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III. The Adsorption of Pyridine on Molybdena–Alumina Catalysts

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Only Lewis-bound pyridine (LPy) was detected in infrared spectra from pyridine which had been adsorbed on Ketjen Alumina (CK-300) and then evacuated to successively higher temperatures. Exposure to H_2O lowered the intensity of the LPy bands. On the oxidized forms of molybdena-, chromia-, rhenia-, and tungsta-alumina catalysts (made with CK-300) both LPy and pyridinium ion (BPy) were observed. The amount of BPy present was increased by added-back H_2O; lowering the pretreatment temperature had the same effect. On reduction, the ability of the catalyst to generate BPy was eliminated although a sufficient extent of reduction was difficult to achieve with the tungsta-alumina catalyst. Added-back H_2O did not produce BPy on reduced catalysts. Coverage with LPy and BPy and heats of adsorption were estimated in separate experiments. These findings appear to be in conflict with our earlier assumption that the facile isomerization of cyclopropane over reduced molybdena-alumina is effected by acid catalysis.

INTRODUCTION

An interesting observation was made some years ago by Kiviat and Petrakis (*1*). These workers reported that pyridinium ion bands appeared in infrared spectra when pyridine was adsorbed on molybdena-alumina catalysts. These bands were completely absent in spectra obtained with the parent alumina. Similar results were obtained with several other, but not all, metal oxides mounted on the same support. Most of this work was done with the oxidized form of the catalyst, but one line of data showed that the effect persisted when the catalyst was reduced. It was not clear from this work whether the Brønsted sites associated with the pyridinium ion were part of the metal oxide complex on the alumina surface or alumina hydroxyl groups activated, perhaps inductively, by the supported transition metal oxide. We note, however, that in the latter case there is no apparent reason why the acidity should increase as the catalyst was reduced, vide infra.

Fransen *et al.* (*2*) made some related studies. They reported that no BPy (only LPy) was formed on the parent alumina surface, even in the presence of H_2O. They prepared a molybdena-alumina catalyst from their (Degussa) alumina by carrying $MoO_2(OH)_2$ on to the support in steam at 600°C. When a platelet of this catalyst was reduced to $e/Mo = 2.0$, the ir spectra were said to contain the BPy bands, but the quality of the spectra were not sufficient to establish this point unambiguously. When additional H_2O was present, however, these bands were unmistakable.

Hall and co-workers (*3, 4*) discovered that when a molybdena-alumina catalyst was reduced with H_2, only about half of the H_2 consumed during the early stages of the reduction was evolved as H_2O at temperatures up to 600°C. Moreover, it was found that the surface chemistry could be satisfactorily described in terms of the new hydroxyl groups formed on reduction (H_I atoms/Mo) and the anion vacancies which were presumed to be produced as oxygen was removed as H_2O from the bound monolayer of molybdena. These were experimental parameters; whatever changes in in-

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terpretation might follow later, these quantities could be used to correlate data.

In view of the foregoing it was supposed (*4*) that the H_I could be identified with a Brønsted acid (a form of supported molybdic acid); thus, studies of the isomerization of cyclopropane were initiated. This molecule is stable thermally to about 450°C, above which a homogeneous isomerization occurs by an intramolecular process. The rate of this process is not affected by passing the gas over a nonacidic solid such as pure silica gel. The isomerization to propylene becomes facile, however, over solid acids such as silica-alumina (*6, 7*). This reaction is an intermolecular process which occurs at room temperature or somewhat above and proceeds via a nonclassical cyclopropyl carbonium ion. The reaction also takes place over pure alumina at temperatures above 200°C, presumably by the same mechanism. Interestingly, the reaction over reduced molybdena-alumina resembled closely that over a silica-alumina cracking catalyst. The reaction became facile above room temperature and a rapid stepwise isotopic scrambling occurred when mixtures of perdeuterio- and perhydrocyclopropane were coisomerized (*5*).

