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# Catalytic decomposition of 2-propanol on $Co_{1+x}Al_{2-x}O_4$ spinel system

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Catalytic activity of the $Co_{1+x}Al_{2-x}O_4$ $(0 < x < 1)$ solid solution system has been evaluated using decomposition of 2-propanol as test reaction. The end members (with $x = 0$ and 1) showed exclusively dehydration and dehydrogenation activities, respectively. Selectivity for dehydrogenation increased with increase in $x$. Dehydration activity was found to occur due to the presence of acid centers as determined by *n*-butyl amine titration and pyridine poisoning experiments. Dehydrogenation activity was found to be caused by $Co^{3+}$ ions. The surface concentrations of cobalt were evaluated by X-ray photoelectron spectroscopy and these were correlated with the catalytic activity.

**Keywords:** cation distribution; 2-propanol decomposition; spinel solid solution; X-ray photoelectron spectroscopy

## 1. Introduction

Ternary oxides crystallizing in spinel structure are well known for their catalytic and solid state properties. Cobalt containing spinels have been well studied as catalysts in various reactions like decomposition of nitrous oxide and hydrogen peroxide, and oxidation of carbon monoxide [1–4]. They have also been used as automotive pollution control catalysts [5]. Alumina supported cobalt sulfide and sulfided cobalt oxide–molybdena catalysts are particularly known for their HDS activity [6]. It has been reported that in $Co/Al_2O_3$ catalysts the surface consists of dispersed $CoAl_2O_4$ spinel at low cobalt loading while at higher loading, crystalline $Co_3O_4$ forms. Arnoldy and Moulijn [7] have identified various phases that had formed in these catalysts through TPR studies. Baker et al. [8] have reported the role of bimetallic phases of cobalt and copper in the catalysts supported on $CoAl_2O_4$ spinel. Their activity for the formation of oxygenates from a carbon monoxide–carbon dioxide–hydrogen mixture was attributed to metallic cobalt. Barbaux et al. [9] studied the oxidation of 1-butene and methane on cobalt–aluminium oxide system and concluded that $Co^{2+}$ is the active site. The X-ray parameters and infrared frequencies of Al-substituted $Co_3O_4$ were reported by Garcia Casado and Rasines [10]. Cd substituted $CoFe_2O_4$ spinels were studied by Gabr et al. [11] through 2-propanol decomposition and correlations were attempted between catalyst composition and surface intermediate concentrations. However, the effect of substitution of $Al^{3+}$ in place of $Co^{3+}$ has not been discussed in detail with respect to the coordination of the metal ions. It is interesting to note that $Co^{3+}$ and $Al^{3+}$ have nearly the same ionic radii (0.545 and 0.535 Å, respectively) [12]. As a result, replacement of $Al^{3+}$ by $Co^{3+}$ in $CoAl_2O_4$ could lead to the spinel system having cobalt in two oxidation states, viz. +2 and +3. Therefore, in the present investigation, the effect of substitution of $Al^{3+}$ by $Co^{3+}$ in $CoAl_2O_4$ on the decomposition of 2-propanol has been reported.

## 2. Experimental

Analytical grade reagents, obtained from E. Merck (India) Ltd., were used throughout the investigation. The solid solution series $Co_{1+x}Al_{2-x}O_4$ has been prepared by coprecipitation technique [7] with compositions having $x = 0.0, 0.02, 0.2, 0.4, 0.6, 0.8$ and 1.0. The hydroxide precursors were obtained from nitrate mixtures of cobalt and aluminium by adding 1 N ammonia solution until pH = 8.2, where the precipitation was found to be complete. The precipitates thus obtained were filtered, washed with slightly alkaline water, dried in air oven at 110°C and calcined at 800°C for 24 h with intermittent grinding. The samples were finally quenched to room temperature by removing from the furnace. X-ray diffractograms (XRD) were recorded in a Phillips X-ray diffractometer (model PW 1140) using iron filtered cobalt $K_\alpha$ radiation ($\lambda = 1.7889$ Å) at a scan speed of 2°/ min. The peaks for the 220 and 440 planes were separately recorded at a scan speed of 0.33°/ min for determination of distribution of cations in tetrahedral and octahedral coordinations. The surface areas of the samples were estimated by BET method using nitrogen as adsorbate at 77 K after evacuation at 250°C upto $10^{-6}$ Torr in a BET sorptometer (PMI Inc., USA). The surface areas, given in table 1 showed a general decrease from 40 to 24 $m^2/g$.

