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Infrared Study of Coke on Alumina and Zeolite

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In situ infrared studies of coke deposited on alumina or on platinum/alumina, by exposure to acetylene at 250°C, show a carboxylate species in the coke. This carboxylate produces a pair of bands at 1580 and 1460 cm^{-1}. This observation is contrary to literature reports of infrared spectra of coke deposits on zeolites, which are equivalent to conventional spectra of carbonaceous materials and do not indicate the presence of an oxidized species in the coke. Study of the hydroxyl bands of alumina during coke deposition shows that only the higher frequency bands are consumed. These high-frequency hydroxyls are considered to be the more basic. This suggests that carboxylates are not formed on zeolites because none of the hydroxyls in zeolites have a sufficiently basic character. Previous work has shown that the addition of tin to alumina lowers both the production of carboxylate and total coke. This is consistent with the decrease in hydroxyls which tin produces. After severe sulfiding, only small quantities of carboxylates and conventional coke are observed on alumina. Conventional coke, but not carboxylate, is observed on sulfided platinum/alumina.

INTRODUCTION

Previous work has shown that a carboxylate was present as a minor constituent in coke deposited by exposing alumina and platinum/alumina to acetylene at 250°C (1). Extensive infrared studies reported in the literature show that molecules which contain a single oxygen atom, such as alcohols or aldehydes, tend to form carboxylates when heated in contact with alumina (2–4). These results are of interest because the mechanisms, which were proposed for the formation of carboxylates from molecules containing only a single oxygen, may be pertinent to the formation of carboxylates from hydrocarbons.

The presence of an oxidized species in a hydrocarbon coke is unexpected because this coke deposition involves reducing conditions. Less carboxylate is formed when rhenium is added to platinum/alumina (1). Addition of rhenium improves catalyst performance without significantly lowering total coke in commercial catalytic reforming. This suggests the interesting, but unproven, possibility that carboxylate in coke may have an especially deleterious effect on reforming catalyst performance.

The observation of carboxylate was not confirmed in infrared studies of coke deposition on zeolites (5, 6). These studies reported what may be considered spectra of conventional coke. For example, Blackmond *et al.* observed a large band near 1585, a moderate band near 1340, and a small band near 1460 cm^{-1} for coke deposited by exposure to hexene at 300°C. The large band near 1585 cm^{-1} is commonly ascribed to the carbon–carbon stretching vibration in aromatic rings.

The work to be reported here focuses on two questions. The first involves the factors which produce carboxylates on alumina and conventional coke on zeolites. This could have been due to differences in surface properties or to differences in experimental procedures. It was found that the nature of alumina surfaces is the critical factor. This shifts the study to the source of the oxygen which produces carboxylates.

When the reactant is a hydrocarbon, the only source of oxygen is the alumina surface. This oxygen might be available through a surface reduction or by hydration reactions involving surface hydroxyls. A nonstoichiometric, oxygen deficient alumina has been reported (7). The production of an aldehydic oxide species, involving oxygen obtained from a surface reduction, has been postulated as the source of catalyst deactivation in the isomerization of olefins over alumina (8). Formate production from fluoroalkyl ether was attributed to a "reactive oxygen center" rather than to hydration by surface hydroxyls of alumina (9). Alumina is an important hydration–dehydration catalyst. Thus, despite the examples which suggest that surface reduction could be the source of carboxylate oxygen, efforts were made to determine the behavior of surface hydroxyls during coke deposition.

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EXPERIMENTAL METHODS

The infrared spectra were obtained with an Analect FX-6160 FTIR spectrometer. This instrument operates efficiently over most of its spectral region with a resolution of 2 cm^{-1} after 200 scans. However, difficulties are encountered at the edge of the spectral region near 3700 cm^{-1}. This is a serious problem because the surface hydroxyl bands are found in this region. To circumvent this difficulty, 2000 scans were used to obtain Fig. 4. Despite a 2-h scanning time, only four of the expected five surface hydroxyl bands of alumina could be resolved. Because of the spectral performance in the 3700-cm^{-1} region, other studies involving surface hydroxyls, such as Figs. 5 and 6, were carried out using samples which had been deuterated by exposure to deuterium at 350°C. Deuteration shifts the bands into the 2700-cm^{-1} region. The deuterated acetic acid which was 99.5% pure was obtained from the Aldrich Chemical Company.

