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High-Temperature Acidity Measurements and Correlation with Catalyst Activity

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A method is described for the determination of catalyst acidity. It is based on the amount of oxygen used for the oxidation of ammonia retained on catalyst samples after they have been exposed to ammonia and outgassed at elevated temperatures.

The method is versatile. It allows for different pretreatments, in the same apparatus, in order to establish conditions for the development and measurement of optimum acidity. It provides a means for detecting changes in the type of acid sites resulting from variations in the preparation and pretreatment procedures.

One of the advantages of this method over the direct determination of adsorbed ammonia lies in its ability to distinguish between different types of acid sites. This distinction can be made on the basis of observed differences in the oxygen consumption pattern with varying adsorption and outgassing temperatures, and in the temperature required for oxidation of ammonia adsorbed on different sites.

Good correlations were obtained between acidity as measured by this method and catalytic activity for fluorided aluminas of different fluoride content, and for silica-aluminas of varying silica–alumina ratios.

The appearance, rise, and decline in one type of acidity with increasing pretreatment temperatures in NH_4-Y, rare earths-X, and rare earths-Y zeolites, coincides with the corresponding activity curve for ethylation of benzene. Another type of acidity, which increases steadily with increasing pretreatment temperatures, apparently has no pronounced influence on the activity. Therefore, any measure of "total" acidity would be misleading. Identification of these two respective types as Brönsted and Lewis acid sites is proposed.

INTRODUCTION

The importance of acid-type catalysis in the petroleum industry has been well established. Extensive research has been carried out to elucidate the nature of acid sites and to develop methods for their quantitative measurement which could be correlated with catalyst activity. The approaches are manifold but the frequent disagreement in the interpretation of results gives some indication of their complexity and ambiguity.

Past attempts in our laboratories to correlate acidity measurements with catalytic activity have met with only limited success, despite a variety of approaches. These included such techniques as adsorption and desorption of ammonia and other basic compounds (*1–4*), indicators in conjunction with amine titrations (*5–9*), IR, UV, and ESR observations of adsorbed species (*10–15*).

It was desirable, therefore, to develop a method for the quantitative measurement of catalyst acidity which could be shown to correlate with activity for such reactions as isomerization, alkylation, and catalytic cracking. Such a method must be capable of distinguishing between different acid sites since, in many cases, and even though more than one species is present, only one may be catalytically active in a given reaction.

Ammonia adsorption at elevated temperatures followed by temperature-programmed oxidations has been found in the present work to yield a measure of experimentally distinguishable types of adsorption sites. It is shown that the oxygen consumption, as a function of ammonia adsorption temperature, can be either independent or dependent upon the ammonia adsorption temperature over a range of temperatures. A distinction between two types of acid sites should be possible on the basis of observed differences in the oxygen consumption with varying ammonia adsorption temperatures.

Also, the onset of oxidation, the maximum oxygen consumption per unit time, and the termination of oxidation usually occur at different temperatures for ammonia retained by different types of acid sites. Thus, a two-step oxidation should be another technique for distinguishing between sites.

APPARATUS

The apparatus indicated schematically in Fig. 1 consists of a U-shaped glass sample tube; facilities for vacuum outgassing to 10^{-6} mm, for ammonia adsorption and for O_2-He flow; an oxygen analyzer (Beckman 39065 Polarographic Oxygen sensor and 96260 Adapter Box), and a recorder.

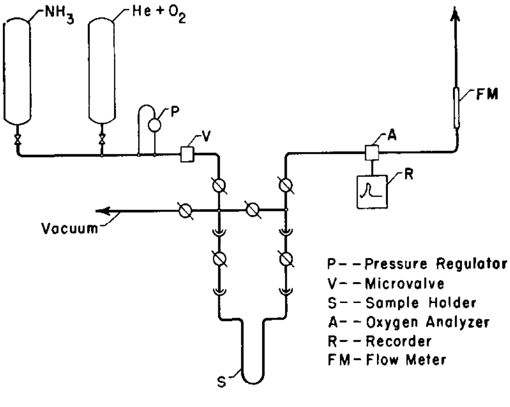


FIG. 1. Apparatus for catalyst acidity determination.

PROCEDURE

The basic experimental procedure consists of the following steps:

(1) Pretreatment by outgassing a 1-g sample for ½ hr in a vacuum at elevated temperature (*Pretreatment Temperature*). In this step, samples which have been previously dried for 1 hr at 110°C, or have been calcined, are subjected to a heat treatment in which the temperature is raised at the rate of 15–20°C/min until the desired temperature is reached. The samples are maintained at this temperature for ½ hr.

(2) Exposure to ammonia at 1 atm pressure and elevated temperature for ½ hr.

(3) Outgassing for ½ hour at the same temperature [(2)+(3); *Adsorption Temperature*].

(4) Cooling to room temperature in vacuum.

(5) Passing a stream of 2% oxygen in helium over the sample while the temperature is being raised to 750°C at a rate of 15°C/min (*Oxidation Temperature*).

(6) Measuring changes in the oxygen level of the exit gas by oxygen analyzer and computing total oxygen consumption.

