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Oxidation of Iodides by Silica–Alumina Catalysts

B. D. FLOCKHART, KONG YONG LIEW, AND R. C. PINK

Department of Chemistry, The Queen's University,
Belfast, BT9 5AG, Northern Ireland

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Aqueous solutions of iodide ion liberate iodine in a continuing reaction in the presence of a silica–alumina catalyst, suitably activated by heat treatment, provided molecular oxygen is present. A similar reaction occurs in benzene solutions of tetramethylammonium iodide. Pure alumina and pure silica are both inactive for the oxidation. Hydrogen Y zeolite has an activity comparable with that of the most active of the amorphous silica–aluminas. The catalytic activity of both the amorphous and crystalline silica–aluminas for the iodide ion oxidation is related to their Bronsted acidity. In the presence of water, the Bronsted sites on the oxide surface are continuously regenerated as the oxidation proceeds.

Although silica–aluminas are active for the oxidation of methyl iodide to iodine, the reaction occurs much more readily on the surface of pure alumina. Alumina samples dehydrated at about 630°C show maximum oxidizing activity and maximum Lewis acid activity. The production of methyl peroxy radicals shows that basic sites are also involved. Dissociative adsorption of methyl iodide probably occurs on the alumina surface and is followed by association of the halogen atoms to produce molecular iodine. Bronsted acid sites are not involved.

INTRODUCTION

Many aspects of the oxidizing properties of silica–alumina and alumina surfaces have been widely studied (*1*). In nearly all cases the oxidations have been observed either at the gas–solid interface or in nonaqueous systems. In several instances, however, investigators have reported that the oxidizing properties of these surfaces are retained even in aqueous solutions. Mellor, Rooney and Wells (*2*) reported that a commercial silica–alumina sample liberated iodine from potassium iodide in aqueous solution at room temperature, and suggested that the reaction might be used as a basis for a simple method of estimating the concentration of oxidizing sites on the silica–alumina surface. Recently, Fiedcrow *et al.* (*3*) reported that out of 10 alumina samples, 2 showed activity for the oxidation of iodide ions in aqueous solution. Both groups of workers have suggested that the sites responsible for the oxidation of iodide ions in aqueous systems may be the same as those responsible for the oxidation at the catalyst surface of hydrocarbons such as perylene or anthracene. On the other hand, the oxidizing power of these surfaces towards hydrocarbons is known to be extremely sensitive to the presence of water vapor, the activity declining rapidly when water is adsorbed (*4*). The present study was therefore initiated to throw further light on the oxidation processes in these aqueous systems and to resolve this apparent discrepancy.

EXPERIMENTAL METHODS

The commercial sample of silica–alumina (wt %, dry basis: Al_2O_3, 13; Fe, 0.043; Na_2O, 0.20), supplied by Joseph Crosfield & Sons Ltd., was washed in distilled water and dried at 120°C before activation. A series of alumina catalysts that contained various percentages of silica was prepared by the hydrolysis of mixtures of aluminum isopropoxide and tetraethyl orthosilicate. Base-exchanged silica–alumina was prepared by digesting activated samples of the commercial catalyst with aqueous sodium acetate solution at 20°C; the samples were washed in water and dried at 120°C before further activation. Union Carbide molecular sieve catalyst SK-40, a Y-type zeolite (wt %, dry basis: Al_2O_3, 23.5; SiO_2, 63.5; Na_2O, 13.0), was modified as required by exchanging the sodium ion with other cations. The ammonium form was prepared by the method described by Lunsford (*5*); exchange with ions other than the ammonium ion was effected using Eberly's method (*6*). Aluminum oxide–hydroxide (boehmite) was supplied by Laporte Industries Ltd. and had the following specifications: Al_2O_3, 75% (w/w); SiO_2, Fe_2O_3, Na_2O, each $<0.01\%$. Activation of all catalyst samples involved heating in flowing oxygen for 30 min and subsequently in air for 4 hr at temperatures between 100 and 1000°C in an electric muffle furnace, followed by cooling at 10^{-2} mm Hg over phosphoric oxide for 30 min.