The effect of varying the extent of reduction of the molybdena-alumina catalyst was studied (*5*). The activity of the unreduced catalyst was negligibly small when compared with that of reduced catalysts. A very good linear correlation was obtained between the percentage conversion per pass and H_I/Mo up to a value of 0.5 for the latter. Interestingly, this was the maximum value of H_I which could be obtained; H_I fell again at higher extents of reduction (*4*) as Mo^{+5} was converted into Mo^{+4}. The rate of conversion of cyclopropane did not fall, however; it continued to increase with the extent of reduction. Nevertheless, these (high) points could be moved back onto a linear plot of the conversion versus $(H_I + \square)/Mo$. It was concluded, therefore, that whereas Brønsted sites were needed to open the ring, the presence of anion vacancies must play a significant role. At least partly, this could be traced to cyclopropane decomposition by other pathways, e.g., the formation of a metallocyclobutane by insertion of the Mo into the cyclopropane ring. As described by Gasman and Johnson (*8*) this led to the liberation of C_2H_4 together with the formation of a surface carbene which then acted as a center for olefin metathesis. Interestingly, metathesis did occur with the propylene produced and an excess of ethylene over butene was always present; this excess correlated with the vacancy concentration (*9*). These reactions could be virtually eliminated by adding H_2 as an additional reactant. Now propane became virtually the sole product illustrating the high hydrogenation ability of the reduced catalyst. Thus, the reactions of cyclopropane provided a useful tool for assaying simultaneously a variety of catalyst functions.

As the work progressed several observations were made which did not fit the simple picture described above. In the first place it was found that catalysts reduced with CO were equally active with those reduced in H_2 for isomerization (*9*). Moreover, deuterium tracer experiments revealed that the maximum number of Brønsted sites which could be effective for isomerization was lower by several orders of magnitude than the amount of H_I introduced when H_2 was used as the reductant. Most damaging was the adverse effect of H_2O on the reaction (*5*). Exposure of a highly active reduced catalyst to the vapor pressure of H_2O at room temperature for the few minutes virtually eliminated its activity for cyclopropane isomerization. Evacuation at 110°C only slightly increased its activity and only about half was restored by evacuation at 300°C. The original activity of the catalyst could be recovered, however, by evacuation at 500°C, thus demonstrating that the catalyst had not been reoxidized by H_2O. Brønsted acidity is usually enhanced by the addition of small amounts of H_2O to a catalyst.

Like H_2O, pyridine and NH_3 were also very effective poisons for isomerization (*10*). Because of experimental difficulties, pyridine was not investigated in much detail, but NH_3 could be used to estimate the surface concentration of active sites. The lethal dose was estimated to be about 0.8 cm^3 (NTP)/g (an amount equivalent to about 3% of the Mo). In this connection NH_3 was a much more effective poison for cyclopropane isomerization than was NO which was a selective poison for olefin hydrogenation (*10*). This was an interesting observation because NH_3 could adsorb on Brønsted centers as well as CUS associated with Mo, whereas NO is thought to be localized on the latter.

In view of the above results, it was decided to make a detailed spectroscopic study of the chemisorption of pyridine, since such experiments are widely used to discriminate between Lewis and Brønsted acidity. Results from this investigation are the topic of this paper.

EXPERIMENTAL

Catalysts investigated. Most preparations were made by the equilibrium adsorption method of Wang and Hall (*11*). The alumina support was Ketjen CK-300 (lot #26919). The preparations investigated contained 1.1 to 7.3×10^{20} Mo/g, 2.1 to 5.6×10^{20} W/g, 3.2×10^{20} Cr/g, and 2.9×10^{20} Re/g of alumina. Data from these catalysts were compared with those from the conventional (8% Mo) molybdena-alumina catalyst used in much of our earlier research.

Infrared measurements. For the ir work, calcined aliquots of the catalysts were pressed into spectroscopic platelets having a thickness of about 10 mg/cm^2. These platelets were mounted on a quartz rack which positioned the platelet between the KBr windows (13 mm path length) of a vacuum tight spectroscopic cell.

The catalyst rack assembly could be moved magnetically upward about 20 cm into a self-contained furnace built around the vacuum tight cell. Temperatures were measured by a thermocouple positioned close to the catalyst platelet. Temperatures up to 700°C were easily maintained.