The alumina was Aluminum Oxide-C which was donated by the Degussa Corporation. This is a γ-alumina of relatively low surface area, about 100 m^2 g, which is similar to Alon-C which was used in early infrared studies. The alumina was pressed into discs which weighed 75–100 mg with a face area of 2.6 cm^2. When spectra are compared, the absorbance scales are normalized to 100 mg discs, i.e., the observed values are multiplied by 100 and divided by the actual weight of the disc. Prior to coke deposition the samples were evacuated at 350°C for one hour and then reduced in the infrared cell at 350°C. Static hydrogen, purified by passage through a Fisher Scientific DEOXO unit, was used at one atmosphere pressure with three changes of hydrogen over a period of 24 h. The effect of hydrogen reduction is of some interest to the interpretation of experimental results. However, the main reason for reducing all samples was related to the fact that the aluminas were also used as references for experiments involving supported metals.

The HY zeolite was pretreated in the same manner as the alumina. It has a silicon/aluminum ratio of 2.6. The HY zeolite was prepared from a NaY zeolite which had been synthesized at the Institute of Industrial Chemistry, Warsaw. The NaY was exchanged with 10% ammonium nitrate to a NH_4/Na ratio of 0.77 and then heated to 450°C.

Sulfiding involved treatment with 10 Torr of H_2S (1 Torr = 133.3 N m^{-2}) for 1 h. The H_2S was obtained from Air Products and was used as received. Sulfiding added 0.8 wt% sulfur to the alumina and 1.4% sulfur to the 3% Pt/Al_2O_3 which had been prepared using chloroplatonic acid and conventional impregnation to incipient wetness methods. The sulfur analyses were provided by Galbraith Laboratories, Inc.

Coke deposition was carried out at 250°C by exposure to acetylene at a pressure of 10 Torr. A temperature of 350°C was used for coke deposition with 10 Torr ethylene. The acetylene, Union Carbide Specialty Grade, was passed through a tube containing glass beads at −78°C to remove acetone. This treatment is critical because the acetylene may contain acetone. A detailed description and evaluation of this purification procedure is available (1). The ethylene, Union Carbide Specialty Grade, was used as received.

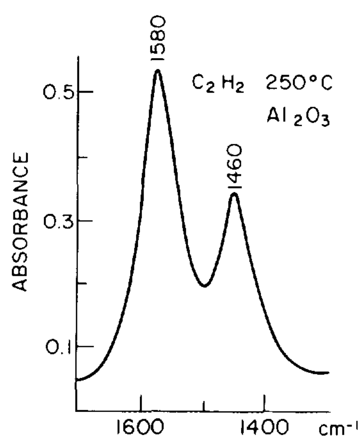


FIG. 1. Carboxylate bands on alumina.

A T-shaped pyrex infrared cell was wound with a heating tape. The two ends of the 5-in. short arm of the cell were sealed to CaF_2 windows with Apiezon W wax and cooled with running water. The samples were suspended from a Cahn 1000 microbalance through the center arm of the T-cell. This made it possible to make an *in situ* measurement of the total weight of the deposited coke.

The 3 wt% Sn/Al_2O_3 sample of Fig. 6 was prepared by impregnation to incipient wetness with a solution of tin chloride in nondeuterated water. After reduction with hydrogen, as described for alumina, the sample was deuterated by exposure to deuterium at 350°C.

EXPERIMENTAL RESULTS

Figure 1 shows the carboxylate bands at 1580 and 1460 cm^{-1} in the spectrum of coke produced by exposure of alumina to acetylene for 6 h. The bands grow at the same rate, as would be expected for a pair of bands from a single species. The total coke level, as measured by the Cahn balance, is about 1 wt%. Calibration, based on comparison of band absorbances with those obtained from addition of acetic acid, indicates that about one-sixth of the total carbon is present as carboxylate (1). The other five-sixths of the coke appears to be poor in hydrogen because only weak carbon–hydrogen bands are observed. Both of the bands show the expected shift of about 20 cm^{-1} when oxygen-16 in the alumina is replaced with oxygen-18 (10). This shift proves only that the bands are

