

Polyphenylaluminumoxosiloxanes as Catalysts

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The isopropyl alcoholate of tris(triphenylsiloxy)aluminum, $[(C_6H_5)_3SiO]_3Al \cdot 3 \text{ iso-C}_3\text{H}_7\text{OH}$, evolves alcohol, propylene, and benzene as it is heated to 350°. The polyphenylaluminumoxosiloxane which is formed retains about two-thirds of the phenyl groups. This material is not active for cumene dealkylation. When it is treated with small amounts of water there is formed one mole of benzene per mole of water and it becomes very active for cumene dealkylation. An apparatus which has been called a twin tube injector was developed for the study of the volatile products formed on heating the catalyst and for determining the activity of the catalyst after any thermal or chemical pretreatment.

INTRODUCTION

Thomas and Gerald described the synthesis of organosilica-aluminas and demonstrated their activity as cracking catalysts (1). Andrianov and co-workers prepared many organosilica-aluminas (2). There has been no systematic study of these organosilica-aluminas as catalysts. Because of their solubility in organic solvents, it seemed that their structural characterization would be simpler than for the silica-alumina cracking catalyst. The solubility in organic solvents might also make it possible to study silica-alumina in a homogeneous catalyst system.

In the present work the condensation polymer obtained by heating the triisopropyl alcoholate of tris(triphenylsiloxy)aluminum, compound (I), has been studied. The compound (I) is representative of a class of organosilica-aluminas which has similar catalytic properties. Thus, other alcoholates of tris(triphenylsiloxy)aluminum and condensation products of triphenylsilanol and diphenylsilanediol with aluminum isopropylate and with partially hydrolyzed aluminum isopropylate gave soluble substances which had catalytic activity after appropriate chemical and thermal pretreatment.

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METHODS

a. Synthesis of the triisopropyl alcoholate of tris(triphenylsiloxy)aluminum (I). Metallic aluminum (0.0195 moles) was allowed to react with 25 ml of anhydrous isopropyl alcohol in the presence of a crystal of mercuric chloride which served as a catalyst. Triphenylsilanol (16.1 g, 0.0586 moles) in 175 ml of anhydrous isopropyl alcohol was added slowly with stirring. The volume of the final solution was reduced to about 125 ml by boiling off the alcohol. The clear solution was stoppered and allowed to cool. Large needlelike crystals formed. The alcohol was decanted. The crystals were dissolved by heating with anhydrous isopropyl alcohol and recrystallized by cooling slowly to room temperature. The alcohol was again decanted and the crystals were pumped under vacuum until the initial high rate of weight loss due to the evaporation of wet alcohol decreased sharply. At this point the crystals appeared dry and were free-flowing. The recovery was about 80% of theory. Continued pumping at room temperature resulted in a slow loss in weight due to the volatilization of isopropyl alcohol and the loss of phenyl groups as benzene.

b. Apparatus. A modification of the microreactor and chromatographic product

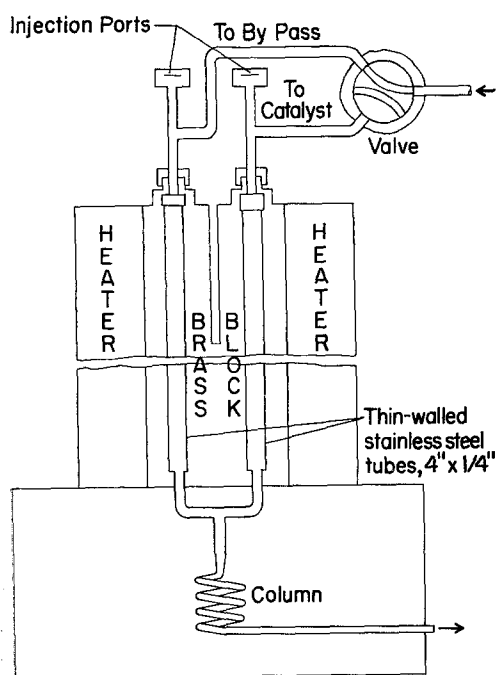


FIG. 1. Diagrammatic representation of the twin tube injector and the accompanying chromatographic column.

analyzer described by Kokes, Tobin, and Emmett (3) was used to determine catalyst activity and to estimate quantitatively the volatile products formed by the chemical and thermal treatment of compound (I). The apparatus has been called a twin tube injector. It is shown diagrammatically in Fig. 1.