The specific temperatures employed in the various steps depend on the type of information desired and will be discussed later in the examples given.

The amount of ammonia retained on catalyst samples was determined by oxidation. The oxidation products and the stoichiometry of the oxidation reaction under experimental conditions were investigated. Oxidation of known amounts of ammonia adsorbed on a variety of catalysts led to oxidation products. These, when separated over a Porapak column, identified by retention times, and quantitatively analyzed by the Dumas method, showed that nitrogen was the major product of oxidation. Trace amounts of oxides of nitrogen were observed. Results indicated that the oxidation of ammonia follows the reaction: $4NH_3 + 3O_2 = 2N_2 + 6H_2O$, nearly exclusively.

SAMPLE DESCRIPTION

Silica-aluminas. All samples were prepared by adding calculated amounts of silicate solution to pH-adjusted aluminum chloride solutions. After gelation and dropping (sphere formation), they were calcined in air at 600°C for 2 hr.

Fluorided aluminas. These samples were prepared by impregnation of γ-alumina with calculated amounts of ammonium fluoride

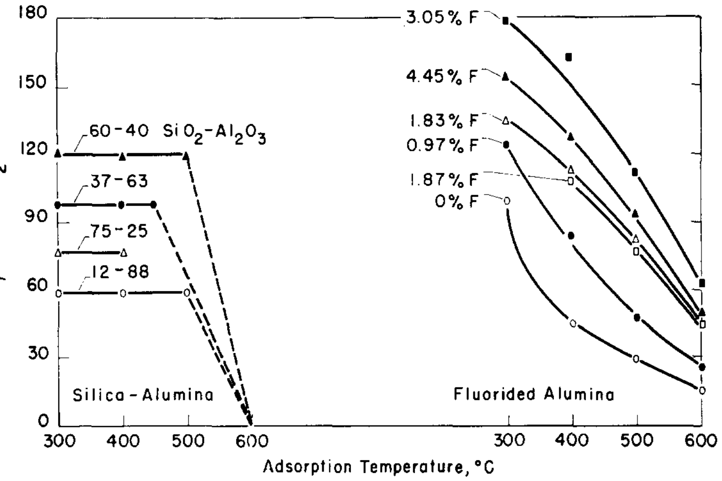


FIG. 2. Oxygen consumption versus ammonia adsorption temperatures for fluorided aluminas and silica-aluminas.

solution at pH = 9. They were dried in perfluent nitrogen at 600°C for 3 hr and sealed in ampoules.

NH_4-Y zeolite. The ammonium form was obtained by conventional ion exchange of Ca-Y zeolite with aqueous ammonium chloride solution at 90°C and subsequently dried at 110°C. Analysis showed the composition to be 5.7% NH_3, 1.62% Na_2O, 2.04% CaO, 63.5% SiO_2, and 22.4% Al_2O_3.

Ce-X zeolite. The cerium form was prepared by conventional ion exchange of Na-X zeolite with aqueous $Ce(NO_3)_3$ solution at 90°C and subsequently dried at 110°C. Analysis gave 29.0% Ce_2O_3, 1.05% Na_2O, 41.8% SiO_2, and 28.5% Al_2O_3.

Ce-Y zeolite. The cerium form was prepared by conventional ion exchange of Na-Y zeolite with $Ce(NO_3)_3$ solution at 90°C and subsequently dried at 110°C. Analysis gave 15.3% Ce_2O_3, 4.3% Na_2O, 59.0% SiO_2, and 21.4% Al_2O_3.

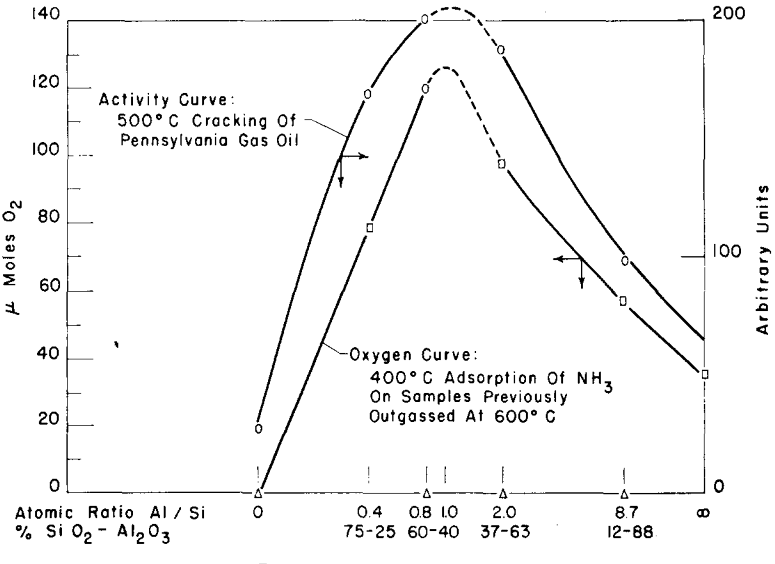


FIG. 3. Acidity of silica-alumina as a function of composition.