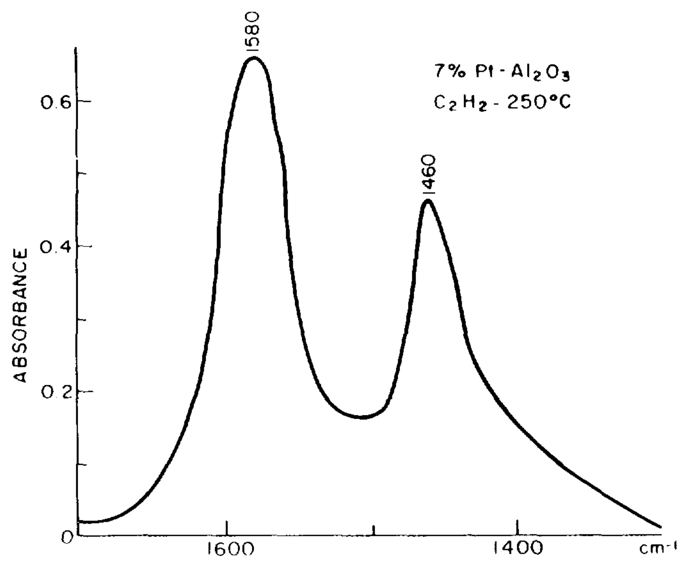


FIG. 2. Carboxylate bands on platinum/alumina.

produced by an oxygen-containing species. This species is referred to as a carboxylate because the bands are similar to those observed after chemisorption of acetic acid. It is not considered to be a formate because formic acid produces bands at 1595 and 1830 cm^{-1}. Carbon dioxide produces bands at 1640 and 1420 cm^{-1}. The carboxylate assignment has a weakness in that bonding to the second carbon is not evident. The methyl group in acetate produces a CH_3 deformation at 1390 cm^{-1}. Despite this weakness the carboxylate assignment appears to be the most reasonable and will be used here. The important question involves the differences between the carboxylate bands and the bands of a conventional coke. The production of carboxylate bands reaches a maximum. This suggests that they are surface-bound. Figure 1 represents about one-half the maximum intensity that can be produced by exposures of 20 h or more. This maximum is reached when the total coke level is about 2 wt%. Above this value total coke increases but carboxylate band intensity does not increase. At the maximum band intensities each carboxylate occupies about 85 Å^2 (1). Thus, Fig. 1 represents a carboxylate surface coverage of about 15%.

Figure 2 shows carboxylate bands, produced by acetylene, on a 7% Pt/Al_2O_3 sample under conditions similar to those of Fig. 1. Platinum causes a small increase in total coke but the spectrum is dominated by carboxylate bands similar to those observed on alumina.

Carboxylate was not observed by Blackmond *et al.* (5) in an in situ study of coke deposition on HY zeolite after exposure to hexene at 300°C. They observed a strong band at 1585, a moderate band at 1340, and a small, barely detectable band near 1460 cm^{-1}. Similar spectra were observed by Lange *et al.* (6) after exposure of hydrogen mordenite to ethylene. Carboxylates were also not observed in a study of coke formation on zeolites containing only Lewis acids or both Lewis and Brønsted acids (11).

Figure 3 shows the spectrum of coke deposited on HY zeolite under experimental conditions similar to those which produced Fig. 1 for alumina, i.e., acetylene at 250°C. The bands in Fig. 3 resemble those which have been described for a conventional coke. Figure 3 is similar to those observed by Blackmond *et al.* The differences between Figs. 1 and 3 are attributable to the characteristics of the alumina and zeolites. Experimental variables, such as the difference between hexene and acetylene, can be excluded.

As stated previously, the strong bands in the 1580–1600 cm^{-1} region are commonly assigned to the carbon–carbon stretch in aromatic rings. The other bands are assigned to carbon–hydrogen deformations. The 1580-cm^{-1} band is observed in carbonaceous materials such as coal, charcoal, and carbon black. Smith *et al.* (12) produced a spectrum similar to Fig. 3 after grinding petroleum based charcoal in air. These bands were not observed when the charcoal was ground under nitrogen. These significant experiments appear to cast doubt on the assignment of the 1580-cm^{-1} region band to aromatic carbon–carbon alone. However, Smith *et al.* continue to support the aromatic carbon–carbon vibration as one component of the 1580-cm^{-1} region absorption (13). Their explanation of the grinding experiments is that the specific intensity of carbon–carbon vibration is enhanced by dissymmetry caused by carbon–oxygen species on the edges of the aromatic rings.

Whatever the band assignments, Fig. 3 shows that observation of carboxylate in Fig. 1 is not attributable to differences in experimental procedure. Rather, they are due to differences in the surface properties between alumina and silica alumina as represented by the HY zeolite. This focuses attention on the role of surface hydroxyls in the formation of carboxylates.