Helium carrier gas enters the two-way valve by which it may be routed to either the catalyst or the bypass chamber. Both chambers contain removable thin-walled stainless steel tubes which fit snugly into 1/4-inch parallel holes in a brass cylindrical block that is 4 inches long and 1 1/4 inches in diameter. The block is enclosed in a heating element and contains a thermocouple well. The temperature of the block can be set at any value and maintained at this value by a stepless controller (West Gardsman, Model JS series).

Each chamber is equipped with its own injection port and a gas entry line which is connected to the block by Swagelok fittings. Exit lines of 1/8-inch stainless steel tubing are connected to the block by silver

solder and by Swagelok fittings to a 5-ft length of 3/16-inch copper tubing which was packed with 30/60 mesh celite (Chromosorb P, Johns-Manville) having 10% of a silicone oil (Dow-Corning 710) as a liquid phase. The column is housed in an insulated box which is thermostatically controlled. Thermal conductivity cells were used to compare entering helium with exit gases and the differences in thermal conductivity were recorded.

The thin-walled stainless steel tubes were charged with acid-washed celite (Chromosorb W, 45/60 mesh, Johns-Manville) which was held in place by glass wool plugs. The capacity of a tube was about 200 mg of celite. In the present study the bypass tube contained only celite and the catalyst tube contained 30 to 60 mg of compound (I) or triphenylsilanol mixed as crystals with enough celite to fill the tube.

When the tubes were in the chambers, carrier gas flow was started and both chambers were purged of air. With carrier gas routed to the bypass tube the controller was set at a desired temperature. As the temperature of the block rose, volatile products from the catalyst formed in the catalyst chamber. When carrier gas flow was switched from bypass to catalyst for 10 sec and then back to bypass the volatile products were swept into the column and were separated. Each turn to the catalyst gave product peaks whose retention times were characteristic of the product and whose areas were proportional to the amount of product. Before or after any turn to the catalyst, accurately measured samples of standards were introduced to the injection port of the twin bypass chamber to establish peak areas per mole and retention times at conditions almost exactly comparable to those at which product peaks were observed. The product peaks were identified and quantitatively determined by comparison with these standards. Supplementary identification of products was made with a Varian 60 NMR Spectrometer.

When carrier gas was routed to the catalyst chamber, the unit functioned as a pulse-charge reactor for the evaluation of catalyst activity. Water could be introduced

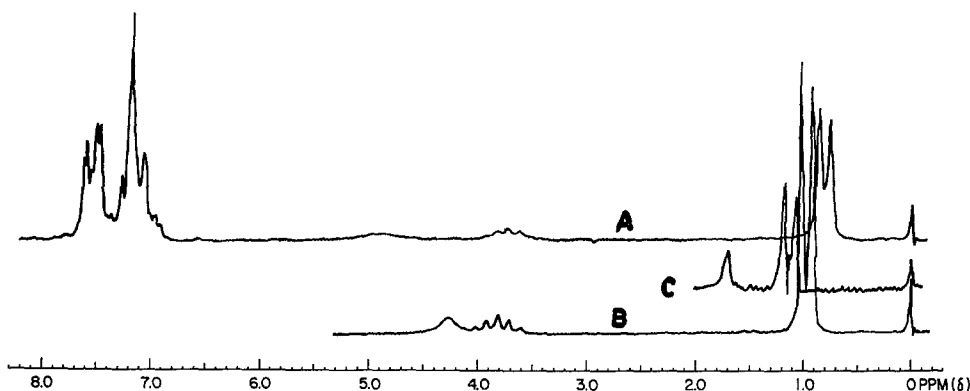


Fig. 2. Proton NMR spectra expressed in ppm downfield from tetramethylsilane; carbon disulfide solvent, 30°C, and 60 MHz. A, Compound (I). B, Compound (I) plus isopropyl alcohol. C, Isopropyl alcohol.

through the injector to the catalyst chamber and the product of its reaction with the polyphenylaluminumoxosiloxane observed and quantitatively estimated.