The potassium iodide was AnalaR grade. Tetramethylammonium iodide from BDH Chemicals Ltd. was recrystallized twice from deionized water and dried at 70°C in an oven evacuated to 20 mm Hg. Methyl iodide was dried with magnesium sulfate and redistilled. Benzene (A.R.) was stored over active silica–alumina and filtered before use.

Oxidation of the iodides was carried out in 50-ml flasks fitted with ground-glass stoppers. Activated samples of catalyst ($\sim$0.5 g, weighed accurately by difference) were rapidly transferred to the flasks containing the iodide solution, the contents were mixed by swirling, and the flasks were either stored in the dark at room temperature or kept in a thermostat at 60°C. After a known time interval the liberated iodine was titrated with standard sodium thiosulfate solution (10^{-4} *M* or 5×10^{-3} *M*), using starch as indicator.

Acidities (*7*) were determined by the method already described. A Decca XI spectrometer was used for obtaining the electron spin resonance (ESR) spectra.

RESULTS

Oxidation of Aqueous Potassium Iodide by Amorphous Silica–Aluminas

No immediate liberation of iodine was apparent when a sample of the commercial silica–alumina (subsequently referred to as cSA) activated at 700°C was added to a 0.1 *M* aqueous solution of potassium iodide at room temperature. Instead, a slow reaction with liberation of iodine continued at a constant rate over a period of at least 30 days. The rate of reaction increased when the potassium iodide + catalyst system was agitated by an ultrasonic generator operating at 22 kHz, e.g., the amount of free iodine present after 2 hr of ultrasonic mixing was 20 times greater than that in a similar system kept at room temperature for 24 hr without such stirring. This result probably indicates that the reaction rate is controlled by diffusion and/or adsorption–desorption processes. The rate of oxidation also increased with temperature (see Table 1). In subsequent experiments a reaction temperature of 60°C was used. Ultrasonic mixing was not employed in these experiments, but the contents of the flasks were swirled frequently.

The amount of iodine liberated over partially dehydrated silica–aluminas at 60°C increased linearly with increase in the iodide concentration of the supernatant

TABLE 1

AMOUNT OF IODINE FORMED IN 0.1 *M* AQUEOUS POTASSIUM IODIDE AFTER 24 hr USING AS CATALYST SILICA–ALUMINA ($\sim$13% Al_2O_3) DEHYDRATED AT 700°C

Reaction temp (°C)	Iodine liberated (10^{-6} g atom iodine/g catalyst)
$\sim$20	0.6
35	2.4
60	5.1
84	9.9

solution between 0.2 and ~2.5 *M*. Above this iodide concentration the iodine liberated was less than that required by the simple linear relationship; above 4–5 *M* the amount was independent of the iodide concentration. All these iodine determinations were made after 24 hr. Immediate liberation of iodine was apparent when iodide solutions more concentrated than ~3 *M* were used. When a sample of cSA activated at 700°C was added to 5 *M* potassium iodide, $\sim 2 \times 10^{-6}$ g atom iodine/g catalyst was present after 5 min and 3.38×10^{-4} g atom iodine/g catalyst after 24 hr. In all but one of the subsequent experiments with potassium iodide, 20 ml of a 0.1 *M* aqueous solution were used. As a test of reproducibility, cSA activated at 700°C was added to five flasks each containing this amount of iodide and was allowed to react for 24 hr at 60°C, the contents of the flasks being swirled frequently. Titers for the iodine produced agreed within 5%. Control experiments showed that the reaction did not occur when silica–alumina was absent.

