

The role of V^{4+} ions in vanadium oxide catalysts

I. Decomposition of 2-propanol

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Abstract. Decomposition of 2-propanol has been studied on vanadium pentoxide with MoO_3 and WO_3 additives. It has been observed that a small amount of the additives increases the dehydration activity of the catalysts, but at 5% or higher concentration, dehydration of 2-propanol decreases. The initial increase followed by a decrease in the dehydration activity with increased amount of additives is due to the change in the rate-determining step. Addition of MoO_3 , WO_3 , and alkali metal oxides to vanadium pentoxide has similar effects on the V^{4+} concentration and catalytic activity. Based on the results of the kinetic and ESR spectral studies, a scheme for the reaction has been proposed. It is concluded that the concentration of V^{4+} ion plays the crucial role in these catalysts.

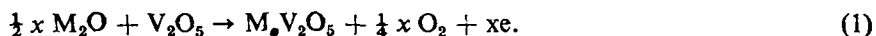
Keywords. Dehydration activity; vanadium concentration; 2-propanol decomposition.

1. Introduction

It has been mentioned in the literature that V^{4+} ions play a very important role in vanadium oxide catalysts. Thus, Mars and Maessen (1968) have shown that during oxidation of sulphur dioxide, V^{5+} is reduced to V^{4+} and the rate of the reaction is determined by the oxidation of V^{4+} by oxygen. It was also shown by Vorontyntsev *et al* (1971) that when silica gel-supported vanadium pentoxide is subjected to thermovacuum treatment, V^{4+} ions are generated at the surface that serve as the centre of adsorption for various molecules. Nakamura *et al* (1974) have shown that the activity and selectivity of vanadium oxide catalysts towards oxidation of butene to maleic anhydride is optimised by a large concentration of V^{4+} ions. Chakrabarty *et al* (1976 and 1977) have shown that by increasing the V^{4+} concentration in the catalyst, dehydration of 2-propanol initially increases and then falls. They have claimed that dehydration increases with V^{4+} concentration as long as desorption of water is the rate-determining step and at still higher concentration of V^{4+} , adsorption of 2-propanol becomes rate-controlling that causes the rate to fall.

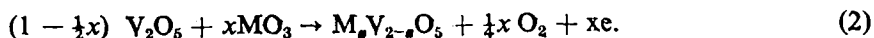
Chakrabarty *et al* (1976 and 1977) used lithium and sodium oxides as additives to control the V^{4+} concentration in the catalysts. It is well-known that alkali metal

ions enter into the vanadium pentoxide lattice interstitially to form the so-called vanadium bronzes according to the reaction



The liberated electrons are trapped at vanadium sites forming V^{4+} ions. If the primary factor that determines the catalytic activity and selectivity of the alkali metal-doped vanadium pentoxide is the concentration of V^{4+} ions (Chakrabarty *et al* 1977) addition of other metal ions should show similar behaviour irrespective of the nature of the additive as long as this alters the V^{4+} concentration in a manner analogous to alkali metal ions.

It is known that MoO_3 and WO_3 dissolve in V_2O_5 . Here Mo^{4+} and W^{4+} enter into the lattice substitutionally and the reaction can be written as



These free electrons may be trapped to form V^{4+} ions. Thus, the effect of dissolving MoO_3 or WO_3 in vanadium pentoxide will be similar to that of dissolving alkali metal oxide so far as the V^{4+} concentration is concerned. The present paper reports the effect of molybdenum and tungsten oxide additives on the V^{4+} concentration and on the activity and selectivity of the catalysts towards the decomposition of 2-propanol. The results show that the effect is quite similar to that of alkali metal doping.

2. Experimental methods

The samples were prepared by mixing appropriate quantities of MoO_3/WO_3 with V_2O_5 on an agate mortar by adding benzene, drying and then by melting it at $750^\circ C$. After cooling, the material was crushed to fine powder. For electrical conductivity measurement, the powdered sample was pelletised at $7 \times 10^6 \text{ kg/m}^2$ pressure and sintered at $530^\circ C$ for 24 hr. The powder was used for surface area measurement, catalytic and ESR studies.

Surface area of the samples were measured by BET nitrogen adsorption by taking about 15 g of the sample. A flow type reactor was used and the reactant was fed by a feeder pump. The total conversion was maintained between 2–15%. The products were analysed by GLC using the internal standardisation method. Initial rates (r_i) were obtained from conversion vs. contact time plots.

ESR spectra were recorded on a Varian E-line X Band 100 kHz spectrometer. Electrical conductivity was measured by the four-probe technique.

3. Results

On all the catalysts studied here, the decomposition of 2-propanol proceeded by the dehydration path to yield propene. Trace amounts of di-isopropyl ether and acetone were also found in the product.

