# 2-PROPANOL DECOMPOSITION ON $La_2MnMO_6$ (M = Co, Ni, Cu) PEROVSKITES

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## Summary

Perovskite catalysts of the type La<sub>2</sub>MnMO<sub>6</sub> (M  $\equiv$  Co, Ni, Cu) were synthesized by means of a ceramic technique. Single-phase formation was checked by means of X-ray diffraction using Cu K $\alpha$  radiation. Electrical conductivity measurements were carried out with a standard two-probe cell. The catalytic activity of the perovskites was tested for the decomposition of 2-propanol in the temperature range 200 - 300 °C in a fixed-bed flow type of reactor. All the perovskites promote dehydrogenation of the alcohol. A possible mechanism for the reaction is proposed by studying the effect of products on the reaction rate and from the variations in the electrical conductivity of the pelletized catalysts in the reactant and product atmospheres.

#### 1. Introduction

The solid state properties of perovskite-like compounds have been widely studied. Recent studies on their catalytic properties have revealed that they are potential catalysts for a variety of reactions [1 - 3]. Perovskites containing rare earth and transition metals have been tested for many reactions and rationalizations of their catalytic activity based on their physicochemical properties are well documented in the literature [4 - 6]. In the present investigation the catalytic activity of a series of ordered perovskites of the type La<sub>2</sub>MnMO<sub>6</sub> (M = Co, Ni, Cu) has been tested for the decomposition of 2-propanol. 2-Propanol decomposition has been studied on various types of catalysts [7 - 9] and has recently been reviewed by Cunningham *et al.* [10]. This reaction is often chosen as a model reaction for studying catalytic activity since it gives information about both the catalytic activity and the selectivity and is often free from undesired side products.

The kinetics of 2-propanol decomposition on perovskites has been studied in a flow type of reactor. A possible mechanism for the decomposition reaction on these catalysts has also been proposed.

## 2. Experimental details

The perovskites  $La_2MnMO_6$  were synthesized by firing the corresponding metal oxalates at 950 °C for 36 h in stoichiometric amounts. X-ray diffractograms of the heated samples were recorded using Cu K $\alpha$  radiation to confirm single-phase formation and to analyse the crystal structure. Electrical conductivity measurements were made with a standard two-probe cell. For the kinetic studies, high purity 2-propanol and acetone were used after distillation. Hydrogen and nitrogen were purified by standard methods.

The catalytic decomposition of 2-propanol was studied in the temperature range 200 - 300 °C in a fixed-bed flow type of reactor [11]. The liquid products and gaseous products of the decomposition reaction were analysed by means of gas chromatography and with an Orsat gas analyser respectively. To establish the effect of the products on the reaction rate, kinetic studies were carried out at various partial pressures of 2-propanol. The partial pressure was varied by addition of either an inert diluent or the products of the reaction.

## 3. Results and discussion

All the perovskites prepared are found to crystallize in a cubic lattice and the unit cell parameters are twice that of  $ABO_3$  perovskites (about 7.9 Å). They are also found to be p-type semiconductors as revealed by the electrical conductivity and Seebeck coefficient measurements. The physicochemical properties of the perovskites are listed in Table 1.

#### TABLE 1

Physicochemical properties of La<sub>2</sub>MnMO<sub>6</sub> perovskites

Compound	Lattice type	Lattice parameter (Å)	E <sub>a</sub> conduction (eV)
La <sub>2</sub> MnCoO <sub>6</sub>	Cubic	7.74	0.25
La <sub>2</sub> MnNiO <sub>6</sub>	Cubic	7.76	0.30
La <sub>2</sub> MnCuO <sub>6</sub>	Cubic	7.80	0.37

The decomposition of 2-propanol on these perovskites was studied at various temperatures (200 - 300  $^{\circ}$ C) and contact times (0.2 - 4.0 s). Analysis of the products reveals that all these catalysts promote only dehydrogenation of the alcohol.

The Arrhenius plots are constructed from the initial rates of conversion at various temperatures (Fig. 1) from which the kinetic parameters, *i.e.* the activation energy  $E_a$  for reaction and the frequency factor A, are computed (Table 2).



Fig. 1. Arrhenius plots for the dehydrogenation of 2-propanol on  $La_2MnMO_6$ : •,  $La_2MnCuO_6$ ;  $\triangle$ ,  $La_2MnNiO_6$ ;  $\bigcirc$ ,  $La_2MnCoO_6$ .

