

## Electronic Factor in Catalysis

### II. Decomposition of Isopropyl Alcohol on Manganese Molybdate ( $MnMoO_4$ )

By

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With 9 figures

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The vapor phase decomposition of isopropanol (IPA) on  $MnMoO_4$  has been studied in the temperature range  $375^\circ$ — $440^\circ\text{C}$  at atmospheric pressure in a flow type reactor. Both dehydrogenation and dehydration reactions occur to almost equal extents with apparent activation energies of 9.7 and 13.1 kcal · mole<sup>-1</sup> respectively. Small amounts of propane are also found in the products.

Addition of acetone and water separately to the feed caused selective suppression of the dehydrogenation and dehydration reactions respectively indicating that the reactions occur independently of each other on separate groups of surface-sites, while addition of hydrogen enhanced both the reactions. Adsorption measurements lend support to the view that the suppression effects of acetone and water are caused by their "blocking" the dehydrogenation and dehydration sites by stronger adsorption. From the inhibiting effect of acetone and the results of electrical conductivity measurements, it is concluded that electronic factors arise only in regard to the dehydrogenation reaction and that the desorption of acetone is the rate-determining step in dehydrogenation and has an acceptor character. On the other hand, dehydration is caused by surface acidity which could be measured by ammonia adsorption.

Evidence based on experiments with deuterated catalyst surfaces suggests that propane is produced by hydrogenolysis of the alcohol.

### Introduction

The dual mode of decomposition of isopropyl alcohol (IPA) is commonly used for evaluating the relative dehydrogenating and

dehydrating activities of oxide catalysts<sup>1</sup>. Activity for dehydrogenation has been related by various authors to the lattice parameters<sup>2</sup>, type of semiconductivity<sup>3</sup>, and the width of the forbidden zone in the electronic energy band<sup>4</sup>, while that for dehydration is generally attributed to the acidic properties of the surface<sup>5</sup>.

There has been a good deal of controversy with regard to the mechanisms of the two reactions. It is generally accepted, however, that each of these reactions proceeds through the successive steps of adsorption of alcohol, surface rearrangements leading to the adsorbed products and finally desorption of the products. The difference between the two modes of decomposition arises from the different modes of adsorption of the alcohol on the catalyst surface.

While WOLKENSTEIN<sup>4</sup> considers the initial step of adsorption of alcohol as rate-determining in the dehydrogenation sequence, HAUFFE<sup>6</sup> regards the final step of desorption of acetone as rate-limiting. Regarding the electronic aspects, the adsorption of alcohol is conceived of as an acceptor process by WOLKENSTEIN and as a donor process by HAUFFE. Both authors regard the desorption of acetone as a donor process. However, these postulates were not based on electrical measurements of any kind. BIELANSKI<sup>7</sup>, ZHABROVA<sup>8</sup> and KRYLOV<sup>9</sup> followed the dehydrogenation of alcohols on *p*-type and *n*-type oxide catalysts by measurements of electrical conductivity<sup>7-9</sup> and work-function<sup>9</sup> during reaction. They concluded that on both types of catalysts the desorption of acetone was rate-determining and that it was an acceptor process.

The dehydration reaction is generally attributed to the action of the protonic acid sites on the adsorbed alcohol, though WOLKENSTEIN associates this reaction also with the electronic character of the catalyst.

<sup>1</sup> O. V. KRYLOV, "Catalysis by non-metals", p. 115, Academic Press, New York 1970.

<sup>2</sup> A. A. TOLSTOPYATOVA, T. N. FILATOVA, E. F. KORYTNYI and A. A. BALANDIN, *Izv. Akad. Nauk SSSR* (1969) 1439.

<sup>3</sup> O. V. KRYLOV and E. A. FOKINA, *Kinetika i Katalis* 5 (1964) 284.

<sup>4</sup> TH. WOLKENSTEIN, "The electronic Theory of Catalysis on semiconductors", p. 66, Pergamon, London 1963.

<sup>5</sup> G.-M. SCHWAB, *Advances Catalysis* 2 (1952) 229.

<sup>6</sup> K. HAUFFE, *Advances Catalysis* 7 (1955) 251.

<sup>7</sup> A. BIELANSKI, "Catalysis and Chemical Kinetics", p. 115, Academic Press, New York 1964.

<sup>8</sup> G. M. ZHABROVA, *Chem. Techn. [Berlin]* 15 (1963) 193.

<sup>9</sup> O. V. KRYLOV, *J. physic. Chem.* 39 (1965) 2911.