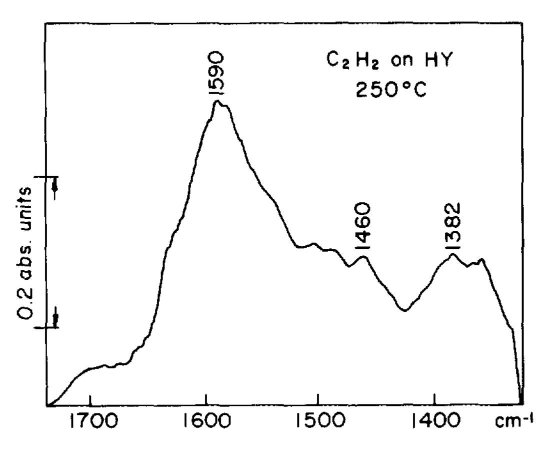


FIG. 3. Coke deposited on HY zeolite from acetylene at 250°C.

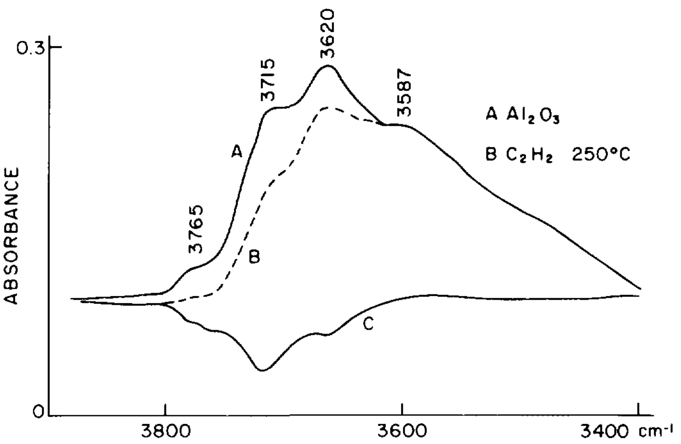


FIG. 4. Effect of carboxylate formation on surface hydroxyl bands: (A) alumina prior to coking, (B) after coking with acetylene, and (C) difference between (A) and (B).

Figure 4 illustrates the effect of carboxylate formation on the surface hydroxyls of alumina. Spectrum (A), observed before exposure to acetylene, shows bands at 3765, 3715, 3670, and 3527 cm^{-1}. Spectrum (B) was observed after exposure to acetylene for 20 h at 250°C. Spectrum (C) is the difference between Spectrum (A) and Spectrum (B). It is apparent that the higher frequency hydroxyl bands decrease during carboxylate formation while the low-frequency bands are relatively unaffected. After deuteration of the alumina, OD bands are found at 2653, 2707, 2737, 2776, and 2798 cm^{-1}. After a 6-h exposure to deuterated acetylene at 250°C, decreases in the OD bands, similar to Fig. 4, are observed.

Figure 5 was observed after a short exposure of deuterated alumina to deuterated acetic acid at 250°C followed by evacuation at 250°C. It is seen that the carboxylate formation, caused by acetic acid, eliminates the higher frequency hydroxyl bands. However, the results are not as well defined as in Figure 4 because the lower frequency bands also show some decrease. The carboxylate bands produced by deuterated acetic acid are found at 1560 and 1454 cm^{-1} (10). Deuteration of acetic acid produces isotopic shifts of 19 and 11 cm^{-1} in the carboxylate bands. These shifts will be discussed below.

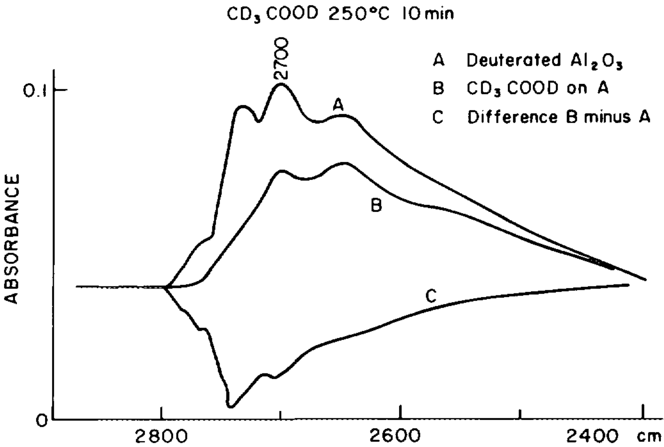


FIG. 5. Effect of deuterated acetic acid on deuterated alumina.