Gases could be passed over the catalyst and evacuated at selected temperatures. The vacuum tight cell was attached to a conventional system which routinely reached 10^{-6} Torr. Oxidation and reduction treatments of the catalyst were made using flowing streams of purified O_2 and H_2, respectively. After pretreatment, the catalysts were evacuated at 500°C for 1 hr and cooled to 200°C before exposure to 4 Torr of pyridine vapor for a period of 1 hr. The catalyst platelet was then evacuated for 2 hr at this or higher temperatures. Finally, the catalyst and its rack assembly were moved back between the KBr windows for spectroscopic investigation.

Spectra were obtained with a Nicolet Model-MX-1 FT spectrometer which was operated in the absorbance mode. The spectrometer resolution was about 2 cm^{-1}. The scan rate was 32/min and the number of scans required to produce the spectra shown were 160 for pyridine and 640 for the surface hydroxyl region. The determination of integrated intensities of the bands at 1450 and 1545 cm^{-1} were determined and used as measures of the amounts of LPy and BPy, respectively (see Figs. 3, 4, 5, and 8). Then the data were normalized to a constant thickness of 10 mg/cm^2 for pyridine and 25 mg/cm^2 for the OH spectra.

Gravimetric measurements. Adsorption measurements were made using a Cahn electrobalance (Model 2000). Equilibrium isobars were determined at several different equilibrium pressures. Clausius–Clapeyron plots could be constructed from these data for different surface coverages yielding a relationship between heat of adsorption and surface coverage. The balance was attached to a vacuum system (1×10^{-5} Torr). Pyridine vapor pressure was varied from $0.5 \sim 4$ Torr and measurements were made over the temperature region between 130°C and 360°C.

Gases and reagents. The tank oxygen

was passed through a Linde 13× molecular sieve purification column before use. The hydrogen was ultrapure; it had been passed through the Pd–Ag thimble of a RSI commercial purifier. The pyridine was dried over 5A molecular sieves; it was distilled and the center cut was collected and redistilled. The final distillate was collected over anhydrous KOH and stored over activated 5A molecular sieves in a tube which could be attached to the vacuum system, frozen, pumped, and surrounded by a constant temperature bath to fix the vapor pressure over the catalyst sample.

RESULTS

Spectra from pyridine adsorbed on the parent alumina following successive 1 hr evacuations at increasing temperatures are shown in Fig. 1. The 19a and 19b breathing vibrations which appear at about 1495 cm^{-1} and in the 1450 cm^{-1} region, respectively, stemmed from Lewis-bound pyridine (LPy). That the ratio of the band intensities remained about constant as pyridine was removed by evacuation at increasing temperatures, while their frequencies increased slightly, suggested that the interaction be-