The product and sample peaks recorded during the chemical and thermal treatment of a substance have been called "thermalchromograms." The thermalchromogram of a substance is characteristic of that substance and both qualitative and quantitative information can be obtained from it.

RESULTS AND DISCUSSION

The fact that compound (I) exerted a pressure of isopropyl alcohol and slowly underwent a reaction forming benzene at room temperature made it difficult to characterize. When compound (I) was prepared as described and carefully pro-

tected from moisture, the analytical data shown in Table 1 were obtained.

The proton NMR spectrum of compound (I) is shown in curve A of Fig. 2. It consists of an aromatic multiplet at 6.9 to 7.7 ppm, a methyl doublet at 0.80 ppm, a methine heptuplet at 3.7 ppm, and a hydroxyl at 4.9 ppm. The spectrum is consistent with the formula $[(C_6H_5)_3SiO]_3Al \cdot 3$ iso- C_3H_7OH . The methyl doublet for isopropyl alcohol, curve C, appears downfield from the methyl doublet of the compound at 1.15 ppm. A mixture of compound and alcohol, curve B, gives only one methyl doublet at 0.97 ppm.

These data suggest that there is a rapid exchange between alcohol in solution and alcohol coordinated with the aluminum. The molecular weight recorded in Table 2 is about half of the theoretical value. This corresponds to the value expected if about 1 mole of alcohol per mole of compound was in solution and was not coordinated with the

TABLE 1

SUMMARY OF ANALYTICAL DATA OBTAINED ON COMPOUND (I), THE TRIISOPROPYL ALCOHOLATE OF TRIS(TRIPHENYLSILOXY)ALUMINUM

	Observed	Theory
% Ash	22.7	22.4
% Carbon	72.21	73.22
% Hydrogen	6.35	6.73
% Aluminum	2.54	2.62
Melting point	132	—
Ratio of phenyl hydrogens to methyl hydrogens NMR integration	2.6	2.5
Molecular weight, by freezing point lowering in benzene	470	1033.5

TABLE 2

SUMMARY OF THERMALCHROMOGRAM OF COMPOUND (I)^a

Volatile products recovered	Moles of product per mole of compound
Isopropyl alcohol	1.71
Propylene	0.39
Benzene	3.67

^a Moles of $[(C_6H_5)_3SiO]_3Al \cdot 3C_3H_7OH$ charged, 3.32×10^{-5} .

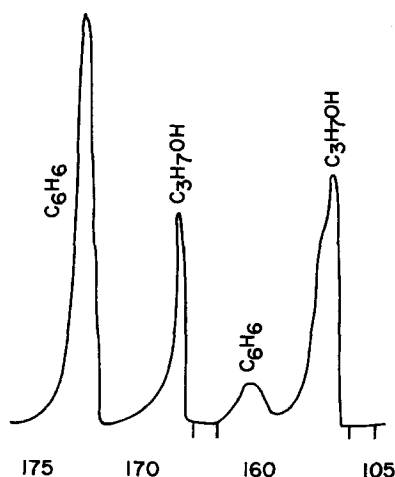


FIG. 3. Tracing of a section of a thermalchromatogram from 105° to 175°. Read from right to left! Short vertical lines below tracing designate turn of carrier gas to catalyst chamber and back to bypass.

aluminum, while 2 moles of alcohol per mole were coordinated with the aluminum.

A structure in which the three triphenylsiloxy groups are at the corners of an equilateral triangle with the aluminum in the center and an alcohol above and below the plane of the triangle and coordinated with the aluminum has a symmetry which seems necessary for the easy formation of the long needlelike crystals. The third alcohol in the formula may be held more loosely in the crystal. It is this uncoordinated alcohol which appears in the solution and causes molecular weights to be lower than theoretical.

