

Dehydrogenation of Isopropyl Alcohol on Zinc Molybdate (ZnMoO_4)

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The vapour phase decomposition of isopropyl alcohol on ZnMoO_4 and on ZnMoO_4 doped with various amounts of Li_2O has been studied in the temperature range $300\text{--}350^\circ$ at atmospheric pressure in a flow type reactor. From kinetic and electrical conductivity measurements and from studies of the effect of acetone, water and hydrogen separately to the feed, it is concluded that the desorption of acetone (an acceptor step), is normally the rate-controlling step in the dehydrogenation reaction. However, on surfaces with a high Fermi level (e.g. pure ZnMoO_4), the adsorption of alcohol by a donor mechanism becomes rate-determining in the same reaction.

IN two earlier papers^{1,2} studies on the catalytic decomposition of isopropyl alcohol on defect zinc oxide and manganese molybdate were reported. It was shown that the dehydrogenation and dehydration reactions occurred independently of each other involving different types of surface characteristics and that only the dehydrogenation reaction seemed to involve electron exchanges between the catalyst and the adsorbed substrate. The rate determining step of the dehydrogenation process also seemed to depend on the nature of the catalyst. These conclusions receive further substantial support from the results of studies reported in this paper on zinc molybdate.

Materials and Methods

Zinc hydroxide was precipitated from zinc nitrate by adding ammonia and the oven-dried precipitate heated for 48 hr at 150° to yield anhydrous ZnO .

Molybdic trioxide was obtained by thermal decomposition of ammonium paramolybdate at 520° .

Zinc molybdate was prepared by co-precipitation from a mixed solution of ammonium paramolybdate and zinc nitrate by dropwise addition of liquor ammonia and heating the oven-dried precipitate for 48 hr at 150° followed by 12 hr at 600° . The zinc content in the final product was estimated by EDTA titration. Its X-ray diffraction pattern conformed to that reported³ for ZnMoO_4 . Its identity was also confirmed by IR spectrum⁴.

Doping of zinc molybdate with Li_2O was carried out by the addition of the calculated amount of lithium nitrate to a mixed solution of zinc nitrate and ammonium paramolybdate prior to co-precipitation. The lithium content was estimated independently by analysis.

The preparation of pure reagents and the procedures for carrying out the reaction studies in a flow-type glass reactor and for making electrical measurements⁵ and adsorption measurements on the catalyst have already been described². The decomposition studies were carried out on ZnO , ZnMoO_4 , and Li-doped

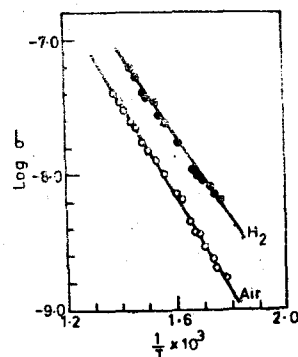


Fig. 1 — Variation of electrical conductivity of zinc molybdate with temperature in air and in hydrogen

ZnMoO_4 in the temperature range $300\text{--}350^\circ$ and on MoO_3 in the range $230\text{--}275^\circ$.

Results

Electrical measurements — Seebeck coefficient measurement showed ZnMoO_4 to be an *n*-type semiconductor. The variation of electrical conductivity (σ) of ZnMoO_4 as a function of temperature in air and in hydrogen is shown in Fig. 1. The activation energy for electrical conduction calculated from these

TABLE 1 — ELECTRICAL CONDUCTIVITY VALUES AT DIFFERENT TEMPERATURES

Temp. °C	ZnMoO_4	$\sigma \times 10^9$ ($\text{ohm}^{-1} \text{cm}^{-1}$) values of	
		$\text{ZnMoO}_4 + 1.5$ mole % Li_2O	$\text{ZnMoO}_4 + 3.0$ mole % Li_2O
299	2.044	0.662	0.638
326	3.716	1.104	0.754
348	7.059	1.813	1.160
370	10.210	3.624	1.450
392	15.340	6.304	2.786
412	23.320	11.040	4.062
432	30.590	18.120	6.094

plots is 0.50 eV in hydrogen as against 0.62 eV in air, thus showing a rise in the Fermi level of the catalyst as a result of hydrogen adsorption.

The data in Table 1 show that the electrical conductivities of Li-doped samples at various temperatures are lower than those of the undoped molybdate thus confirming the lowering of the Fermi level of $ZnMoO_4$ as a result of doping with Li^+ ions.

