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Oxidation Sites on Silica-Alumina*

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An investigation of the nature of the oxidation sites on silica-alumina and their role in various reactions has been carried out. Positive ion radical formation with adsorbed anthracene and perylene was examined along with the effects of silica-alumina on propylene polymerization, alkylation of aromatic hydrocarbons, and the decomposition of a carbonyl compound, pivalaldehyde. The effects of sodium ion exchange and ammonia adsorption on the activity of silica-alumina for these reactions were also examined. The results indicate that Bronsted acid sites are responsible for propylene polymerization and alkylation of aromatic hydrocarbons, while oxidation sites are responsible for aromatic ion radical formation. A spectrum of both Bronsted and oxidation sites is proposed to account for the activity of silica-alumina.

INTRODUCTION

The acidity of silica-alumina is generally attributed to both Bronsted and Lewis acid sites (*1*). Recent work has indicated which of these sites are responsible for catalyzing various reactions. Brouwer (*2*) has demonstrated that cumene cracking occurs at Bronsted acid sites and perylene oxidation at Lewis acid sites; Shepard, Rooney, and Kemball (*3*) and Rooney and Pink (*4*) have shown that olefin polymerization occurs at Bronsted acid sites and ion radical formation at Lewis acid sites. The oxidation of triphenylmethane to triphenylmethyl carbonium ion has been attributed to Lewis acid sites by Leftin and Hall (*5*) and to Bronsted acid sites by Hirschler and Hudson (*6*).

We have examined the activity of silica-alumina for aromatic ion radical formation, propylene polymerization, alkylation of aromatics, and decomposition of an aldehyde in an attempt to delineate further the functions of the various acid sites on silica-alumina.

EXPERIMENTAL METHODS

Adsorption of Aromatic

American Cyanamid MSA-3 silica-alumina cracking catalyst was used throughout this investigation (~25% Al_2O_3, surface area ~500 m^2/g, pore volume ~1.1 ml/g). The silica-alumina was usually pretreated by heating in moderate vacuum to 500–550°C. For most of this investigation about 1 wt % aromatic was adsorbed on the silica-alumina. With anthracene, about 19 wt % would give complete coverage if distributed as a monolayer (calculated by using the area of an anthracene molecule, 67×10^{-16} cm^2, as determined by X-ray studies) (*7*); however, 1 wt % is more than sufficient, by a factor of at least 3, to saturate the sites capable of oxidizing the aromatic (*2, 4*). The anthracene or perylene was adsorbed on silica-alumina either by mechanically mixing and heating to 200°C in vacuum or from solution. The preferred technique was a combination of these two methods, i.e., the aromatic and silica-alumina were mixed and heated to 200°C in vacuum, benzene was added to cover the solid and allowed to stand for a few minutes, then removed by filtration, after

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which the solid was once again heated to 200°C in vacuum.

The Na^+-exchanged silica-alumina was prepared by stirring with 0.05 M $NaNO_3$ at pH 6–7 (adjusted with NaOH) for 24 hr, filtering, washing, and calcining in air several days at ~550°C (wt % $Na^+ = 0.6$). Alternatively, it was prepared by treating with three successive portions of 0.5 M Na acetate for 20, 6, and 20 hr, washing with 10 portions of water, and calcining 20 hr at 530°C (wt % $Na^+ = 0.9$). The NH_3-treated silica-alumina was prepared by exposing the solid to 76 cm of NH_3 vapor for 1 hr at room temperature followed by evacuation for 3 hr at 200°C.

Electron Spin Resonance Spectra

The ESR studies were carried out with a Varian EPR spectrometer with a V-4531 cavity operating at 9490 Mc/sec with a magnetic field modulation of 100 kc/sec. Samples were sealed in 3-mm ID quartz tubing under a nitrogen atmosphere or, in some cases, in an atmosphere containing H_2O, CO_2, O_2, or C_3H_6.