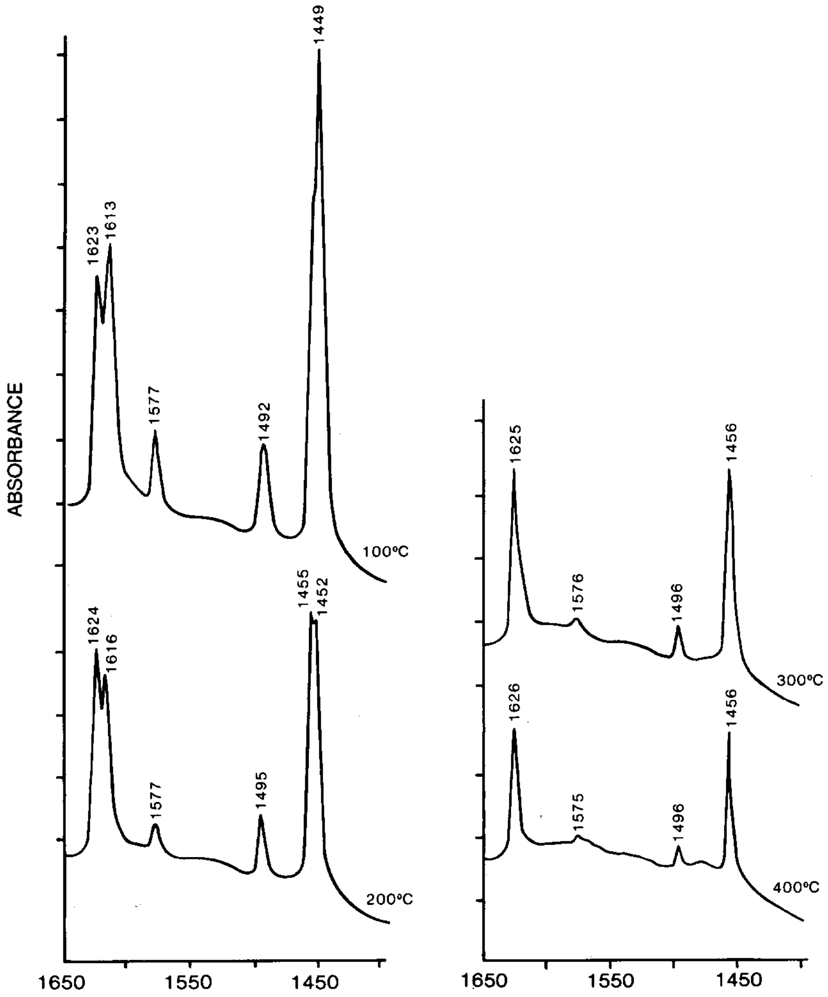

FIG. 1. Spectra from pyridine adsorbed on alumina after evacuation at various temperatures.

came stronger as the surface coverage was lowered. Note, also, the absence of a band in the 1545 cm^{-1} region which would correspond to BPy (pyridinium ion); the slight curvature shown in this region was also present without pyridine. The bands at higher frequency may be assigned as follows: the 8a and 8b vibrations of LPy appear at about 1620 and 1577 cm^{-1}; the same vibrations for BPy are found at 1638 and 1620 cm^{-1}, respectively, the latter being superimposed on the 8a mode of LPy.

Spectra obtained from pyridine adsorbed on a molybdena-alumina catalyst are presented in Fig. 2. Note the appearance of the 19b band at about 1540 cm^{-1} from pyridinium ion as well as the new band at 1638 cm^{-1} from the 8a mode of this species. When H_2O (0.2 mmol/g) was added to the dry catalyst, Spectrum A was converted into Spectrum B. The bands at 1542 and 1638 cm^{-1} were strengthened as was the 19a vibration at 1491 cm^{-1}. The enhancement of Brønsted acidity by the addition H_2O has been frequently observed with solid acids such as silica-alumina.

The data of Fig. 3 show that the Brønsted acidity is not due to H_2O adsorbed on Lewis sites of the alumina surfaces. The integrated intensities for the Lewis and Brønsted bands are plotted as a function of the temperature at which the oxidized form of the molybdena-alumina catalyst was evacuated following addition of H_2O at 200°C. The concentration of Brønsted sites fell linearly while concentration of Lewis sites remained essentially constant at temperatures up to 400°C, but then increased

