7	12.7	12.4	9.8	19.9	24.8	55.3
$Zn_3(VO_4)_2$ [f]	−0.76	28	20.0	11.3	13.8	0.7	17.0	8.0	8.0	8.4	4.4	40.0	41.4
$CrVO_4$	−0.42	139	0.76	11.1	0.0	2.6	8.5	0.0	0.0	0.0	55.1	33.8	8.5
$EuVO_4$ [d]	−0.35	100	0.01	15.7	3.6	1.8	18.1	7.3	7.3	1.8	10.9	49.0	34.5
$Ni_3VO_4)_2$	−0.26	139	0.5	12.7	0.0	4.3	10.4	1.0	2.1	0.0	47.0	35.3	13.5
$Cu_3(VO_4)_2$	+0.32	100	1.1	11.3	0.0	0.0	2.2	0.0	0.0	0.0	1.3	96.5	2.2
$FeVO_4$	+0.77	139	5.02	13.7	0.0	3.9	8.3	0.0	0.0	0.0	57.6	29.9	8.3

[a] Feed composition: butane/O_2/helium = 4/8/88.

[b] Selectivity on carbon basis.

[c] Sum of butenes and butadiene.

[d] Data obtained from ref. [5].

[e] Reaction temperature = 540°C.

[f] Reaction temperature = 530°C.

[g] Aqueous reduction potential, from: *Standard Potentials in Aqueous Solution*, eds. A.J. Bard, R. Parsons and J. Jordan (Marcel Dekker Publ., 1985).

Table 2
Product selectivities and conversions for Mg orthovanadate and Mg pyrovanadate [a]

Catalyst	Temp. (°C)	Feed O_2/HC/He	Conv. (%)	Product selectivities (%)			
				CO	CO_2	Alkenes	1,3-butadiene
Oxidation of butane							
$Mg_3(VO_4)_2$	540	2/1/22	8.5	13.0	14.0	53.2	12.7
	540	2/1/22	17.0	16.0	20.0	43.3	12.7
$Mg_2V_2O_7$	540	2/1/22	11.1	40.0	33.9	24.5	1.5
	503	2/1/22	17.7	44.2	38.7	15.2	1.9
Oxidation of propane							
$Mg_3(VO_4)_2$	541	10/1/39	6.7	10.1	26.3	63.6	
$Mg_2V_2O_7$	502	11/1/88	7.9	20.9	17.7	61.4	
	510	2/1/22	12.0	27.2	18.4	54.4	

[a] Catalysts were prepared as described in ref. [2], using $Mg(NO_3)_2$ and $(NH_4)_2CO_3$ as precursors.

difficult. The observed correlation implies that the easier it is to reduce the oxide, that is, to remove a lattice oxygen, the more likely it is for the oxide to react with the surface hydrocarbon intermediates to result in carbon oxides, perhaps due to a higher tendency to attack C-C and C-H bonds indiscriminately.

The successful correlation also implies that the reduction potentials of the cations in solids of very similar structures parallel those in aqueous solutions. We have further shown that the rate of reduction by H_2, as measured by the on-set temperature of reduction in temperature programmed reduction, also paralleled the reduction potential [7].

The conclusion derived from the results presented thus far can be used to explain the difference in the catalytic properties of Mg orthovanadate and Mg pyrovanadate in butane oxidation. As shown in table 2, under similar experimental conditions and comparable conversions, Mg orthovanadate was a much more selective catalyst for the oxidative dehydrogenation of butane than Mg pyrovanadate, similar to our results reported earlier [2]. This is consistent with the picture that in Mg pyrovanadate, there are V-O-V bonds. Because of the higher reducibility of the V^{5+} ions, the oxygen ion in these bonds can be more easily removed than those in the Mg-O-V bonds. Thus the pyrovanadate is more active in combustion.

However, this simple picture does not seem to apply to the oxidation of propane. As shown in table 2, under comparable conditions, Mg pyrovanadate and orthovandate showed similar selectivites for dehydrogenation. This observation was consistent with the fact that similar selectivities were obtained on mixed oxides of V-Mg-O that contained mixtures of MgO, Mg orthovanadate and pyrovanadate [8] and on those that contained only Mg orthovanadate and MgO [3].

The large difference in the behavior of butane and propane on Mg pyrovanadate was unexpected. It has been shown earlier that these two compounds behaved similarly on Mg orthovanadate [2,3]. They showed similar dependence of conversion on selectivity, and based on kinetic arguments, reacted with similar rate limiting steps. We propose that their different catalytic behavior on Mg pyrovanadate is a result of the structure of the solid. In Mg orthovanadate, the isolated VO_4 units result in a condition that the adsorbed molecule can only interact with one VO_4 unit. In Mg pyrovanadate, on the other hand, the V_2O_7 units, which consist of two corner-shared VO_4 units, provide the opportunity for a surface species to react with two VO_4 units simultaneously, provided that the size of the molecule is sufficiently large to do so. Propane is too small to do so. Thus it interacts with only one VO_4 unit and does not distinguish between orthovanadate and pyrovanadate. Butane is sufficiently large that its two end carbons could interact with the two VO_4 units in the V_2O_7 group simultaneously. Such an interaction leads to the ready formation of π-allyl and eventually combustion of the molecule.

The results reported here demonstrate again that the interaction between a surface intermediate and the catalyst is specific to the nature of the molecule and the solid. When comparing the reaction of one molecule with different oxides of the same structure, it is shown that the redox property of the cations is a primary factor that determines selectivity. On the other hand, when different molecules are compared, the specific interaction between the molecule and the surface must be considered. In the case of propane and butane oxidation, the mode with which the molecule interacts with the surface will determine how the structure of the solid influences the catalytic results.

Acknowledgements

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