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Surface Structure and Catalytic Cracking Properties of the SiO_2/BCl_3, $SiO_2/AlMe_3$ and $SiO_2/AlCl_3$ Systems

II. Catalytic Studies

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Samples of characterized Aerosil silicas have been examined for cumene cracking activity before and after treatment with either aluminium trimethyl, aluminium trichloride or boron trichloride in a fixed bed catalytic microreactor connected by means of a fine capillary to a mass spectrometer. To provide a standard to which these samples could be compared, a commercial silica alumina catalyst was also examined under identical reaction conditions. After hydrolysis, the $SiO_2/AlMe_3$ samples showed a comparable cracking activity to that of the commercial sample, while the $SiO_2/AlCl_3$ samples were less active. The hydrolyzed SiO_2/BCl_3 catalyst was found to be inactive for cumene cracking, having virtually no activity over and above that of the parent silica.

On examining the adsorption of pyridine on the catalysts by infrared spectroscopic techniques, a correlation between the catalytic activity and the ability of the catalyst to produce and retain pyridinium ions was noted. The results support a hypothesis that the catalytically active sites are ionic centers as suggested by previous authors (*3*, *11*).

INTRODUCTION

There has been continuing interest in the surface structure of silica–alumina cracking catalysts with particular reference to the acidic properties of the catalytically active sites. Some recent workers postulate that the catalytic cracking process involves the concerted action of both Lewis and Lowry–Brönsted acidic surface sites (*1–3*) although others suggest that Lowry–Brönsted acidity is only of secondary importance (*4*). It has also been postulated that another essential feature of the surface structure of cracking catalysts is that they carry surface ions which promote the ionic dissociation of adsorbed hydrocarbons, thereby leading to the transient existence of adsorbed, mechanistically viable, reaction intermediates (*3*).

The object of the present work was to use oxide systems which enabled us to provide direct evidence concerning some of the crucial features of these theories.

EXPERIMENTAL METHODS AND MATERIALS

Determination of the Catalytic Cracking Activities

It was thought to be desirable to determine the cracking activities of the catalysts in a manner that minimized the effect of physical variables such as hydrocarbon feed rate, heat exchange, diffusion, etc., on the observed activities. This was achieved by use of a fixed bed catalytic reactor system. The reaction vessel of about 40-ml capacity was made from Pyrex glass. Powdered catalyst was weighed in and formed a thin (~0.5 mm) layer over the bottom of the vessel. After the required pretreatment, cumene at its ambient saturated vapor pressure (≈8 mm) was admitted to the reactor, which was then sealed immediately by the greaseless tap. The concentration of propylene in the gas phase was then monitored continuously by means of an A.E.I. M.S. 10 mass spectrometer connected directly to the reactor via a fine capillary leak. Control experiments showed that the rate of removal of cumene through the leak and the purely thermal cracking rate were both negligible (~1%) compared with the rates of cumene removal caused by the active catalysts studied under identical experimental conditions. It was also found that the rate of cumene removal was always equal to the rate of propylene production to within 2%. The most essential control experiments, however, were those carried out to determine the optimum catalyst weight. A 13% Al_2O_3–SiO_2 cracking catalyst (J. Crosfield & Sons Ltd.) was used for these experiments. It was found that with catalyst weights of <0.25 g, the rate constant for propylene production per unit catalyst weight was constant.

The reactor system proved extremely robust in practice and allowed for the rapid and accurate evaluation of a very large number of catalytic activities over a wide range of temperatures. All the catalytic cracking rates reported in this paper are the result of at least two independent determinations. The reproducibility was good, with a variability of less than 2% between the rate constants obtained from separate determinations. The results obtained on all the catalytically active samples are presented in Figs. 2, 3, and 4 in the form of Arrhenius plots. It must be stressed, however, that this particular method of testing cracking activity determines largely the "chemical" activity of the catalysts used. As such the results would not necessarily relate precisely to other testing methods where "physical" factors may become of equal importance.

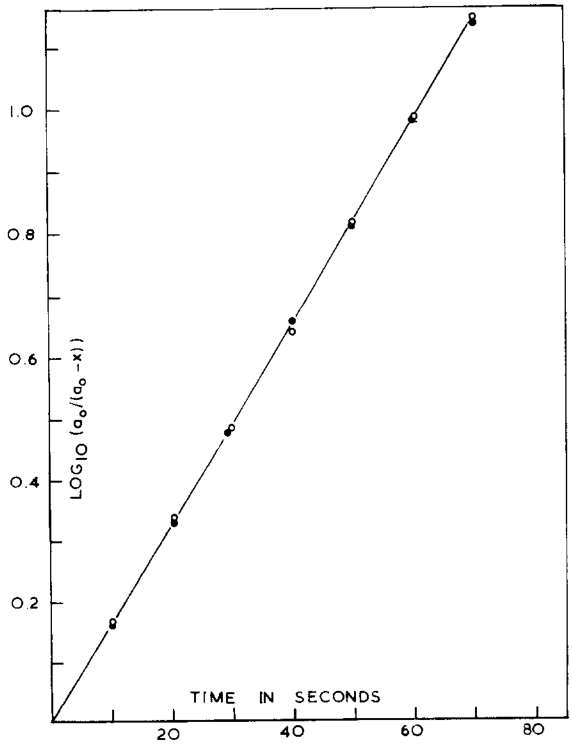

FIG. 1. A first-order plot for propylene formation over 13% Al_2O_3–SiO_2 cracking catalyst at 450°C.