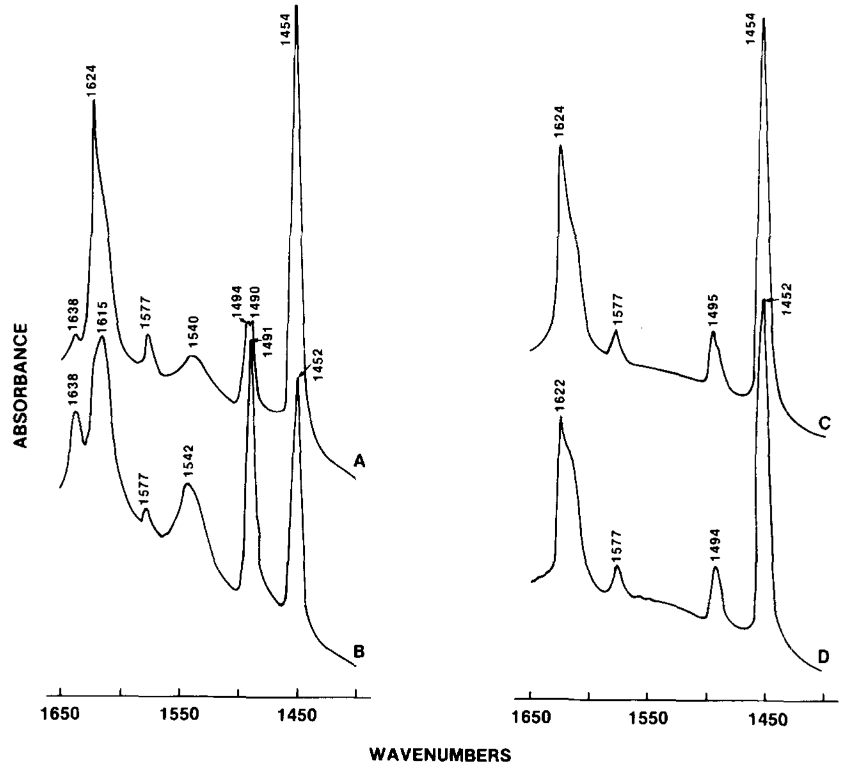

FIG. 2. Spectra from pyridine adsorbed on an 8% Mo molybdena-alumina catalyst (5×10^{20} Mo/g). Spectrum A is for the freshly oxidized catalyst after evacuation at 500°C; Spectrum B resulted from the addition of 0.2 mmol/g of H_2O to the cell after Spectrum A. Spectrum C is from the same catalyst platelet after reduction with H_2 for 1 hr at 500°C; Spectrum D was taken after adding 0.2 mmol/g of H_2O after C.

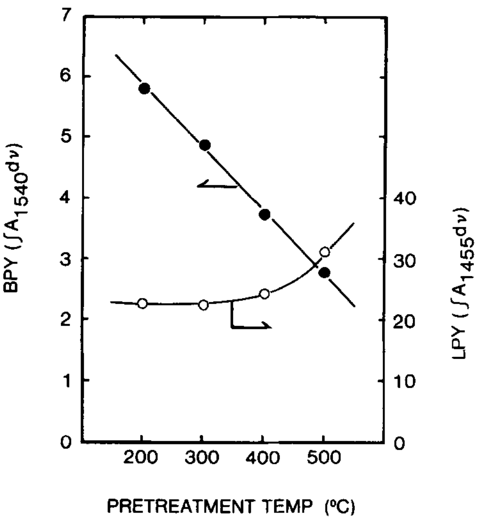

FIG. 3. Variation of acidity of an oxidized molybdena-alumina catalyst (8% Mo) following evacuation at various temperatures. The catalyst was exposed to 5 Torr of H_2O at 200°C for 30 min in each case and evacuated at T before exposure to pyridine.

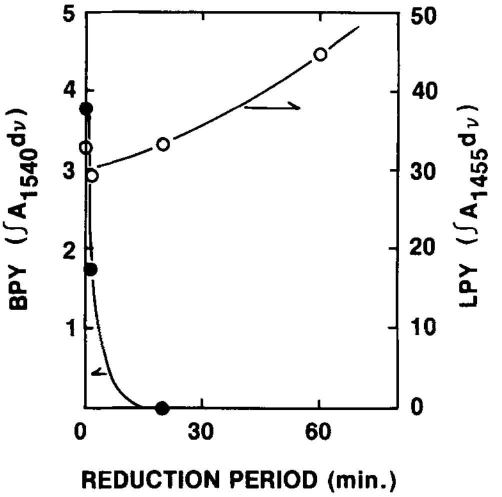

FIG. 4. Loss of Brønsted acidity with time (extent) of reduction at 500°C (8% Mo).

noticeably at 500°C. Interestingly, when the experiment of Fig. 3 was repeated with a reduced catalyst (e/Mo ≈ 1.3), only the LPy bands were produced and the addition of H_2O weakened the band intensities slightly (Spectra C and D of Fig. 2). No bands ascribable to pyridinium ion were formed. The effectiveness of reduction in eliminating the Brønsted acidity is shown in Fig. 4. These experiments were made by passing H_2 flowing at about 100 cm^3 (NTP)/min over the catalyst at 500°C for different periods of time. The ability of the catalyst to form BPy was eliminated in about 15 min under these conditions, but could be restored by reoxidation.

