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Catalytic Decomposition of Isopropanol over Chromite Spinels MCr_2O_4 (M = Ni, Mn and Mg)

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The decomposition of isopropanol over nickel, manganese and magnesium chromite spinel catalysts has been investigated in the vapour phase in an integral reactor. Its decomposition follows first-order kinetics. Kinetic and thermodynamic parameters have been calculated using the Arrhenius and Eyring equations. The activity pattern is found to be NiCr₂O₄ > MnCr₂O₄ > MgCr₂O₄. The chromite spinels have been characterised by X-ray studies, i.r. spectral analysis, conductivity and thermoelectric potential measurements. All three chromites were found to be p-type semiconductors in the temperature range 150–400 °C. Exclusive dehydrogenation is shown by NiCr₂O₄ and MnCr₂O₄, whereas MgCr₂O₄ functions as a dehydrogenation and dehydration catalyst. A linear correlation exists between the entropy of activation and the activation energy for electrical conduction for the chromite spinels studied.

Spinels are a group of inorganic compounds represented by a general formula AB_2O_4 ,¹⁻³ where A and B are bivalent (Mg, Mn, Co, Ni, Cu and Zn) and trivalent (Al, Cr, Fe) metals, respectively. Spinels are thermally stable and they maintain enhanced and sustained activities for a variety of industrially important reactions such as decomposition of nitrous oxide,⁴ hydrodesulphurisation of crude petroleum,⁵ oxidation and dehydrogenation of hydrocarbons^{6, 7} and oxidation and methanation of carbon monoxide.^{8, 9} This study involves the preparation, characterisation and comparison of the catalytic activity of nickel, manganese and magnesium chromite spinels.

Experimental

Catalyst Preparation

A mixture of a 10% solution of the metal nitrates was taken in the ratio of Cr: M = 2:1 and the mixture was heated to 60–80 °C. To this hot mixture a 5% ammonia solution was added dropwise with constant and uniform stirring. The solution was maintained at pH 9 during the precipitation. The mixture was digested for another 2 h at this temperature to complete precipitation. The precipitate was filtered and dried at 105 °C for 24 h. Calcination of magnesium and nickel chromites was done at 700 °C in a muffle furnace for 8 h in a current of pure dry air and manganese chromite in hydrogen.

The purity of isopropanol (AR, BDH) was tested by gas chromatography.

Catalytic Decomposition of Isopropanol

plane	NiCr ₂ O ₄		MnCr ₂ O ₄		MgCr ₂ O ₄	
	$d_{\rm obs.}^{a}$	$d_{\rm lit.}{}^b$	$d_{\rm obs.}{}^a$	$d_{\rm calc.}$	$d_{\rm obs.}^{a}$	$d_{\rm lit.}{}^b$
111	4.78 w	4.79 (20)		<u> </u>	4.80 m	4.813 (65)
220	2.90 m	2.93 (30)	3.145 m	2.98	2.94 w	2.95 (14)
311	2.49 vs	2.50 (100)	2.542 vs	2.54	2.51 vs	2.51 (100)
400	2.05 m	2.07 (35)	2.11 m	2.11	2.10 s	2.08 (55)
422	1.68 w	1.70 (15)	1.72 w	1.72		
511, 333	1.58 s	1.60 (60)	1.625 s	1.624	1.587 m	1.603 (40)
440	1.47 s	1.47 (80)	1.496 s	1.492	1.468 s	1.473 (55)

Table 1. X-Ray d spacing data (Å) on $NiCr_2O_4$, $MnCr_2O_4$ and $MgCr_2O_4$

^{*a*} vs = Very strong; s = strong; m = medium; w = weak. ^{*b*} Peak intensity in parentheses. Powder diffraction file lattice parameter: NiCr₂O₄ = 8.331 Å, MnCr₂O₄ = 8.437 Å, MgCr₂O₄ = 8.329 Å.