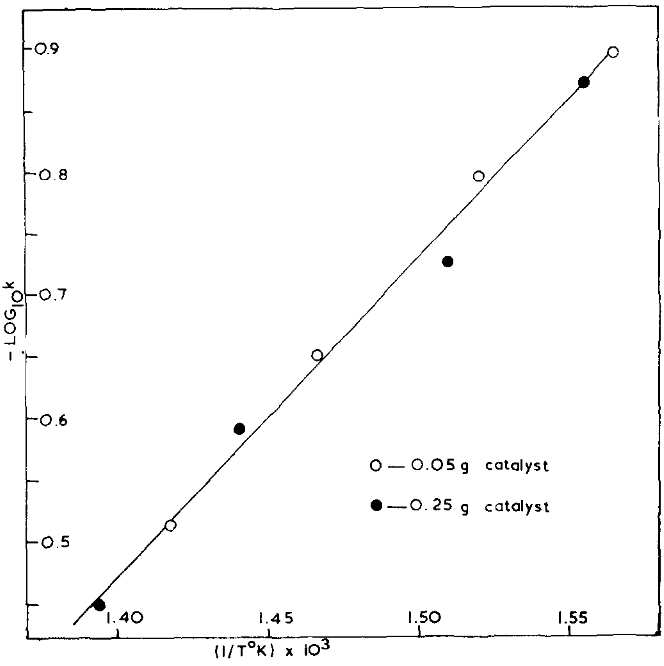

FIG. 2. Årrhenius plot for 13% Al_2O_3–SiO_2 cracking catalyst over the range 350–450°C.

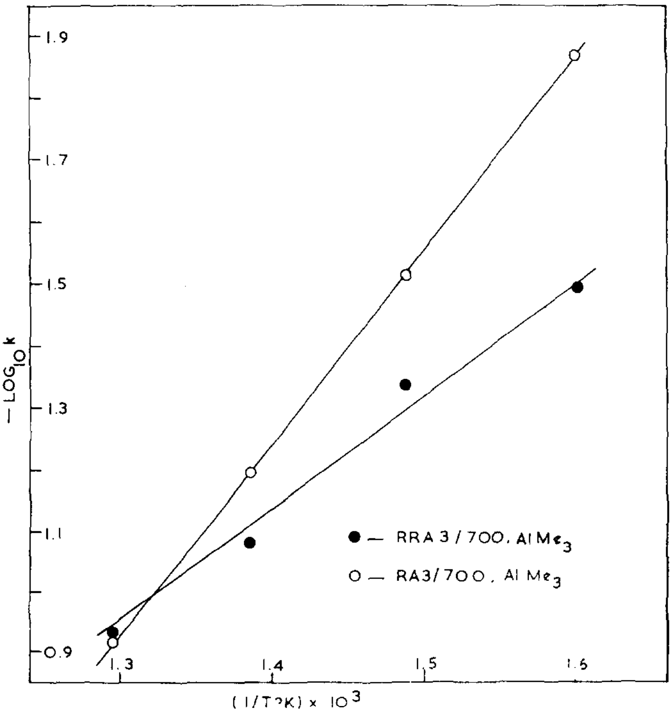

FIG. 3. Årrhenius plot for hydrolyzed SiO_2–$AlMe_3$ catalysts over the range 350–500°C.

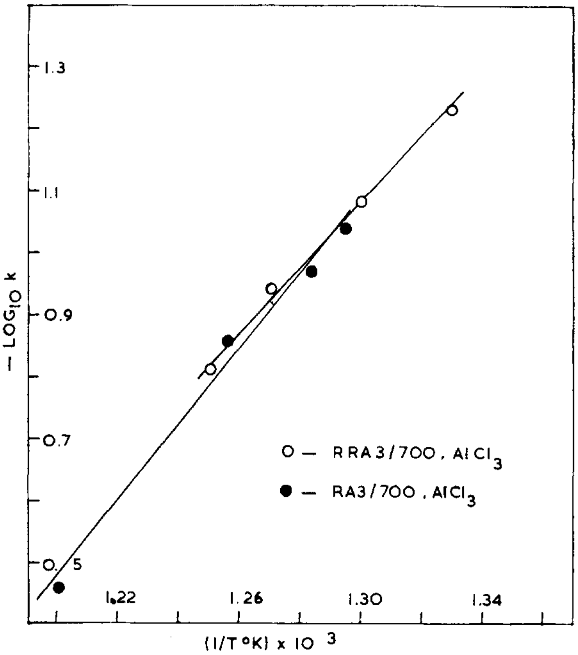

FIG. 4. Arrhenius plot for hydrolyzed SiO_2–$AlCl_3$ catalysts over the range 470–560°C.