Tracings of sections of a thermalchromatogram for the compound (I) are shown for

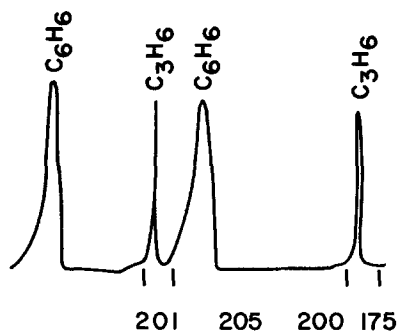
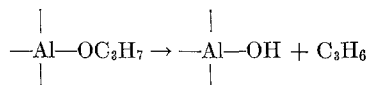


FIG. 4. Tracing of thermalchromatogram of compound (I) in the range of temperature from 175° to 205°.

the temperature ranges 100° to 175° and 175° to 205° in Figs. 3 and 4. Below 175° isopropyl alcohol and benzene are evolved; above 175° propylene and benzene are evolved. Although the relative amounts of alcohol, propylene, and benzene determined from thermalchromograms of the compound (I) were slightly dependent upon the rate of heating and very dependent upon the presence of atmospheric moisture inadvertently introduced when handling the sample, a representative thermalchromogram for the dry compound gave the data which are summarized in Table 2. The benzene evolved was somewhat more than 3 moles per mole of compound, representing a little more than one-third of the phenyl groups in the original compound. In the absence of added water the remaining phenyl groups were quite stable at 350° and 400°. The relative amounts of propylene and isopropyl alcohol were sensitive to the rate of heating. It was generally observed, however, that the 3 moles of isopropyl alcohol in the formula were not completely accounted for in the volatile products. Some of the propylene may have remained on the catalyst as polymer. In the example of Table 2 only 2.1 moles/mole of compound was accounted for as isopropyl alcohol and propylene. It seems likely that propylene was formed by the decomposition of an aluminum isopropoxide group in the polymer structure as shown in the equation:



A thermalchromatogram for triphenylsilanol showed that benzene was the only volatile product formed in detectable quantities. No benzene appeared below the melting point of 155°. Between about 170° and 200° benzene was evolved rapidly. When heated to 250° there was evolved 0.69 moles of benzene per mole of triphenylsilanol. Additional benzene could be removed at high temperatures but in many thermalchromograms of triphenylsilanol, the moles of benzene formed per mole of triphenylsilanol did not exceed 1.

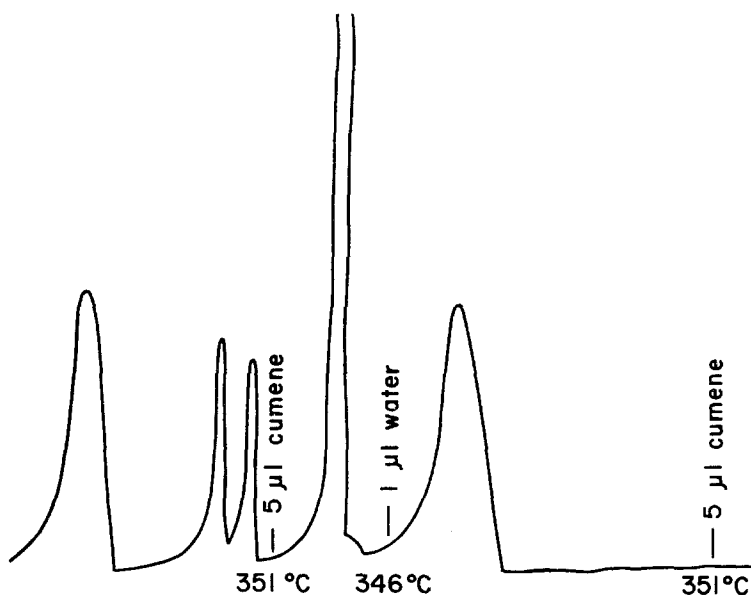
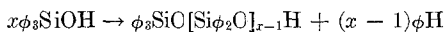


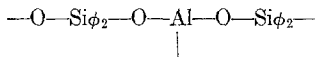
Fig. 5. Tracing from thermalchromogram of compound (I) at 350° showing conversions of cumene before and after water treatment.