Manganese (II) oxide has been found to possess a high selectivity for dehydrogenation of IPA<sup>10,11</sup>, while molybdenum trioxide is predominantly dehydrating<sup>12</sup>. In view of the synergetic behaviour reported in the case of several mixed (ternary) oxides in catalysis, and of the rapidly advancing interest in the catalytic applications of several molybdates, a study of the catalytic properties of mixed oxides of manganese and molybdenum has been undertaken. The present paper reports studies on kinetic and mechanistic aspects of the decomposition of IPA on manganese (II) molybdate ( $MnMoO_4$ ), and the role of the electronic factor therein.

## Experimental

### Materials

The catalyst,  $MnMoO_4$ , was prepared by heating an intimate equimolar mixture of  $MnCO_3$  (Merck "Reagent Grade") and  $MoO_3$  (prepared from ammonium paramolybdate by the method described by PALMER<sup>13</sup>) at 580°C for 2 hours. The completion of the reaction and the identity of the product as  $MnMoO_4$  were confirmed by chemical analysis and X-ray diffraction. The IR absorption pattern obtained in Nujol-mull conformed to that reported for  $MnMoO_4$  by BROWN et al.<sup>14</sup>. The surface area of the catalyst by BET method using nitrogen at liquid nitrogen temperature = 12.1 m<sup>2</sup>/g.

Merck "Reagent Grade" isopropanol and acetone were redistilled and purity-checked by VPC before use. Hydrogen was obtained from an Elhygen electrolytic hydrogen generator (Milton Roy Co., St. Petersburg, Fla., U.S.A.) which was provided with a cathode made of silver-palladium alloy tube to yield hydrogen of absolute purity and dryness straightaway.

### Reaction procedure

The decomposition studies were carried out in a flow type reactor similar to that described by UPRETI et al.<sup>15</sup> except for the use of a syringe pump (Sage Instruments Co., White Plains, New York,

<sup>10</sup> A. A. BALANDIN, A. A. TOLSTOPYATOVA and V. K. MATYSCHENKO, *Izv. Akad. Nauk SSSR* (1960) 1333.

<sup>11</sup> D. G. KLISSURSKI, E. F. McCAFFREY and R. A. ROSS, *Canad. J. Chem.* **49** (1971) 3778.

<sup>12</sup> A. A. BALANDIN and I. D. ROZHDESTVENSKAYA, *Izv. Akad. Nauk SSSR* (1959) 1889.

<sup>13</sup> W. G. PALMER, "Experimental Inorganic Chemistry", p. 412, Cambridge Univ. Press, London 1959.

<sup>14</sup> R. G. BROWN, J. DENNING, A. HALLETT and S. D. ROSS, *Spectrochim. Acta* [London] **26 A** (1970) 1963.

<sup>15</sup> M. C. UPRETI, J. C. KURIAKOSE and M. V. C. SASTRI, *Bull. polon. Akad. Sci. Ser. Sci. Chim.* **11** (1963) 651.

U.S.A., Model 255.2) for accurate control and metering of the feed rate. Prior to each run the catalyst was activated by heating in a stream of dry air at 500°C for 4 hours. After each run, the reactor was flushed with dry nitrogen while the temperature of the catalyst was gradually raised to 500°C for reactivation. The decomposition of IPA was studied in the temperature range 375–440°C with contact times varied between 0.5 seconds and 4 seconds. The liquid products were analysed by VPC, using a Carbowax 20 M on Chromosorb column at 80°C. The gaseous products were analysed by VPC using dimethyl sulpholane as column material.

In order to understand the mode of formation of propane in the reaction products, the catalyst was treated with  $D_2$  at 420°C for 24 hours to replace the surface  $H$ -atoms by  $D$ -atoms. The decomposition of isopropyl alcohol on the “deuterated” catalyst was carried out at 420°C at a contact time of 2.5 seconds. The gaseous products were analysed by a Varian CH-7 mass spectrometer.

### Electrical measurements

It was established by the thermal probe method<sup>16</sup> that the catalyst  $MnMoO_4$  behaved predominantly as an  $n$ -type semiconductor in the temperature range 300–500°C.

Using an arrangement similar to that described by BIELANSKI et al.<sup>17</sup>, changes in the electrical conductivity of the catalyst were followed during the decomposition of isopropanol and under the following environmental conditions:

- a) In air, at various temperatures up to 500°C.
- b) In hydrogen at various temperatures, after pretreatment in flowing hydrogen for 20 minutes at 500°C.
- c) At 420°C, in mixtures of acetone and isopropanol vapours and of nitrogen and isopropanol vapour in different proportions.
- d) In acetone vapour at 220°, 300° and 420°C to ascertain the effect of adsorption of acetone on the electrical conductivity of the catalyst.