Materials. The precise methods used for making the catalysts are given at the convenient points in the results and discussion section of the paper.

Cumene (B.D.H.) was fractionally distilled over sodium wire and the liquid passed (at room temperature) under a sufficient pressure of dry nitrogen through a meter column of activated kaolinite. This procedure removed water and hydroperoxides from the cumene. The final product gave a mass spectrum corresponding to that recorded in the A.P.I. index.

"Analar" pyridine (Hopkins & Williams) was refluxed and distilled from KOH. The middle cut from the final distillate was collected directly into predried ampoules, sealed by greaseless taps, transferred to the vacuum line and used immediately. The silicas, $AlMe_3$, BCl_3, $AlCl_3$, etc., were prepared and used as described in the preceding paper (*12*).

The 13% Al_2O_3–SiO_2 Catalyst

Samples of the powdered catalyst weighing 0.05–1.0 g were placed in the catalytic reactor which was then glass-blown onto the vacuum manifold. The reactor was heated under vacuum for 1 hr at 500°C and the catalytic activities were determined by the procedure described above. It was found for all the silica–aluminas studied that the cracking process followed first-order kinetics with respect to the disappearance of cumene. (A typical first-order plot is shown in Fig. 1.) For comparison of the catalytic activities exhibited by different catalysts, the calculated first-order rate constants were divided by the weight of the catalyst sample used to yield a "cracking rate" per gram of catalyst. As the results shown in Fig. 2 indicate, the cracking rates per gram of catalyst were independent of the actual quantity of catalyst, provided less than 250 mg were used. The experiments showed that a catalyst bed thickness of greater than ~1–2 mm gave a unit weight cracking rate less than those shown in Fig. 2, indicating that all the catalyst in the bed was not equally available to the cumene vapor. Experiments at cumene vapor pressures up to 40 mm were also carried out by heating the vacuum manifold and cumene reservoir.

With catalyst weights of less than 250 mg, the first-order cracking rates per unit weight were the same as those shown in Fig. 2.

The $SiO_2/BCl_3/H_2O$ System

About 200 mg of each of two silicas were reacted and tested separately. R.A.3/700 was weighed into the reactor, evacuated at 500°C for 1 hr and then cooled to room temperature, whereas R.R.A.3/700 was merely evacuated overnight at room temperature. The samples were then exposed to excess BCl_3 vapor and after about 10 min the excess reagent and product gases were evacuated. (The mass spectrometer was protected by a break seal during the BCl_3 treatment.) Two samples of each of the BCl_3-treated silicas were heated *in vacuo* at 500°C for 1 hr and then tested for cracking activity at this temperature by admission of cumene vapor as above; similarly two of each type were first exposed to excess water vapor after BCl_3 treatment at room temperature and then heated *in vacuo* at 500°C for 1 hr prior to testing at this temperature. All the samples exhibited a catalytic activity for cumene cracking of less than 1% of that of the industrial catalyst. Since the hydrolyzed R.R.A.3/700-BCl_3 samples carry about 1.6 $>$B—OH groups per 100 Å^2 of their surface this virtual absence of catalytic activity was a surprising result.

The results of the infrared studies of pyridine adsorption on these surfaces are also of interest. Figure 5 shows that, when pyridine is adsorbed on an R.A.3/5/700 sample, only two new absorption bands appear in the 1400–1650 cm^{-1} region of the spectrum. The new bands are at 1440 and 1595 cm^{-1}and are characteristic of pyridine hydrogen-bonded (HPY) to OH groups (*1*, *8*). As expected, there are no absorption bands in the spectrum corresponding to pyridine coordinated to Lewis acid surface sites (LPY) or to pyridinium ions (BPY) produced by proton transfer from a Lowry–Brönsted surface acid site to a pyridine molecule. Figure 6b shows that when pyridine is adsorbed on an SiOH/BOH surface both HPY and LPY forms are present; the bands at 1595 and 1620 cm^{-1} correspond to the HPY and LPY species, respectively (*1*, *8*). The HPY species is easily removed by mild heating (Fig. 6c) but the LPY form persists as indicated by the continued