The results of dehydration of 2-propanol on the catalysis are presented in table 1. The Arrhenius plots are shown in figure 1. It can be seen from the results that

Table 1. Kinetic parameters for the dehydration of 2-propanol in the range 200–260° C.

Catalyst	Surface area $m^2 g^{-1}$	E_a $kcal \cdot mole^{-1}$	K_0 $m^{-2} sec^{-1}$
Pure V_2O_5	1.8	9.33	2.48×10^6
0.1% MoO_3	0.9	5.23	9.09×10^4
1% MoO_3	0.87	6.24	4.83×10^5
5% MoO_3	1.2	4.81	3.54×10^4
10% MoO_3	0.87	6.01	1.1×10^5
0.1% WO_3	1.7	4.01	3.5×10^4
1% WO_3	1.2	4.02	5.63×10^4
5% WO_3	1.2	5.51	1.23×10^5

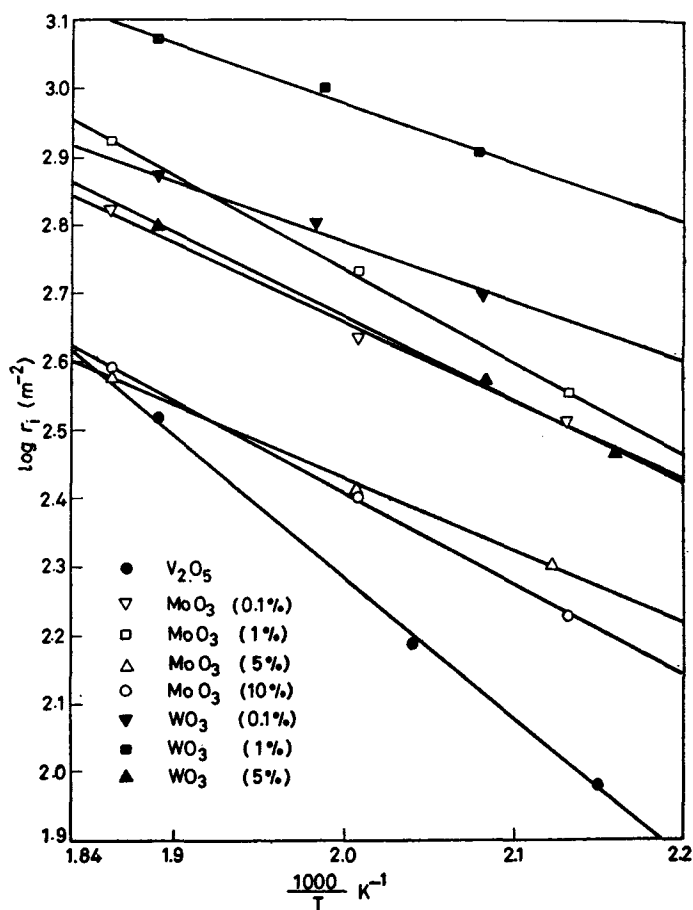


Figure 1. Kinetic plots for the dehydration of 2-propanol on the various catalysts.

addition of small amounts of MoO₃ or WO₃ to V₂O₅ increases the dehydration activity of the catalyst. At 5% or higher concentration, activity falls although it still remains higher than that of pure vanadium pentoxide. Activation energy (E_a) of the reaction is lower on the doped sample, but there is no systematic change in either in E_a or in the frequency factor (K_a).

The ESR spectra of all the samples showed a signal near $g = 1.97-1.98$ which can be easily assigned to the V⁴⁺ ion. The intensity of the signal increased systematically with the increase in the concentration of the additives indicating that this increases the V⁴⁺ concentration.

Table 2 gives the room temperature, electrical conductivity, activation energy of conduction (E_σ) and charge carrier concentration of the samples. As can be seen the charge carrier concentration obtained from electrical conductivity data are much lower than what is to be expected if each Mo/W atom donates a free electron to the lattice as given in equation (2). E_σ is lowered systematically with the additives.

Figure 2 shows the ESR spectra of the sample with 1% WO₃ before and after adsorption of 2-propanol at 200° C. It can be seen that adsorption of 2-propanol at 200° C increases V⁴⁺ concentration. However, no such change was noticed after 2-propanol adsorption on the sample containing 5% WO₃.

The rate of 2-propanol dehydration was found to be suppressed by the presence of water vapour in the reactant if V₂O₅ or samples with 1% MoO₃/WO₃ were employed. However, on samples with 5% MoO₃/WO₃, dehydration was not effected by the presence of water vapour.

4. Discussion

Although V₂O₅ lattice cannot take up more than 5% WO₃ as evidenced by x-ray analysis, it can dissolve upto 20% MoO₃ according to equation (2). With the

Table 2. Electrical conductivity and charge carrier concentration in various catalysts.