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<sup>16</sup> W. C. DUNLAP, “An Introduction to Semiconductors”, p. 89, John Wiley, New York 1960.

<sup>17</sup> A. BIELANSKI, J. DEREN, J. HABER and J. NEDOMA, *Przemysl. chem.* **12** (1956) 642.

### Adsorption measurements

Measurements of the adsorption of acetone, water, IPA and ammonia were made with an electrical vacuum microbalance (Cahn, Model RG) having a sensitivity of  $0.1 \mu\text{g}$ . The surface acidity of the catalyst was estimated from ammonia adsorption.

To ascertain the effect of adsorbed acetone and water on the subsequent adsorption of isopropyl alcohol the catalyst was first exposed to acetone vapour or water vapour at  $420^\circ\text{C}$  and 50 Torr pressure for 2 hours, then cooled to room temperature ( $30^\circ\text{C}$ ) and pumped down to  $10^{-4}$  Torr. The amounts of acetone or water vapour retained by the catalyst was noted. The catalyst was then heated to the required temperature. Constancy of weight indicated that the adsorbed acetone or water vapour was retained intact. The adsorption of alcohol was then followed as a function of pressure. The adsorption of ammonia after prior adsorption of hydrogen or acetone was determined likewise.

### Results

#### a) Reaction studies

The catalyst  $MnMoO_4$  was found to catalyze both modes of decomposition of isopropanol almost equally. In addition to the usual products of these reactions, minor amounts of propane and traces of *di*-isopropyl ether were also found in the reaction products. From the plots of moles of acetone and water formed by dehydrogenation or dehydration per 100 moles of alcohol fed versus contact time (defined as the ratio of the volume of the catalyst to the volumetric feed rate under the experimental conditions) shown in Figs. 1 and 2, the initial rates were evaluated and were utilised in the construction of Arrhenius plots shown in Fig. 3. The apparent activation energies,  $E_a$ , and the pre-exponential factors,  $k_0$  for the dehydrogenation and dehydration processes were as follows:

Dehydrogenation  $E_a = 9.7 \text{ kcal/mole.}, k_0 = 9.4 \times 10^4 \text{ min}^{-1} \text{ m}^{-2}$ .

Dehydration  $E_a = 13.1 \text{ kcal/mole.}, k_0 = 9.3 \times 10^5 \text{ min}^{-1} \text{ m}^{-2}$ .

The effect of admixture of acetone, hydrogen, water and nitrogen (the last-mentioned provided for comparative purposes) with the alcohol feed is shown in Figs. 4 and 5 as moles of the respective products formed per hour as a function of the partial pressure of the alcohol in the feed. It is seen from the results shown in these figures that

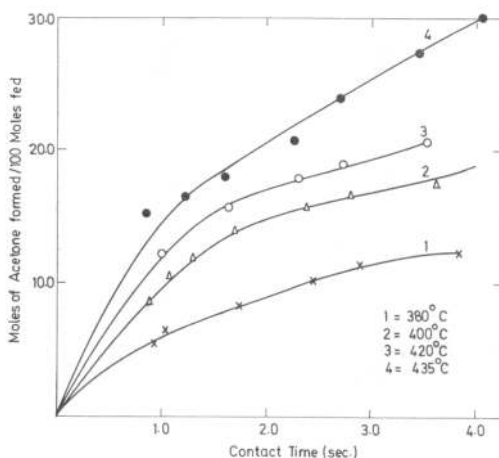


Fig. 1. Effect of temperature and contact time on the extent of dehydrogenation of isopropanol

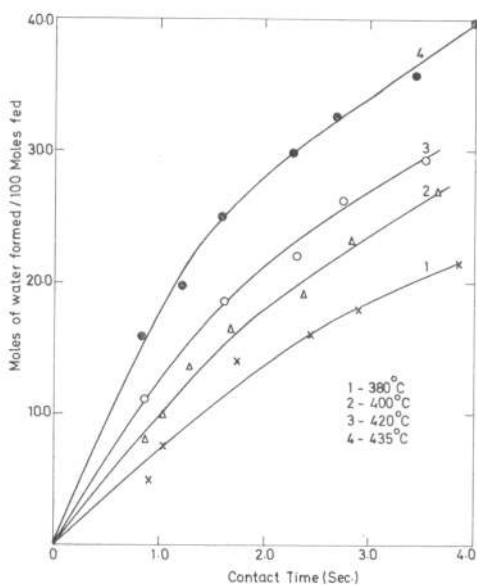


Fig. 2. Effect of temperature and contact time on the extent of dehydration of isopropanol