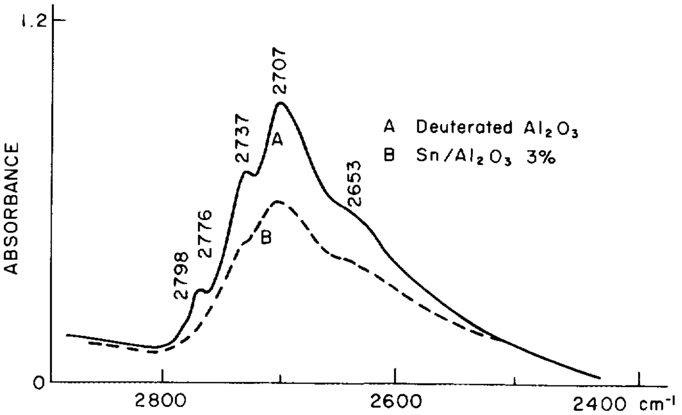


FIG. 6. Effect of tin on deuterated hydroxyl groups of alumina.

Carboxylate formation is decreased by addition of tin to alumina (14). Figure 6 shows the effect of tin on deuterated hydroxyl groups of alumina. Spectrum A is from deuterated alumina and Spectrum (B) is from a deuterated 3 wt% Sn/Al_2O_3. Both the high- and low-frequency bands of Spectrum B have been decreased compared to Spectrum (A). Since both high- and low-frequency bands have been affected by tin, the results are also not as well defined as those in Fig. 4. However, Fig. 6 is consistent with the concept that tin decreases carboxylate formation because it decreases surface hydroxyls. The general decrease in hydroxyl bands observed in Spectrum (B) of Fig. 6 is similar to published observations of this effect when difficulty reduced metals are added to alumina (15, 16).

Treatment with H_2S at 350°C is expected to affect the hydroxyls of alumina. Spectrum (A) of Fig. 7 shows the spectrum of coke deposited on a 3 wt% Pt/alumina sample that had been treated with H_2S until the sulfur content was 1.4%. The coke was deposited by exposure to ethylene at 350°C. Spectrum (A) resembles Fig. 3. The spectrum is that of a conventional carbonaceous coke and there is no evidence for significant amounts of carboxylate. Figure 2 shows that exposure of unsulfided Pt/Al_2O_3 to ethylene at 350°C produces carboxylate spectra similar to Fig. 1. Addition of 3% Pt to alumina has a negligible effect on carboxylate formation but it produces a moderate increase of 15–25% in total coke (1, 14). These increases in total coke are not observable in the infrared spectra. Exposure of unplatinized alumina, sulfided to 0.8% sulfur, to ethylene at 350°C, produces only weak, poorly defined bands. This is shown in Spectrum (B). These bands clearly do

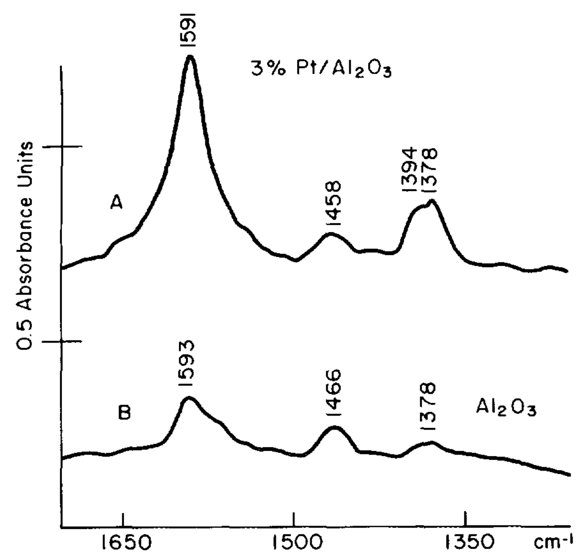


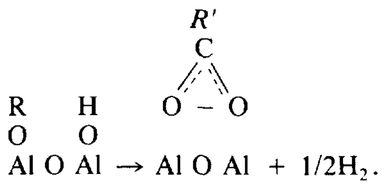
FIG. 7. Spectrum (A): Coke deposition from ethylene at 350°C on sulfided platinum/alumina. Spectrum (B): Coke deposition on sulfided alumina.

not represent significant carboxylate formation and any bands that could represent conventional coke are small compared to the bands of Spectrum (A).