Propylene Polymerization and Alkylation of Aromatics

The sample (4 g) of silica-alumina was placed in a glass tube (~20 cc) in a vacuum system and the aromatic added to the solid. After being degassed in vacuum at 200°C, the solid was cooled to 100°C in vacuum. A charge (2.7 cc STP) of propylene vapor was then admitted at 100°C and the propylene and solid were held at 100°C for 5–10 min (the pressure in the system became constant in less than 5 min). The system at 100°C was then evacuated through a liquid N_2 trap for 30 min and through a second liquid N_2 trap while the temperature of the solid was raised to 400°C and for 30 min at that temperature. The trapped products were analyzed first by gas-liquid chromatography (GLC) and then mass spectrometry (MS). The solid was examined by ESR at various stages in the procedure. In one case a larger scale preparation of the products from the reaction of excess propylene with anthracene on silica-alumina at 100°C was carried out. The products were extracted from the solid with benzene-water in a Soxhlet apparatus and analyzed by MS and infrared spectrometry.

Pivalaldehyde Decomposition

Samples (4 g) of silica-alumina containing the adsorbed aromatic were prepared as in the experiments with propylene. Pivalaldehyde, previously purified by passage through a 60 ft/1 inch SF-96 GLC column at 70°C, was then admitted as a gas to the solid held at 100° to 200°C. After several hours the volume of products was determined and their identity determined by GLC and MS.

RESULTS

Formation of Ion Radicals

The adsorption of aromatics on silica-alumina produced colored solids, green in the case of anthracene and brownish-purple with perylene. Both materials gave strong ESR signals which were quite stable over several months in a nitrogen atmosphere. The spectrum for adsorbed perylene given in Fig. 1A is in agreement with that reported elsewhere for this species (*2, 3, 8–10*) and with the spectrum of the positive ion radical of perylene in sulfuric acid solution (*11*). Similarly, the spectrum for adsorbed anthracene given in Fig. 1C is in agreement with that reported for this species prepared by adsorption from carbon disulfide (*9*) or benzene (*4*) solution and with the spectrum of the positive ion radical of anthracene in sulfuric acid solution (*9*). With anthracene we obtained two different spectra depending primarily on the conditions of catalyst preparation. The spectrum in Fig. 1C was obtained only with silica-alumina which had been treated with ammonia or exchanged with Na^+. With untreated silica-alumina the spectrum given in Fig. 1B was obtained. This spectrum has fewer lines and wider spacing and does not agree with previously reported spectra for the anthracene positive ion radical. The one electron species responsible for the

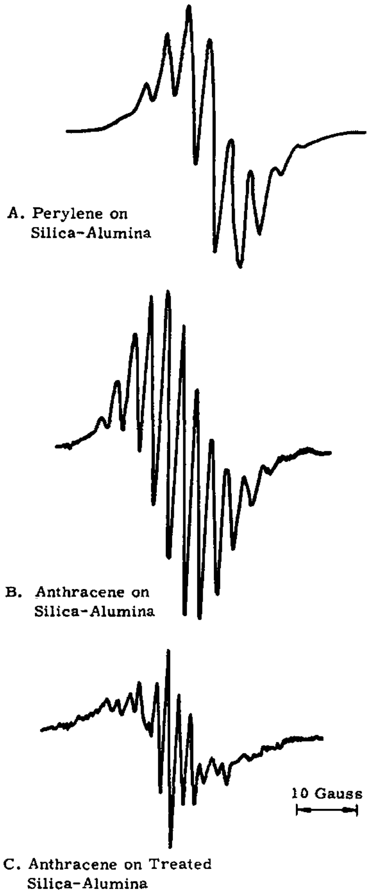

FIG. 1. Electron spin resonance spectra of adsorbed aromatic ion radicals.

different spectrum is thermally stable, the ESR signal being essentially the same before and after heating to 400°C. By contrast, the ESR signal of the perylene ion radical is almost completely eliminated after heating, probably by a coupling reaction similar to that reported by Rooney and Pink (*4*).