- i) acetone suppresses the dehydrogenation reaction severely (eliminating it completely above 0.6 mole fraction of acetone) but does not affect the dehydration activity,

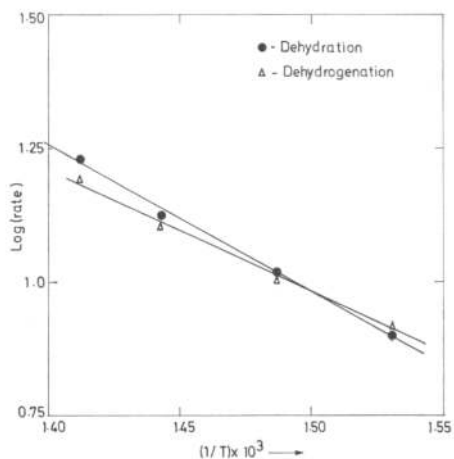


Fig. 3. Arrhenius plots for the decomposition of isopropanol

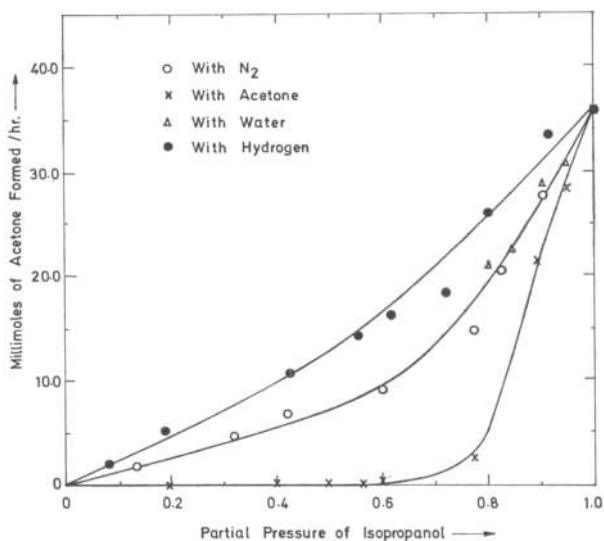


Fig. 4. Effect of nitrogen, acetone, water and hydrogen on the dehydrogenation of isopropanol

- ii) conversely, water suppresses the dehydration reaction alone, and
- iii) hydrogen enhances both dehydrogenation and dehydration activities.

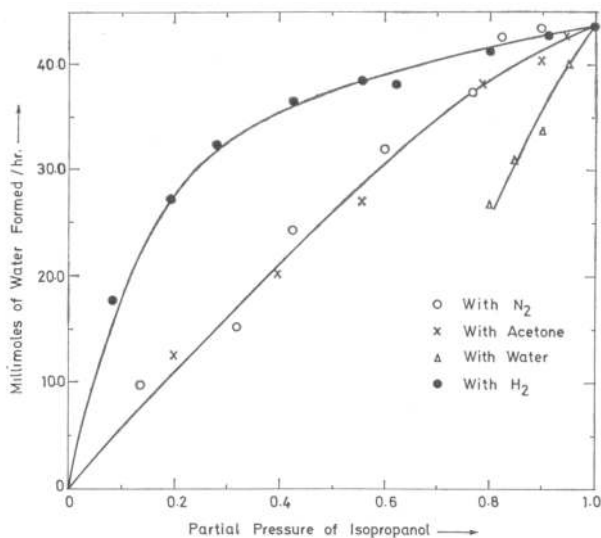


Fig. 5. Effect of nitrogen, acetone, water and hydrogen on the dehydration of isopropanol

