

10. WELLS, A. F., "Structural Inorganic Chemistry," p. 346. Oxford University Press, 1962.
11. WALTON, R. A., *Spectrochim. Acta* **21**, 1795 (1965).
12. WALKER, D. G., *J. Phys. Chem.* **65**, 1367 (1961).
13. DONATI, M., AND CONTI, F., *Inorg. Nucl. Chem. Lett.* **2**, 343 (1966).
14. KABANOV, V. A., ZUBOV, V. P., KOVALEVA, V. P., AND KARGIN, V. A., *J. Polym. Sci., Part C*, **1**, 1009 (1963).

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Catalytic Activity and Selectivity of Alumina-Spinel Oxides in Decomposition of Ethyl Alcohol Vapor

In studies of the decomposition of ethyl alcohol vapor on a range of pure aluminum oxides (1) and on these oxides doped with known concentrations of sodium, cobalt, calcium, and magnesium ions (2), results indicated that both selectivity and activity were affected by changes in crystal structure and apparent Brønsted acidity of the catalysts. For example, catalysts with the γ -alumina structure promoted dehydration reactions while α -alumina catalysts were active also in dehydrogenation (1). The structural aspect has now been extended to include an examination of three alumina-spinel oxides; the "normal" spinels, ZnAl_2O_4 and MgAl_2O_4 ; and the "intermediate" spinel, NiAl_2O_4 (3).

The spinel oxides were prepared from high purity samples of the divalent oxides and γ -alumina. Equimolar quantities were intimately ground and heated for 48 hr at 1100°C. Heating was then continued at 1350°C for several days until X-ray powder diffraction patterns showed the disappearance of unreacted components and gave d -spacings in agreement with those in the ASTM index for each spinel. A final 24 hr treatment at 1350°C was then given. Details of other materials, apparatus and procedure have been reported (1, 2). Surface area determinations (BET: N_2 : -196°C) indicated values around 10 m²/g for each

sample, which bordered on the limit of the BET nitrogen technique. Hence a separate evaluation was carried out by B. P. Research Centre, Sunbury-on-Thames, England, who confirmed the measurements.

Spinel was held in the catalyst chamber as powders dispersed on quartz wool supported on platinum gauze. Blank runs on the wool and gauze showed less than 0.5% ethyl alcohol decomposition at 400°C. All flow runs were made with 5.84 mm Hg ethyl alcohol partial pressure, space velocity range from 3.5 to 4.3 ml of gas/ml of catalyst/sec. with temperatures from 350 to 480°C. Steady level conditions of catalysis were generally reached after 30-min exposure time.

Figure 1 shows the effect of temperature on the organic products obtained from the decomposition of ethyl alcohol on ZnAl_2O_4 catalysts with surface areas taken as 10 m²/g. The distribution of the components in the reaction products and their variation with temperature were similar to that found with α -aluminas (1). Ethylene production was low at 360°C, 0.2 to 0.3%/m², but it rose sharply with temperature; became the major contribution at about 370°C and reached 2.7%/m² at 480°C. While the diethyl ether production decayed slowly, the acetaldehyde fraction remained steady at

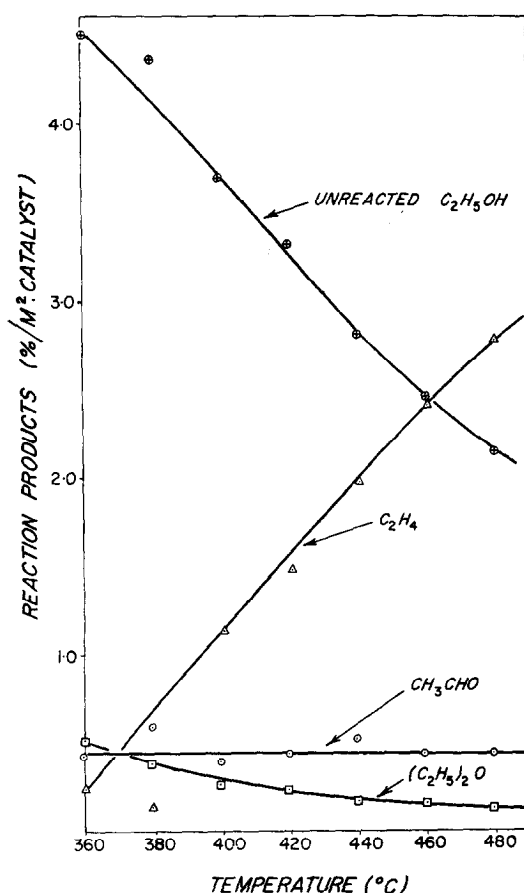


FIG. 1. Products from ethyl alcohol decomposition on ZnAl_2O_4 .

about $0.4\%/m^2$ over the entire temperature range.