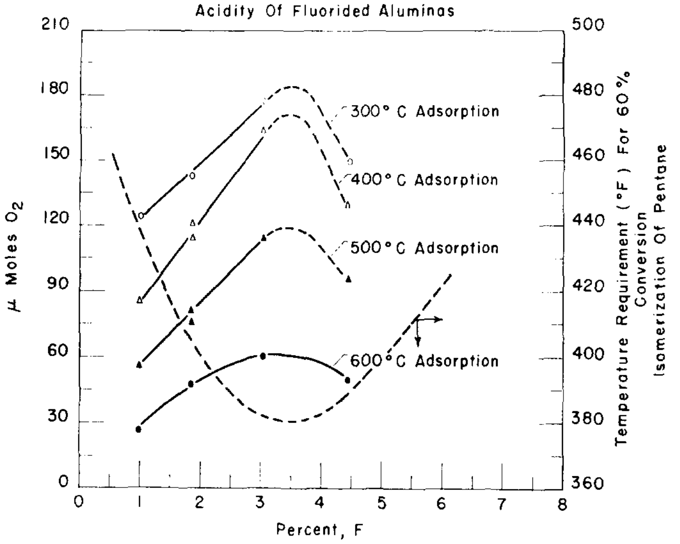


FIG. 4. Acidity of fluorided aluminas as a function of composition.

RESULTS

Silica-Aluminas

The oxygen consumptions for silica-aluminas of various composition after pretreatment at 600°C and NH_3 adsorption at 300°, 400°, 500°, and 600°C, respectively, are plotted in Fig. 2 as a function of adsorption temperature. Experimental data for silica-aluminas having different Al/Si ratios, 100% silica, and 100% alumina correlate well (Fig. 3) with an activity curve for Pennsylvania gas oil cracking (*16*). Maximum acidity and activity are observed for silica-aluminas having an Al/Si ratio of unity.

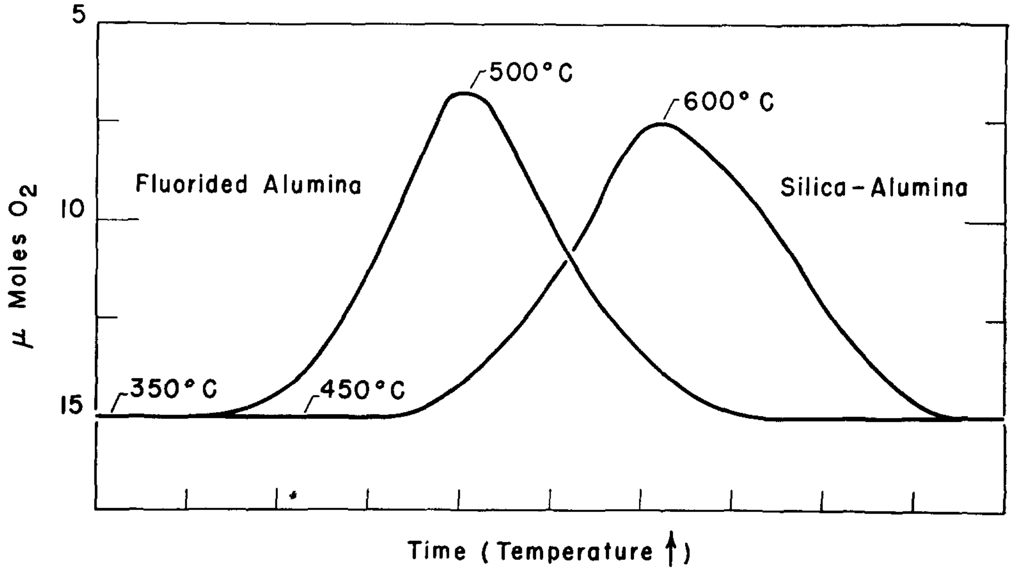


FIG. 5. Response of oxygen analyzer versus temperature for ammoniated samples (linear temperature increase of 15°C/min).

Fluorided Aluminas

The oxygen consumption for fluorided aluminas containing from 0% to 4.45% F, after pretreatment at 600°C and NH_3 adsorption at 300°, 400°, 500°, and 600°C, respectively, are plotted in Fig. 2 as a function of NH_3 adsorption temperature.

The reproducibility of the method is exemplified by inclusion of a sample from another series of fluorided aluminas (1.87% F).

The amounts of oxygen used for the oxidation of ammonia retained on these fluorided aluminas at various adsorption temperatures, plotted in Fig. 4 versus fluoride content, correlate with an activity curve based on the temperature requirement for 60% isomerization of pentane. (*17*) The maximum oxygen consumption for alumina containing 3.5% F coincides with a minimum temperature requirement and, therefore, maximum activity.

A comparison of the results plotted in Fig. 2 for silica-aluminas and fluorided aluminas indicates a substantial difference in the behavior of the two types of catalysts toward ammonia adsorption and oxidation. A further difference in the behavior of the two catalyst systems is given in Fig. 5, which indicates different temperature requirements for the oxidation of ammonia retained by the two catalyst types.