The oxidizing activity of silica–alumina for potassium iodide in aqueous solution depends markedly on both the temperature at which the catalyst has been dehydrated and its alumina content. Figure 1 shows the variation of the amount of iodine produced with activation temperature of the cSA catalyst. The catalyst possesses two optimum temperatures of activation for the reaction: 100 and 800°C, approximately; for samples activated at these temperatures the amount of iodine present after 24 hr at 60°C was 0.9×10^{-8} and 1.6×10^{-8} g atom iodine m^{-2} of catalyst surface, respectively. In Fig. 2 the amount of iodine liberated is plotted as a function of alumina content for catalysts activated at 700°C. Pure silica and pure alumina are both catalytically inactive for the reaction. Whereas the introduction of a small amount of alumina into pure silica results in a dramatic increase in oxidizing activity, the incorporation of up to 40% silica into pure alumina produces little effect.

Comparative data for the surface acidity were obtained by dehydration of the silica–alumina samples under identical conditions to those used for the oxidation studies. The results obtained using triphenylmethanol as indicator are presented in Figs. 1 and 2. The shapes of the corresponding graphs are sufficiently similar to suggest that the measured acidity, which is probably Bronsted acidity [see, for example, Ref. (*8*)], may be involved in the

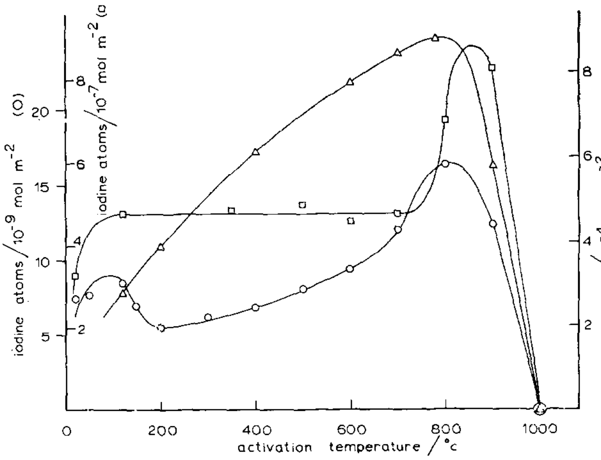

FIG. 1. Amount of iodine formed in: 0.1 *M* aqueous potassium iodide after 24 hr at 60°C (○), and saturated solution of tetramethylammonium iodide in benzene after 10 days at 60°C (□), as a function of the activation temperature of silica–alumina (~13% Al_2O_3). Surface acidity as a function of the activation temperature of silica–alumina (~13% Al_2O_3) using triphenylmethanol as indicator (△).

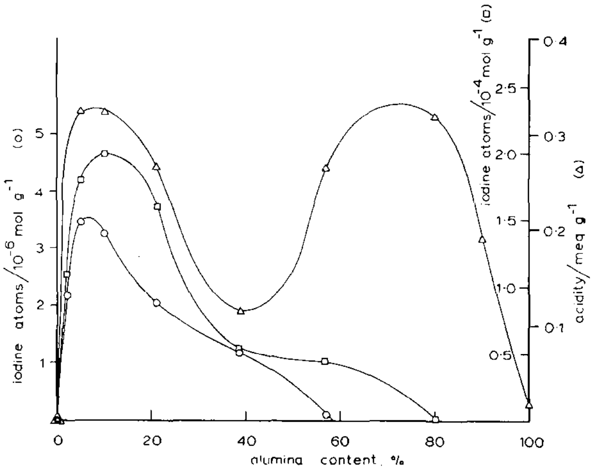

FIG. 2. Amount of iodine formed in: 0.1 *M* aqueous potassium iodide after 24 hr at 60°C as a function of alumina content for silica–aluminas dehydrated at 700°C (○), and saturated solution of tetramethylammonium iodide in benzene after 10 days at 60°C as a function of alumina content for silica–aluminas dehydrated at 550°C (□). Surface acidity as a function of alumina content for silica–aluminas dehydrated at 700°C using triphenylmethanol as indicator (△).