Table 2. I.r., conductivity and Seeback potential data on NiCr₂O₄, MnCr₂O₄ and MgCr₂O₄

		v _{max} /				
metal chromites and colour	Cr—O obtained	Cr—O reported	M—O obtained	M-O reported	E_{σ}/eV	$lpha^a$ / μ V °C ⁻¹
Ni Cr_2O_4 (green)	575-585	510	630–640	630	1.066	380
$MnCr_2O_4$ (grey)	490–510	490	610–630	620	1.054	92
$\begin{array}{c} MgCr_2O_4 \\ (grey-green) \end{array}$	525	525	600-620	650	0.652	6.8

^a Positive Seeback potential indicates that all three chromite spinels are p-type semiconductors in the temperature range studied.

Catalyst Characterization

X-Ray Study

The spinels were characterised by X-ray powder pattern studies¹⁰ using a Philips X-ray diffractometer (PW 1050), and 'd' spacings and lattice parameter values are given in table 1, along with the reported data for comparison.¹¹

I.R. Study

The i.r. spectra of spinels were obtained in a double-beam spectrophotometer (Perkin-Elmer 983). The maxima of the absorption bands for Cr—O (580–490 cm⁻¹) and M—O (650–620 cm⁻¹) are given in table 2, along with the reported data for comparison.¹¹

Conductivity and Thermoelectric Potential Measurements

Electrical conductivity measurements¹² were carried out using a two-probe conductivity cell in the temperature range 150–400 °C. The activation energies for electrical conduction (E_{σ}) were obtained from the slope of the plot of log σ vs. $T^{1/2}$ and the values are included in table 2. Thermoelectric (Seeback) potential, α measurements¹³ for all three chromites were also carried out in this temperature range. The nature of charge carriers (holes or

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electrons) was determined by checking the sign of the Seeback potential. For this purpose the following modification in the conductivity measuring apparatus was made. An auxiliary heating element was wound over a silica tube and kept at one end of the conductivity cell containing the catalyst pellet. After equilibrating the sample at each temperature for 15 min, the auxiliary heater was switched on and a temperature difference of *ca*. 10 K was maintained between the sample ends. After a steady state had been attained the Seeback potential was measured using a d.c. microvoltmeter. In this way, the Seeback potential has been measured at various temperatures. The cold end of the conductivity cell was positive, indicating p-type semiconduction (hole conduction) and the α values are given in table 2.

Conductivity data of many spinels have been related to their magnetic properties, both of which in turn depend on the crystal structure.^{14, 15} Goodenough,¹⁶ using a one-electron energy diagram, has found out that it is the octahedral (B site) cations which are responsible for electrical conduction by virtue of site symmetry in an AB₂O₄ spinel. Neel¹⁷ has explained the magnetic behaviour of ferrite spinels on the basis of exchange interactions that occur between the transition-metal ions at A and B sites in the spinel structure. The three possible interactions are A–A, A–B and B–B. A–B interactions can occur through 125° A–O–B super-exchange type, while B–B interactions can be either 90° B–O–B super-exchange type or a direct B–B one. The A–A interaction is usually very weak owing to the large distance between the A-site cations. Thus the relative magnitude of interaction in spinels is in the following order: AB > BB > AA. All three exchange interactions are normally antiferromagnetic and the spin vector would tend to align antiparallel.^{18, 19}

In NiCr₂O₄ and MnCr₂O₄ all the three exchange interactions are present and the distance between the Cr³⁺–Cr³⁺ ions is shortened owing to the higher ionic radii of Ni²⁺ (0.69 Å) and Mn²⁺ (0.80 Å). The resulting antiferromagnetic order thus enhances the activation energy for electrical conduction (table 2). MgCr₂O₄ has a much lower activation energy for electrical conduction owing to the very weak B–B interaction (Mg²⁺ non-magnetic, radius 0.66 Å).