Use will be made in subsequent examples of the different shapes of the oxygen consumption-versus-temperature curves, to distinguish between the two types of acid sites when both are present in a sample.

The results shown in Fig. 5 should be further clarified as follows:

The oxygen sensor located in the effluent from the sample holder measures the partial pressure of oxygen. Since oxidations are carried out with a blend of 2% oxygen in helium, the recorder base line represents 15.2-mm partial pressure of oxygen in the effluent. In the case of fluorided aluminas which had been subjected to steps (1) through (4) of the procedure, linear temperature programming of the oxygen-helium flow produces a recorder deflection indicative of the onset of oxidation at about 400°C. Maximum oxygen consumption per unit time is observed at 500°C, while the ammonia oxidation is essentially completed at 600°C. For ammoniated silica-aluminas the onset, maximum rate, and termination of the oxidation reaction occurred at temperatures about 100°C higher than those needed for the oxidation of ammonia on fluorided aluminas (Fig. 4). The integrated area under the curves is a measure of the total oxygen consumption for each sample.

A mechanical 50–50 mixture of fluorided alumina, containing 3.05% of fluorine, and a 37–63 silica-alumina, was outgassed at 600°C, exposed to ammonia at 500°C, and then subjected to a two-step oxidation. The temperature was first raised to 475°C and held at this temperature until the oxygen sensor output returned to base line. The integrated area under the oxygen consumption curve for the mixed sample was one-half of that obtained for the acid sites of a 100% fluorided alumina. By increasing the temperature to 625°C, the oxygen consumption for the oxidation of ammonia retained on the acid sites of the silica-alumina was determined. This also matched one-half of the oxygen uptake required for 100% silica-alumina.

Zeolites

In preliminary studies of various ion-exchanged zeolites, major changes were observed in the type of acid sites as well as in their concentrations, and depended on the pretreatment temperatures used. Having available the catalytic activity-versus-calcination temperature information for RE-X, RE-Y, and NH_4-Y zeolites (*18*), we considered these systems to be good test cases for establishing whether or not a correlation with ammonia adsorption and oxidation patterns can be observed.

NH_4-Y Zeolite

Since the range of pretreatment temperatures employed coincides to some extent with the temperatures observed for the transition of the ammonium to the hydrogen form, corrections for the intrinsic oxygen consumption by the samples must be made. The oxygen consumption was determined for samples of NH_4-Y zeolite which have been pretreated by outgassing at 400°, 500°, 600°, 650°, and 750°C, respectively, and which have not been exposed to ammonia (Fig. 6, filled circles). It can be seen that, under the experimental conditions, complete conversions of the ammonium form to the hydrogen form of the zeolite are accomplished only after treatment at 600°C. The total consumption for samples pretreated at the same temperatures, but which have subsequently been exposed to ammonia and outgassed at 500°C only (Fig. 6), and when corrected for the blank, show that acidity increases essentially linearly with increasing pretreatment temperatures. As will be shown in Fig. 8, this acidity measurement does not correlate with catalytic activity.

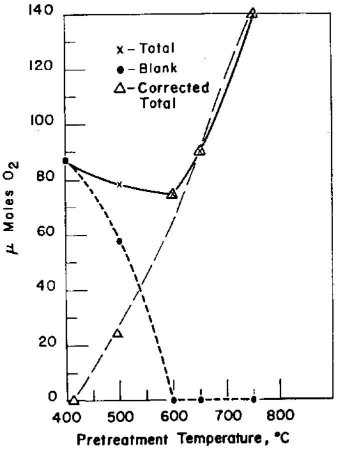


Fig. 6. Acidity of NH_4-Y zeolite as a function of pretreatment temperature.

A plot of oxygen consumption versus ammonia adsorption temperatures for samples outgassed at various temperatures prior to exposure to ammonia (Fig. 7) shows that, for samples pretreated at 500° and 600°C, acid sites strong enough to be measured by this technique are of the type encountered in silica-aluminas. This is indicated by the constant oxygen consumption observed for samples which were exposed to ammonia at 300°, 400°, and 500°C and then outgassed at the same temperatures, respectively. However, pretreatment at 750°C produces only sites of the fluoride alumina type, for which oxygen consumption decreases with increasing ammonia adsorption temperatures. Pretreatment at 650°C produces a mixture of the two types. No acidity is observed after pretreatment at 400°C.