oxidation of aqueous potassium iodide by silica–alumina. Evidence in support of this view was obtained from the results of base exchange measurements and from a comparison of the behavior of the oxide catalyst with that of a protonic acid. For a sample of cSA previously dehydrated at 700°C, exchange with sodium ion followed by reactivation at 700°C caused a drop in activity to about one-third of the original value. Repeated ion-exchange–dehydration cycles produced a well-defined stepwise reduction in activity, as indicated by the results shown in Table 2. In Fig. 3 the amount of iodine liberated from aqueous potassium iodide as a function of time, using as catalyst a sample of cSA dehydrated at 700°C, is compared with the corresponding plot for an aqueous solution of potassium iodide that contained 1×10^{-4} mol sulfuric acid. The curves differ only in slope and the Arrhenius activation energies for the two reactions are in close agreement (~8 kcal mol^{-1}). From a comparison of the amount of iodine present in a potassium iodide solution containing cSA ac-

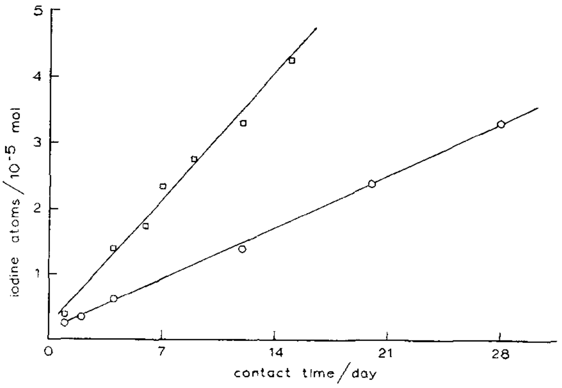

FIG. 3. Amount of iodine formed in 0.1 *M* aqueous potassium iodide at 60°C as a function of time: 0.5 g silica–alumina (~13% Al_2O_3) dehydrated at 700°C (○); 1×10^{-4} mol sulfuric acid (□).

TABLE 2
AMOUNT OF IODINE FORMED IN 0.1 *M* AQUEOUS POTASSIUM IODIDE AFTER 24 hr USING SODIUM-EXCHANGED SILICA–ALUMINAS DEHYDRATED AT 700°C

No. of sodium-exchange-dehydration cycles	Iodine liberated (10^{-6} g atom iodine/g catalyst)
0	5.1
1	1.6
2	1.2
3	0.8

tivated at 700°C with that produced in similar intervals of time in an iodide solution containing a known amount of sulfuric acid, the protonic acidity of the oxide sample was estimated to be 0.16 mEq g^{-1}, corresponding to 2.4×10^{17} acidic sites m^{-2} of oxide surface.

Figure 4 shows the amount of iodine liberated from a 1 *M* aqueous solution of potassium iodide as a function of time using as catalyst a sample of cSA activated at 700°C, and the corresponding plot obtained when the oxide was replaced by 1×10^{-4} mol sulfuric acid. In contrast to the results observed with the 0.1 *M* iodide solution, the plots differ markedly in shape, that obtained using sulfuric acid as catalyst showing pronounced curvature concave towards the axis indicating time.

Since molecular oxygen is known to be responsible for the oxidation of iodide ion to iodine in aqueous solutions that contain a protonic acid, the role of oxygen in the presence of a silica–alumina catalyst was of interest. For this experiment the cSA sample was activated at 700°C following the usual procedure, but it was subsequently outgassed at the same temperature for 15 hr at a pressure of 10^{-5} mm Hg or better. The aqueous potassium iodide solution was deaerated by 3 freeze–evacuate–thaw cycles. No trace of iodine could be detected, even after the catalyst had been in contact with the degassed iodine solution for 24 hr at 60°C. When air was admitted and the system was kept at 60°C for 24 hr, 4.0×10^{-6} g atom iodine/g catalyst was produced. Molecular oxygen therefore plays as decisive a role in the oxidation of iodide ion in aqueous solution in the presence of a solid acid catalyst as in aqueous solutions that contain a dissolved protonic acid.