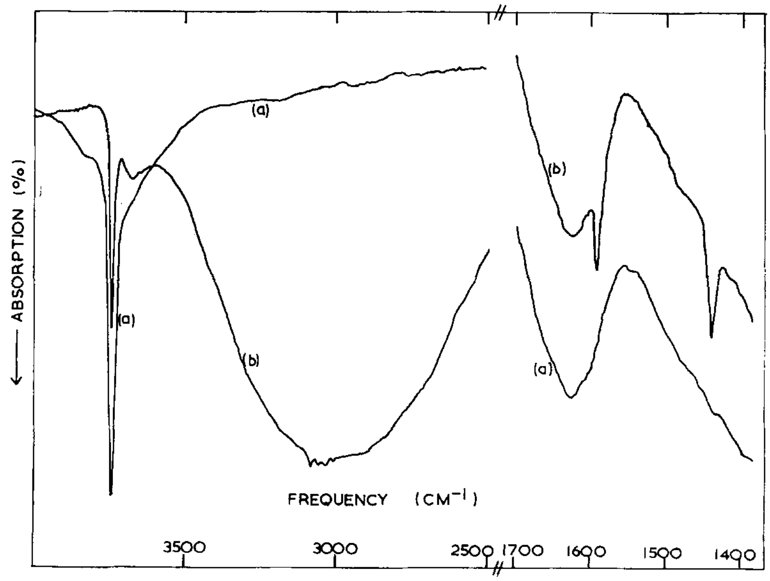

FIG. 5. (a) R.A.3/5/700 after evacuation at 500°C. (b) After exposure to pyridine vapor, ambient saturated vapor pressure (SVP), and evacuation for 30 min at room temp.

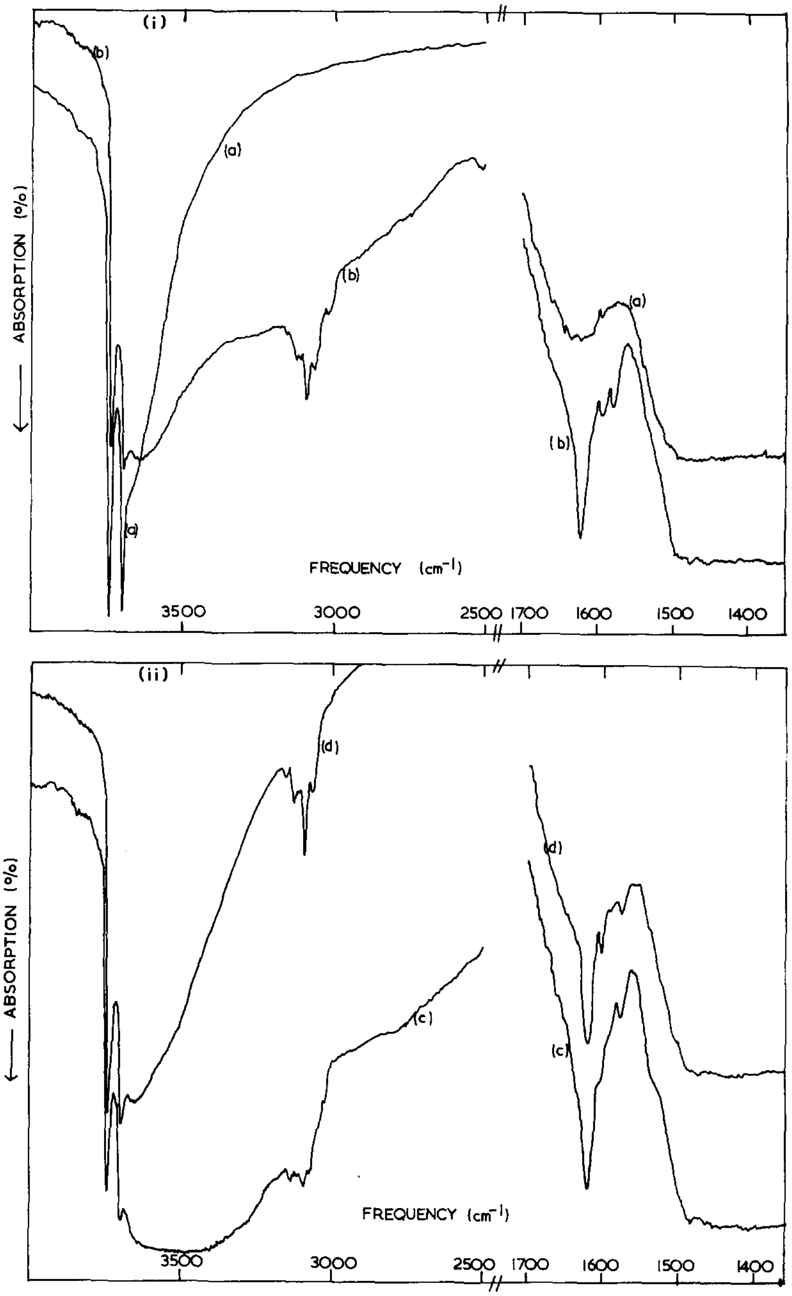

FIG. 6. (a) A hydrolyzed SiO_2–BCl_3 sample prepared from an R.R.A. 3/5/700 disc (see text) after evacuation at 500°C for 1 hr. (b) After exposure to pyridine vapor (SVP) and evacuation for 30 min at room temperature. (c) After exposure for 5 min to H_2O vapor at its saturated ambient vapor pressure (SVP) followed by evacuation at room temperature for 30 min. (d) After evacuation at 125°C for 30 min.

presence of the 1620 cm^{-1} absorption band. Addition of water vapor to the sample at this stage leads to no detectable increase in absorption intensity at 1540 cm^{-1} nor to any decrease at 1620 cm^{-1}. We conclude that, unlike all the SiO_2/Al_2O_3 systems described below, no detectable BPY species is produced by this treatment. In total the results obtained for this catalytically inactive material suggest that, although this SiOH/BOH surface carries sites of Lewis acidity comparable to the silica–aluminas studied, it does not carry Lowry–Brönsted sites of comparable strength to those present on the silica–aluminas, either in the presence or absence of molecular water.