DISCUSSION

The higher frequency hydroxyl bands of alumina are generally ascribed to the most basic hydroxy groups. Boehm and Knozinger (17) relate the higher stretching frequency to the higher negative charge of these hydroxyls. Peri (18) attributes the higher frequency to hydroxyls which have a larger number of close neighbor negative oxygen ions. Both of these interpretations imply a stronger hydroxyl basicity. Boehm (19) has reported that the basic hydroxyls of titania react with olefins to produce a surface alcoholate, Ti–O–*R*. The corresponding reactions of unsaturated hydrocarbons and hydroxyls of alumina would produce Al–O–*R*. This is equivalent to the alkoxide which Kagel (3) visualizes as the precursor of carboxylates on alumina from alcohol. The disappearance of the basic hydroxyl groups shown in Fig. 4, coupled with the conclusions of Boehm and Kagel, indicates that the formation of carboxylates may be related to basic groups that are found on alumina but not on zeolites. Therefore, concepts involving reduction of the alumina are not favored. The reduction of alumina as the source of the carboxylate oxygen is also not consistent with the fact that the alumina had been reduced with hydrogen prior to coke deposition. Prereduction has no detectable effect on carboxylate formation. The lack of effect of pretreatment with hydrogen has also been reported by Greenler (2) in his study of carboxylate formation from alcohol.

Kagel (3) and Deo and Dalla Lana (4) postulate that the carboxylate, produced by heating alumina with alcohol, is produced by reaction of the surface alcoholate with a hydroxyl to add a second oxygen and evolve H_2:



$$\begin{matrix} R & H \\ O & O \\ \mathrm{Al} & \mathrm{O} & \mathrm{Al} \end{matrix} \rightarrow \begin{matrix} & R' & \\ & C & \\ O & - & O \\ \mathrm{Al} & \mathrm{O} & \mathrm{Al} \end{matrix} + 1/2H_2.$$

Hydrogen evolution is observed during carboxylate formation on alumina (1). A negative finding for hydrogen evolution would be significant. However, the observation of hydrogen is necessary, but not sufficient, evidence for a mechanism such as outlined above. Hydrogen could be evolved by simple dehydrogenation of the hydrocarbon during formation of conventional coke.

The results of the deuterated acetic acid, tin, and H_2S experiments of Figs. 5, 6, and 7 do not prove the concept that it is the basic hydroxyls which are necessary for carboxylate formation. However, these results do indicate that surface hydroxyls are important factors. Thus, they indirectly add credibility to the basic hydroxyl concept.

The experimental study of the effect of carboxylate formation on hydroxyls was undertaken to determine whether surface hydroxyls or an "active surface oxygen" was the source of oxygen for converting hydrocarbons to carboxylates. The observation that the higher frequency hydroxyls were the most active led to the concept that the difference between alumina and zeolite was attributable to the lack of basic hydroxyls on zeolites. Other reasons for the difference between alumina and zeolites can be visualized. For example, the above mechanism for the conversion of an alkoxide to a carboxylate might be due to the absence of close neighbor aluminums in the zeolites. The favored mechanism, which is taken from publications (2–4) involving alcohols shows an Al–O–Al structure which is not found in pure zeolites. This structural reason for the observed differences in carboxylate formation is not favored because there is no experimental result that can be quoted to support it.

Eisenbach and Gallei reported an infrared study of the effect of coke deposition on the hydroxyls of HY zeolite (20). Exposure of the zeolite to hexene or hexane at temperatures up to 500°C produced coke spectra similar to Fig. 3. The HY zeolite spectrum showed hydroxyl bands at 3740 and 3640 cm^{-1}. The 3640-cm^{-1} band decreased as coke was deposited but the 3740-cm^{-1} band was not affected. They attributed the 3640-cm^{-1} band to OH groups in supercages and the 3740-cm^{-1} band to external OHs. Overall they visualize an acid catalysed carbonion ion mechanism for the coke deposition. They also observed a band at 3585 cm^{-1} for a PtCa Y zeolite. This band, which was attributed to $Ca(OH)^+$, has basic properties and its lack of activity is not consistent with the conclusion relating to basic hydroxyls of alumina. However, the difference between a hydroxyl in a $Ca(OH)^+$ cation and a surface hydroxyl on alumina is so great that the comparison is not pertinent.