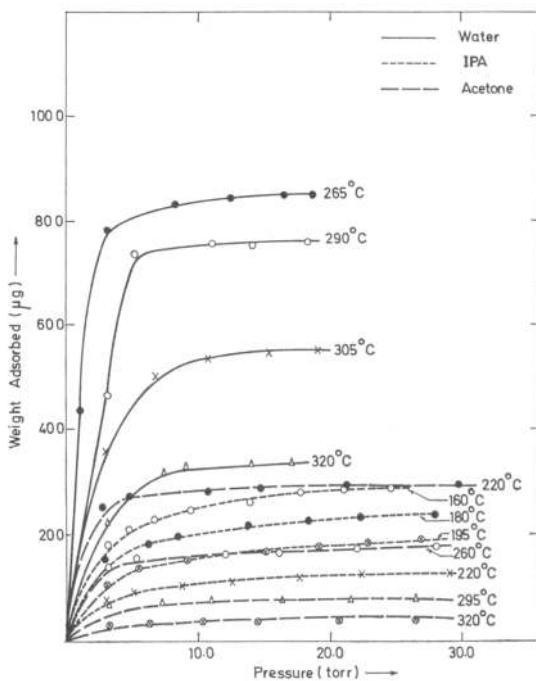


Fig. 6. Adsorption isotherms of isopropanol, acetone and water



## b) Adsorption measurements

The adsorption isotherms of isopropanol, acetone and water on the catalyst are shown in Fig. 6 and the Clapeyron heats of adsorption deduced therefrom are given in Table 1.

Table 1. *Heats of adsorption of various substances*

Adsorptive	Temperature range °C	$\Delta H$ kcal/mole
Acetone	220–320	20.9
Isopropylalcohol	140–220	11.6
Water	260–320	15.7

In order to understand the effect of acetone (completely suppressing dehydrogenation above 0.6 atm) and hydrogen (enhancing both the reactions) the following adsorption measurements have also been carried out:

- i) Adsorption of isopropanol on the catalyst containing previously adsorbed (presorbed) acetone and water.
- ii) Adsorption of ammonia on the fresh catalyst as well as on the catalyst containing presorbed hydrogen and acetone.

The results of these experiments are given in Tables 2 and 3.

## c) Electrical measurements

Under all conditions of reaction the conductivity ( $\sigma$ ) of the catalyst registered a steady and significant rise during reaction (Fig. 7). To identify the particular reaction associated with the conductivity-increase, measurements were also made during decomposition of isopropanol mixed with various proportions of acetone. The results of these measurements are summarised in Table 4.

While exposure to acetone caused only a slight increase in conductivity of catalyst (Table 5) exposure to hydrogen produced a marked increase. The conductivities of the evacuated (adsorbate-free) catalyst sample and of the same after 20 minutes exposure to flowing hydrogen at 500°C were measured at several temperatures in the range 100–500°C. The results plotted as  $\log \sigma$  vs  $1/T$ , are shown

Table 2. Adsorption of isopropanol at 195° C on MnMoO<sub>4</sub> in presence of presorbed acetone and water

Adsorption of IPA on acetone presorbed catalyst		Adsorption of IPA on water presorbed catalyst		Total IPA adsorbed on acetone and water presorbed catalyst (mg/g catalyst) (col. 2 + col. 4)	Amount of IPA adsorbed on free catalyst (mg/g catalyst)
Amount acetone presorbed <sup>a</sup> (mg/g catalyst)	Amount IPA adsorbed (mg/g catalyst)	Amount water presorbed <sup>a</sup> (mg/g catalyst)	Amount IPA adsorbed (mg/g catalyst)		
1	2	3	4	5	6
0.115	0.189	0.111	0.174	0.363	0.379
0.119	0.184	0.116	0.169	0.353	0.368

<sup>a</sup> Presorption has been carried out at 420° C and 50 Torr pressure for 2 hours.

Table 3. Adsorption of ammonia

Temperature °C	Amount adsorbed on fresh catalyst (mg/g catalyst)	Nature of pretreatment (prior adsorbate)	Amount adsorbed on pretreated catalyst (mg/g catalyst)
320	0.569	Acetone at 420° (0.116 mg) <sup>a</sup>	0.575
320	0.564	Acetone at 420° (0.114 mg) <sup>a</sup>	0.579
170	0.550	Hydrogen at 420° (0.082 mg) <sup>b</sup>	0.650
320	0.502	Hydrogen at 420° (0.085 mg) <sup>b</sup>	0.590

<sup>a</sup> Amount of acetone retained after pretreatment.

<sup>b</sup> Amount of hydrogen retained after pretreatment.

