

The Decomposition of Isopropanol over MgO and CoO-MgO Solid Solutions

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The decomposition of isopropanol is studied over well-outgassed MgO and $\text{Co}_x\text{Mg}_{1-x}\text{O}$ ($x = 0.07, 0.30$) as catalysts in the temperature range from 180 to 250°C. A micropulse technique is used, with high-temperature outgassing between pulses. The dependence of conversion on flow rate, pulse size, and temperature is investigated for $\text{Co}_x\text{Mg}_{1-x}\text{O}$. All the catalysts are selective for dehydrogenation, producing acetone. The effect of incorporating cobalt ions is to increase the activity of MgO; small amounts ($x = 0.07$) have a relatively greater effect than large amounts ($x = 0.30$). A mechanism involving coordinatively unsaturated cations and changes in cation-anion bond character is proposed to account for the reactions and for the enhanced activity of the cobalt-containing MgO.

INTRODUCTION

Dehydrogenation of isopropanol leads to acetone, and dehydration, to propylene or isopropyl ether. These reactions are catalyzed by oxides, and there are marked differences in both activity and selectivity as between one oxide and another (1). In seeking to understand these differences, some workers have stressed electronic and ionic properties (2, 3) as being the determining features, while others have emphasized acidity, basicity, and hydroxylation (1, 4). The possible interplay between these features is imperfectly understood.

The broadest simple correlation (1) is that acidic oxides are those most active in dehydration, while basic oxides, such as the triad of MgO, CaO, and SrO recently studied by Szabó, Jover, and Ohmacht (5), are mainly active in dehydrogenation. Moreover, at least for MgO (6), the higher

the preparation temperature the more selective is the oxide for dehydrogenation. Selectivity, however, is also affected by the temperature at which the catalysis is conducted, higher temperatures (typically above 350°C) favoring dehydration. Thus to obtain high selectivity toward dehydrogenation one needs a basic catalyst, and preferably a basic catalyst prepared at high temperature, but also a low temperature for the catalysis. These last two conditions both militate against high activity, as can be appreciated by considering the Arrhenius relation $k = k_0 \exp(-E/RT)$. The first condition decreases k_0 (because of lowering the specific surface area) and the second decreases the exponential term.

A possible way to increase the activity of a basic oxide catalyst in dehydrogenation is to modify its composition by adding a foreign oxide. Benbenek and Tokarczyk (7) took an interesting step in this direction by studying MgO impregnated and coprecipi-

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tated with MnO. They showed that, in comparison to pure MgO, activity for isopropanol dehydrogenation was indeed increased and even selectivity was improved. A more direct comparison between MgO and a modified MgO would be obtained by choosing for the latter a solid solution, that is, a catalyst in which the foreign ion has actually been incorporated in the structure rather than simply being supported (possibly as particles of the foreign oxide) on MgO.

This is the line which we have followed in the present study. We have explored the influence of Co^{2+} ions on the activity and selectivity of MgO for isopropanol decomposition by studying MgO and two CoO-MgO solid solutions as catalysts. Co^{2+} behaves as a high-spin ion in MgO, and the radii of Co^{2+} and Mg^{2+} are then virtually identical (0.74 and 0.72 Å, respectively); the charge/radius ratio of the cations, sometimes regarded as a parameter affecting selectivity (3, 8), is thus kept constant, but the nature of the cation-anion bond is changed by virtue of the cobalt ion having *d*-electrons. The experiments have been conducted using a micropulse technique, outgassing between pulses at 800°C. In this way we have been able to study the

reaction on a largely dehydroxylated surface.

EXPERIMENTAL

Catalyst preparation and characterization. CoO-MgO solid solutions of composition $\text{Co}_{0.07}\text{Mg}_{0.93}\text{O}$ and $\text{Co}_{0.30}\text{Mg}_{0.70}\text{O}$ were prepared by impregnating MgO (Johnson & Matthey Speepure) with a comparable volume of Co-nitrate solution (Johnson & Matthey Speepure). The soaked MgO was dried at 110°C, ground, heated for 1 h in air at 600°C, reground, and then fired for 5 h at 1200°C in air. MgO used for the reference catalyst was similarly treated at 1200°C.