The effect of loading on spectra from both oxidized and reduced molybdena-alumina catalysts is shown in Fig. 5. These data have been corrected to constant platelet thickness. Reduced catalysts, which evidenced only Lewis acidity, produced integrated intensities which were almost independent of loading. This behavior may be contrasted with that for the oxidized catalysts where the Lewis acidity fell off sharply with increasing loading. The catalyst which had the lowest loading (about 1.1×10^{20} Mo/g) showed no Brønsted acidity. This catalyst had been prepared at high pH and contained only tetrahedrally coordinated monomeric MoO_4^{-2}, a species suggested in earlier work (*3*, *4*) as a model describing the surface chemistry. Catalysts containing higher loadings were all pre-

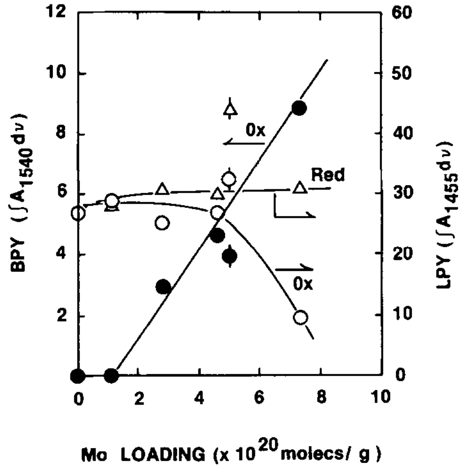

FIG. 5. The effect of molybdena loading on the acidity. Catalysts were made by the equilibrium adsorption method (*11*), except for the marked points (ϕ, ●, and △) which correspond to an 8% Mo catalyst made by the usual incipient wetness method. All preparations were exposed to 4 Torr of pyridine vapor at 200°C for 1 hr and then evacuated at this temperature for 2 hr.

pared at pH < 7.0 and the oxidized form of these catalysts has been identified as polymolybdate species bound to the alumina surface (*11*). Interestingly, with these, the Brønsted acidity increased about linearly with loading.

The spectra of Fig. 6 show the changes in the hydroxyl region as the loading of the alumina was increased (oxidized form) of the catalysts. The gradual to almost complete replacement of the alumina hydroxyl groups (*2*) is evident. This information coupled with the data of Fig. 5 suggested that on oxidized catalysts the Lewis sites may be associated with the alumina surface whereas the Brønsted sites are strongly dependent on the presence of polymolybdate species. After reduction the CUS associated with molybdena may also function as Lewis sites. The marked points are for a sample prepared by the incipient wetness technique. Its Lewis acidity was somewhat higher and its Brønsted acidity lower, as might be expected if the molybdena dispersion was less uniform. In all cases the alumina hydroxyl concentration increased markedly on reduction as previously reported (*16*).

Heats of adsorption were determined by the method of Deeba and Hall (*13*) for pyridine on the alumina and the oxidized and reduced forms of a molybdena-alumina catalyst made from it. This involved the determination of equilibrium isobars for adsorbed pyridine using a microbalance. From isobars for differing pyridine partial pressures Clausius–Claperon plots were generated for different surface coverages. The heats of adsorption calculated from the slopes of these are shown in Fig. 7. These data show that the spectra described above corresponded to species having fairly high heats and provide an indication of the coverage range being examined.

The microbalance data showed that when equilibrium had been obtained at a given vapor pressure of pyridine and then the catalyst was evacuated, a portion of the pyridine desorbed. The irreversible pyridine