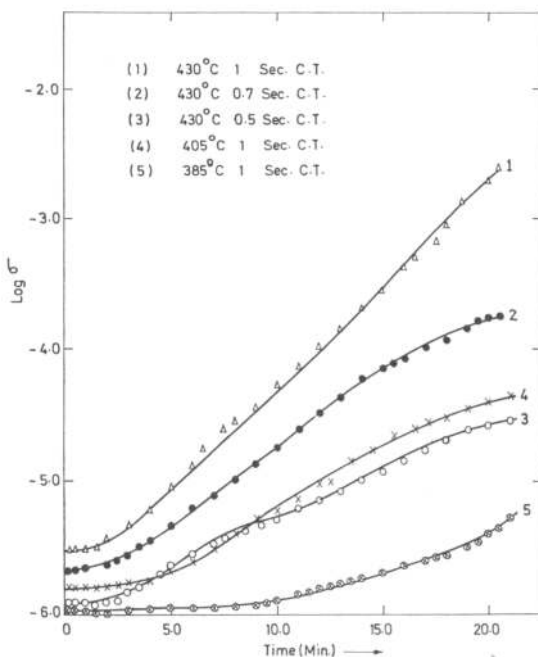


Fig. 7. Variation of the electrical conductivity of the pelleted catalyst during the decomposition of isopropanol. (C.T. = Contact Time)

Table 4. Summary of the electrical conductivity data on  $MnMoO_4$  in presence of acetone and IPA ( $N_2$  is diluent)

Partial pressure (atm)		Temperature : 420°C						Total feed rate 0.155 moles/hour									
		Acetone		Water		Amount of product formed moles/hour · 10 <sup>3</sup>			$\sigma_i$ Ohm <sup>-1</sup>			$\sigma_{20}$ Ohm <sup>-1</sup>			$\Delta \log \sigma$		
Nitrogen	Alcohol	Acetone	in $N_2$	in acetone	in $N_2$	in acetone	in $N_2$	in acetone	in $N_2$	in acetone	$\sigma_i$	$\sigma_{20}$	$\Delta \log \sigma$				
—	1.00	—	3.67	—	4.96	—	8.76 · 10 <sup>-6</sup>	0.104	4.5256	—	—	—	—				
0.25	0.75	—	3.03	—	3.89	—	1.143 · 10 <sup>-5</sup>	7.09 · 10 <sup>-2</sup>	3.7928	—	—	—	—				
—	0.75	0.25	—	2.81	3.09	3.94	6.85 · 10 <sup>-6</sup>	6.71 · 10 <sup>-2</sup>	3.673	—	—	—	—				
—	0.50	—	2.95	0.506	2.72	3.05	1.155 · 10 <sup>-5</sup>	8.69 · 10 <sup>-2</sup>	0.4397	—	—	—	—				
—	0.50	0.50	2.66	—	—	2.86	1.164 · 10 <sup>-5</sup>	—	—	—	—	—	—				
0.65	0.35	—	—	—	—	—	—	—	—	—	—	—	—				
—	0.35	0.65	—	—	—	—	—	—	—	—	—	—	—				
—	0.20	0.80	—	—	—	—	—	—	—	—	—	—	—				

$\Delta \log \sigma = \log \sigma_{20} - \log \sigma_i$  where  $\sigma_i$  and  $\sigma_{20}$  are the initial conductivity and conductivity at the end of the 20th minute respectively.

Table 5. Results of conductivity measurements during adsorption of acetone at atmospheric pressure

Temp. °C	$-\log \sigma_i$	$-\log \sigma_{20}$	$\Delta \log \sigma$
220	4.8921	4.2553	0.6368
300	4.0170	2.8573	1.1597
420	5.2201	3.5575	1.6626

$\sigma_i$  = initial conductivity of catalyst pellet at the start.

$\sigma_{20}$  = conductivity at 20 minutes from the start.

in Fig. 8. From these, the "band gap" values were evaluated using the equation<sup>18</sup>

$$\log_e \sigma = \log_e \sigma_0 - \varepsilon/2 kT$$

where  $\sigma$  represents the conductivity at any temperature,  $\varepsilon$  the band gap and  $\sigma_0$  is a constant.

The values obtained for  $\varepsilon$  are 1.57 eV for the plain catalyst and 1.05 eV after hydrogen pre-treatment pointing to a significant rise in the Fermi level of the catalyst as a result of hydrogen adsorption.