The $SiO_2/AlCl_3/H_2O$ and $SiO_2/AlMe_3/H_2O$ Systems

The $SiO_2/AlMe_3$ catalysts were made *in situ* in the catalytic reactor by the same procedure as that used for preparing the SiO_2/BCl_3 samples. The $SiO_2/AlCl_3$ samples were made in the same way as in the corresponding infrared samples (*12*) and were then weighed into the catalytic reactor. It was therefore only possible to study the hydrolyzed form of the latter system. Once again complete series of experiments were carried out using each of the R.A.3/700 and R/R.A.3/700 silicas as the "support" materials.

After heating the nonhydrolyzed $AlMe_3$-treated silicas *in vacuo* at 500°C for one hr, infrared studies showed that their surfaces carried no detectable OH groups (*12*). They exhibited negligible catalytic for cumene cracking. Exposure of these 500° evacuated samples to an excess of water vapor at room temperature followed by evacuation for 1 hr at 500°C led (for both R/R.A.3/700 and R.A.3/700) to an infrared spectrum similar to that shown in Fig. 7(a) of the preceding paper (*12*). The corresponding catalytic activities for cumene cracking at 500°C were about 25% of those observed for those $SiO_2/AlMe_3$ samples that were hydrolyzed as described below. The manifestation of catalytic activity by these $SiO_2/AlMe_3$ samples on hydrolysis suggests that the presence of surface OH groups is essential for cumene cracking activity; it certainly seems to suggest that protonic acidity (i.e., available protons) is essential for cumene cracking activity.

The hydrolyzed $SiO_2/AlMe_3$ and $SiO_2/AlCl_3$ catalysts were prepared from silicas that had been reacted with $AlMe_3$ and $AlCl_3$ under the experimental conditions described in the preceding paper (*12*). After reaction, the samples were hydrolyzed by heating them to 500°C over a period of 1 hr in the presence of excess water vapor. When prepared in this way the hydrolyzed catalysts remained colorless (*12*).

The hydrolyzed $SiO_2/AlCl_3$ catalysts were less effective for cumene cracking in the 350–450°C temperature range than the hydrolyzed $SiO_2/AlMe_3$ systems. The activation energies observed for the two systems were also different (Figs. 3 and 4). These differences in catalytic activity and activation energy no doubt reflect differences in the surface structure of the catalysts and, while it would be possible to suggest reasons for the differences, such speculation is perhaps best left until such time as their detailed surface structures are better understood. However, some general features are worthy of present note. Firstly, all the hydrolyzed catalysts exhibited cracking activity for cumene. Secondly, the hydrolyzed R.R.A.3/700/$AlMe_3$ catalyst exhibits a cumene cracking activity comparable on a unit BET area basis with the industrial catalyst used. Also, whereas the industrial catalyst was black after testing, the hydrolyzed $SiO_2/AlMe_3$ samples showed only very slight discoloration after a comparable series of activity tests, indicating a much lesser tendency for carbonization during cumene cracking.

Infrared studies of pyridine adsorption were carried out on both the hydrolyzed and nonhydrolyzed silica–alumina catalysts. The results are summarized in Figs. 7, 8, and 9. On adsorbing pyridine at room temperature on a hydrolyzed R.A.3/5/700/$AlMe_3$ sample evacuated at 500°C, it can be seen (Figure 7ia) that three forms of adsorbed pyridine are detectable, namely, HPY, characteristic band at 1595 cm^{-1} (also band at 1443 cm^{-1}); LPY, characteristic band at 1620 cm^{-1} (also bands at 1450 and 1490 cm^{-1}); and BPY, characteristic band at 1540 cm^{-1} (also bands at 1640 and 1490 cm^{-1}). Addition of water vapor to this sample (Fig. 7 ib) causes a decrease in absorption intensity at 1595 (HPY) and