Tetramethylammonium iodide contains the halogen in the ionized form. When an aqueous solution of tetramethylammonium iodide was brought into contact with partially dehydrated silica–alumina, a slow

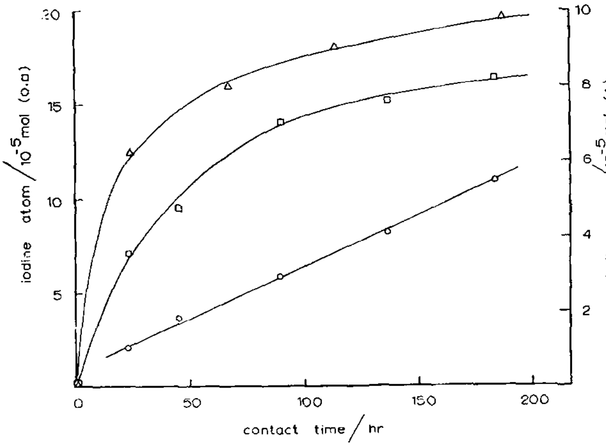

FIG. 4. Amount of iodine formed in 1 *M* aqueous potassium iodide at 60°C as a function of time: 0.5 g silica–alumina (~13% Al_2O_3) dehydrated at 700°C (○); 1×10^{-4} mol sulfuric acid (□). Amount of iodine formed in a saturated solution of tetramethylammonium iodide in benzene at 60°C as a function of time using as catalyst 0.5 g silica–alumina (~13% Al_2O_3) dehydrated at 700°C (△).

continuing reaction with liberation of iodine was observed. Because tetramethylammonium iodide is sparingly soluble in water at room temperature, the experiment was carried out at 60°C.

Oxidation of Aqueous Potassium Iodide by Crystalline Aluminosilicates

The sodium-form type Y zeolite was catalytically inactive for the iodide–iodine reaction; no iodine could be detected in the supernatant solution after a sample had been in contact with 0.1 *M* aqueous potassium iodide for 24 hr at 60°C. Partial replacement of the sodium ion by other cations produced zeolites that had this activity, but the magnitude of the property was greatly dependent on the substituted ion and the activation temperature. Figure 5 shows the variation of the amount of iodine produced with activation temperature for zeolite 90% exchanged with ammonium ion. Maximum activity was obtained with samples heated at about 500°C, 1.60×10^{-5} g atom iodine/g catalyst, corresponding to 2.59×10^{-8} g atom iodine/m^2 catalyst surface, being formed after 24 hr at 60°C. The resurgence of activity for samples dehydroxylated at around 700°C is of particular interest because of the marked increase in the rate of isomerization of cyclopropane on similar zeolite samples activated in this temperature range (*9*). Zeolite 50% exchanged with ammonium ion gave broadly similar results to those obtained with the 90%-exchanged sample, but the activity was lower. At 500°C the amount of iodine produced per gram of 50%-exchanged zeolite was 9.8×10^{-6} g atom.

The following values were obtained for the amount of iodine liberated when other exchanged zeolite samples were activated at 500°C and left in contact with aqueous potassium iodide for 24 hr at 60°C: 58% of the Na^+ ion replaced by Ni^{2+}, 0.6×10^{-6} g atom iodine/g catalyst; 63% of the Na^+ ion replaced by Ca^{2+}, 2.3×10^{-6} g atom iodine/g catalyst; 61% of the Na^+ ion replaced by La^{3+}, 19.9×10^{-6} g atom iodine/g catalyst.