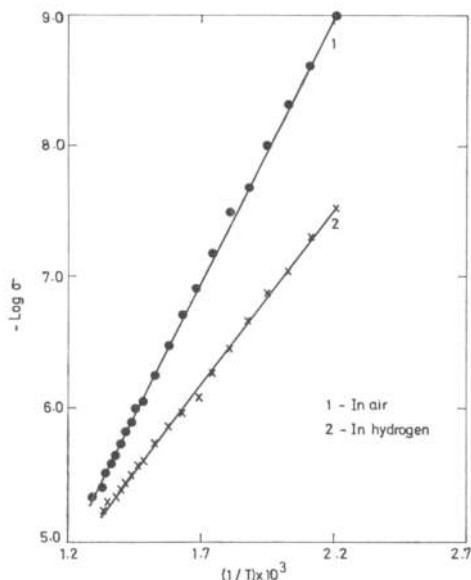


Fig. 8. Variation of the electrical conductivity of  $MnMoO_4$  with temperature in air and in hydrogen

<sup>18</sup> J. M. PEACOCK, A. J. PARKER, P. G. ASHMORE and J. A. HOCKEY, *J. Catalysis* **15** (1969) 387.

### Discussion

The observation that acetone and water selectively suppress the dehydrogenation and dehydration reactions respectively suggests that the two activities are independent of each other and are associated with different types of sites or different surface reaction conditions. That the selective poisoning effects of acetone and water are due to their preferential adsorption on the catalyst is supported by the data of heats of adsorption (Table 1), which show that acetone

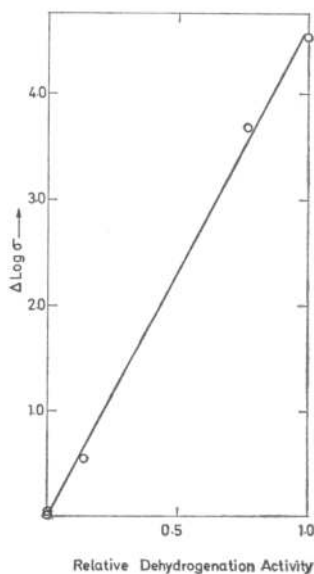


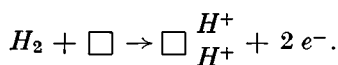
Fig. 9. Dependence of the electrical conductivity change during reaction on the relative dehydrogenation activity. (Based on data of Table 4. Basis: Extent dehydrogenation of pure isopropanol = 1)

and water-vapour are more strongly adsorbed than the alcohol. That acetone and water are adsorbed sufficiently at reaction temperatures to interfere significantly with alcohol adsorption is confirmed by the data of Table 2. The figures in the last two columns show that the amounts of isopropanol adsorbed in presence of presorbed acetone and water respectively add up very nearly to the amount of alcohol adsorbed on the bare surface. This is a strong indication that acetone and water are adsorbed on different groups of sites which are presumably those responsible separately for the dehydrogenation and dehydration activities.

That the surface possesses acidic sites which presumably account for its dehydrating activity is evidenced by the data of ammonia adsorption given in Table 3. It is seen that prior adsorption of acetone has virtually no effect on the ammonia adsorption, thereby confirming the presumption that acetone is not adsorbed to any extent on the acidic (dehydrating) sites.

The data of Table 4 show that with progressive suppression of the dehydrogenation reaction by addition of acetone to the reactant feed, the conductivity increase ( $\Delta \log \sigma$ ) decreases in proportion and finally vanishes when the reaction is completely suppressed. This is brought out clearly by Fig. 9, wherein the abscissa represents the relative dehydrogenation activity with reference to pure isopropanol. It is evident from these data that only dehydrogenation is attended with electron-exchange and that the dehydration reaction is unrelated to the electronic properties of the catalyst.

The action of hydrogen which enhances both the reactions seems to be two-fold: (a) to increase the density of acid sites as shown by the increase in ammonia adsorption following exposure to hydrogen (Table 3, Col. 3 and 4) and (b) to raise the Fermi level by contraction of the band gap (Fig. 7). The two effects can be represented by the equation



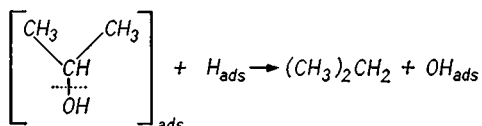
The former accounts for the enhancement of dehydration on addition of hydrogen. The latter effect and the attendant promotion of the dehydrogenation reaction are in agreement with our earlier observations<sup>19</sup> with zinc oxide catalysts which related the dehydrogenation activity with the Fermi level. Thus, it may reasonably be concluded that, on *n*-type oxide catalysts, activity for dehydrogenation of alcohols is associated with the donor-levels or the chemical potential of the electrons in the solid and is rate-limited by an acceptor process. This is in accord with the mechanism put forward by WOLKENSTEIN<sup>4</sup> on theoretical considerations insofar as it relates to the dehydrogenation reaction only. With regard to dehydration, however, the observed enhancement of this reaction also by added hydrogen is completely at variance with Wolkenstein's theory which expects the dehydrating activity to *decrease* with elevation of the Fermi level. This is because Wolkenstein's theory completely excludes the role of protonic acid sites from the mechanism of dehydration.