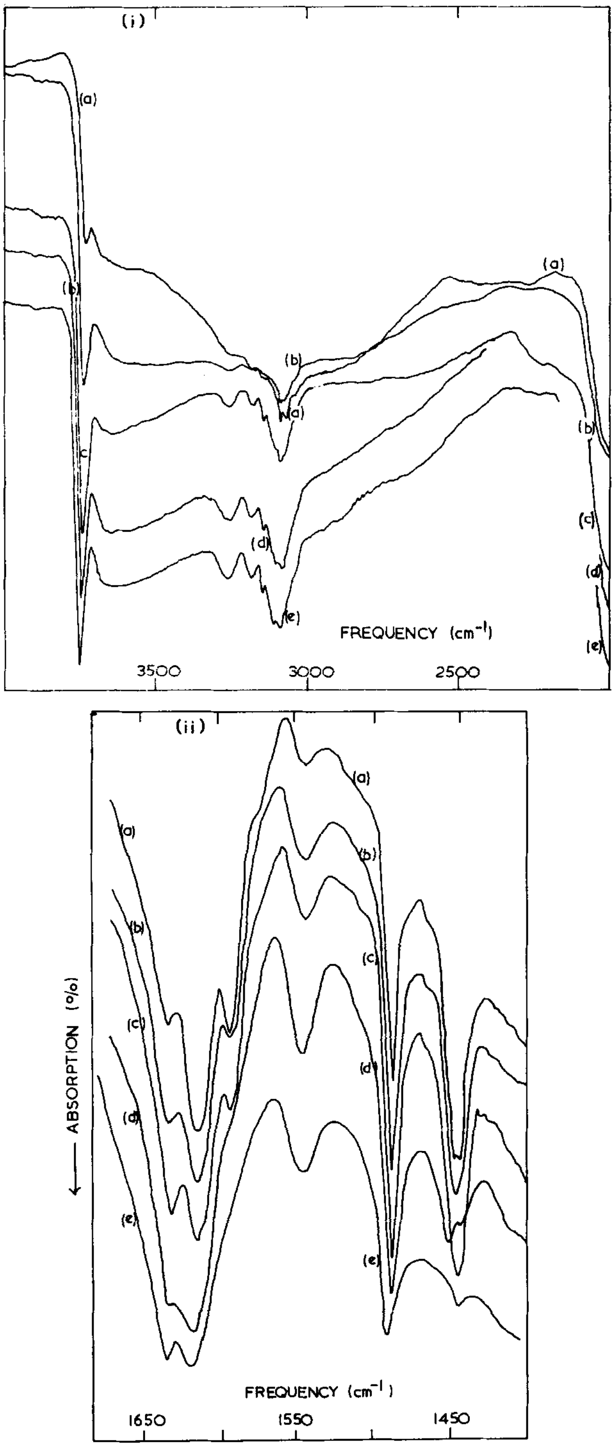

FIG. 7. (a) A hydrolyzed R.A.3/5/700/AlMe$_3$ catalyst (see text), evacuated at 500°C for 1 hr, cooled to room temperature, exposed to pyridine vapor (SVP) and evacuated at room temperature for 30 min. (b) After exposure for 5 min to H_2O vapor (SVP) and evacuation at room temperature for 30 min. (c) After evacuation at 150°C for 30 min. (d) After evacuation at 300°C for 30 min. (e) After evacuation at 500°C for 10 min.