Apparatus and Procedure

The reactions were carried out in a fixed-bed flow-type integral reactor, 50 cm long with 1.5 cm internal diameter in the temperature range 290–380 °C and at different contact times, W/F (W is the weight of the catalyst and F is the weight rate of the reactant per hour). Pyrex glass beads (4 mm diameter) were placed above the catalyst bed to a height of 5 cm. The reactor tube was inserted into a cylindrical furnace and heated electrically to the requisite temperature. Using a thermocouple the temperature was monitored along the length of the catalyst bed and the temperature required for a particular run was maintained constant.

The liquid products, containing acetone and unreacted isopropanol, were identified and estimated by a CIC gas chromatograph (FFAP column, f.i.d. detector, column temperature 90 °C, injection port temperature 150 °C, detector temperature 90 °C, carrier gas argon, 1.75 kg cm⁻², fuel H₂, 1.2 kg cm⁻², sample size 10⁻³ cm³). The gaseous products consisted mainly of H₂ with all three catalysts, with a measurable amount of propene over MgCr₂O₄. Products were estimated using Orsat's gas analyser. At higher contact times, traces of carbon dioxide were noticed and measured.

Results and Discussion

A plot of $\log_{10}[100/(100-x)]$ vs. contact time (fig. 1), where x is the percentage isopropanol converted to acetone, results in straight lines passing through the origin, indicating that the decomposition of isopropanol follows first-order kinetics. The rate



Fig. 1. First-order plot for the formation of acetone at 290 °C. \bigcirc , NiCr₂O₄; \triangle , MnCr₂O₄; \bigcirc , MgCr₂O₄.

			rate constant/h ⁻¹		
catalyst	$T/^{\circ}\mathrm{C}$	first-order plot	initial rate	Guggenheim	
NiCr ₂ O ₄	290	1.49	1.33	1.11	
2 ¥	340	2.41	2.87	2.70	
	380	4.14	4.23	4.1	
MnCr ₂ O ₄	290	0.69	0.77	0.63	
2 4	340	1.26	1.50	1.14	
	380	2.07	2.54	1.97	
MgCr _a O ₄	290	0.46	0.46	0.37	
0 2 4	340	1.12	1.11	1.25	
	380	2.16	1.92	2.71	

Table 3. Rate constants for dehydrogenation

constants calculated from the slopes of these plots are presented in table 3, along with the values obtained by the method of initial rate. The first-order rate constants obtained by Guggenheim's²⁰ finite contact time method are also included in table 3 for comparison.

The formation of acetone as a function of contact time over NiCr₂O₄, MnCr₂O₄ and MgCr₂O₄ at 340 °C is plotted in fig. 2. The rate of formation of acetone decreases with increasing contact time. Increase of contact time may facilitate the adsorbed acetone to react with lattice oxygen to form CO₂. This is evident from the liberation of CO₂ (table 4). Oxidation of acetone to CO₂ was confirmed by adding acetone and identifying the liberated CO₂. The decrease of acetone may also be due to the occurrence of the reverse reaction, as reported by Daniel and Kuriakose.²¹ Over magnesium chromites, dehydration also occurs and the extent of dehydrogenation and dehydration are shown in fig. 3. The effect of temperature on the formation of acetone for the above three catalysts is illustrated in fig. 4. The activation energy (E_a) obtained from the Arrhenius plots and thermodynamic parameters ΔH^{\ddagger} , ΔS^{\ddagger} and ΔG^{\ddagger} evaluated for the activated state²² of the system are given in table 5.



Fig. 2. Effect of contact time on the formation of acetone at 340 °C. \bullet , NiCr₂O₄; \triangle , MnCr₂O₄; \bigcirc , MgCr₂O₄.

Table 4. CO_2 (mol %) liberated during the decomposition of isopropranol over chromite spinels

	CO_2 liberated/mol%									
	NiCr ₂ O ₄			MnCr ₂ O ₄			MgCr ₂ O ₄			
T/°C	0.2^{a}	0.3	0.4	0.2	0.3	0.4	0.2	0.3	0.4	
290	0.56	1.1	2.1	0.21	0.64	0.9	0.16	0.4	0.7	
340	0.69	1.6	2.7	0.32	0.85	1.4	0.28	0.65	0.9	
380	0.9	2.25	3.2	0.42	1.2	1.8	0.4	1.0	1.3	

^a Contact time/h.