On purely kinetic considerations, since the dehydrogenation reaction is inhibited by acetone, the final step in the reaction, namely, the desorption of acetone, seems to be rate determining. This conclusion is supported by the high value of the energy of activation of the desorption of acetone ( $\cong 21$  kcal/mole, the heat of adsorption of acetone). Combining the two conclusions regarding the rate-controlling step, it follows that the desorption of acetone is an acceptor process. The results on manganese molybdate therefore lead to practically the same conclusions as those deduced by BIELANSKI<sup>7</sup>, ZHABROVA<sup>8</sup> and KRYLOV<sup>9</sup> on the basis of similar experiments on other oxide catalysts. The results on zinc oxide catalysts reported in Part I of this series<sup>19</sup> can also be interpreted on the same principles.

### Propane formation

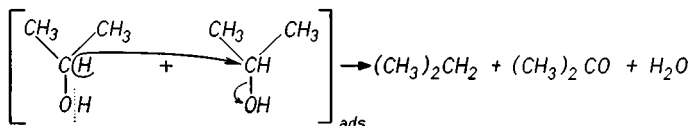
There are three possible means by which propane found in the reaction products could have been formed:

- by hydrogenation of propylene obtained through dehydration, with hydrogen yielded by dehydrogenation
- by hydrogen transfer between two adsorbed alcohol molecules



and

- by hydrogenolysis of adsorbed isopropanol



The first of the above possibilities is ruled out, firstly, by the appearance of propane in the products (with increased propane: propylene ratio) even under conditions of total elimination of the dehydrogenation reaction by acetone—addition and, secondly, by

<sup>19</sup> B. VISWANATHAN, M. V. C. SASTRI and V. SRINIVASAN, *Z. physik. Chem. Neue Folge* **79** (1972) 216.



Table 6. Decomposition of isopropanol and *ter-butanol* on deuterated catalyst

Deuteration procedure	Reaction	Mass spectral data		Moles propane/ isobutane formed per 100 moles alcohol decomposed	Per cent $C_3H_7D$ or $C_4H_9D$ of total propane or isobutane formed
		( <i>m/e</i> )	intensity		
Passed pure $D_2$ , 24 hours, 420°C	Decomposition of isopropanol, 420°C, 2.5 seconds contact time	44 <sup>a</sup>	95.0	14.1	21.7
		45 <sup>b</sup>	29.5		
		46 <sup>c</sup>	0.5		
Passed pure $D_2O$ vapour at 4 ml (1)/hour, 360°–420°, 3 hours and flushed with dry $N_2$ at 420° for 8 hours	Decomposition of isopropanol, 420°C, 2.5 seconds contact time	44	14.8	14.7	14.0
		45	2.8		
		46	—		
Passed $D_2$ , 24 hours, 420°C	Decomposition of <i>ter-butanol</i> , 420°C, 2.5 seconds contact time	43 <sup>a</sup>	20.0	11.2	59.2
		44 <sup>e</sup>	30.0		

<sup>a</sup> molecular ion peak for  $C_3H_8$ ; <sup>b</sup> molecular ion peak for  $C_3H_7D$ ; <sup>c</sup> molecular ion peak for  $C_3H_6D_2$ ; <sup>d</sup> base peak for iso- $C_4H_{10}$ ;  
<sup>e</sup> base peak for iso- $C_4H_9D$ .

the absence of hydrogenation when propylene-hydrogen mixture is circulated over the catalyst in the temperature range 400–430 °C.

The hydrogen transfer mechanism (b) should yield acetone and propane in equimolar amounts. The complete absence of acetone increase in the decomposition experiments carried out with acetone-isopropanol mixtures containing  $> 65\%$  of the former, though considerable amounts of propane are formed under these conditions, rules out this possibility also.

When the decomposition of isopropanol is carried out over the catalyst previously treated with flowing pure  $D_2$  or pure  $D_2O$  for 24 hours at 420 °C, 14 to 22 percent of the propane formed is found to be monodeuterated with virtually no dideuterated product (Table 6). This provides strong evidence for a hydrogenolysis mechanism (c), which is further confirmed by the formation of 2  $d_1$ -isobutane to the extent of nearly 60 percent of total isobutane formed (Table 6), when *t*-butanol is used as the reactant.

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