Adsorption measurements—The adsorption isotherms of isopropyl alcohol, acetone and water on $ZnMoO_4$ are shown in Figs. 2 and 3 and the Clapeyron heats of adsorption deduced therefrom are given in Table 2. It is seen from Table 2 that the computed isosteric heats of adsorption of isopropyl alcohol and acetone are less than the heats of vaporization at their boiling points but higher than the heats of vaporization reckoned at the temperatures at which the reaction was studied.

The surface acidity of the $ZnMoO_4$ catalyst was estimated by measurement of ammonia adsorption at 320° and 30 torr pressure. The fresh catalyst adsorbed 1.51 mg NH_3/g of the catalyst, whereas the catalyst containing presorbed hydrogen (1.3 mg/g) took up ~ 2.4 mg NH_3/g thus showing a marked increase in acidity as a result of hydrogen adsorption.

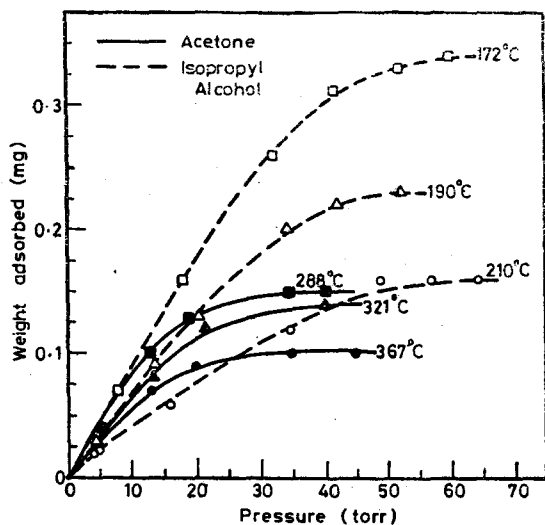


Fig. 2—Adsorption isotherms of isopropyl alcohol and acetone on zinc molybdate

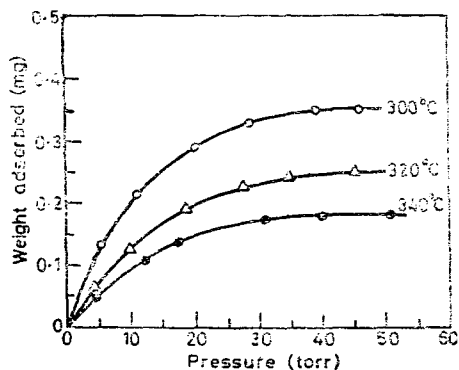


Fig. 3—Adsorption isotherms of water on zinc molybdate

TABLE 2—HEAT OF ADSORPTION OF VARIOUS SUBSTRATES

Adsorbate	Temp. range (°C)	ΔH (kcal/mole)	ΔH_v^* (kcal/mole)
Isopropyl alcohol	170-210	7.9	9.56 (82.3°) 0.0 (238°)
Acetone	280-370	4.7	7.2 (56.1°) 6.5 (100°) 0.0 (235°)
Water	280-370	12.7	9.7 (100°) 9.2 (140°) 8.6 (180°)

*Computed heat of vaporization values at various temperatures. (Ref.: *International critical Tables*, Vol. V, p. 138).

Decomposition kinetics: Studies on undoped $ZnMoO_4$ and its component oxides—Zinc molybdate catalyst was found to be predominantly dehydrogenating, the selectivity for dehydrogenation being about 85% of the total decomposition. Of the component oxides, MoO_3 was predominantly dehydrating and

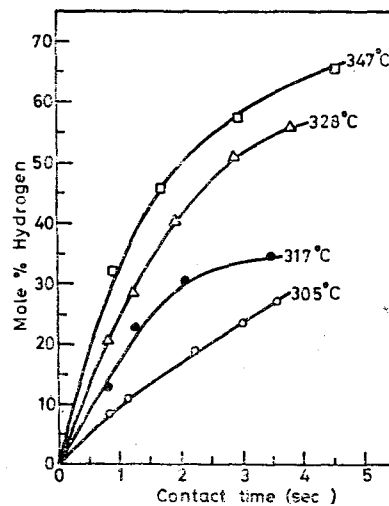


Fig. 4—Concentration-time plots for the dehydrogenation of isopropyl alcohol on zinc molybdate