The cobalt content of the solid solutions was determined by the method of Laitinen and Burdett (9). Surface areas were obtained by the BET method using krypton at 77 K. X-Ray analysis, magnetic studies, and reflectance measurements were carried out by methods described elsewhere (10, 11).

Apparatus and procedure for catalysis measurements. A block diagram of the apparatus is shown in Fig. 1. The reaction vessel (volume $\sim 5 \text{ cm}^3$) consisted of a narrow silica tube across which a sintered

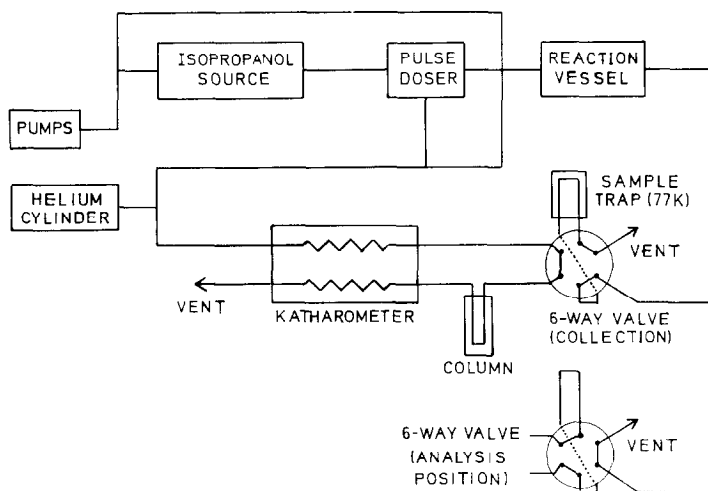


FIG. 1. Schematic diagram of apparatus for catalysis measurements.

silica disk was sealed. The catalyst, typically ~ 50 mg, was spread on the sinter and was pretreated by heating *in vacuo* ($\sim 10^{-5}$ Torr) at 800°C (or, in the case of one catalyst sample, at 440°C , as specified later). Helium was used as the carrier gas: pulses of isopropanol were added to the He stream from a doser of ~ 3 cm³ total volume, the pressure in the doser being varied between 9 and 23 Torr. These conditions implied $\sim 10^{18}$ molecules per pulse and a catalyst capacity of $\sim 10^{19}$ molecules at monolayer coverage.

Reaction products and unchanged isopropanol were collected beyond the reaction vessel in a copper trap cooled at 77 K. The collection time τ was long enough to ensure 90 to 100% recovery, 100% recovery (total recovery) meaning that the sum of the collected isopropanol, acetone, and propylene (when present) equaled the amount of isopropanol injected. Furthermore, the collection time was adjusted in indirect proportion to the flow rate F , i.e., the product $F\tau$ was kept constant, thereby ensuring that conversion was determined on the basis of the same volume of gas having passed through the trap. Analysis of isopropanol, acetone, and propylene was made by flash evaporation into a gas chromatograph, separation being achieved by a 2-m column of Carbowax 1500 operated at 115°C and a carrier gas flow of 73 cm³ min⁻¹. Peak heights were linear with concentration for each gas over the full range of pressures used.

As already indicated, the pulses were

"submonolayer" in size, as advocated by Stone and Agudo (12) and by Szabó *et al.* (5). To preserve the significance of these conditions, the catalyst was outgassed at a high temperature *between each pulse* (for particular details, see Results), and in this respect our conditions differed from those used by Szabó *et al.* (5) in their isopropanol decomposition study.

RESULTS

1. Catalyst Characterization

The results of the chemical and physical analysis are mostly summarized in Table 1. For convenience the symbolism MCo 8 and MCo 44 will be used to describe the solid solutions [cf. Cimino and Pepe (11)]. The lattice parameters agree with those expected for CoO-MgO solid solution (10), and the magnetic moments accord with high-spin octahedral Co²⁺ (d^7). MCo 44 has the larger Weiss constant, as would be anticipated. The decrease in surface area with increasing cobalt content is also expected (11). The reflectance spectra showed absorption in each solid solution at 500 and 1200 nm, as is normal for Co²⁺ in an octahedral field of O²⁻ ions, the intensity ratios $I(\text{MCo } 8)/I(\text{MCo } 44)$ being commensurate with their cobalt contents. All these results are consistent with the MCo 8 and MCo 44 catalysts being homogeneous solid solutions isomorphous with MgO.