Iodide Oxidation in Nonaqueous Media

When 0.1 g tetramethylammonium iodide was added to 20 ml benzene, only part of the iodide dissolved. A 0.5-g sample of cSA activated at 700°C was added to this two-phase system and allowed to react at 60°C over a 10-day period, with frequent shaking of the flask. During this time the color of the catalyst surface changed from white through a greenish fluorescence and orange to red, which gradually became darker. At the end of 10 days the supernatant solution had the red color typical of an iodine-in-

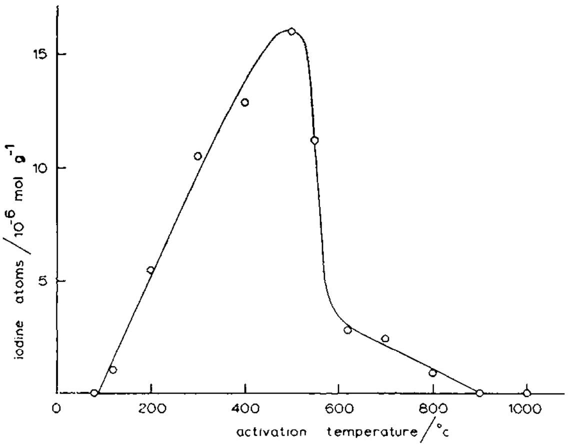

FIG. 5. Amount of iodine formed in 0.1 *M* aqueous potassium iodide after 24 hr at 60°C as a function of activation temperature of Y-type zeolite 90% exchanged with ammonium ion.

benzene solution. The iodine was determined by titration with sodium thiosulfate solution, after the addition of 10 ml of 0.1 *M* aqueous potassium iodide. The amount of iodine formed in 10 days under these conditions was 4.9×10^{-7} g atom iodine m^{-2} of catalyst surface. Reproducibility was within ~8% and, as in the oxidation of iodide ion in aqueous solution catalyzed by silica–alumina, molecular oxygen plays a decisive role. A plot of the amount of iodine liberated from tetramethylammonium iodide in benzene as a function of time using as catalyst a sample of cSA activated at 700°C is shown in Fig. 4. In contrast to the linear relationship observed for this catalyst with 0.1 and 1 *M* aqueous solutions of potassium iodide, the corresponding plot for tetramethylammonium iodide in benzene exhibits pronounced curvature concave towards the axis indicating time.

The above procedure for studying the oxidation of tetramethylammonium iodide in benzene solution was repeated with samples of cSA activated at other temperatures and the results are presented in Fig. 1. Maximum activity was obtained with samples dehydrated at ~900°C. In contrast to the results obtained when an aqueous potassium iodide solution was used (Fig. 1), no maximum was observed at dehydration temperatures of around 100°C. All samples activated between 100 and 700°C, however, were about equally active in oxidizing iodide ion in benzene solution when the comparison was made per unit area of catalyst surface. Experiments similar to those described above but substituting carbon tetrachloride for benzene gave broadly similar results.

The amount of iodine liberated from a saturated solution of tetramethylammonium iodide in benzene after 10 days at 60°C is plotted in Fig. 2 as a function of alumina content for catalysts activated at 550°C. Pure silica and pure alumina are both inactive for this oxidation; samples containing ~10% Al_2O_3 showed maximum catalytic activity.

Oxidation of Methyl Iodide

Samples of cSA activated at various temperatures were added to 5 ml quantities of methyl iodide and the systems left in the dark at room temperature (~20°C) for 10 days. At the end of this period the supernatant solution in many of the flasks had turned reddish orange. The iodine was titrated with sodium thiosulfate solution after adding 0.1 *M* aqueous potassium iodide. Exact determination of the end point was difficult because the color change from dark blue (starch in-