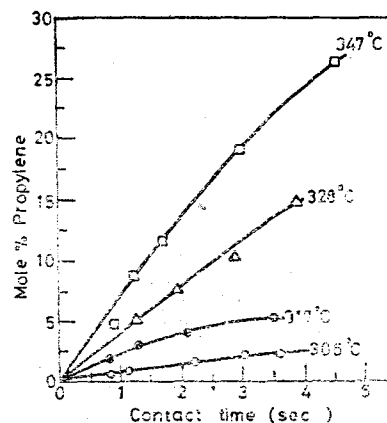


Fig. 5—Concentration-time plots for the dehydration of isopropyl alcohol on zinc molybdate

TABLE 3 — KINETIC PARAMETERS FOR THE DECOMPOSITION OF ISOPROPYL ALCOHOL

Catalyst	Dehydrogenation		Dehydration		Selectivity (dehydrogenation)
	E_{app} kcal/mole	K_0 $\text{min}^{-1} \text{m}^{-2}$	E_{app} kcal/mole	K_0 $\text{min}^{-1} \text{m}^{-2}$	
ZnO	10.9	1.8×10^8	—	—	1.00
MoO ₃	27.0	8.5×10^{10}	17.6	2.0×10^7	0.30
ZnMoO ₄	24.4	4.0×10^8	23.5	3.1×10^7	0.85

TABLE 4 — DECOMPOSITION OF ISOPROPYL ALCOHOL ON PURE AND DOPED ZINC MOLYBDATE

Contact time (sec)	ZnMoO ₄		ZnMoO ₄ + 0.5 mole % Li ₂ O		ZnMoO ₄ + 1.0 mole % Li ₂ O		ZnMoO ₄ + 1.5 mole % Li ₂ O	
	% A	% B	% A	% B	% A	% B	% A	% B
TEMP.: 330° ± 2°								
0.5	15.0	2.5	22.5	21.5	20.0	18.5	18.5	19.0
1.0	25.0	4.0	33.0	35.0	29.0	30.0	26.0	33.0
1.5	35.0	6.0	37.5	41.0	29.0	36.0	31.0	43.5
2.0	42.0	8.0	38.5	42.0	33.0	38.0	35.0	50.0
TEMP.: 350° ± 3°								
1.0	32.5	7.5	38.5	44.5	32.0	37.5	32.0	46.0
1.5	43.5	11.0	40.5	47.0	34.5	41.0	36.5	49.0
2.0	51.0	13.5	40.5	47.0	35.0	42.0	40.0	52.0

(A) refers to dehydrogenation and (B) to dehydration.

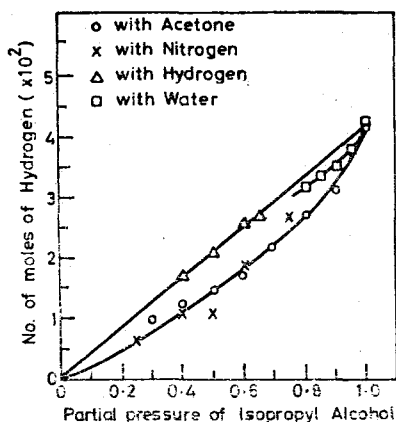


Fig. 6 — Effect of substrates on the dehydrogenation of isopropyl alcohol on zinc molybdate

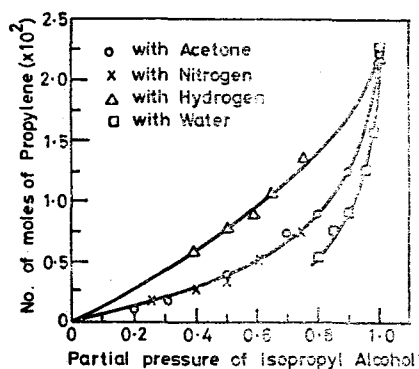


Fig. 7 — Effect of substrates on the dehydration of isopropyl alcohol on zinc molybdate

 TABLE 5 — ACTIVATION ENERGY VALUES FOR DOPED ZnMoO₄ CATALYSTS

Mole % Li ₂ O doped with ZnMoO ₄	Activation energy (kcal/mole)	
	Dehydrogenation	Dehydration
0.5	14.3	24.1
1.0	16.5	19.6
1.5	12.4	17.2
3.0	17.0	30.5

ZnO possessed almost exclusively dehydrogenating activity. The initial rates of the two reactions were derived from the plots of concentration vs time (Figs. 4 and 5) and the values of apparent energies of activation and frequency factors evaluated therefrom are given in Table 3.