Low activity towards alcohol decomposition was shown by the MgAl_2O_4 catalysts, Fig. 2. Thus, at 350°C only $0.5\%/m^2$ of the total ethyl alcohol had reacted, otherwise the nature of the reaction products was identical to those for ZnAl_2O_4 . A steady acetaldehyde content was found up to 430°C while the ethylene production rose more slowly than with ZnAl_2O_4 catalysts. The acetaldehyde content exceeded that of diethyl ether just above 380°C , when the amounts of diethyl ether decreased slowly with further increase in temperature in a similar fashion to Fig. 1.

The products of catalysis on NiAl_2O_4 from 350 to 430°C contained only ethylene, acetaldehyde, water, and unreacted ethyl alcohol, Fig. 3. Diethyl ether was not de-

tected. In terms of the percentage alcohol reacted/ m^2 of catalyst surface at comparable temperatures, this spinel had the highest activity of the three examined. At 350°C , the amount of acetaldehyde produced was $1.5\%/m^2$ which remained almost constant to about 400°C when it decreased to $1.1\%/m^2$. The production of ethylene rose slowly and smoothly with temperature to $0.5\%/m^2$ at 390°C and then sharply to $1.5\%/m^2$ to 410°C , when it settled again to a slower rise.

The effect of temperature on the overall ethyl alcohol decomposition on the three catalysts was determined by plotting the first order rate constants (k) against $1/T^\circ\text{K}$ in the Arrhenius fashion. From the line slopes, activation energies of 10.7, 16.4, and 11.3 kcal mole⁻¹ were calculated, respectively, for NiAl_2O_4 , ZnAl_2O_4 , and MgAl_2O_4 . Since the nickel spinel did not form diethyl ether, comparison of activation energies is obscured by the selectivity effect which could imply differences in the reaction mechanisms. However, the products from the magnesium and zinc spinels were the same as found with $\alpha\text{-Al}_2\text{O}_3$ which gave an activation energy between 13.0 and 11.0 kcal mole⁻¹, depending on surface treatment (1). The activation energy for NiAl_2O_4 was very close to that of $\gamma\text{-Al}_2\text{O}_3$, 10.8 kcal mole⁻¹ (1).

Essentially, the unit cell of the alumina spinels has 32 oxygen atoms in an almost cubic close-packed arrangement (3). In both MgAl_2O_4 and ZnAl_2O_4 , 8 divalent metal atoms are surrounded tetrahedrally by oxygen while 16 aluminum atoms are surrounded octahedrally. The metal atom distribution in the nickel spinel is more complex (3) with normally two nickel and six aluminum atoms in tetrahedral sites with the balance of metal atoms in octahedral positions. The selectivities of the catalysts show relationships to the different coordinations of the aluminum atoms in these spinels and in the α - and γ -aluminas. Thus, while all catalysts produce ethylene only those containing octahedrally coordinated aluminum produce diethyl ether above 320°C , $\alpha\text{-Al}_2\text{O}_3$, ZnAl_2O_4 , and MgAl_2O_4 , while acetaldehyde is not detect-

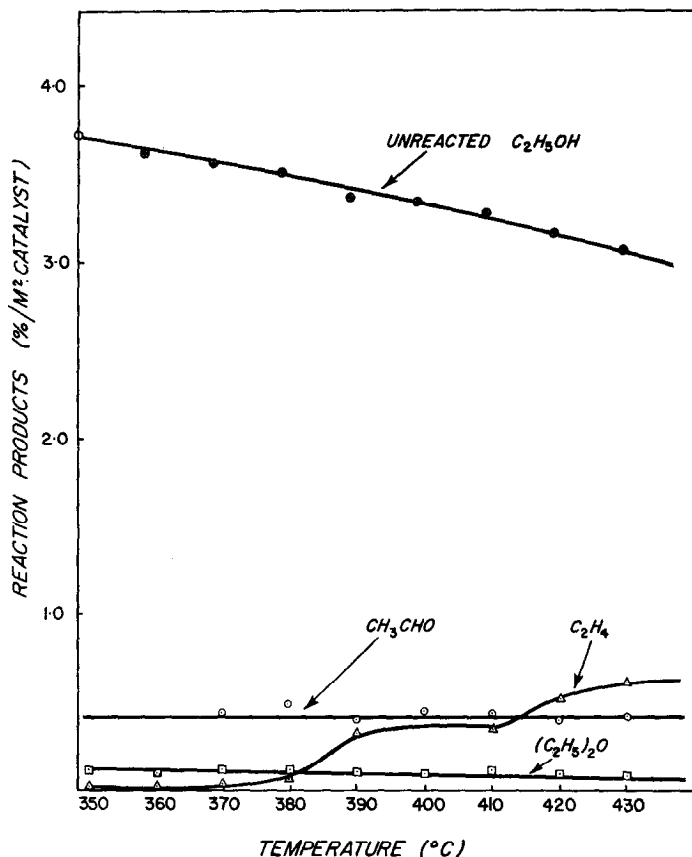


FIG. 2. Products from ethyl alcohol decomposition on MgAl_2O_4 .

able in products from catalysts with only tetrahedrally coordinated aluminum, $\gamma\text{-Al}_2\text{O}_3$.