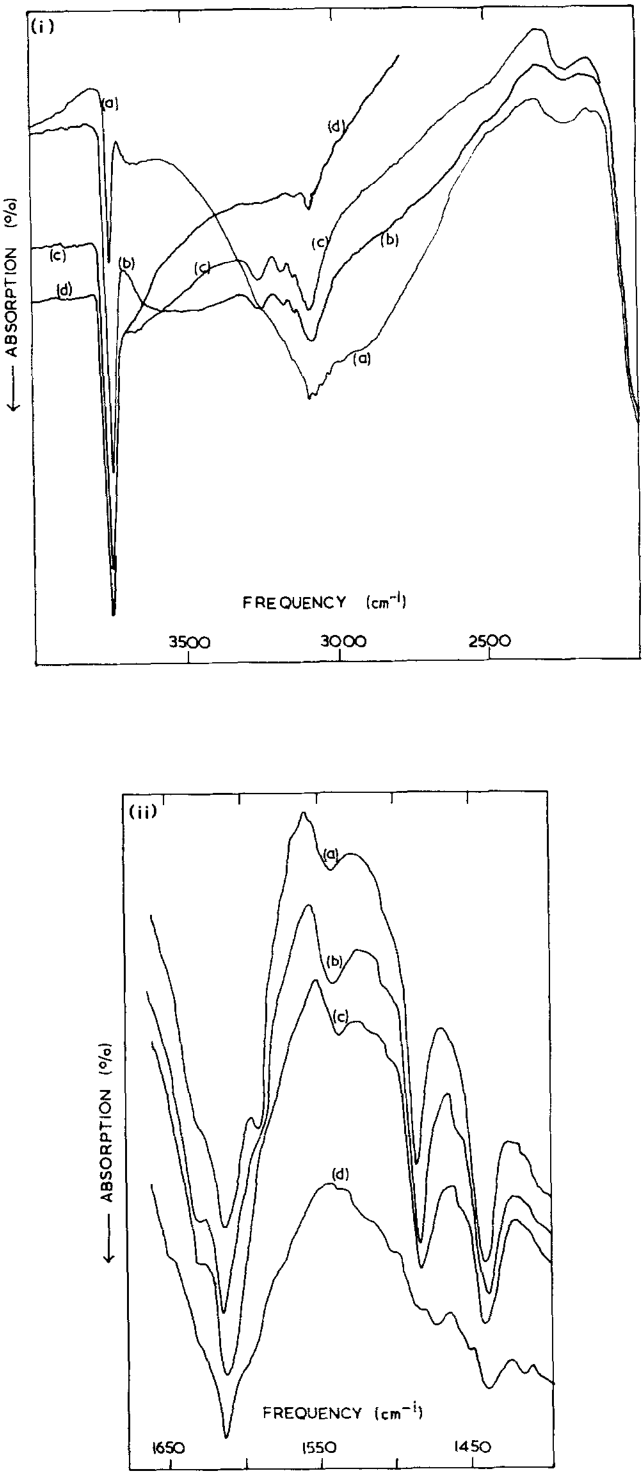

FIG. 8. (a) A hydrolyzed R.A.3/5/700/$AlCl_3$ catalyst (see text), evacuated at 500°C for 1 hr, cooled to room temperature, exposed to pyridine vapor (SVP) for 5 min and finally evacuated at room temperature for 30 min. (b) After exposure for 5 min to H_2O vapor (SVP) and evacuation at room temperature for 30 min. (c) After evacuation at 150°C for 30 min. (d) After evacuation at 300°C for 30 min.

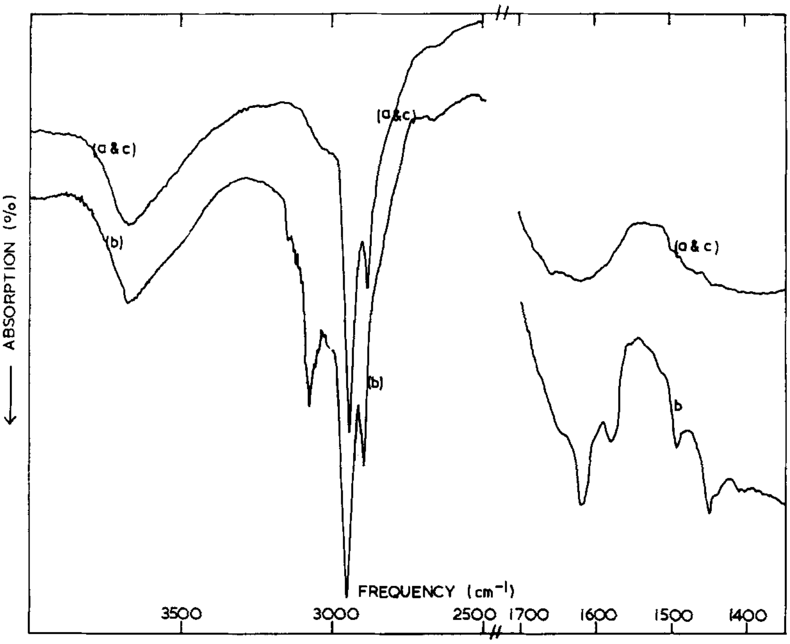

FIG. 9. (a) An R.A.3/5/700 silica after treatment with $AlMe_3$ (see text), followed by evacuation at 500°C for 30 min. (b) After exposure to pyridine vapor (SVP) and evacuation at room temperature for 30 min. (c) After evacuation at 300°C for 30 min.

1620 cm^{-1} (LPY) and an increase at 1540 cm^{-1} (BPY). There is also a marked increase in absorption intensity in the 3600 cm^{-1} region of the spectrum. Heating the sample to higher temperatures (Fig. 7 ic, d, and e) leads to the disappearance of HPY from the surface at 150°C and a further increase in the concentration of BPY at the expense of LPY as the temperature is further raised to 300°C. It is interesting to note that the persistence of the BPY species on the catalyst surface is matched by the presence of the broad absorption band in the 3600–3700 cm^{-1} spectral region. This is an expected result when it is realized that the formation of some of the pyridinium ions is due to the reaction between pyridine and water.

$$\mathrm{Py} + \mathrm{H_2O} \rightarrow \mathrm{PyH^+} + \mathrm{OH^-} \qquad (1)$$

Whatever the initial coordination of the pyridine molecule, and the results on balance suggest, in agreement with previous workers (*1*, *2*, *8*), that the BPY species arises from the conversion of the LPY form, the preservation of electrical neutrality requires the corresponding presence of a hydroxyl ion when protonation of pyridine (or any other molecule) occurs by reaction with water (*9*).

The results obtained with the hydrolyzed R.R.A.3/5/700/$AlMe_3$ catalysts show essentially the same features as those described for the R.A.3/700 based material, namely the LPY to BPY conversion on heating the pyridine carrying catalysts and the relative temperature stability of the BPY form and its accompanying absorption in the 3600 cm^{-1} spectral region.