2. Isopropanol Decomposition

In the absence of catalyst, no reaction occurred below 430°C . The experimental

TABLE 1
Chemical Analysis and Physical Characterization of MgO and
CoO-MgO Solid Solution Catalysts

Catalyst	Symbol	Co ²⁺ content (atom %)	Lattice parameter a_0 (Å)	Magnetic moment μ (B.M.)	Weiss constant $-\theta$ (K)	Surface area (m ² /g)
MgO	MgO	0	4.2116	0	0	20.4
CoO-MgO	MCo 8 ^a	7.2	4.2147	5.3 ± 0.05	52 ± 10	7.3
CoO-MgO	MCo 44 ^a	30.3	4.228	5.2 ± 0.05	114 ± 10	3.6

^a The numeral indicates the number of Co atoms per 100 Mg atoms (11).

data reported below, which mostly refer to the temperature range 200 to 250°C, have therefore been obtained at temperatures well below the region where homogeneous decomposition or wall reactions on silica occur.

All the catalysts (MgO, MCo 8, and MCo 44) were active for the dehydrogenation of isopropanol at 200 to 250°C, yielding acetone. For the first few pulses, however, small and decreasing amounts of propylene were also observed. With subsequent pulses, acetone was the only reaction product. The dehydrogenating activity increased slightly with successive pulses up to a reproducible and constant value of conversion. Unless otherwise indicated, conversions quoted in the following sections refer to these constant values.

No isopropyl ether was detected as a reaction product in the temperature range explored.

We present below the individual results for MgO, MCo 8, and MCo 44 outgassed at 800°C. For MCo 44 the effect of outgassing at the lower temperature of 440°C was also investigated. The designations MCo 44 (800) and MCo 44 (440) are used to distinguish the catalysts in this case.

(a) *MgO*. Since the activity of MgO in isopropanol decomposition has already been well investigated (1, 2, 5, 6, 7), the present studies were restricted to the minimum necessary for comparison with the cobalt-containing catalysts.

The activity of MgO was explored over

the range 150 to 250°C. Isopropanol pulses (doser pressure $p_0 = 8.9$ Torr) were passed through the catalyst (54 mg) at a flow rate $F = 30$ cm³ min⁻¹, and a collection time of $\tau = 10$ min was used. Between pulses of isopropanol the catalyst was treated for 1 hr at 800°C under vacuum (10^{-5} Torr). The extent of decomposition was 13% at 240°C and 10% at 180°C; the product was acetone.

These results agree well with those of previous authors, who have consistently reported MgO to be a dehydrogenating catalyst for isopropanol in the temperature range studied here. Our conversions depended only slightly on temperature, implying a low apparent activation energy.

(b) *MCo 8*. As with MgO, the catalyst was outgassed for 1 hr at 800°C between pulses.

The conversion α for the dehydrogenation of isopropanol to acetone at 240°C is shown in Table 2 as a function of p_0 , the pressure of isopropanol in the doser before injection of the pulse into the He stream. Thus p_0 is proportional to the partial pressure of isopropanol seen by the catalyst. The table shows that the conversion is independent of p_0 . The conversion at $p_0 = 8.9$ Torr and $F = 32$ cm³ min⁻¹ enables the activity of MCo 8 to be compared with that of MgO. Reference to the previous section shows that the respective conversions at 240°C and $F = 30$ to 32 cm³ min⁻¹ are 13% for MgO and 32% for MCo 8 (differences in collection time are not significant in the range $10 < \tau < 60$ min, as is shown later). The activity of MCo 8 is thus substantially greater than that of MgO, especially when account is taken of the larger surface area of MgO (Table 1).

The effect of varying the flow rate is shown in more detail in Fig. 2. Following Bassett and Habgood (13), data for $p_0 = 23$ Torr and 240°C are represented as a plot of $\log\{1/(1 - \alpha)\}$ vs $1/F$. At high flow rates (low $1/F$) the experimental points show a greater conversion than is expected on the basis of extrapolation to infinite flow rate

TABLE 2

Conversion of Isopropanol as a Function of Pulse Size, Flow Rate and Trap Collection Time^a

Isopropanol pressure in doser p_0 (Torr)	Flow rate F (cm ³ min ⁻¹)	Collection time τ (min)	Conversion α (%)
23.0	12	60	52
17.0	12	60	49
12.1	12	60	49
8.9	12	60	49
8.9	32	20	32

^a Catalyst = MCo 8; weight of catalyst = 46 mg; $T = 240^\circ\text{C}$.