The order of activity, based on the values of activation energy for dehydrogenation, is: NiCr₂O₄ > MnCr₂O₄ > MgCr₂O₄. The negative ΔS^{\ddagger} values indicate the formation of an ordered activated complex by absorption of isopropanol on the spinel, with resultant loss in the internal degrees of freedom. The higher entropy of activation $(-210 \text{ J mol}^{-1} \text{ K}^{-1})$ and lower energy of activation (38.37 kJ mol}^{-1}) for dehydration of isopropanol over MgCr₂O₄ compared to the respective values of dehydrogenation shows that activated complex for the former process is relatively stable and easily attainable. This is clear evidence for the prevalence of a different active site over MgCr₂O₄ for isopropanol decomposition.

In situ electrical conductivity measurements in ambient atmospheres have been carried out on the three catalysts. The initial conductivities at 340 °C for NiCr₂O₄, MnCr₂O₄

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Fig. 3. Effect of contact time on the product distribution over $MgCr_2O_4$ at 340 °C. \triangle , Unchanged isopropanol; \bigcirc , acetone; \bigcirc , propylene.



Fig. 4. Effect of temperature on the formation of acetone. \bullet , NiCr₂O₄; \triangle , MnCr₂O₄; \bigcirc , MgCr₂O₄.

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catalyst	$E_{ m a}$ /kJ mol ⁻¹	ΔH^{\ddagger} /kJ mol ⁻¹	ΔG^{\ddagger} /kJ mol ⁻¹	ΔS^{\ddagger} /J mol ⁻¹ K ⁻¹
		dehydrogenation		
NiCr ₂ O ₄	34.46	29.78	130.56	-175.16
MnCr ₂ O ₄	37.44	32.76	141.95	- 193.95
MgCr ₂ O ₄	51.06	46.38	149.83	-183.75
		dehydration		
MgCr ₂ O ₄	38.37	33.69	158.22	-210.2

Table 5. Activation and thermodynamic parameters at 563 K



Fig. 5. Relationship between entropy of activation and activation energy for electrical conduction. □, $CoCr_2O_4$; \blacksquare , $CuCr_2O_4$; \bigotimes , $ZnCr_2O_4$; \triangle , $MnCr_2O_4$; \bigcirc , $NiCr_2O_4$; \bigcirc , $MgCr_2O_4$.

and MgCr₂O₄ were 6.13×10^{-4} , 2.49×10^{-4} and $1.36 \times 10^{-3} \Omega^{-1}$ cm⁻¹, respectively. When isopropanol vapour was introduced the conductivity decreased slowly and attained a constant value of 4.41×10^{-4} , 1.83×10^{-4} and $0.79 \times 10^{-3} \Omega^{-1}$ cm⁻¹, respectively, after 10 min. The decrease in conductivity is attributed to the transfer of electrons from the oxygen of isopropanol to the catalyst during the process of adsorption. This lends further support to the p-type nature of the chromite spinels. The constant value of conductivity may be due to the attainment of adsorption–desorption equilibrium. An exactly similar trend is observed in presence of acetone vapour, except that the conductivity decrease is drastic, while there is no change in conductivity in the atmosphere of hydrogen.

The existence of a linear correlation between activation energy for electrical conduction (E_{σ}) and entropy of activation (ΔS^{\ddagger}) for Mn, Co, Ni, Cu and Zn chromites is shown

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in fig. 5 (the values for Co, Cu and Zn are taken from our earlier work²³), which indicates the exclusive dehydrogenating nature of these spinels, while the dual-function $MgCr_2O_4$ catalyst does not fit into the linear plot (fig. 5).

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