TABLE 1
PERCENTAGES OF THE DEUTERIZED HYDROCARBONS IN THE CHARGE-TRANSFER COMPLEX

Complex	Deuterized hydrocarbon		E
Perylene–Cs	$C_{20}H_{11}D$	$C_{20}H_{10}D_2$ and others	—
	5%	2–4%	ca. 8–9 kcal/mole
Violanthrene B–Cs	All of deuterized violanthrene B		
		5–6%	17 kcal/mole

and then the aromatic hydrocarbon was isolated. From the result of mass spectroscopic analysis of the isolated hydrocarbon, we found that a part of the hydrogen of the hydrocarbon has definitely been exchanged with deuterium in a gaseous phase, as is shown in Table 1.

The concentration of deuterized aromatic hydrocarbon in the complex, however, was fairly low in comparison with the findings of the decay of D_2 concentration, mentioned in Fig. 1. This discrepancy may take place from the hydrogen exchange between the deuterized hydrocarbon and ethyl alcohol used for the decomposition of the complex.

This hydrogen exchange reaction occurs *reversibly*. This reversible behavior suggests that the complexes between certain aromatic compounds and alkali metal atoms may be similar to the model for hydrogenase, a biological enzyme (4).

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Effect of Sodium Ion Impurities in γ-Alumina on the Catalytic, Vapor-Phase Dehydration of Ethyl Alcohol

During studies of the kinetics of dehydration of ethyl alcohol vapor on alumina catalysts (1), we have examined how the activity and selectivity of highly pure γ-alumina (<100 ppm total impurities; Cu, Ni, Pb, Zn, Fe, and Mn) was affected by

addition of sodium ions in a range of concentrations. Only general qualitative reports of this effect have been made by different authors and their findings are contradictory. In a study of the selective poisoning of alumina and silica-alumina catalysts by sodium ions, impregnated from aqueous salt solutions, Topchieva, Yun-Pin, and Smirnova (2) reported that catalyst activity towards ethyl alcohol dehydration was not affected by the presence of such ions. In contrast, Pines and Haag (3) found that the activity of active aluminas, in the dehydration of 1-butyl alcohol, was almost destroyed on addition of 1.5 wt % sodium by impregnation from sodium chloride or sodium hydroxide solutions. Neither of these groups of workers found any change in the selectivity of their alumina catalysts following sodium-ion impregnation.

Gamma alumina was prepared by slow precipitation at pH 9 from solutions of aluminum sulfate and ammonia. The dried precipitate was heat-treated for 2 hr at 240°C and at 300°C followed by 24 hr at 360°C. The material was shown by X-ray analysis to be entirely γ-alumina. The series of catalysts was prepared by impregnation of the γ-alumina with aqueous solutions of sodium chloride for 24 hr at 80°C, with continuous stirring. After filtration and washing, the materials were dried at 120°C for 3 hr, pelleted, and then heated in the catalyst reactor in flowing nitrogen for 4 hr at 360°C. Sodium uptake was measured by flame photometry following sulfuric acid digestion. The presence of chloride impurity was not detected by microanalytical methods even following alkali fusion. Surface areas were measured by the standard gas adsorption method (BET; N_2; -196°C). These results are given in Table 1.

The activity of each sample was examined in a flow reactor (4) at 360°C, space velocity = 3.60 cc gas/cc catalyst per sec, and 380°C, space velocity = 3.71 cc gas/cc catalyst per sec, with alcohol partial pressures of 5.84 and 9.75 mm Hg. High-purity nitrogen was used as the carrier gas. The results in Table 2 represent steady-level catalytic activities achieved normally after 1 hr exposure. They clearly show a loss in activity with increase in sodium content.

TABLE 1
SODIUM CONTENT AND SURFACE AREAS
OF IMPREGNATED ALUMINAS

Catalyst sample number	Conc. of sodium chloride impregnation solution (% w/v)	Conc. of sodium ions in 100 g catalyst (% w/w)	Surface area ($m^2 g^{-1}$)
1	0	0.00	425
2	5	0.39	395
3	10	1.10	375
4	15	1.45	390
5	20	0.86	375
6	25	2.20	340
7	30	2.87	340

The results are expressed as mole percentage of ethyl alcohol reacted per 100 m^2 of catalyst and hence the poisoning effect cannot be attributed simply to loss of area through solution of alumina in the sodium chloride hydrolysis products on impregnation.

The poisoning effect was consistently more pronounced at the higher alcohol partial pressure while the catalyst activity was enhanced with increase in temperature. Vapor-phase chromatographic analysis of the reaction products showed that while pure γ-alumina gave ethylene, water, and unreacted ethyl alcohol as the only products at both temperatures, all sodium-containing samples gave diethyl ether also. Trace amounts of another unidentified component were detected at 380° with the impregnated

TABLE 2
EFFECT OF SODIUM CHLORIDE IMPREGNATION
ON THE ACTIVITY OF γ-ALUMINA AT
360° AND 380°C[a]

Catalyst sample number	Ethyl alcohol reacted (mole %/100 m²)			
	360°C		380°C	
	5.84 mm Hg	9.73 mm Hg	5.84 mm Hg	9.73 mm Hg
1	12.9	12.8	13.0	12.9
2	12.5	12.2	12.9	12.7
3	10.5	10.1	11.3	10.9
4	8.4	8.2	9.0	8.8
5	10.2	9.8	10.8	10.5
6	8.3	8.2	9.5	9.2
7	8.2	7.7	9.1	8.9

[a] Ethyl alcohol partial pressures, 5.84 and 9.73 mm Hg.