(zero conversion at $1/F = 0$). It is inferred from this that isopropanol is strongly adsorbed on some sites but that a decrease in F leads to an increasing amount of less strongly adsorbed isopropanol on other sites. A further indication of the presence of a strongly adsorbed form is shown in Fig. 3, which relates to experiments at the same flow rate but different collection times. The data points for $\tau = 15$ min and $\tau = 60$ min correspond to conditions of total recovery. However, when τ is reduced below 10 min the amount of acetone collected decreases (see data points for $\tau = 5$ min and $\tau = 2$ min). As the dead time for transfer of the pulse is less than 1 min, the result shows that a slow surface process or a slow product desorption is taking place.

Figure 3 also shows the dependence of $\log \alpha$ on $1/T$. The data for $F = 12 \text{ cm}^3 \text{ min}^{-1}$ and $\tau = 60$ min, obtained with two

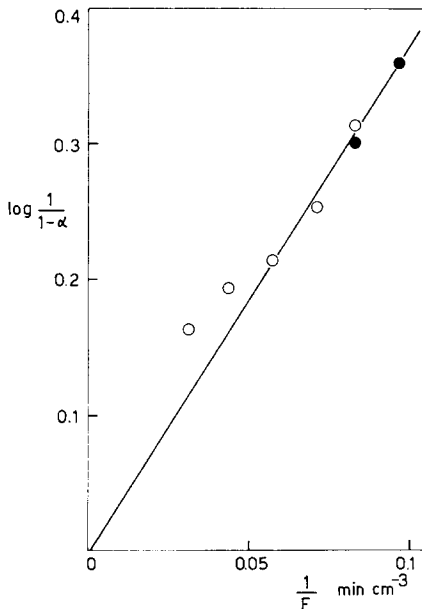


Fig. 2. Plot of $\log \{1/(1 - \alpha)\}$ vs $1/F$, where α is the fraction of the isopropanol pulse converted to acetone and F is the flow rate. Catalyst: MCo 8 (46 mg). Temperature: 240°C . Open and filled circles correspond to experiments with different batches of catalyst.

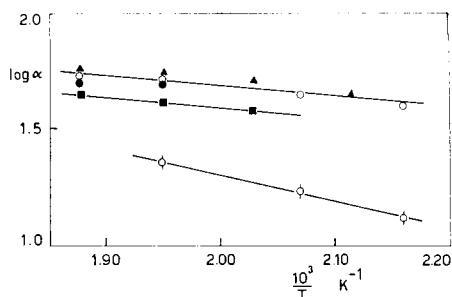


Fig. 3. Plot of $\log \alpha$ vs $1/T$ for isopropanol conversion (α in %) on MCo 8 at different trap collection times τ ($\tau = 15$ min and $\tau = 60$ min correspond to conditions of total recovery). (\circ , \bullet) $\tau = 60$ min; (\blacktriangle) $\tau = 15$ min; (\blacksquare) $\tau = 5$ min; (\diamond) $\tau = 2$ min.

different 46-mg samples of MCo 8, illustrate that the reproducibility of the catalytic experiments is very satisfactory.

(c) *MCo 44 (800)*. In common with MgO and MCo 8, the catalyst was outgassed for 1 hr at 800°C between pulses.

Figure 4 shows the variation of $\log \alpha$ with $1/T$ for $p_0 = 8.9$ Torr and three values of flow rate F . α does not significantly change with F over the range from 60 to $20.5 \text{ cm}^3 \text{ min}^{-1}$. The results of experiments on the dependence of α on p_0 are shown in Table 3. It is evident that the conversion is essentially independent of p_0 at both 160 and 266°C .