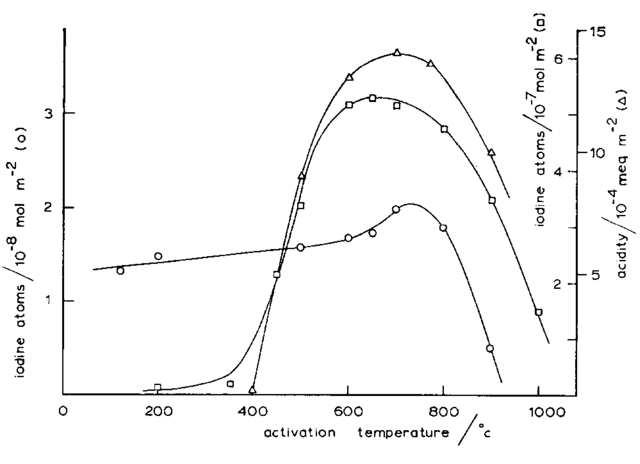

FIG. 6. Amount of iodine formed in neat methyl iodide after 10 days at ~20°C as a function of activation temperature of: silica–alumina (~13% Al_2O_3) (○), alumina (□). Surface acidity as a function of activation temperature of alumina using *p*-dimethylaminoazobenzene as indicator (△).

dicator) to colorless was gradual with an intermediate grayish yellow stage; in these titrations the complete disappearance of the yellow tint was taken as the end point. Figure 6 shows a plot of the amount of iodine liberated versus the activation temperature of the catalyst. Maximum catalytic activity occurs in samples dehydrated at ~750°C, the amount of iodine formed after 10 days at ~20°C being 2.3×10^{-8} g atom iodine m^{-2} of surface.

The oxidation of methyl iodide by silica–alumina samples is markedly dependent on the alumina content of the catalyst (Table 3). Alumina samples are much more active than silica–aluminas and even a small decrease in the alumina content results in a sharp reduction in oxidizing activity. The plot of the amount of iodine produced in neat methyl iodide as a function of the activation temperature of boehmite is shown in Fig. 6, the procedure followed being the same as described for silica–alumina. Maximum activity was observed with samples dehydrated at about 630°C, which corresponds closely with the maximum in Lewis acidity for this catalyst (Fig. 6). Pure silica is catalytically inactive for the oxidation of methyl iodide.

Strong ESR signals were obtained when methyl iodide was adsorbed on alumina surfaces active for the oxidation of the iodide (Fig. 7). From the line shape and g value (2.011) it seems probable that the adsorbed paramagnetic species is the methyl peroxy radical *(10)*.

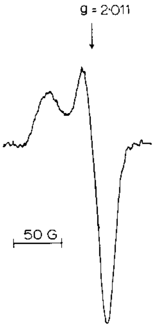

Fig. 7. ESR spectrum (first derivative) obtained when methyl iodide was adsorbed from hexane at 20°C on alumina activated at 650°C.

Discussion

Aqueous solutions of potassium iodide liberate iodine in a continuing reaction in the presence of a silica–alumina catalyst, provided molecular oxygen is present. Pure alumina, activated at a temperature that confers upon it powerful oxidizing powers with respect to hydrocarbons, is inactive for this oxidation, as is pure silica. These findings show that iodide oxidation in aqueous systems is not a useful measure of the activity of oxide surfaces for hydrocarbon oxidation, as suggested earlier. The results indicate, on the other hand, that the iodide oxidation is related to the Bronsted acidity of the catalyst. A closely similar oxidation occurs in an aqueous solution of potassium iodide acidified with sulfuric acid and exposed to air. The activation energies of these two processes are in close agreement, and an estimate of the protonic acid activity of the silica–alumina catalyst based on a comparison of the rates of iodine liberation from the same iodide solution gave a value of 2.4×10^{17} sites m^{-2} of catalyst surface, in reasonable agreement with the value of 5.0×10^{17} sites m^{-2} with acidity stronger than 50% sulfuric acid, obtained by titration with an arylmethanol (H_R) indicator. Further evidence for the close relationship between the Bronsted activity of the silica–alumina catalyst and its oxidizing activity in aqueous solution lies in the correlation between the optimum activation temperature of the catalyst for H_R acidity and for its oxidizing power in iodide solution (Fig. 1), and in the effect of varying alumina content on these prop-