Catalyst	σ_{RT} ohm ⁻¹ cm ⁻¹	E_σ eV	Charge carrier concentration cm ⁻³	
			A	B
V ₂ O ₅	0.28×10^{-3}	0.245	5.82×10^{16}	..
0. % MoO ₃	1.02×10^{-3}	0.236	2.12×10^{17}	1.11×10^{19}
1% MoO ₃	1.07×10^{-3}	0.215	2.23×10^{17}	1.11×10^{20}
5% MoO ₃	1.12×10^{-3}	0.198	2.33×10^{17}	5.57×10^{20}
10% MoO ₃	2.32×10^{-3}	0.19	4.83×10^{17}	1.11×10^{21}
0. % WO ₃	0.78×10^{-3}	0.225	1.64×10^{17}	1.09×10^{18}
1% WO ₃	1.05×10^{-3}	0.2	2.18×10^{17}	1.09×10^{20}
5% WO ₃	4.2×10^{-3}	0.19	8.7×10^{17}	5.49×10^{20}

A : Obtained from electrical conductivity using mobility $\mu = 0.03$ cm²/V · sec. taken from Ioffe and Patrino (1970).

B : Calculated from dopant concentration.

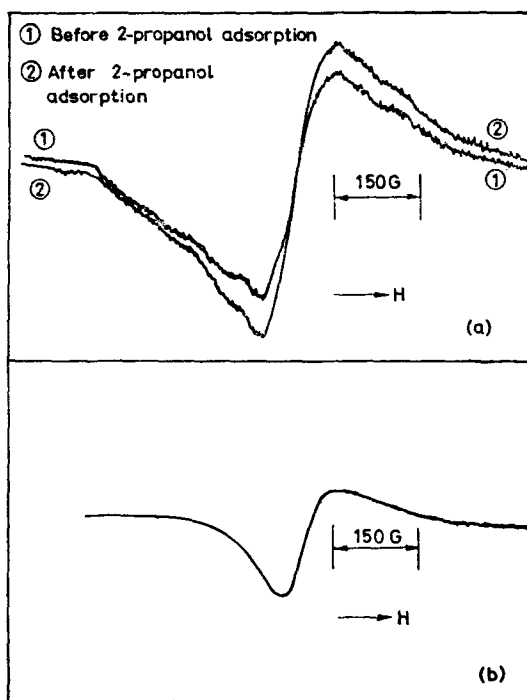


Figure 2. ESR spectra of (a) 1% WO_3 doped V_2O_5 , (b) 5% WO_3 doped V_2O_5 (at lower amplifier gain): no change after 2-propanol adsorption.

increase in molybdenum or tungsten substitution, V^{4+} content in the solid increases. This is evidenced by the increase in the ESR signal. The increase in V^{4+} concentration is, however, much lower than what should be expected if each molybdenum or tungsten atom created one V^{4+} site as proposed by Tarama *et al* (1964). This conclusion is drawn from the fact that the charge carrier concentration calculated from electrical conductivity data is much lower than what is expected if each Mo/W atom contributes one electron available for conduction (table 2). Similar results were obtained for the alkali metal vanadium bronzes (*a*-phase) (Chakrabarty *et al* 1976). Since vanadium pentoxide is a hopping semiconductor and the conductivity is due to a thermally activated electron jump from a V^{4+} site to a neighbouring V^{5+} site separated by a distance 3.08 \AA , electrical conductivity is a measure of V^{4+} concentration. It was proposed that in the case of the vanadium bronzes, each alkali metal atom donates one electron to the lattice, but they are initially trapped at oxygen vacancies (Chakrabarty *et al* 1976). The same argument seems to hold good for the molybdenum and tungsten-doped samples. This will explain the lower than expected V^{4+} concentration in the samples and also the rather high activation energy ($\sim 0.2 \text{ eV}$). The hopping model proposed above requires a low activation energy ($< 0.1 \text{ eV}$). The observed high value is because additional energy is needed to raise the electrons from an oxygen defect trap to form a V^{4+} centre. However, addition of alkali metal ion (interstitial) or that of molybdenum or tungsten (substitutional) definitely increases V^{4+} concentration and hence can be used as a handle for regulating V^{4+} ions in the host lattice.