It is now possible to compare the activity of 800°C -outgassed MgO, MCo 8, and MCo 44, and this is done in Table 4. Taking note of the differences in surface area, it can be seen that: (i) MgO is much less active than MCo 8 or MCo 44; and (ii) the conversions on MCo 8 and MCo 44 are

TABLE 3
Dependence of Isopropanol Conversion on Pressure for MCo 44 (800) Catalyst

Pressure p_0 (Torr)	Conversion α (%)	
	$T = 160^\circ\text{C}$	$T = 266^\circ\text{C}$
8.9	18	33
12.1	20	34
17.0	18	31

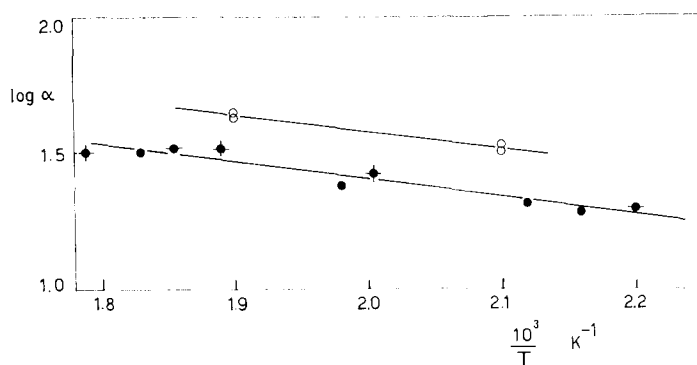


FIG. 4. Plot of $\log \alpha$ vs $1/T$ for isopropanol conversion (α in %) on MCo 44 (800) and MCo 44 (440).

	weight (mg)	τ (min)	F ($\text{cm}^3 \text{min}^{-1}$)
MCo 44 (800)			
●	73	10	60
◆	73	20	32
●	73	30	20.5
MCo 44 (440)			
○	146	10	60

similar, hence MCo 44 is much less active *per cobalt ion* than MCo 8.

(d) *MCo 44 (440)*. After installation in the reaction vessel, a sample of MCo 44 was treated at 440°C *in vacuo* overnight; catalytic experiments were then conducted as before except that between pulses the sample was outgassed for 1 hr at 440 instead of 800°C. Thus, in comparison with MCo 44 (800), the surface of this catalyst was appreciably more hydroxylated. In this way the influence of hydroxylation on the catalytic activity could be examined.

The conversion (acetone production) for

conditions of $p_0 = 8.9$ Torr, $F = 60 \text{ cm}^3 \text{min}^{-1}$, $\tau = 10$ min, and a sample weight of 146 mg was 36% at 200°C and 45% at 250°C. These results are included in Fig. 4 for comparison with results under equivalent conditions on MCo 44 (800). Bearing in mind the smaller sample weight (73 mg) in the experiments with MCo 44 (800), it would appear that MCo 44 (440) is slightly less active.

Reference has already been made at the beginning of the catalysis results section to the fact that propylene could be detected in the product from the initial pulses. This effect was especially studied with MCo 44 (440), and results are given in Table 5. No propylene was present in the product from the fourth and subsequent pulses. In a separate sequence, pulses of water vapor were admitted to the catalyst before the outgassing at 440°C; no dehydration (propylene production) was then observed when the isopropanol pulse was passed, but only dehydrogenation (acetone production) at the normal value. We conclude that some

TABLE 4

Comparison of the Activity of 800°C-Outgassed MgO and CoO-MgO for Dehydrogenation of Isopropanol^a

Catalyst	Weight used (mg)	Surface area (m^2)	Flow rate ($\text{cm}^3 \text{min}^{-1}$)	τ (min)	α (%)
MgO	54	1.08	30	10	13
MCo 8	46	0.34	32	20	32
MCo 44	73	0.26	32	20	30

^a $T = 240^\circ\text{C}$; pulse size = 8.6×10^{17} molecules,

hydroxylation of the surface improves the selectivity of the dehydrogenation reaction.

The presence of sites able to dehydrate isopropanol was shown by the following further observation. By raising the temperature of the catalyst just after the main part of a pulse had cleared the reactor and simultaneously directing the He stream into a separate, clean trap cooled at 77 K, only propylene was collected. This not only shows that acetone is not strongly adsorbed, but also indicates that some isopropanol does not readily react on the surface. Separate adsorption experiments at the temperatures concerned (200–300°C) showed that there is no measurable adsorption of propylene at these temperatures. Thus the propylene collected must have been the result of isopropanol decomposition made possible by raising the temperature.