TABLE 3
Oxidation of Neat Methyl Iodide by Silica–Aluminas Dehydrated at 550°C

Al_2O_3 (% by wt)	Iodine liberated (10^{-9} g atom iodine m^{-2} oxide surface)
99.9	455
95	80
80	13
13 (commercial catalyst)	16

erties (Fig. 2). The effect of base exchange on the oxidizing power of amorphous silica–alumina (Table 2) and the results obtained with crystalline aluminosilicates also fit this general pattern. Whereas the oxidizing activity for iodide of the sodium form of Y zeolite is negligible, the activity of hydrogen Y zeolite is comparable with that of the most active of the amorphous silica–aluminas. Bronsted acidity is a well-developed property in hydrogen Y zeolite heated below ~500°C, but is not exhibited by NaY zeolite irrespective of the calcination temperature. For activation temperatures above ~500°C, the marked decrease in the iodide oxidizing activity of hydrogen Y zeolite (Fig. 5) is accompanied by a sharp decline in the Bronsted acidity (*11*). As with the amorphous catalysts, molecular oxygen is necessary for the oxidation to occur.

The mechanism of the reaction in sulfuric acid solution, in the absence of a catalyst, initiator and light, involves the steps indicated below (*12*):

$$O_2 + H^+ + I^- + H_2O = H_2O_2 + IOH,$$
$$H_2O_2 + H^+ + I^- = H_2O + IOH,$$
$$IOH + H^+ + I^- = H_2O + I_2.$$

The agreement between the activation energies of the sulfuric acid and silica–alumina reactions and the fact that both reactions are first order with respect to the hydrogen ion concentration suggests that a similar mechanism operates in the system containing silica–alumina. An important difference, however, between the two oxidations is that in the presence of the amorphous or crystalline silica–aluminas the reaction is catalytic in nature and continues so long as a supply of iodide ion and oxygen is present (see Fig. 4). Experiments with one amorphous silica–alumina catalyst showed that even after 5 wk the amount of iodine in solution was still increasing linearly with time. It appears that, in the presence of water, the Bronsted sites on the oxide surface are being continuously regenerated as the oxidation proceeds. This is consistent with the view that the Bronsted acidity of silica–alumina arises from dissociative adsorption of water at sites in the lattice where the isomorphous substitution of aluminum for silicon has created the necessary redistribution of charge.

Tetramethylammonium iodide, in water or benzene, also liberates iodine in the presence of a silica–alumina catalyst, provided molecular oxygen is present. In benzene solution, however, the iodine concentration does not increase linearly with time, as is observed in water. Instead the plot exhibits marked curvature concave towards the axis representing time. Evidently, the hydrogen ion concentration is not being restored in the absence of water, a result that is to be expected if the explanation given above for aqueous systems is correct. Since there is no evidence of poisoning of the active surface sites by the tetramethylammonia residue in aqueous systems, similar poisoning in benzene solution seems unlikely.

Although silica–aluminas are active for the oxidation of methyl iodide, this activity is apparently determined by the alumina content of the mixed oxide. Pure alumina is 30 times more active than a typical cracking catalyst for methyl iodide oxidation (Table 3). Even the introduction of a small amount of silica into pure alumina results in a marked reduction in oxidizing activity. Because the temperature of activation that leads to maximum oxidizing power in alumina corresponds closely with the maximum in Lewis acidity (Fig. 6), Lewis acid sites may be involved in this oxidation. The production of methyl peroxy radicals upon the adsorption of methyl iodide on partially dehydroxylated alumina shows that basic sites may also be involved. Dissociative adsorption of methyl iodide may occur at a pair of adjacent Lewis acid–Lewis base sites, followed by association of the halogen atoms to produce molecular iodine.

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