#### TABLE 2

Kinetic parameters for the dehydrogenation of 2-propanol on La<sub>2</sub>MnMO<sub>6</sub> catalysts

Catalyst	$E_{a}$ (kcal mol <sup>-1</sup> )	$\ln A$	
La <sub>2</sub> MnCoO <sub>6</sub>	6.7	8.75	
$La_2MnNiO_6$	9.1	11.63	
$La_2MnCuO_6$	12.5	14.00	

#### 3.1. Effect of products on the reaction rate

Kinetic studies were carried out at various partial pressures of 2propanol at a constant contact time (1.2 s). The partial pressure was varied by addition of either the dehydrogenation products (acetone and hydrogen) or an inert diluent (nitrogen). The following observations were made from these studies (Table 3).

(i) Admission of hydrogen together with 2-propanol does not have any influence on the reaction rate.

(ii) Admission of acetone with 2-propanol decreases the reaction rate considerably (by about 25%) at all partial pressures.

It can be inferred that hydrogen acts as a mere diluent whereas acetone has an additional inhibiting effect which may be due to its slow desorption.

## 3.2. Effect of the reactant and products on the electrical conductivity of the catalysts

The conductivity changes in the presence of the reactant or the products of the dehydrogenation reaction were measured as a function of

Catalyst	Partial pressure of 2-propanol (atm)	Amount (×10 <sup>2</sup> mol h <sup>-1</sup> ) of $H_2$ formed in the presence of the following		
		$H_2$	Acetone	N <sub>2</sub>
La <sub>2</sub> MnCoO <sub>6</sub>	0.21	0.43	0.32	0.45
	0.43	0.63	0.47	0.65
	0.61	0.78	0.59	0.79
	0.91	0.84	0.63	0.86
	1.00	0.85	0.85	0.85
La <sub>2</sub> MnNiO <sub>6</sub>	0.21	0.56	0.39	0.58
	0.43	0.83	0.67	0.89
	0.70	1.10	0.89	1.06
	0.91	1.12	1.05	
	1.00	1.12	1.12	1.12
La <sub>2</sub> MnCuO <sub>6</sub>	0.21	1.05	0.46	0.98
	0.43	1.41	0.90	1.46
	0.61	1.88		1.92
	0.91	2.09	1.74	
	1.00	2.10	2.10	2.10

Effect of products on the dehydrogenation of 2-propanol on  $La_2MnMO_6$  catalysts

Temperature, 260 °C; contact time, 1.2 s.

time at a constant flow rate (1.5 ml min<sup>-1</sup>) at and below the reaction temperature. The factor  $\Delta\sigma/\sigma_0$ , where  $\sigma$  is the conductivity in the desired atmosphere and  $\sigma_0$  is that in air at the same temperature, was used as a measure of the change in conductivity.

The conductivity changes brought about by the presence of acetone at low temperatures are much less compared with those brought about by the presence of 2-propanol. However, at the reaction temperatures the effects of both acetone and 2-propanol are similar. The conductivity changes in the presence of hydrogen are much less compared with those in the presence of either 2-propanol or acetone (Table 4 and Fig. 2).

The decrease in conductivity of these p-type semiconductor catalysts in the presence of 2-propanol may be due to adsorption by a donor mechanism. The dehydrogenation products, acetone and hydrogen, also have the same effect of decreasing the conductivity of the catalysts, indicating that the adsorption in these cases also takes place by donation of electrons to the catalyst surface.

The effect of admitting acetone (or 2-propanol) to surfaces pretreated with 2-propanol (or acetone) on the electrical conductivity of the catalysts was also studied at the reaction temperature. 2-Propanol was admitted first and acetone was introduced after the conductivity had reached a constant value for the adsorption of 2-propanol. The experiment was repeated at the same temperature by reversing the order of admission. Irrespective of the

TABLE 3

Catalyst	Temperature (°C)	$\Delta\sigma/\sigma_0^{a}$	
		Acetone	2-Propanol
La2MnCoO6	150 260	$-0.20 \\ -0.30$	-0.26 -0.28
$La_2MnNiO_6$	150 260	-0.48 -0.83	-0.62 -0.88
La <sub>2</sub> MnCuO <sub>6</sub>	150 260	$\begin{array}{c} -0.24 \\ -0.36 \end{array}$	$-0.32 \\ -0.37$

Variation in electrical conductivity of La2MnMO6 in ambient atmospheres

<sup>a</sup> After 20 min.



Fig. 2. Variation in electrical conductivity of  $La_2MnCuO_6$  in various ambient atmospheres:  $\triangle$ , hydrogen;  $\bullet$ , acetone;  $\bigcirc$ , 2-propanol.

order of admission, the observed steady state conductivity values were the same. The observations can be rationalized as follows.

The changes in conductivity in the presence of 2-propanol or acetone are of the same extent at the reaction temperatures, which means that the surface is predominantly covered with acetone under the reaction conditions. The fact that acetone vapour when passed over a surface previously covered with alcohol does not have much influence on the conductivity may correspond to one of two possibilities.