The effects of addition of hydrogen, acetone and water to the alcohol-feed and of varying the alcohol partial pressure by dilution with nitrogen are shown in Figs. 6 and 7. It is seen that (i) addition of acetone has no effect on either of the reactions, (ii) hydrogen enhances both, and (iii) addition of water decreases the dehydration rate preferentially.

Studies on ZnMoO₄ doped with Li₂O — Typical values of the extents of dehydrogenation and dehydration as a function of contact time and temperature are given in Table 4. The selectivity (for dehydrogenation) of the catalyst doped with 1.5 mole per cent Li₂O was found to be almost 50% of the total decomposition as against 80% for pure ZnMoO₄. The activation energy for dehydration reaction on Li-doped catalysts (Table 5) is 20 ± 3.0 kcal/mole

TABLE 6 — EFFECT OF SUBSTRATES ON THE DECOMPOSITION OF ISOPROPYL ALCOHOL ON ZINC MOLYBDATE DOPED WITH 1.5 MOLE % Li_2O

(Temp.: 330°; contact time: 1.0 sec)

Partial pressure of alcohol (atm)	Amount of products formed in 1 hr (moles $\times 10^3$)					
	Propylene	Hydrogen	Propylene	Hydrogen	Propylene	Hydrogen
	In presence of N_2		In presence of acetone		In presence of H_2	
0.5	2.43	2.65	2.32	2.21	—	—
0.7	3.17	3.10	3.07	2.49	4.14	4.53
0.8	3.43	3.92	3.59	3.25	5.20	4.76
0.9	3.71	4.26	3.88	3.27	5.49	5.22

which is comparable with that obtained on pure ZnMoO_4 . On the other hand, the value of the activation energy for dehydrogenation reaction on Li-doped ZnMoO_4 (14.0 ± 2.0 kcal/mole) is considerably lower than that on pure ZnMoO_4 (24.5 kcal/mole). This reveals a difference in the mechanism of dehydrogenation reaction on doped and undoped ZnMoO_4 catalysts.

In order to understand this mechanistic difference, the decomposition of isopropyl alcohol was studied in presence of acetone, hydrogen and nitrogen on zinc molybdate doped with 1.5 mole per cent Li_2O at 330°. It is seen from the values given in Table 6 that as compared with undoped catalyst, addition of acetone decreases the dehydrogenation rate preferentially and the presence of hydrogen enhances both dehydrogenation and dehydration rates.

Discussion

Mechanism of the dehydrogenation reaction — The adsorption of alcohol by a donor mechanism and the desorption of acetone by an acceptor process^{6,7} are considered to be the two kinetically important steps of the dehydrogenation reaction. Depending upon the nature of the catalyst and the position of the Fermi level, one or the other of these two steps can be rate-controlling. From studies of the decomposition of isopropyl alcohol on ZnO catalyst, it has been concluded that the adsorption of alcohol through oxygen of the hydroxyl group and the subsequent rearrangements of adsorbed alcohol is the rate-determining step². However, on MnMoO_4 catalyst, the desorption of acetone was found to be the rate-controlling step. It is evident, therefore, that the rate-determining step is dependent on the nature of the catalyst surface under examination.

It was observed that on pure ZnMoO_4 the reaction was not inhibited by addition of acetone to the feed. Further, the heat of adsorption of acetone (Table 2) being less than that of either alcohol or water, it follows that on ZnMoO_4 , the desorption of acetone cannot be rate-controlling in the overall reaction.

Li-doped ZnMoO_4 samples have lower conductivity values than pure ZnMoO_4 . It is known that addition of monovalent oxides to *n*-type catalysts lowers the Fermi level and decreases the concentration of charge carriers. Seebeck coefficient measurements have confirmed this expectation. Consequently, the acceptor step of the reaction sequence (desorption of acetone) is slowed down to become the rate-determining step of the dehydrogenation reaction. On Li-doped ZnMoO_4 the overall rate is inhibited in the presence of acetone as shown by the results reported in Table 6. This observation supports the above conclusion.

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