DISCUSSION

The principal result is that the incorporation of cobalt ions into MgO to form a solid solution increases the activity for isopropanol decomposition without changing the selectivity: the oxide remains a dehydrogenating catalyst. The dilute solid solution $\text{Co}_{0.07}\text{Mg}_{0.93}\text{O}$ (MCo 8) is almost as active as the much more concentrated solution $\text{Co}_{0.30}\text{Mg}_{0.70}\text{O}$ (MCo 44), so the effect of cobalt is greater when it has magnesium ions as neighbor cations.

The linear relation between $\log \{1/(1 - \alpha)\}$ and $1/F$ (Fig. 2) is indicative of a process involving an adsorption equilibrium for the reactant and a low coverage (regime of first-order kinetics). This is compatible with the submonolayer conditions contrived by using small pulses and also explains the low temperature coefficients found with both MgO and CoO–MgO, the latter being clearly seen in the shallow slopes of Figs. 3 and 4. The apparent activation energy will be lower than the true activation energy by the amount of the heat of adsorption of isopropanol.

Although there is the above evidence for reversible isopropanol adsorption (and accompanying dehydrogenation to acetone) there is also evidence for strong adsorption of isopropanol. For MCo 8 at high flow rates ($F > 20 \text{ cm}^3 \text{ min}^{-1}$, or $1/F < 0.05 \text{ min cm}^{-3}$ in Fig. 2) the conversion no longer falls as rapidly as expected. For MCo 44 (800), interpolation between the data points in Fig. 4 for $F = 20.5, 30$, and $60 \text{ cm}^3 \text{ min}^{-1}$ shows that α scarcely responds at all to flow rate changes in this range. This implies that isopropanol adsorption is stronger on MCo 44 than on MCo 8. A strong adsorption of isopropanol on MgO is implicit in the infrared studies of Miyata *et al.* (14), where dissociative adsorption producing isopropoxide was reported.

If dissociative adsorption of isopropanol to give isopropoxide is occurring, as seems likely, there will also be hydrogen atoms to consider. The obvious model is one in which isopropoxide radicals are chemisorbed on cations (previously coordinatively unsaturated by the outgassing) and hydrogen on anions. Loss of a second hydrogen atom, this time from the secondary carbon, leads to acetone formation and hence dehydrogenation. If, however, the surface has been very well outgassed, there will be a higher concentration of *cus* cations and anions. An adsorption in which the dissociative mode is $(\text{CH}_3)_2\text{CH}\cdot\text{OH} \rightarrow (\text{CH}_3)_2\text{CH}\cdot + \cdot\text{OH}$,

TABLE 5
Incipient Dehydration during Decomposition of
Initial Pulses of Isopropanol^a

Pulse No.	<i>T</i> (°C)	Conversion (%)	
		Acetone	Propylene
1	204	33	12
2	200	35	3
3	200	35	3
>3	200	36	0

^a Catalyst: MCo 44 (440); weight of catalyst = 146 mg; $F = 60 \text{ cm}^3 \text{ min}^{-1}$; pulse size = 8.6×10^{17} molecules ($p_0 = 8.9 \text{ Torr}$); $\tau = 10 \text{ min}$.

with OH bonding to a *cus* cation, can now be envisaged. Loss of a hydrogen atom from a methyl group of $(\text{CH}_3)_2\text{CH}_{\text{ads}}$ to an adjacent *cus* anion then yields propylene. This mechanism would account for the incipient propylene yields which we have observed. It can also explain why dosing with a small amount of water vapor, as in the experiment with MCo 44 (440), suppresses propylene formation. Limited hydroxylation may even be beneficial for dehydrogenation by preventing the most coordinatively unsaturated sites from interacting with isopropanol so as to break the C-O bond. Indeed, such a situation would also enable hydrogen-bonded forms of adsorbed isopropanol to be present, and especially under conditions of low flow rate these forms could assist in maintaining the coverage of the reacting species. The mechanism also enables us to understand why MCo 44 (440) is not appreciably less active for dehydrogenation than MCo 44 (800). Both catalysts acquire hydroxylation by limited dehydration, so provided the outgassing temperature is great enough to destroy most of the OH blanket which forms on atmospheric exposure (and 440°C is certainly adequate for that), further dehydroxylation is not greatly important.