TABLE 1
BEHAVIOR OF PROPYLENE IN THE PRESENCE OF ADSORBED AROMATICS ON SILICA-ALUMINA

Experiment no.	Solid (~4 g)	Aromatic (~1 wt %)	C_3 Removed (% of charge) at each temperature 100°C	400°C
37	MSA-3	None	Trace	7
77	MSA-3	None	4	11
43	MSA-3	Perylene	3	79
48	MSA-3	Perylene	28	72
53	MSA-3	Perylene	0	69
54	MSA-3	Perylene	7	80
30	MSA-3	Anthracene	5	72
31	Solid + aromatic	from Expt 30	10	9
34	MSA-3	Anthracene	2	75
35	Solid + aromatic	from Expt 34	14	8
79a	MSA-3	Anthracene	15	31
79b	Solid + aromatic	from Expt 79a	20	10
33	MSA-3	Anthracene	28	35
74	MSA-3-Na^{+a}	None	90	3
76	MSA-3-Na^{+a}	Perylene	93	7
75	MSA-3-Na^{+a}	Anthracene	94	6
75X	Solid + aromatic	from Expt 75	97	2
85	MSA-3-Na^{+b}	None	67	7
40	MSA-3-Na^{+b}	Anthracene	81	19
44	MSA-3-Na^{+b}	Anthracene	87	8
81	MSA-3-NH_3[c]	None	100	Trace
82	MSA-3-NH_3[c]	Anthracene	99	1
80	MSA-3-NH_3[d]	Anthracene	81	Trace

[a] MSA-3 treated with 0.5 *M* Na acetate, wt % $Na^+ = 0.9$.

[b] MSA-3 treated with 0.05 *M* $NaNO_3$ at pH 6–7, wt % $Na^+ = 0.6$.

[c] MSA-3 exposed to NH_3 at room temperature and evacuated at 200°C, wt % $NH_3 = 0.5$.

[d] Anthracene adsorbed on MSA-3 then exposed to NH_3 at room temperature and evacuated at 200°C.

Propylene Polymerization and Alkylation of Aromatics

The results of reacting propylene in the presence of silica-alumina with or without an aromatic adsorbed on the solid are summarized in Table 1. In the absence of an aromatic on the silica-alumina, only a small portion of the propylene could be recovered from the solid by evacuation at either 100°C (0–4%) or 400°C (7–11%). The unrecovered propylene is assumed to have been polymerized on the solid. Propylene in the presence of anthracene on silica gel (Davison Grade 62) was largely recovered at 100°C. When anthracene or perylene was adsorbed on silica-alumina, reaction of the propylene occurred but polymerization was no longer the major reaction, since a large fraction of the propylene could be recovered at 400°C (average recovery with anthracene, 53%; with perylene, 75%). That a different reaction is occurring is also indicated by the reduced amounts of C_4–C_5 products when an aromatic is present. Re-exposure to propylene of a solid with adsorbed aromatic thereon and from which the initial propylene had been removed at 400°C resulted largely in polymerization of the second charge of propylene. The major products from a larger scale reaction of excess propylene with anthracene on silica-alumina at 100°C were poly-C_3-anthracenes, -dihydroanthracenes, and -tetrahydroanthracenes with the C_3 groups all on ring positions and not present as C_6 or longer chains.

After treatment of the silica-alumina with Na^+ ions to replace the protons at the Bronsted acid sites, activity for propylene polymerization and alkylation was almost eliminated, but it was still possible to oxidize either anthracene or perylene to ion radicals. The extent to which the polymerization and alkylation were eliminated was a function of the Na^+ content of the treated silica-alumina, i.e. at 0.6 wt % Na^+ some polymerization and alkylation were still occurring, but at 0.9 wt % both reactions were essentially absent. Silica-alumina treated with ammonia before and after adsorbing anthracene on the solid was inactive for both polymerization and alkylation. Once the anthracene was adsorbed on the surface, ammonia treatment did not reduce the ESR signal.

Pivalaldehyde Decomposition

Pivalaldehyde, $(CH_3)_3CCHO$, was observed to be rapidly adsorbed on silica-alumina then slowly decompose at 200°C to isopentane and isobutane without appreciable CO formation. The reaction was essentially the same with or without an aromatic on the silica-alumina. The use of silica-alumina which had been sodium ion-exchanged (0.6 wt % Na^+) to remove protons also did not alter these results. That the absence of CO in the products was not the result of CO adsorption after its formation was demonstrated by observing that CO itself was not adsorbed by anthracene on silica-alumina. In the absence of any solid, pivalaldehyde decomposed to CO and C_4 hydrocarbon, the expected products from a free radical reaction, to the extent of about 6% in 3 hr at 200°C, but this reaction was not observed when silica-alumina was present. A likely ionic reaction intermediate, 2-methyl-2-butene, was exposed to silica-alumina, with and without adsorbed anthracene, at 200°C. Isopentane and isobutane were again the major products.