There are two possible mechanisms for the decrease in hydroxyl groups which is shown in Fig. 6. The hydrochloric acid, formed by hydrolysis of tin chloride during sample preparation, might react with the surface hydroxyls. However, it is more likely that tin could react to form an Al–O–Sn species. Reactions similar to this tin reaction have been reported for vanadium, molybdenum, chromium and rhenium (16). It is less reasonable to attribute lowering of carboxylate formation to hydrochloric acid because preparations using chloroplatinic acid do not show this effect. Moreover, auxiliary experiments in the study of oxygen-18 band shifts showed that treatment of alumina with hydrochloric acid did not affect carboxylate formation (10). Although it might be expected that hydrochloric acid would affect basic hydroxyls, any such effect appears to be vitiated by the high temperature evacuation prior to reduction with hydrogen. It is therefore reasonable to assume that the lowering of carboxylate formation by tin and rhenium and the absence of this effect for platinum are related to the ease of reducing the metal. Tin or rhenium cations would be attracted to the more negative basic sites.

The assignment of the two bands in Figs. 1 and 2 to carboxylates draws heavily on the previous work with alcohols, especially that of Greenler (2). Greenler showed that the bands observed after heating ethyl alcohol on alumina are similar to the bands of aluminum acetate. He also showed that the bands at 1572 and 1466 cm^{-1} are shifted by 12 and 13 cm^{-1}, respectively, in deuterated systems. These small shifts are consistent with those observed with deuterated sodium acetate (21, 22). Galuszka and Amenomiya reported an infrared study of coke deposition from acetylene over Ni/Al_2O_3 and Al_2O_3 at temperatures up to 250°C (23). They observed bands at 1580 and 1460 cm^{-1}. For Ni/Al_2O_3 the 1580-cm^{-1} region was complex and there appeared to be three bands. After deuteration the 1589-cm^{-1} band for Ni/Al_2O_3 shifted by 37 cm^{-1} and the 1459-cm^{-1} band decreased and new bands were observed at 1444 and 1338 cm^{-1}. No bands attributable to C–D vibrations were observed. On the basis of the more pronounced shifts, Galuszka and Amenomiya attributed the bands to aromatic species and did not accept the carboxylate assignments of Refs. (1, 2). The oxygen-18 experiments of Ref. (10) were not then available.

A report by Espinat *et al.* (24) describes a Raman study of coke deposition on alumina and commercial reforming catalysts. Heptane was the primary hydrocarbon but in some cases this was supplemented with hexene or benzene. Carbon deposits, which range from 0.29 to 20 wt% show strong bands near 1600 and 1350 cm^{-1}. There is little or no evidence for a band near 1460 cm^{-1} which would indicate the possibility of carboxylate. Since the samples used by Espinat *et al.* were alumina, or alumina with supported metals, it at first appears that there is a major discrepancy between their findings and those which are the basis of conclusions based on results reported above. The absence of carboxylates in the spectra of Espinat *et al.* is best explained on the basis of the high coke deposition temperatures which they used. Most of their coke depositions were carried out at temperatures of 500°C or higher. It is expected that carboxylates would have decomposed at these high temperatures. They carried out one experiment at 350°C but this involved only heptane as the hydrocarbon source and the amount of coke was 0.29%. It is also possible that higher sample pretreatment may be a factor. Their samples were dried at 530°C. It is known that severe dehydroxylation will limit carboxylate formation (1).

Spectrum (A) of Fig. 7 is similar to Fig. 3. It can be assigned to a conventional coke with an aromatic C–C stretching band at 1591 cm^{-1} and CH_2 and CH_3 bendings at 1458, 1394, and 1378 cm^{-1}. There is no evidence for carboxylates as seen for unsulfided Pt/Al_2O_3 in Fig. 2. Small quantities of carboxylate might be concealed in the 1591- and 1458-cm^{-1} bands. However, assignment of the 1458-cm^{-1} band to the symmetric carboxylate vibration is not consistent with the moderately stronger bands at 1394 and 1378 cm^{-1}. In Spectrum (B) the coke bands for sulfided Al_2O_3 are so small that it is dificult to interpret them. They probably represent a mixture of carboxylate and conventional coke. Thus it appears that Spectrum (A) of Fig. 7 can be attributed to coke on sulfided platinum. Sulfiding has a strong effect on the ability of the platinum to chemisorb carbon monoxide. At 100°C a barely detectable small band at 2109 cm^{-1} attributable to chemisorbed carbon monoxide is retained after evacuation. An unsulfided platinum will chemisorb carbon monoxide under these conditions as shown by a strong chemisorbed CO band in the 2060-cm^{-1} region. No comprehensive effort was made to study the effect of coking sulfided Pt/Al_2O_3 and Al_2O_3 as was made for Fig. 3. Using short times, one tenth as long as for Fig. 3, the hydroxyl bands could not be resolved. Overall the hydroxyl band on sulfided samples did not appear to be affected by coke deposition.