Using this information from Fig. 7, the oxygen consumption for the oxidation of ammonia on the two types of adsorption sites can be plotted independently as a function of pretreatment temperatures (Fig. 8). Good agreement between the measurement for the temperature-independent acid sites and the activity for the alkylation of benzene is found. The slight discrepancy in the lower calcination temperature range

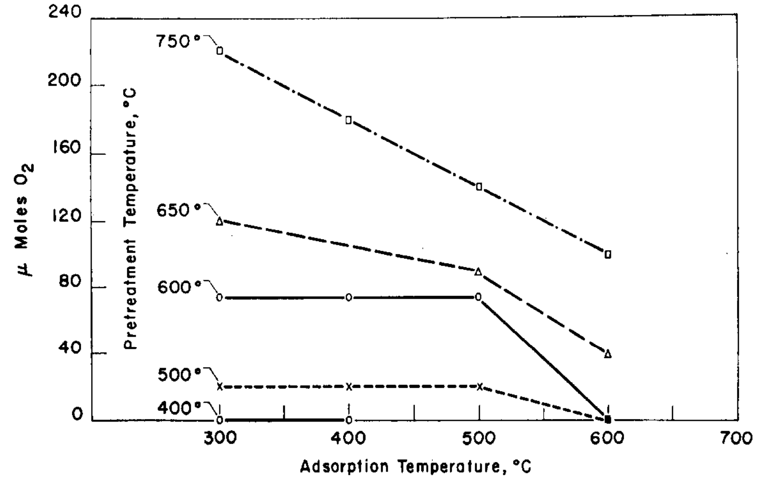


Fig. 7. Oxygen consumption versus adsorption temperatures for NH_4-Y zeolites.

results from the difference in the conversion of the NH_4 form to the H form and depends on the pretreatment of the samples. Venuto (*18*) states that calcination in nitrogen instead of oxygen shifted the activity curve by 50°C toward higher temperatures, which would then coincide with our acidity curve. This is expected because outgassing would be more readily comparable to pretreatment in nitrogen rather than in oxygen. It is readily seen that the other type of acid sites does not contribute to the activity of the zeolite for this reaction.

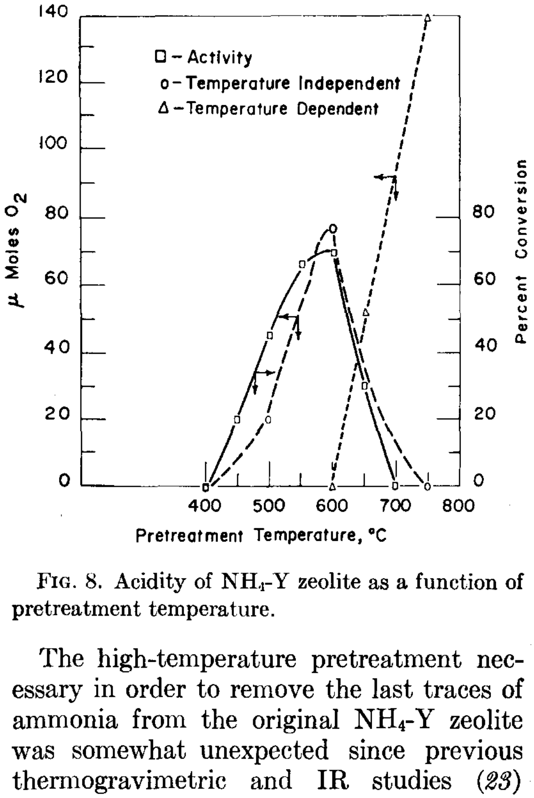


FIG. 8. Acidity of NH_4-Y zeolite as a function of pretreatment temperature.

The high-temperature pretreatment necessary in order to remove the last traces of ammonia from the original NH_4-Y zeolite was somewhat unexpected since previous thermogravimetric and IR studies (*23*) indicate that NH_4 is no longer present above 400°C. The apparent absence of available strong acid sites on these zeolites pretreated at 500° in vacuum is reasonable when one considers that, even after 97% deamination, there remains enough ammonia to satisfy the strongest acid sites. The oxygen consumption after pretreatment at 500°C indicates the presence of 80 μmoles of NH_3 (60 μmoles of O_2). Chemical analysis for NH_3 gave 90 μmoles, which is in good agreement with that obtained by oxidation. A sample outgassed at 500°C overnight still retained 70 μmoles of NH_3 (54 μmoles O_2).

These observations are in agreement with the pretreatment temperatures necessary to obtain activity for the alkylation of benzene (*18*) or for the disproportionation of toluene. (*22*)

Cerium-X Zeolite

Corrections had to be made in this case for oxygen uptake by outgassed samples which had not been exposed to ammonia. This is presumably the result of oxidation of some Ce^{3+} to Ce^{4+}. Also, preliminary work indicated the presence of both types of acid sites for samples pretreated between 200° and 600°C. As pointed out before, samples having ammonia adsorbed on different types of acid sites required different temperatures for their oxidation. Use of this finding was made here. A programmed temperature oxidation indeed showed two maxima—one at 400°C, the other at 600°C. All samples were, therefore, subjected to oxidation at 400°C until the oxygen trace from the oxygen detector returned to base line; this was followed by oxidation at 600°C. Corrections for the intrinsic oxidizability under these conditions are shown in Fig. 9.

Oxygen consumption for samples of Ce-X zeolite pretreated at 200°, 300°, 400°, 500°, and 600°C, and on which ammonia had been adsorbed at 200°C, show the 400°C portion of each oxidation, when corrected for the blank, to be in good agreement with the activity curve for the ethylation of benzene (Fig. 9) (*18*). The oxygen consumption for the subsequent oxidation at 600°C in each sample increases essentially linearly with temperature and does not correlate with activity; neither does the combined total oxygen consumption, which is a measure of total acidity.