The condensation polymeric siloxane remaining might be linear or cyclic or a mixture of the two. The formation of a linear polymer may be represented by the equation:



The polyphenylsiloxane is stable in the presence of steam at 300°C.

The polymeric condensation product which forms on heating compound (I) seems likely to contain diphenylsiloxy units with interspersed aluminoxy units. A section of this aluminosiloxane may be represented as



The aluminum has a coordination number of three in this representation. It is also possible to place the aluminum in a position of four coordination. Thus, if $[\phi_3\text{SiO}]_3\text{Al}$ -1 iso- $\text{C}_3\text{H}_7\text{OH}$ splits out a benzene by the reaction of the alcohol hydrogen with an *adjacent* molecule and then loses propylene, the aluminum will be surrounded by four Si—O groups and will retain a proton to balance the charge. Except for the phenyl groups on the silicon this structure is the same as that suggested by Thomas for silica-alumina cracking catalysts (4).

It is interesting to report that when mixtures of triphenylcarbinol and compound (I) are heated in a melting point tube, a yellowing characteristic of the triphenylcarbonium ion begins at 150° to 160° and an intense red appears at 170°C. Above this temperature the color darkens to a deep blue or black. The appearance of yellow near the temperature range at which propylene begins to form in the thermalchromogram is consistent with formation of a proton by the loss of propylene. Either this proton is not retained at higher temperatures or it is not the catalyst because thermal treatment to 350°C does not produce an active catalyst for cumene dealkylation. The material does display activity for alcohol dehydration and for the cracking of diisobutylene so it is not without some of the catalytic properties that are usually associated with acidity.

Figure 5 shows a tracing from a thermalchromogram obtained when volatile products had ceased to form after heating compound (I) to 350°. With helium passing through the catalyst a pulse charge of 5 μl of cumene gave only a cumene peak. After the cumene peak, 1 μl of water was charged. A large benzene peak which is off scale in this test is observed. Immediately afterwards a

5- μ l pulse charge of cumene showed a conversion in excess of 30%. This conversion was observed on only 34 mg of substance dispersed as agglomerates in the celite packing. A tube containing 200 mg of a commercial silica-alumina bead catalyst of a surface area of 420 m²/g gave only 20% conversion of cumene under these conditions. In repeated tests conversions changed from 0 before water to the range of 30% to 50% by the addition of only 1 μ l of water. Additional water did not increase the conversion.

Within the error of the experiment a mole of benzene was formed per mole of water. Since the polyphenylsiloxane did not react with water, it seems clear that the aluminum is the site through which a water molecule can strip a phenyl group from an adjacent silicon. When the phenyl group is removed, an OH is added to the structure. Whether the aluminum in the polyphenylaluminumoxosiloxane is four- or three-coordinated, there are several ways by which the formation of the catalyst site can be shown.

At one extreme the hydroxide ion may remain at the point of attack, the aluminum, and an adjacent positive silicon is formed when the phenyl group is converted to benzene. Although such a picture seems unlikely, it does produce a charge separation. A charge separation has been suggested as the source of catalytic activity of alkaline-earth-exchanged molecular sieves (5).

In a simpler picture the hydroxyl group merely takes the place of the phenyl group on the silicon atom, producing a silicon hydroxyl which is adjacent to the Lewis site of the aluminum.

A picture that is more consistent with current suggestions (6) would show the

oxygen of the hydroxyl shared between the Lewis site of the aluminum and the positively charged Lewis site on the adjacent silicon. This arrangement would probably give a strong protonic acid and catalyst activity would be attributed to the proton.

Whatever may be the geometric structure of a catalyst site, it is clearly established that by the thermal treatment of compound (I) it develops acidity in the temperature range in which propylene is evolved. The polyphenylaluminumoxosiloxane, however, is not active for cumene dealkylation but it becomes very active when it is treated with water. Treatment with water introduces an hydroxyl and eliminates a phenyl group from the structure. The hydroxyl group appears to be the source of catalyst activity but there is more than one structure that will account for the presence of a hydroxyl.

ACKNOWLEDGMENT

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