Catalytic studies were carried out in an all-glass fixed bed continuous flow reactor operating at atmospheric pressure. Details of the reactor are available elsewhere [13]. The reaction conditions for the decomposition of 2-propanol have been chosen such that the conversions were low, in order to avoid diffusion limitations. The conversions at each temperature were plotted against contact time and the rates are calculated from the slopes of the initial straight line portions of these

Table 1
Surface areas and cation distributions of the solid solution

| $x$ | Surface area ($m^2/g$) | Inversion parameter, $y$ | Cation distribution |
|---|---|---|---|
| 0.0 | 39.5 | 0.16 | $Co^{2+}_{0.84}Al^{3+}_{0.16}[Co^{2+}_{0.16}Al^{3+}_{1.84}]O_4$ |
| 0.02 | 41.4 | 0.16 | $Co^{2+}_{0.84}Al^{3+}_{0.16}[Co^{2+}_{0.16}Al^{3+}_{1.82}Co^{3+}_{0.02}]O_4$ |
| 0.2 | 37.1 | 0.14 | $Co^{2+}_{0.86}Al^{3+}_{0.14}[Co^{2+}_{0.14}Al^{3+}_{1.66}Co^{3+}_{0.20}]O_4$ |
| 0.4 | 34.3 | 0.11 | $Co^{2+}_{0.89}Al^{3+}_{0.11}[Co^{2+}_{0.11}Al^{3+}_{1.49}Co^{3+}_{0.40}]O_4$ |
| 0.6 | 24.6 | 0.07 | $Co^{2+}_{0.93}Al^{3+}_{0.07}[Co^{2+}_{0.07}Al^{3+}_{1.33}Co^{3+}_{0.60}]O_4$ |
| 0.8 | 23.2 | 0.03 | $Co^{2+}_{0.97}Al^{3+}_{0.03}[Co^{2+}_{0.03}Al^{3+}_{1.17}Co^{3+}_{0.80}]O_4$ |
| 1.0 | 24.6 | 0.0 | $Co^{2+}_{1.0}[Co^{2+}_{1.0}Al^{3+}_{1.0}]O_4$ |

curves. The activation energies were calculated from Arrhenius plots drawn using these rates. For specific poisoning studies, mixtures of feed having known concentrations of pyridine in 2-propanol were used. Prior to each experiment, the catalysts were activated in a flow of dry air at 400°C for 3 h. The gaseous products were analyzed in an Orsat apparatus and the liquid products in a gas chromatograph (Chromatography Instruments Corporation, India).

X-ray photoelectron spectroscopic (XPS) studies were carried out in an ESCALAB Mark II instrument (Vacuum Generators, UK) which utilized Mg $K_\alpha$ radiation ($h\nu = 1253.6$ eV). The instrument was operated at a pressure of $10^{-8}$ Torr or less. The samples were mounted in the form of powder on nickel holders. The binding energy (BE) scale was calibrated taking the 2p line of the aluminium in the sample, centered at 74.5 eV, as internal reference [14]. The Co $2p_{3/2}$ spectra were deconvoluted using a BASIC program after background correction. The surface acidity of the catalysts was estimated by *n*-butyl amine titration method [15]. The acidity measurement involved the estimation of *n*-butyl amine consumed by the acid centers on the surface.

## 3. Results and discussion

### 3.1. X-RAY DIFFRACTION STUDIES

All the compounds have been found to crystallize in spinel structure. The cation distribution of the $Co_{1+x}Al_{2-x}O_4$ solid solution was determined by evaluating inversion parameters from the X-ray diffractograms. Inversion parameter $y$ in a spinel is defined as the fraction of tetrahedrally coordinated trivalent ions, or the fraction of octahedrally coordinated divalent ions. Hence, the cation distribution is denoted by the formula $(A^{2+}_{1-y}B^{3+}_{y})_{tet}[A^{2+}_{y}B^{3+}_{2-y}]_{oct}O_4$. The X-ray determination of the inversion parameter involved the comparison of theoretical and experimental intensity ratios, as suggested by Furuhashi et al. [16]. In this method, the intensity ratio $I_{220}/I_{440}$ was calculated theoretically at each $y$ and was compared with the experimentally observed ratio. That value of inversion parameter was chosen to be the correct one for which the theoretical intensity ratio $I_{220}/I_{440}$ agrees closely with the corresponding observed intensity ratio. The inversion parameters and cation distributions are shown in table 1. As the value of $x$ in the spinel solid solution $Co_{1+x}Al_{2-x}O_4$ increases, the substitution of $Al^{3+}$ by $Co^{3+}$ increases. The inversion parameter varied from a value of 0.16 to 0 across the series with increasing value of $x$. The value of the inversion parameter decreased, indicating cobalt substitution. Thus, the inversion parameter is inversely related to the $Co^{3+}$ concentration in octahedral sites.