In order to establish which of the two oxidations may be a measure of the temperature-independent adsorption sites which correlated with activity in the case of the ammonium-Y zeolites, adsorption of ammonia was also carried out at 400°C. As shown in Table 1, it is the oxygen consumption at 400°C which remains the same for the two adsorption temperatures, while the

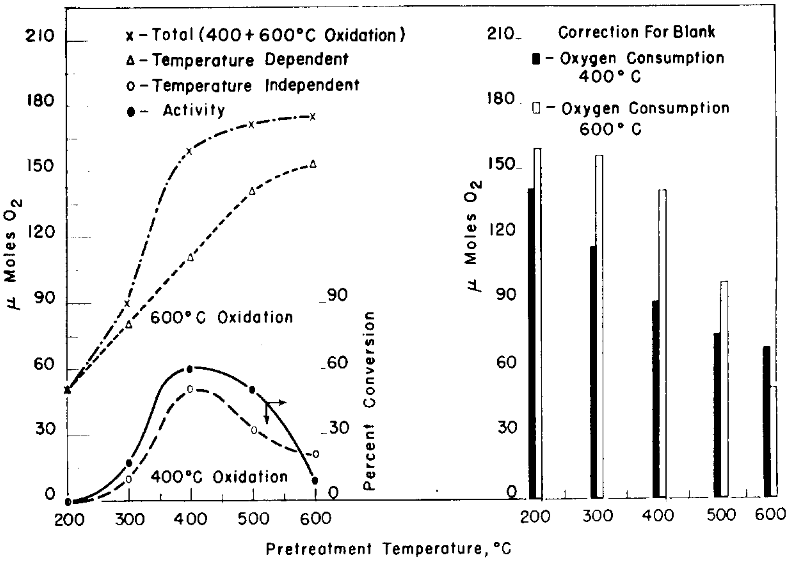
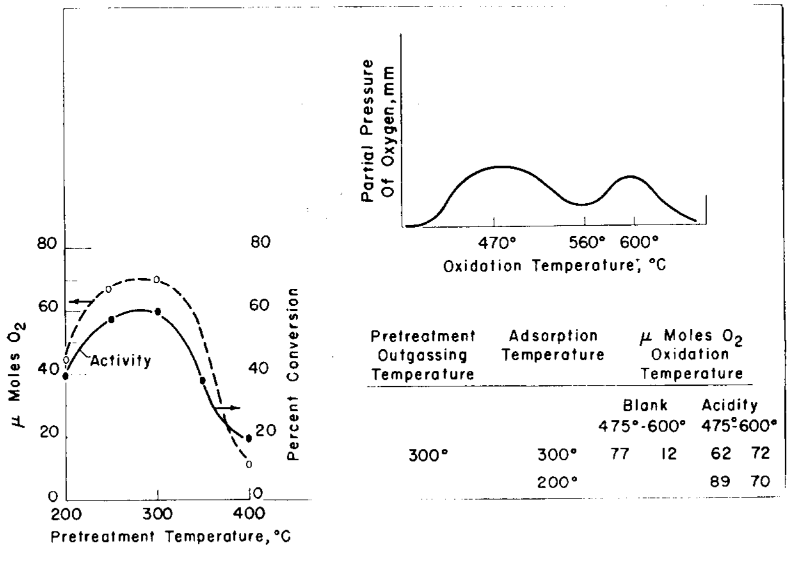


FIG. 9. Acidity of Ce-X zeolite as a function of pretreatment temperature.

oxygen consumption at 600°C decreases at the higher adsorption temperature. Again, as is the case with decationated NH_4-Y zeolite, it is the temperature-independent portion which correlates with activity. Considering the high blank correction that had to be made and the necessity for stepwise oxidation to distinguish between acid sites, the agreement between specific acid sites and activity is surprisingly good.

Cerium-Y Zeolite

Results with Ce-Y zeolites indicate the same dependence of activity on temperature-independent acid sites as seen in the other zeolites studied. Here, again, programmed temperature oxidation of ammoniated samples exhibits two maxima which establish the choice of temperature to be used in the stepwise oxidation to determine separately the ammonia adsorbed



Pretreatment Outgassing Temperature	Adsorption Temperature	μ Moles O_2 Oxidation Temperature			
		Blank		Acidity	
		475°	600°	475°	600°
300°	300°	77	12	62	72
	200°			89	70

FIG. 10. Acidity of Ce-Y zeolite as a function of pretreatment temperature.

TABLE 1
OXYGEN CONSUMPTION AS A FUNCTION OF ADSORPTION TEMPERATURE FOR Ce-X ZEOLITE

Pretreatment outgassing temperature	Adsorption temperature	μMoles O_2 at oxidation temperature of—	
		400°C	600°C
200°	200°	0	49
300°	200°	10	80
400°	200°	*50*	110
400°	400°	*50*	42
500°	200°	31	140
600°	200°	*20*	153
600°	400°	*19*	90

Italicized figures show temperature independence.

on different types of sites. In this instance the two temperatures were 475° and 600°C. Included in Fig. 10 is a set of data which establishes the oxygen consumption at 600°C to be a measure of the temperature-independent sites. Only this portion of the oxygen consumption is plotted and, again, excellent agreement with activity is obtained. Examination of various zeolites by X-ray diffraction indicates that the high-temperature treatments used caused no structural damage to the zeolites.