It is seen from the results that dehydration of 2-propanol increases with increased addition of molybdenum and tungsten oxides. At about 5% concentration dehydration falls but still remains higher than that on pure V_2O_5 and a further increase in molybdenum concentration further lowers the dehydration activity (figure 1). These observations agree with the results on lithium and sodium vanadium bronzes except that in the latter, the fall in dehydration needed a higher additive ion concentration. This difference is possibly due to the fact that the non-stoichiometry in the case of the alkali metal-doped samples was less as they were prepared at only 500°C whereas solid solutions of MoO_3 and WO_3 with V_2O_5 could be prepared at 750°C. If this is correct, then at the same concentration of the additives, the latter samples would have a higher V^{4+} concentration. The analogous effect of the monovalent and hexavalent ion impurities on the 2-propanol dehydration on these catalysts suggests that it is the concentration of V^{4+} ions that is important. The only common feature of these two sets of impurity ions is that both of them increase the V^{4+} ion concentration.

It was shown earlier (Chakrabarty *et al* 1977) that the rate-controlling step for dehydration on V_2O_5 and the α -bronzes (lower concentration of Li^+/Na^+) was desorption of water and that on the β -bronzes (high alkali metal concentration) was adsorption of 2-propanol. In the present work, we observed that the conversion of 2-propanol on the 5% tungsten catalyst is unaffected by the presence of water vapour in the reaction mixture, whereas it is severely hampered by water vapour on those catalysts with lower tungsten concentration. This suggests that the rate-controlling step on the low Mo/W tungsten doped samples is the same as on the α -bronzes i.e. the desorption of water. On catalysis with higher concentration of the additives, the rate-determining step possibly changes to the adsorption of 2-propanol, i.e. same as that on the β -bronzes. The mechanism of dehydration of 2-propanol is then essentially the same as proposed by us (Chakrabarty *et al* 1977) for the α - and β -bronzes. This is schematically shown in figure 3.

On V_2O_5 and the catalysts with low Mo/W content, the last step is rate-controlling. As this step would need an electron to be extracted from the lattice, this is favoured by increase in V^{4+} concentration, i.e. increased additive concentration. When V^{4+}

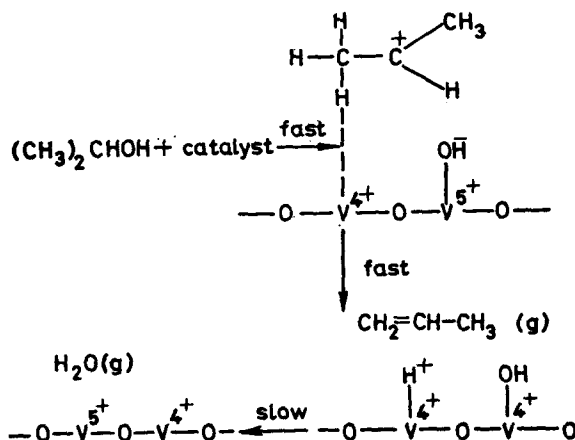


Figure 3. Scheme for 2-propanol dehydration on the doped V_2O_5 catalysts.

concentration further increases, this step becomes faster and ceases to be rate-controlling. If the first step now becomes rate-controlling, increase in V^{4+} will reduce the rate because the OH^- gets adsorbed at a V^{5+} site according to the mechanism suggested. This is the reason why further addition of impurity ions decreases the rate of dehydration.

ESR spectra of the catalyst with 1% W^{6+} before and after 2-propanol adsorption also support the proposed model (figure 2). It is seen that adsorption of the alcohol at 200° C enhances the ESR signal. According to the proposed mechanism, V^{4+} concentration increases in the rapid second step and this accounts for the enhanced ESR signal. No increase in the ESR signal was observed by adsorbing the alcohol at room temperature. No such increase in the ESR signal on 2-propanol adsorption at 200° C was observed for the catalyst with 5% W^{6+} . Since on this catalyst, the first step is the slowest one and both the second and third steps are fast, no steady-state increase in V^{4+} concentration is likely.

It appears that the dehydration of 2-propanol on vanadium pentoxide is controlled by the V^{4+} concentration. The influence of additives is determined by their ability to produce V^{4+} ions in the lattice and that is why such diverse ions as lithium and sodium on the one hand and molybdenum and tungsten on the other, have similar influence on the catalytic behaviour of vanadium pentoxide.

Tarama *et al* (1964) studied the effect of MoO_3 doping on the catalytic activity of V_2O_5 towards CO oxidation and observed that the activity increases upto 25 mole % MoO_3 content. They also observed a shift in the $V = O$ infrared band from 1025 to 1015 cm^{-1} and concluded that this terminal oxygen which is responsible for CO oxidation becomes more active due to the weakening of the $V = O$ bond. The authors suggest that lattice oxygen takes part in CO oxidation. We, however, did not observe any change in $V = O$ frequency by adding MoO_3 . It is doubtful if it is at all necessary to distinguish chemisorbed oxygen from lattice oxygen in explaining catalytic activity. At least in the dehydration of an alcohol, no lattice oxygen is involved and hence it is the V^{4+} concentration and not $V = O$ bond strength that determines catalytic behaviour.

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