### 3.2. X-RAY PHOTOELECTRON SPECTROSCOPIC STUDIES

XPS studies were carried out in order to understand the surface composition of the catalysts, especially for the estimation of $Co^{3+}$ on the surface. The Co $2p_{3/2}$ spectra are shown in fig. 1. The binding energy values, spin–orbit splitting values, relative intensity ratios of main peak ($I_p$) to total peak ($I_p + I_s$) are given in table 2. Based on the BE values, it is not possible to assign any particular valence state

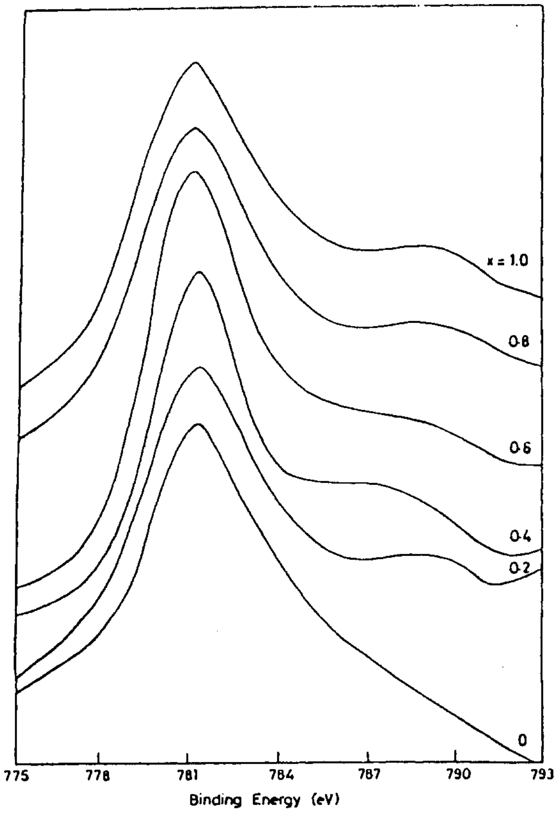

Fig. 1. XP $2p_{3/2}$ spectra of $Co_{1+x}Al_{2-x}O_4$.

Table 2
XPS data for $Co_{1+x}Al_{2-x}O_4$

| $x$ | BE (eV) | | Spin–orbit splitting energy (eV) | BE (eV) for Co $3p_{3/2}$ | $I_p/(I_p+I_s)$ for Co $2p_{3/2}$ |
|---|---|---|---|---|---|
| | $2p_{3/2}$ | $2p_{1/2}$ | | | |
| 0.0 | 781.7 | 797.8 | 15.9 | 62.4 | 0.56 |
| 0.02 | 781.7 | 797.6 | 15.9 | 62.5 | 0.56 |
| 0.2 | 781.8 | 797.7 | 15.6 | 62.5 | 0.69 |
| 0.4 | 781.4 | 796.9 | 15.5 | 62.1 | 0.66 |
| 0.6 | 781.3 | 796.6 | 15.3 | 62.1 | 0.67 |
| 0.8 | 781.4 | 796.4 | 15.0 | 62.1 | 0.64 |
| 1.0 | 781.4 | 796.3 | 14.9 | 62.1 | 0.65 |

(+2 or +3) for cobalt. However, the spin–orbit splitting energy values of the Co 2p level can be used to sense the valence state. Okamoto et al. [17] suggested that the spin–orbit splitting value is 16.0 eV for $Co^{2+}$ compounds and it is 15.0 eV for $Co^{3+}$ compounds. Any intermediate value indicates mixed valence state for cobalt. It can be seen from table 2 that the binding energy values show a decreasing trend both for Co $2p_{3/2}$ and $2p_{1/2}$ peaks, suggesting the presence of $Co^{3+}$ in the system but this cannot be taken as conclusive proof. The spin–orbit splitting value was 15.9 for $CoAl_2O_4$ where cobalt is in +2 state. This value gradually decreases with the decrease in the value of $x$ in the system. These values are in agreement with the suggestion made by Okamoto et al. The spin–orbit splitting values suggest that $CoAl_2O_4$ and $Co_{1.02}Al_{1.98}O_4$ possess relatively high concentrations of $Co^{2+}$ ions while others show the presence of $Co^{2+}$ as well as $Co^{3+}$ ions on their surface.