DISCUSSION

The complex nature of the surface of silica-alumina provides a variety of active sites capable of catalyzing a number of different reactions. In addition to the usual types of interaction of aromatics with solid acids, i.e., carbonium ion formation by reaction with either a proton or a Lewis acid (*12*), our results confirm an interaction, oxidation by one-electron transfer, to form a positive ion radical. That this oxidation does not occur on Bronsted acid sites is indicated by the formation of these ion radicals on Na^+-exchanged silica-alumina.

Propylene ordinarily polymerizes in the presence of silica-alumina. However, with an aromatic on the surface this reaction is overshadowed by a competing reaction either as a result of poisoning of the polymerization sites or because the competing reaction has a higher rate at 100°C. This new reaction produces a product from which propylene can be recovered on heating to 400°C and is identified as an alkylation of the aromatic by the isolation of alkylation products. On reuse of a solid from which the propylene had been removed at 400°C, propylene polymerization became large, indicating that the aromatic had been removed from the surface or altered so that it was less alkylatable. These observations might also be indicative of different active sites for the two reactions. The marked reduction in both these reactions by Na^+ exchange of the silica-alumina indicates that the catalytic sites for both these reactions are Bronsted acids. The level of Na^+ exchange (0.6–0.9 wt % = 0.26–0.39 meq/g) at which alkylation and polymerization are eliminated corresponds with the value of 0.3 meq Na$^+$/g reported by Topchieva *et al.* (*13*) for elimination of cumene cracking activity and with the value of 0.2 meq K$^+$/g reported by Rijnders and Schuit (*14*) for protonic activity for propylene polymerization. Shepard, Rooney, and Kemball (*3*) have recently reported on the polymerization of propylene on silica-alumina. Based on only a small recovery of carbon as products, they conclude that perylene on silica-alumina does not appreciably alter the solid's effectiveness for propylene polymerization. The results of the present investigation indicate that, although propylene still reacts on perylene-treated silica-alumina, the nature of the reaction is markedly changed.

The decomposition of pivalaldehyde could be occurring either at Bronsted acid sites which are less readily exchanged by Na$^+$ or at electron-deficient oxidation sites capable of two-electron acceptance reactions. In the former case proton donation to the carbonyl produces a carbonium ion. In the latter case the aldehyde would donate two electrons from the carbonyl linkage, thereby developing a positive charge on the carbonyl carbon. A methyl migration in either species would give tertiary carbonium ions which at 200°C could decompose to isoamylene with loss of the oxygen to the surface. Isoamylene could then be converted to isopentane, isobutane, etc., by reactions on the silica-alumina, with the necessary hydrogen probably supplied by nonvolatile condensation products of the aldehyde.

It is now possible to consider all these reactions in relation to the catalytically active sites on silica-alumina. The number of sites capable of oxidizing perylene by a one-electron acceptance has been estimated by Brouwer (*2*) and Hall (*10*) as about 2×10^{16}/m^2 [Rooney and Pink (*4*) report 2×10^{15}/m^2 for anthracene oxidation]. The number of sites capable of oxidizing triphenylmethane has been determined by Leftin and Hall (*5*) as about 5×10^{16}/m^2. From the results of the present investigation it is estimated that the reaction of pivalaldehyde on silica-alumina occurs at least on 7×10^{16} sites/m^2 (calculated from the amount of isobutane and isopentane produced) and that polymerization and alkylation are catalyzed by about 40×10^{16} sites/m^2 (calculated from the amount of Na$^+$ required to eliminate these reactions). It is not surprising that there is such a variation in the number of catalytically active sites since there is no *a priori* reason why these different reactions should occur on identical sites. In fact, since polymerization, alkylation, and cracking involve proton transfer; perylene oxidation, a one-electron transfer; pivalaldehyde decomposition, the transfer of either a proton or a pair of electrons; and triphenylmethane oxidation, either a hydride ion transfer (*5*) or a triphenylcarbinol intermediate (*6*), it seems more likely that these reactions do not involve the same sites or even just two types of sites, i.e. Bronsted and oxidation sites. Rather, it is suggested that the best description of silica-alumina activity is a spectrum of sites having different electron-accepting affinities and protonic activities. Some sites accept single electrons, others perhaps electron pairs, and still others hydride ions. Overlap of activity might be expected so that some sites could function in more than one type of reaction, thereby giving a complete spectrum of electron-accepting ability. Similarly, Bronsted acid sites which are responsible for olefin polymerization, aromatics alkylation, cumene cracking, and possibly pivalaldehyde decomposition show a spectrum of proton activity for catalysis.

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