It remains to discuss the enhancement of the activity as between MgO and CoO-MgO. This could be an effect of Co^{2+} ions per se or an effect of Co^{2+} ions by virtue of activating adjacent Mg^{2+} or O^{2-} ions. CoO and Co_3O_4 both have high activity for the catalysis of H_2 - D_2 exchange (15), so the role of cobalt could in principle be seen as providing an active site for chemisorption of H atoms and desorption of H_2 . However, we regard it as unlikely that H atoms are chemisorbed on cations in isopropanol decomposition. More relevant might be their chemisorption on O^{2-} ions adjacent to Co^{2+} , which very probably occurs in H_2 - D_2 exchange. In general, however, we prefer to interpret the effect of Co^{2+} in this system

through an influence on the isopropanol and isopropoxide species.

It has recently been shown (16) that Co^{2+} in well-outgassed CoO-MgO solid solutions of high surface area ($\text{SA} > 100 \text{ m}^2 \text{ g}^{-1}$), where the contribution of surface ions to the total is large, has a reflectance spectrum which implies the presence of some *tetrahedrally coordinated* Co^{2+} in addition to the expected octahedral absorption of the ions in the bulk. This suggests that at least some of the Co^{2+} ions in the surface are in 4-coordination with oxygen ions. A similar situation may occur in low surface area CoO-MgO, as used in the present study, but may not be observable because of the dominant concentration of ions of the bulk. Co^{2+} is more commonly found in 4-coordination than Mg^{2+} , so that the effect of replacing Mg^{2+} with Co^{2+} could be to develop more easily surface cations of low coordination. Such ions would be favored sites for the dissociative chemisorption of the bulky isopropanol molecule. Low (fourfold) coordination of Co^{2+} ions can only be achieved on the surface of charge-balanced CoO-MgO by a compensating high (sixfold) coordination of some residual cations, typically Mg^{2+} . In view of this, one would not expect the concentration of fourfold Co^{2+} to rise as rapidly as the concentration of total Co^{2+} when CoO-MgO solutions of increasing Co content are prepared. This would afford an explanation of the more pronounced effect of cobalt at low concentration.

An alternative proposal for the effect of cobalt is to consider its implications for the cation-anion bonding. Cobalt, being a transition element, is likely to engage more in covalent bonding than magnesium, and one may envisage as a consequence a stronger bond (greater activation) with adsorbed isopropanol, or more relevantly, isopropoxide. There is some evidence for such an effect from the ir work of Miyata *et al.* (14), where a lower C-O stretching frequency (weaker bond) is observed for

adsorbed isopropoxide on NiO than on MgO (and hence a stronger bond between the carbon and the surface cation). The effect in this case should be cumulative with increase in cobalt content, and there was some indication of this in the greater insensitivity of MCo 44 to increasing flow rate. The two descriptions of the possible effect of cobalt are not entirely independent, since a low coordination for surface cobalt ions is only made possible by a modification of the carbon-anion bonding in the direction of greater covalent character.

The view that increasing covalency in the metal-oxygen bond character improves activity and selectivity for dehydrogenation is already implicit in early general considerations of the activity patterns of different oxides. For instance, Winfield (17) noted that dehydrogenation is favored if the cations in the oxide are transition metal ions and hence capable of giving $d-\pi$ covalent character to the metal-oxygen bonds. However, to our knowledge the concept has never been specifically examined with the structural parameters well controlled. One result in the literature which adventitiously comes close to a standardized comparison is the report by Kibby and Hall (18) of alcohol decomposition catalyzed by calcium hydroxyapatite and by hydroxyapatites containing nickel or copper ions. The replacement of small amounts of Ca^{2+} ions with Cu^{2+} or Ni^{2+} leads interestingly to a selectivity favoring dehydrogenation. The ionic radius of Ca^{2+} is about 30% greater than that of Ni^{2+} or Cu^{2+} but in other respects the comparison (at least between Ca^{2+} and Ni^{2+}) is presumably isostructural. The significance of our work in this context is that the bond character in the comparison between MgO and $\text{Co}_x\text{Mg}_{1-x}\text{O}$ is changed under extremely close control of other chemical variables, and the correlation between increased covalency in the metal-oxygen bond and

increased dehydrogenation activity is accordingly more firmly based.

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