Gajardo et al. [18] suggested a method for the quantitative estimation of valence states of cobalt on the catalyst surface by considering the XPS intensities of $2p_{3/2}$ of main peak ($I_p$) and its satellite ($I_s$). The estimation was based on the fact that $Co^{2+}$ exhibits intense satellite features due to the presence of unpaired electrons while in $Co^{3+}$ they were absent and hence no satellite peaks occurred. The authors found that the ratio $r$, given by $I_p/(I_p+I_s)$, is proportional to the amount of $Co^{3+}$ on the surface. In other words, this ratio may be taken to indicate the relative concentration of the $Co^{3+}$ on the surface, with respect to the total Co available. The Co 2p spectra for the present series are shown in fig. 1. As the Co 2p spectra are asymmetric, it was necessary to deconvolute the curve in order to get the main peak and its satellite. The ratios for the present catalysts have been calculated from the Co $2p_{3/2}$ peak. The $r$ values are listed in table 2. The ratios at $x = 0$ and 0.02 are equal (0.56) and agree with that reported for $CoAl_2O_4$ by Gajardo et al. [18].

The main peak to total peak ratios, i.e., $I_p/(I_p+I_s)$ show an increasing trend indicating that the $Co^{3+}$ ion concentration is gradually increasing. It is interesting to recall that the inversion parameter showed an exactly opposite trend, indicating the increasing $Co^{3+}$ concentration with the increase in the value of $x$. Since the total Co varies with $x$, Co may be preferentially concentrated at the surface (or in the bulk). However, this ratio gives the fraction of $Co^{3+}$ ions with respect to the total surface Co available.

The conclusion that can be drawn based on XPS and inversion parameters is that the concentration of $Co^{3+}$ is increasing. It is interesting to see how it will affect the catalytic activity. Acidity is one of the parameters that can be affected by the substitution of $Co^{3+}$ by $Al^{3+}$ in $CoAl_2O_4$ spinel. The *n*-butyl amine titration showed a decreasing trend in the acidity. The acidity decreased from a value of $5.38 \times 10^{-2}$ to $0.54 \times 10^{-2}$ mmol/g. It is also interesting to note that the tetrahedral $Al^{3+}$ also showed a similar trend. One of the products of 2-propanol decomposition viz. propene is produced through dehydration and it is well known that dehydration reactions are acid catalyzed reactions [19]. The influence of this acidity variation and its activity will be dealt with in the following discussion on the catalytic activity.

### 3.3. CATALYTIC ACTIVITY

The results of decomposition of 2-propanol on the solid solution series are summarized in table 3. The reactions were conducted in the temperature range 240–330°C. $CoAl_2O_4$ ($x = 0$) showed exclusively dehydration activity, yielding propene and water as products. $Co_2AlO_4$ ($x = 1$) on the other hand showed exclusively dehydrogenation activity, yielding acetone and hydrogen. The remaining catalysts showed both dehydration and dehydrogenation activities. In order to compare the relative extents of dehydrogenation and dehydration activities on each catalyst, the selectivity parameter is made use of. Here, the selectivity for dehydration of 2-propanol, i.e. propene formation, $S_{\text{propene}}$, is defined as

$$S_{\text{propene}} = \frac{\text{yield of propene}}{\text{conversion of 2-propanol}} \times 100 .$$

As the conversion of 2-propanol is stoichiometrically equivalent to the sum of the

Table 3
Results of 2-propanol decomposition on $Co_{1+x}Al_{2-x}O_4$ and acidity values

| $x$ | Temp. range (°C) | $E_a$ (kJ mol$^{-1}$ m$^{-2}$) |  | Acidity (mmol/g × $10^2$) | $S_{\text{propene}}$ [a] |
|---|---|---|---|---|---|
|  |  | dehydration | dehydrogenation |  |  |
| 0.0 | 240–280 | 2.81 | – | 5.36 | 100.0 |
| 0.02 | 240–280 | 2.87 | – | 5.99 | 98.4 |
| 0.2 | 290–330 | 1.82 | 2.67 | 4.72 | 67.5 |
| 0.4 | 290–330 | 2.15 | 3.58 | 3.97 | 35.3 |
| 0.6 | 290–330 | 2.95 | 3.40 | 3.79 | 10.3 |
| 0.8 | 290–330 | 3.49 | 3.90 | 3.0 | 8.9 |
| 1.0 | 290–330 | – | 4.14 | 0.54 | 0.0 |