TABLE 3
EFFECT OF SODIUM CHLORIDE IMPREGNATION ON THE SELECTIVITY OF γ-ALUMINA AT 360°C[a]

Catalyst sample number	Ethyl alcohol partial pressure					
	5.84 mm Hg			9.73 mm Hg		
	Ethyl alcohol reacted (%/100 m²)	Ethyl alcohol→ ethylene (%/100 m²)	Ethyl alcohol→ ether (%/100 m²)	Ethyl alcohol reacted (%/100 m²)	Ethyl alcohol→ ethylene (%/100 m²)	Ethyl alcohol→ ether (%/100m²)
1	12.9	12.9	0	12.8	12.8	0
2	12.5	11.6	0.9	12.2	11.1	1.1
3	10.5	8.3	2.2	10.1	7.6	2.5
4	8.4	6.0	2.4	8.2	5.4	2.8
5	10.2	8.0	2.2	9.8	7.4	2.4
6	8.3	4.6	3.7	8.2	4.8	2.4
7	8.2	4.3	3.9	7.7	3.8	3.9

[a] Ethyl alcohol partial pressures, 5.84 and 9.73 mm Hg.

samples. Its amount remained constant for each sample and it was assumed to be either (i) a dehydrogenation product or (ii) a breakdown product of one of the major components—trace amounts of carbon were detected on the catalysts when removed from the reactor.

The selectivity of the catalysts was examined at 360° at both alcohol partial pressures, Table 3. The percentage of ethyl alcohol decomposed to ether readily increased with increase in catalyst sodium content, while the percentage decomposed to ethylene decreased. In general, this effect was even more pronounced at the higher alcohol partial pressure. Similar results were also obtained at 380°.

There are several different views (5) of the mechanism of the surface dehydration of alcohols on alumina. The results of our kinetic experiments (1) favor a mechanism based on the "carbonium ion" scheme (6) in which reaction initiation proceeds by proton transfer from surface hydroxyl groups (7) to adsorbed alcohol molecules. This initiation step is probably also rate-controlling on alumina surfaces which have been heated below 700°. However, if it is accepted that Lewis acid sites, such as incompletely coordinated aluminum ions in the surface, are abundant on dehydrated alumina (8) then, it can be postulated (3) that these sites act as initiation centers. Poisoning by sodium chloride would probably then arise through formation of the acid/base surface complex:

$$\left[-\overset{|}{\underset{|}{Al}}-Cl \right]^{-} Na^{+}$$
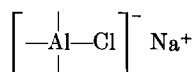
In our work we can find no evidence for the formation of such a complex in any detectable amount. Alternatively, if sodium ions exchange with protons from surface hydroxyl groups, Brönsted acid sites, then the continuous decrease in the total activity of the catalysts with increase in sodium content (Table 2), can be explained by a fall in concentration of these reaction-initiation centers.

Although the total catalyst activity and the activity towards ethylene formation falls with increase in sodium content, the activity towards diethyl ether formation increases at the same time. It is proposed that these changes are brought about by the intervention of an alternative mechanism by which alcohol molecules adsorbed on sodium ion sites can no longer obtain a proton for dehydration initiation. Instead these molecules may react with neighboring alcohol molecules, perhaps from a van der Waals adsorbed layer, to give diethyl ether on the elimination of water bimolecularly. Our kinetic experiments with pure alumina gave a first order rate dependence on ethyl alcohol partial pressure at 360° and 380°C with alcohol partial pressures from 2 to 12 mm Hg. Hence the small but significant decrease in the fraction of ethylene produced with increase in pressure in the present experiments cannot be explained on the basis of these kinetic results. It is most

TABLE 4

THE EFFECT OF CALCIUM, MAGNESIUM, AND COBALTOUS CHLORIDE IMPREGNATIONS ON THE
ACTIVITY OF γ-ALUMINA AT 360° AND 380°C

| | | | Ethyl alcohol reacted (mole %/100 m²) | | | |
| | | | 360°C | | 380°C | |
Catalyst	Surface area (m²/g)	Metal ion concentration (% w/w)	5.84 mm Hg	9.73 mm Hg	5.84 mm Hg	9.73 mm Hg
Al₂O₃	425	0.00	12.9	12.8	13.0	12.9
Al₂O₃ + CoCl₂	355	8.16	12.5	12.4	12.7	12.6
Al₂O₃ + CaCl₂	355	3.11	12.5	12.3	12.7	12.5
Al₂O₃ + MgCl₂	395	0.44	11.6	11.5	11.7	11.7

likely brought about also by the intervention of the alternative mechanism which produces diethyl ether.

Experiments were also carried out with γ-alumina impregnated with other selected metal halides to determine whether the above effects were peculiar to the alkali metal ion. The alumina was impregnated with 10% w/v solutions of cobaltous chloride, calcium chloride, and magnesium chloride by the same method as that used with sodium chloride. A high catalytic activity was shown by all these samples at 360° and 380°C at both alcohol partial pressures, Table 4.

The overall drop in activity was greatest for the magnesium chloride impregnate at both temperatures. This amounted to 1.3% per 100 m² of catalyst and was independent of the alcohol partial pressure. The cobaltous chloride and calcium chloride impregnates gave very small activity drops from 0.3 to 0.4% per 100 m² at both temperatures and both alcohol partial pressures. In all cases the reaction route to ethylene was favored since only very small amounts of diethyl ether could be detected, and these amounts were too small to be estimated quantitatively.

Magnesium and calcium contents were obtained by gravimetric analysis and the cobalt content by instrumental colorimetry. Following alkali fusion, only minute traces of chloride were detected in both the magnesium and calcium samples while the cobalt sample contained 0.7100 g Cl⁻ ion per 100 g catalyst, as estimated by potentiometric titration using a silver/silver chloride electrode.

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