Extended high temperature treatment of aluminum oxides gives rise to vacant anion sites (4), considered also as octahedral and tetrahedral "holes" (4). These "holes," especially the tetrahedral, can be powerful acceptors of nucleophilic reagents (4), thereby acting initially on ethyl alcohol to produce ethylene and two hydroxylated surface centers per hole in a reverse manner to that suggested for surface dehydration (4). These newly hydroxylated centers would be expected to become active in the continuous catalytic dehydration of ethyl alcohol to ethylene through the carbonium ion mechanism (5) at tetrahedral centers with diethyl ether formed by interaction of two alcohol molecules perhaps through a Rideal-Eley mechanism (6) at octahedral sites.

However, it is not possible to achieve a quantitative description of the total catalytic effects in such terms at present since, with respect to dehydrogenation activity, the nickel spinel is between three and four times more active than the zinc and magnesium spinels at a given temperature. Hence in addition to "hole" and aluminum atom effects (1), an added source of dehydrogenation activity may be present in NiAl_2O_4 , such as octahedral nickel atoms in a +3 oxidation state—a nonstoichiometric condition known to exist in nickel oxides; see for example Ref. (7).

REFERENCES

1. BENNETT, D. E. R., AND ROSS, R. A., *J. Chem. Soc., A* 1968, 1524.
2. BENNETT, D. E. R., AND ROSS, R. A., *J. Catal.* 8, 289 (1967).
3. WELLS, A. F., "Structural Inorganic Chemistry,"

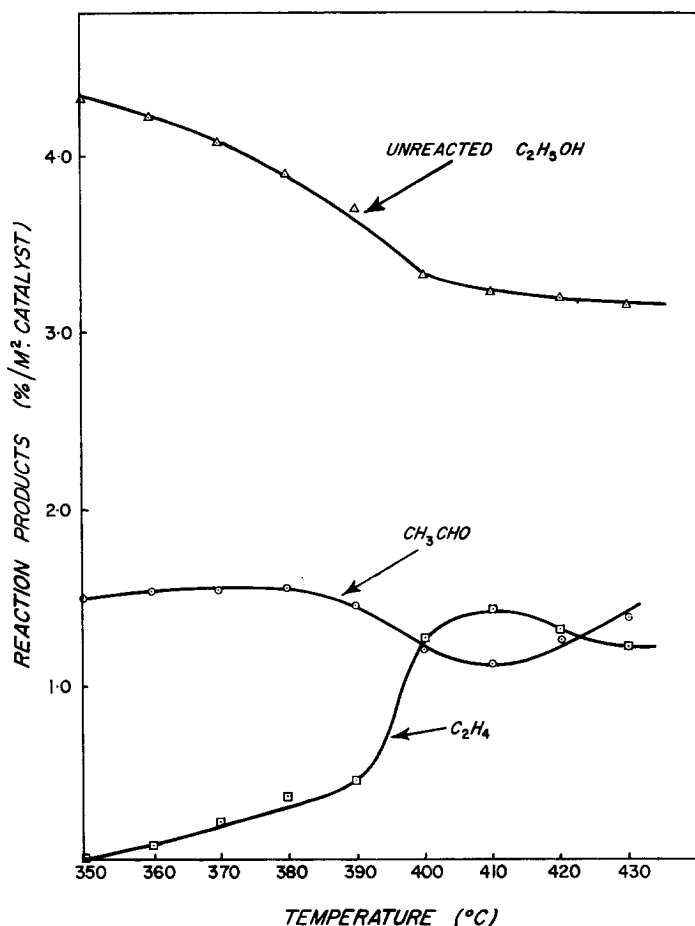


FIG. 3. Products from ethyl alcohol decomposition on NiAl_2O_4 .

3rd ed. Oxford Univ. Press, London/New York, 1962.

4. BOEHM, H. P., *Advan. Catal.* **16**, 262 (1966).
5. WHITMORE, F. C., *J. Amer. Chem. Soc.* **54**, 3274 (1932).
6. DEBOER, J. H., FAHIM, R. B., LINSEN, B. G., VISSEREN, W. J., AND DEVLEESSCHAUWER, W. F. N. M., *J. Catal.* **7**, 163 (1967).
7. GREENWOOD, N. N., "Ionic Crystals, Lattice Defects and Nonstoichiometry," p. 166. Butterworths, London, 1968.

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