[a] At 300°C and contact time 1.6 s for all catalysts except for $x = 0.0$ and 0.02, where the temperature = 260°C.

yields of propene and acetone, selectivity for dehydrogenation will be $100 - S_{\text{propene}}$. Returning to table 3, one may note that the selectivity patterns for dehydration follow a decreasing trend. Another interesting observation is that the introduction of $Co^{3+}$ by substituting for $Al^{3+}$, even in small amounts (0.02 mol), generated dehydrogenation activity in the system. The selectivity towards propene formation, $S_{\text{propene}}$ decreased with increase in $x$. Dehydrogenation activity completely disappeared on $Co_2AlO_4$.

Let us now discuss what happens to solid state and catalytic properties, namely cation distribution and acidity, when cobalt is introduced into octahedral position. $CoAl_2O_4$ is an inverse spinel, which means that some of its Al ions are in tetrahedral coordination. With the substitution of $Al^{3+}$ by $Co^{3+}$, the $Al^{3+}$ population in tetrahedral coordination decreases and the inversion parameter and $Co^{3+}$ in octahedral coordination increase. Acidity of the system is expected predominantly due to $Al^{3+}$ in tetrahedral coordination. Therefore, it is not surprising that $Al^{3+}$ in tetrahedral coordination and acidity follow similar trends.

Coming back to activities, the dehydration activity is generally believed to be generated by interaction of 2-propanol with acid sites. As can be seen from the acidity and selectivity for propene formation following similar trends (fig. 2, table 3), $Al^{3+}$ in tetrahedral coordination is indeed to active site for dehydration. The fact that $Co_2AlO_4$, $Al^{3+}$ is in octahedral coordination, did not show any dehydration activity also supports the suggestion. The trends of variation of acidity and dehydration activity agree with the general notion that the dehydration function is related to the acidity of the catalyst and this acidity is generated by tetrahedral $Al^{3+}$ ions. Specific poisoning studies were carried out in order to understand the nature of the active sites, using pyridine. Pyridine, when added to the catalyst, suppresses

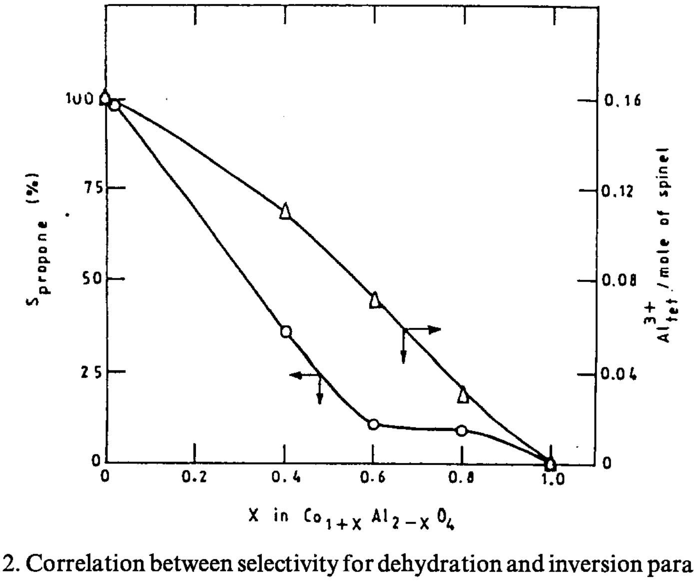

Fig. 2. Correlation between selectivity for dehydration and inversion parameter.

the activity of acid centers. Hence, experiments were performed with the reactant feed containing known quantities of pyridine in 2-propanol. The reaction temperature was 300°C except for the first two catalysts, where it was 260°C. The contact time was 1.60 s for all the samples. The results are given in table 4. It can be seen from the table that the dehydration activity was suppressed to a great extent even by a small quantitity of pyridine (about 2 mol%) in the feed, while the dehydrogenation activity was nearly unaffected. This indicates that pyridine was poisoning the acid sites that were responsible for dehydration activity.