DISCUSSION AND CONCLUSIONS

From the examples presented in this paper it can be seen that at least two experimentally distinguishable types of acidic adsorption sites can be obtained by making use of the differences in oxygen consumption patterns with varying adsorption and outgassing temperatures, and in the temperature requirement for the oxidation of ammonia on different sites. The question then arises as to whether or not the two observed types could be shown to correspond to the usual classification of Brönsted and Lewis acidity.

In order to establish this correspondence, the two types of oxygen consumption patterns, as shown in Fig. 2, must first be reconciled with NH_3 adsorption behavior expected from Brönsted and Lewis sites, respectively. For a heterogeneous acid strength distribution, neither Brönsted nor Lewis sites would be expected to yield a constant oxygen consumption for ammonia adsorbed at 300°, 400°, or 500°C. However, the high-temperature adsorption, outgassing, and oxidation would only measure the strongly acidic sites and, therefore, it may be reasonable to consider these to be essentially homogeneous and having an acid strength of concentrated sulfuric acid or stronger.

In the case of salt formation with a strong protonic acid, the amount of ammonia held would have to be essentially independent of temperature up to the decomposition temperature which, from the break in the oxygen consumption curve between 500° and 600°C, would have to occur in this range. This proposed behavior of ammonium salts of strong acids is inconsistent with the usual observations during thermal treatment of salts like NH_4Cl or $(NH_4)_2SO_4$. However, examples can be cited where no measurable amounts of ammonia are evolved between 300° and 500°C and where complete decomposition occurs above 500°C. For example, a sample of ammonium paratungstate $(NH_4)_6H_7\,O_{24}\cdot 6H_2O$ was subjected to successively higher temperatures in a stream of helium. One-half of the stoichiometric amount of ammonia was released at about 250°C. No further evolution was observed until complete decomposition occurred around 550°C. The amount of ammonia retained was constant between 300° and 500°C, as found in the case of silica-aluminas.

The partial release of NH_3 before 300°C would be equivalent to ammonia which can be adsorbed on catalysts at lower temperatures or higher pressures, but does not remain associated with the acid sites under our experimental conditions of high-temperature adsorption, outgassing, and oxidation.

Similarly, on heating of ammonium alum, $NH_4Al(H_2O)_2(SO_6H_4)_2\cdot 6H_2O$, after loss of 12 molecules of H_2O below 300°C the resultant $NH_4Al(SO_4)_2$ is stable up to 524° and no weight loss is observed between 300° and 500°C (*19*).

One may conclude, therefore, that constant oxygen consumption between 300° and 500°, with no consumption after the adsorption at 600°C, can be consistent with the behavior of strong acids toward ammonia. This behavior may be the result of a combination of kinetic and thermodynamic factors (*25*). This is supported to some extent by the observation that, for example, a 60–40 silica-alumina on which 120 μmoles of oxygen are consumed after ammonia adsorption at 300°, 400°, and 500°C, and outgassing for ½ hr at the respective temperatures, has its oxygen consumption reduced to 85 μmoles after adsorption of ammonia and outgassing for 4 hr at 500°C. Longer outgassing times do not reduce the oxygen consumption significantly and some variations in acid site strength may come into play.

On the other hand, in the case of Lewis acidity, where ammonia would be in equilibrium with acceptor sites, there exists a temperature dependence—that is, a decrease in the amount of ammonia adsorbed with increasing temperature of adsorption.

If, on the basis of these observations, the temperature-independent oxygen consumption could be assigned as being caused by oxidation of ammonia on Brönsted sites, and the temperature-dependent consumption to ammonia on Lewis sites, the following corroborating evidence can be brought forth:

In the case of NH_4-Y zeolite, the acidity developed at lower temperatures would be designated as Brönsted acidity, and the one developed at higher temperatures would be due to Lewis acidity, which would then constitute an acceptable sequence. Also, on addition of water to samples pretreated at the higher temperatures, the temperature-dependent oxygen consumption reverts to the temperature-independent one. This indicated conversion of Lewis to Brönsted sites is also found with other zeolites such as, for example, Mg-Y faujasite.

Further support in the assignment of Lewis or Brönsted acidity to catalysts, based on the shape of these oxygen consumption-versus-ammonia adsorption temperature curves, was obtained from our infrared investigation of adsorbed pyridine (*12, 20, 21*). Pyridine bands observed at elevated temperatures on a sample of NH_4-Y zeolite, pretreated by outgassing at 550°C, were nearly exclusively due to pyridinium ions, while those in a sample pretreated at 750°C arose nearly exclusively from coordinately bonded pyridine. Both observations are in agreement with our assignment of the types of sites.