The results obtained with the hydrolyzed $AlMe_3$ samples contrast somewhat with those obtained with either of the hydrolyzed SiO_2–$AlCl_3$ catalysts. Comparable infrared studies (Fig. 8) on these latter catalysts show once again the LPY–BPY conversion on treating the pyridine-carrying catalysts with water and heating them, but the resulting BPY species is more easily removed. Its presence is still marked, however, by the intensity of the 3600–3700 cm^{-1} absorption band. The difference in behavior of this band between these two types of catalysts is marked. After evacuation at 300°C it is still very evident (Fig. 7 id) on the hydrolyzed SiO_2–$AlMe_3$ catalysts, but after comparable treatment the hydrolyzed SiO_2–$AlCl_3$ catalysts exhibit only a much weaker absorption band in this region (Fig. 8 id).

The relation between the initial quantity of BPY produced on the 500°C evacuated surface, together with the temperature stability of the BPY species, and the cumene cracking activity of the catalysts is marked. The results, when taken in conjunction with those of earlier workers (*1, 2, 4, 8*), suggest that those catalysts which can form temperature-stable protonated species (e.g., pyridinium ions) will crack cumene with a low activation energy.

CONCLUSIONS

Considering the results of these studies, we note that all the silica–borias and silica–aluminas exhibited Lewis acidity. Also, after evacuation at 500°C, all the hydrolyzed samples carried surface hydroxyls which may be possible proton sources for carbonium or pyridinium ion formation in the manner suggested by Basila and his co-workers (*1*). The silica–borias, however, produced no pyridinium ions nor would they crack cumene. Considering the theory of critical interaction distances proposed by Basila *et al.* (*1*), there can be little doubt that the $>$B—OH site possesses a hydrogen atom within the critical distance of a hydrocarbon molecule coordinated to the Lewis acidic boron atom of the surface moiety. It follows that, although Lewis centers may be the primary adsorption centers on cracking catalysts (*1*), the active centers must also possess another essential property.

In this context, it is pertinent to note that the infrared spectra of the silica borias, with their discrete and narrow OH stretching absorption bands corresponding to the B–OH and Si–OH surface sites, demonstrate the predominantly covalent character of the bonding present in these surface structures (*10*). The absence of such discrete absorptions assignable to Al–OH species in the case of the silica–aluminas implies a greater ionic character in the bonding of the surface structures involving this more metallic element. Such a view is supported by the work of Peri (*3*) concerning the adsorption of CO_2 and HCl on hydrolyzed $SiO_2/AlCl_3$ catalysts. This author concludes that aluminium exists on such silica–alumina surfaces as exposed Al^+ ions in conjunction with neighboring negatively charged oxide ions.

Thus it seems that cumene cracking activity is associated with an ionic surface rather than with an array of surface Lewis acid sites. However, as the lack of cracking activity of the nonhydrolyzed $SiO_2/AlMe_3$ catalysts shows (Fig. 9), the presence of available protons is also an essential feature of an active surface. Therefore, when taken in conjunction with the work of previous authors (*1, 3*), the results of this study suggest that the active sites for cumene cracking on silica–aluminas are comprised of aluminium ions in an environment which promotes a sufficient asymmetry of charge distribution (*11*) within the adsorbed molecule for its protonation by a sufficiently proximate hydrogen. Such adsorption sites, or others, may well exhibit Lewis acidity but the present work does not answer the question whether Lewis acid sites are essential for cracking activity.

It is perhaps irrelevant to discuss whether the SiOH groups on the silica aluminas are strong Lowry–Brönsted acid sites. The concept of Lowry–Brönsted acidity is such that provided a Lowry–Brönsted base is of sufficient strength then it will accept a proton even from a weak Lowry–Brönsted acid. The activity of the more ionic surface is best regarded as resulting from the fact that the ions, or more likely a fraction of them, are so sited as to cause sufficient polarization of adsorbed molecules for them each to accept a proton from a neighboring hydroxyl at a point of induced high negative charge density.

The presence of such ionic sites can also explain the results observed on pyridine adsorption. For example, pyridine may be held at the aluminium ionic centers proposed by Peri (*3*) as $\begin{array}{l}\text{Py}\\ \downarrow\\ \text{Al}^+\text{O}^-.\end{array}$

Addition of H_2O to this system could then lead to its conversion to the relatively stable surface arrangement of the type

$$\begin{array}{ll}\text{OH}^- & \text{PyH}^+\\ \text{Al}^+ & \text{O}^-.\end{array}$$

This would account for the formation of BPY from LPY and also the concomitant appearance of a broad OH absorption band in the 3600 cm^{-1} region of the spectrum.

The differences between the activities of the hydrolyzed $SiO_2/AlMe_3$ and $SiO_2/AlCl_3$ catalysts is puzzling. Speculation is unwarranted until more is known about the reactions and surface rearrangement that almost certainly occur on hydrolysis.

ACKNOWLEDGMENTS

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