It can be noted that dehydrogenation activity was noticed on all the catalysts possessing $Co^{3+}$ and its selectivity increases with increasing $Co^{3+}$ content. Hence, the role of $Co^{3+}$ in generating the dehydrogenation activity is clear.

Now in the dehydrogenation reaction, where 2-propanol decomposes to acetone and hydrogen, it can be seen that the inverse spinels did not exhibit any activity. These catalysts contain $Co^{2+}$ in both tetrahedral and octahedral positions. With the increase of $x$, some of the $Co^{2+}$ in octahedral position is converted to $Co^{3+}$ in octahedral position. It can be seen from table 2 that introduction of even small amount of Co in octahedral position generates dehydrogenation activity. It is further confirmed by the fact that increase of $Co^{3+}$ in octahedral position did increase the activity. All this discussion is based on charge balancing in the spinel structure. It is desirable to experimentally show that the concentration of $Co^{3+}$ on the surface indeed had changed and that it had a relationship to the dehydrogenation parameter. In the earlier discussion of XPS results, it is shown that the $Co^{3+}$ surface concentration increases with $x$. In order to further understand the relationship of the dehydrogenation activity parameter and $Co^{3+}$, the activation energy for dehydrogenation is plotted against the ratio of Co $2p_{3/2}$ main peak to total peak intensity ($r$) in fig. 3. It can be seen that there exists a linear relationship with $r$, which indicates that $Co^{3+}$ is the active site for dehydrogenation in this system. A similar observation has been made from the same laboratory on $MgAl_{2-x}Fe_xO_4$ system [20].

Table 4
Effect of pyridine poisoning on the yields of propene and acetone in the decomposition of 2-propanol on $Co_{1+x}Al_{2-x}O_4$. Reaction temperature= 300°C, contact time= 1.60 s

| $x$ | Yield of propene (mol%) | | | Yield of acetone (mol%) | | |
|---|---|---|---|---|---|---|
| | 0% pyridine | 1.98% pyridine | 11.40% pyridine | 0% pyridine | 1.98% pyridine | 11.40% pyridine |
| 0.0[a] | 34.5 | 9.5 | 7.3 | – | – | – |
| 0.02[a] | 33.4 | 8.8 | 7.1 | tr. | – | – |
| 0.2 | 28.7 | 3.4 | 2.8 | 6.1 | 4.6 | 2.2 |
| 0.4 | 6.27 | 2.8 | 1.9 | 11.5 | 9.8 | 8.7 |
| 0.6 | 1.79 | tr. | – | 15.6 | 13.2 | 10.4 |
| 0.8 | 19.2 | tr. | – | 18.3 | 14.9 | 12.1 |

[a] Reaction temperature = 260°C.

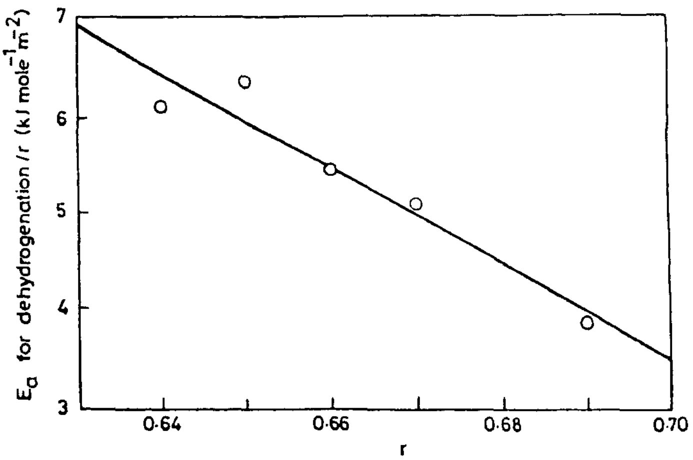

Fig. 3. Dependence of $E_a$ for dehydrogenation on $Co^{3+}$ content.

## 4. Conclusions

(1) Distribution of cobalt cation in octahedral and tetrahedral positions profoundly influences both dehydration and dehydrogenation activities.

(2) The tetrahedral $Al^{3+}$ ion is responsible for acidity generation and also dehydration activity. There exists a linear relationship between the acidity and dehydration activity.

(3) Dehydrogenation activity of the spinel solid solution is caused by $Co^{3+}$ ions in octahedral coordination.

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