The assignment of Lewis acidity to the fluorided alumina on the basis of a temperature-dependent oxygen consumption is supported by the fact that a 1-g sample of fluorided alumina, containing 4.45% fluorine, had a hydroxyl level of 85 μmoles (as determined by H_2/D_2 exchange) after outgassing at 600°C, while the amount of ammonia adsorbed at 300°C on the same sample was 150 μmoles (Fig. 2). Also, on addition of water to the highly dehydrated fluorided aluminas, oxidation of ammonia now yields temperature-independent oxygen consumption patterns. This would, therefore, again indicate a conversion of Lewis to Brönsted acid sites. However, this conversion could not be obtained in the case of unfluorided alumina. The inability to convert alumina Lewis sites to Brönsted sites is well established. The correlation between pentane isomerization over fluorided aluminas and Lewis acidity does not, therefore, necessarily imply a reaction via Lewis sites. The latter may be converted to Brönsted sites by trace amounts of water in the feed.

All the observations discussed so far support the proposal that the method for acidity determination discussed in this paper is capable of distinguishing between Brönsted and Lewis acid sites.

The one case where the assignment of acid types based on oxygen consumption patterns is in contradiction with the interpretation of IR spectra from pyridine adsorption (*12, 13*) is that of silica-aluminas: interpretation of our results would indicate the presence of strong protonic acid sites only. The postulation by Hirschler (*24*) of observed Lewis sites on silica-alumina being the hydrogen atom of an unsolvated, strongly acidic OH group may possibly have some bearing on the two observations. Further work is being carried out with the silica-alumina system to clarify this point.

The different temperature requirements for the oxidation of ammonia on Brönsted sites is not fully understood and no explanation can be given at this time. For silica-alumina and cerium-Y zeolite this temperature requirement is 625° and 600°C, respectively, but only 400°C for cerium-X. In the case of H-Y zeolite, distinction between ammonia on the two sites was possible only when the standard temperature programming of 15°C/min was reduced to 7.5°C/min. Under these conditions the maximum rate of oxidation for ammonia on Brönsted and Lewis sites occurred at 600° and 525°C, respectively. Even though the temperature differential is small, a higher temperature again is required for the oxidation of ammonia on Brönsted sites.

In spite of the uncertainties on some points which need further clarification, it has been shown that ammonia adsorption and oxidation at high temperature is capable of distinguishing between two different types of acid sites on catalysts, and that correlations between activity and oxygen consumptions are obtained. We have found the method to be most useful and applicable to a wide variety of catalysts.

REFERENCES

1. HOLM, V. C. F., BAILEY, G. C., AND CLARK, A., *J. Phys. Chem.* **63,** 129 (1959).
2. WEBB, A. N., *Ind. Eng. Chem.* **49,** 261 (1957).
3. BARTH, R. T., AND BALLOU, E. V., *Anal. Chem.* **33,** 1080 (1961).
4. KUBSKAWOL, Y., *J. Phys. Chem.* **67,** 769 (1963).
5. WALLING, C., *J. Am. Chem. Soc.* **72,** 1164 (1950).
6. BENESI, H., *J. Phys. Chem.* **61,** 970 (1957).
7. HIRSCHLER, A. E., AND SCHNEIDER, A., *J. Chem. Eng. Data* **6,** 313 (1961).
8. HIRSCHLER, A. E., *J. Catalysis* **2,** 428 (1963).
9. HIRSCHLER, A. E., *J. Catalysis* **6,** 1 (1966).
10. MAPES, J. E., AND EISCHENS, R. R., *J. Phys. Chem.* **58,** 1059 (1954).
11. PLISKIN, W. A., AND EISCHENS, R. R., *J. Phys. Chem.* **59,** 1156 (1955).
12. PARRY, E. P., *J. Catalysis* **2,** 371 (1963).
13. BASILA, M. R., KANTNER, T. R., AND RHEE, K. H., *J. Phys. Chem.* **68,** 3197 (1964).
14. HIRSCHLER, A. E., AND HUDSON, J. O., *J. Catalysis* **3,** 239 (1964).
15. PORTER, R. P., AND HALL, K., *J. Catalysis* **5,** 366 (1966).
16. THOMAS, C. L., *Ind. Eng. Chem.* **41,** 2564 (1949).
17. Universal Oil Products Co., unpublished data.
18. VENUTO, P. B., HAMILTON, L. A., LOINDIS, P. S., AND WISE, J. J., *J. Catalysis* **5,** 81 (1966).
19. DUVAL, C., *Anal. Chim. Acta* **20,** 21 (1959).
20. WARD, J. W., Abstract of Papers, 154th Meeting, American Chemical Society, Chicago, Sept. 1967.
21. EBERLY, P. E., JR., Abstract of Papers, 154th Meeting, American Chemical Society, Chicago, Sept. 1967.
22. BENESI, H. A., *J. Catalysis* **8,** 368 (1967).
23. UYTTERHOEVEN, J. B., CHRISTNER, L. G., AND HALL, W. K., *J. Phys. Chem.* **69,** 2117 (1965).
24. HIRSCHLER, A. E., *J. Catalysis* **6,** 1 (1966).
25. EMMETT, P. H., private communication.