(i) The chemisorbed 2-propanol molecules are desorbed by acetone and the number of acetone molecules adsorbed happens to be exactly that necessary to give the same change in conductivity as in the 2-propanol atmosphere.

(ii) After adsorption 2-propanol is decomposed to hydrogen which desorbs quickly and to acetone which desorbs slowly and the steady state conductivity value is due to acetone itself and hence further introduction of acetone does not have any influence as the surface is already covered with acetone.

Hence it can be inferred that acetone desorption is a slow process.

The slow step of the dehydrogenation reaction can be any of the following:

 $(CH_3)_2CHOH \longrightarrow (CH_3)_2CHOH(ads)$  $(CH_3)_2CHOH(ads) \longrightarrow (CH_3)_2CO(ads) + 2H(ads)$  $(CH_3)_2CO(ads) \longrightarrow (CH_3)_2CO(vap)$  $2H(ads) \longrightarrow H_2(g)$ 

The conductivity of these p-type catalysts decreases when they are exposed to 2-propanol vapour. This can only be possible if the alcohol molecules are adsorbed by a donor mechanism. Such a donor type of adsorption is much easier on p-type surfaces. Hence the initial adsorption of alcohol is expected to be fast. Moreover, if the adsorption of alcohol were the slow



Fig. 3. Correlation between  $E_a$  for electrical conduction and  $E_a$  for 2-propanol dehydrogenation on La<sub>2</sub>MnMO<sub>6</sub>:  $\bigcirc$ , La<sub>2</sub>MnCoO<sub>6</sub>;  $\bigcirc$ , La<sub>2</sub>MnNiO<sub>6</sub>;  $\bigcirc$ , La<sub>2</sub>MnCuO<sub>6</sub>.

step, the surface would be predominantly covered with 2-propanol under the reaction conditions. In such a case, if acetone were introduced to the surface previously saturated with 2-propanol, there would be a distinct change in the conductivity. No such change in conductivity is observed in the present case, suggesting that alcohol adsorption is not a slow process.

A linear correlation could be obtained between the activation energy for the dehydrogenation reaction and that for electrical conduction (Fig. 3). Such a correlation corresponds to a slow process in which there is electron transfer between the catalyst surface and the adsorbed species. Since the surface reaction does not involve any such electron transfer, no correlation of the above kind would have been expected. Hence the surface reaction is expected to be a rapid step.

The conductivity studies reveal that the surface is predominantly covered with acetone under the reaction conditions. The study of the effect of the products on the reaction rate suggests that acetone decreases the rate of reaction. Together these facts indicate that desorption of acetone is the slow step of the reaction. Since acetone adsorbs by a donor mechanism, as shown by the decrease in conductivity on its adsorption, its desorption involving electron transfer from the p-type catalyst to the adsorbed species can be expected to be a slow process.

### 4. Conclusions

All these perovskites promote dehydrogenation of the alcohol. Acetone desorption is the rate-limiting step of the reaction.

#### References

- 1 R. J. H. Voorhoeve, J. P. Remeika and L. E. Trimble, Ann. N.Y. Acad. Sci., 272 (1976) 3.
- 2 D. W. Johnson, Jr., P. K. Gallagher, G. K. Wertheim and E. M. Vogel, J. Catal., 48 (1977) 87.
- 3 S. B. Patil, A Bandyopadhyay, D. K. Chakrabarty and H. V. Keer, *Thermochim. Acta*, 61 (1983) 269.
- 4 V. Srinivasan, C. S. Swamy, G. Muralidharan, S. Lewis Raj, R. Pitchai and K. M. Vijayakumar, Proc. 7th Int. Congr. on Catalysis, Elsevier, Amsterdam, 1981, p. 1458.
- 5 T. Shimizu, Chem. Lett., (1980) 1.
- 6 T. Wolfram, E. A. Kraut and F. J. Morin, Phys. Rev. B, 7 (1973) 1677.
- 7 D. V. Fikis, W. J. Murphy and R. Ross, Can. J. Chem., 56 (1978) 2530.
- 8 M. I. Zaki and N. Sheppard, J. Catal., 80 (1983) 114.
- 9 B. H. Davis, J. Catal., 79 (1983) 58.
- 10 J. Cunningham, B. K. Hodnett, M. Ilyas, J. Tobin and E. L. Leahy, Faraday Discuss. Chem. Soc., 72 (1981) 283.
- 11 T. Kawai, K. Kumimon, T. Kondow, T. Onishi and K. Tamaru, Z. Phys. Chem. (Frankfurt am Main), 86 (1973) 268.