The study of the effect of carboxylate formation on alumina hydroxyls is part of a broader study of bimetallic reforming catalysts. This bimetallic study is based on the observation that addition of tin or rhenium both lowers carboxylate formation and improves the performance of bimetallic reforming catalysts. In the case of rhenium the improved performance can be partially attributed to a difference in the nature of coke deposits. The hydroxyl study, which is reported here, does provide supplemental information which may be relevant to bimetallics. However, the specific relationship between carboxylates in coke and catalyst performance has not been clarified.

CONCLUSIONS

It is concluded that formation of carboxylate during coke deposition on alumina is attributable to reactions which involve the presence of basic hydroxyl groups on alumina and not due to differences in experimental procedures. This conclusion is mainly based on the disappearance of the high-frequency bands during carboxylate formation. The absence of carboxylates during coke formation on HY zeolites under equivalent experimental conditions is attributed to the absence of basic hydroxyls on these zeolites. This is consistent with reports in the literature which relate coke formation on zeolites to acidity (11, 20, 25).

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REFERENCES

1. Ludlum, K. H., and Eischens, R. P., "Preprints of the Petroleum Division, American Chemical Society Meeting, April 1976."
2. Greenler, R. G., *J. Chem. Phys.* **37,** 2094 (1962).
3. Kagel, R. O., *J. Phys. Chem.* **71,** 844 (1967).
4. Deo, A. V., and Della Lana, I. C., *J. Phys. Chem.* **73,** 716 (1969).
5. Blackmond, D. G., Goodwin, J. G., Jr., and Lester, J. E., *J. Catal.* **78,** 34 (1982).
6. Lange, J-P., Gutsze, A., Allgeier, J., and Karge, H. G., *Appl. Catal.* **45,** 345 (1988).
7. Teichner, S., Jullet, F., and Arghiropoulos, B., *Bull. Soc. Chim. Fr.*, 1491 (1959).
8. Corado, A., Kiss, A., Knozinger, H., and Muller, H.-D., *J. Catal.* **37,** 68 (1975).
9. Basu, P., Ballinger, T. H., and Yates, J. T., *Langmuir* **5,** 502 (1989).
10. Najbar, J., and Eischens, R. P., "Proceedings of the 9th International Congress on Catalysis, Calgary 1988," Paper 184 Ab.
11. Datka, J., *Zeolites* **1,** 145 (1981).
12. Smith, D. M., Griffin, J. J., and Goldberg, E. D., *Anal. Chem.* **47,** 233 (1975).
13. Akhter, M. S., Kiefer, J. R., Chughtai, A. R., and Smith, D. M., *Carbon* **23,** 589 (1985).
14. Datka, J., and Eischens, R. P., *in* "Proceedings of the 5th International Symposium on Catalyst Deactivation, Evanston 1991" (C. H. Bartholomew and J. B. Butt, Eds.). Elsevier, Amsterdam, 1991.
15. Millman, W. S., Crespin, M., Cirilla, A. C., Abdo, S., and Hall, W. K., *J. Catal.* **60,** 404 (1979).
16. Wachs, I. E., *Chem. Eng. Sci.* **45,** 2561 (1990).
17. Boehm, H. P., and Knozinger, H., "Catalysis Science and Technology" (M. Boudart, Ed.), Vol. 4. Springer-Verlag, Berlin/New York, 1983.
18. Peri, J., *J. Phys. Chem.* **65,** 220 (1969).
19. Boehm, H. P., *Kolloid Z. Z. Polym.* **227,** 17 (1968).
20. Eisenbach, D., and Gallei, E., *J. Catal.* **56,** 377 (1979).
21. Jones, L. H., and McLaren, E., *J. Chem. Phys.* **22,** 1796 (1954).
22. Ito, K., and Bernstein, H. J., *Can. J. Chem.* **34,** 170 (1956).
23. Galuszka, J., and Amenomiya, Y., *in* "Proceedings, 9th International Congress on Catalysis, Calgary, 1988" (M. J. Phillips and M. Ternon, Eds.), Vol. 2, p. 697. Chemical Institute of Canada, Ottawa, 1988.
24. Espinat, D., Dexpert, H., Freund, E., Martino, G., Couzi, M., Lespade, P., and Cruege, F., *Appl. Catal.* **16,** 343 (1985).
25. Karge, H. G., *in* "Introduction to Zeolite Science and Technology" (H. van Bekkum, E. M. Flanigan, and J. C. Jansen, Eds.), Chap. 4. Elsevier, Amsterdam, 1991.