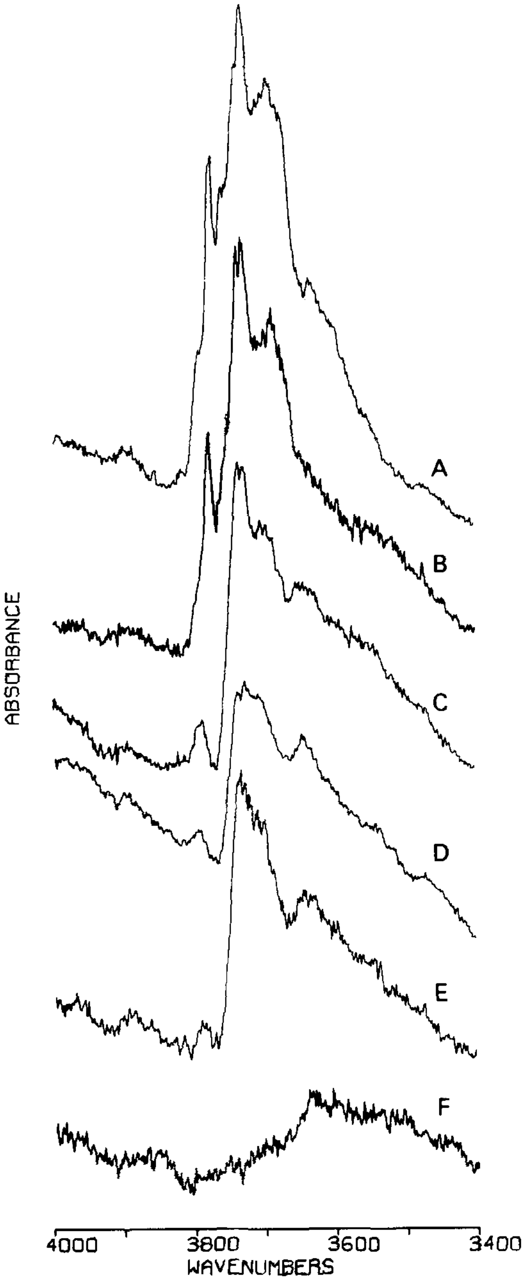

FIG. 6. Photographs of ir spectra of the O–H region from catalysts of increasing molybdena loading. The preparations were calcined in O_2 for 12 hr and evacuated for 0.5 hr at 500°C before the spectra were taken. The pressed platelets had constant thickness of 25 mg/cm^2. Spectra were: A, Al_2O_3; B, 1.1×10^{20}; C, 2.8×10^{20}; D, 4.6×10^{20}; E, 5.0×10^{20}; and F, 7.3×10^{20} Mo/g. Catalysts were made by the equilibrium adsorption method (*11*), except for Spectrum E which corresponds to an 8% Mo catalyst made by the incipient wetness method.

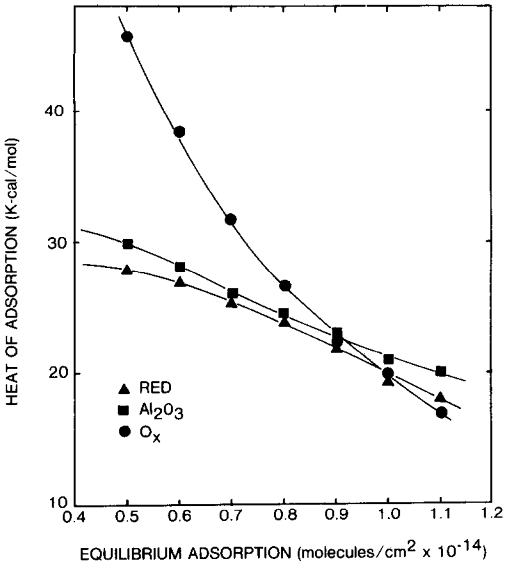

FIG. 7. Heats of adsorption of pyridine on alumina and a molybdena-alumina catalyst (2.7 × 10^{14} Mo/cm^2 or 5 × 10^{20} Mo/g) prepared from it. Determinations made by method of Deeba and Hall (*13*); see text.

which was left was an important fraction (up to one-half) of the equilibrium value. In the experiments reported here, it was this portion of the pyridine (having still higher heats of adsorption) which was observed. Some related data are presented in Fig. 8. Upon evacuation of adsorbed pyridine at higher and higher temperatures, LPy was removed preferentially up to about 300°C. Above this temperature all of the BPy desorbed abruptly, leaving behind a small amount of more strongly held LPy. Since the more weakly held pyridine will desorb at the lower temperature leaving behind the more strongly bound pyridine, these data describe a distribution of acid sites.

Related spectroscopic studies of tungsta-, chromia-, and rhenia-alumina were made. Spectrum A of Fig. 9 is for the oxidized W-catalyst. As found for molybdena-alumina, the BPy band could be enhanced by the adsorption of a small amount of H_2O. Spectrum B corresponds to the same catalyst platelet after reduction for 20 hr at 550°C. Tungsta-alumina catalysts are much more difficult to reduce than molybdena-alumina; separate measurements suggested that this treatment produced an extent of reduction of e/W ≈ 0.25. The extent of reduction could be increased by raising the reduction temperature to 700°C (e/W = 2.0). Spectrum C shows that when this was accomplished, the BPy band disappeared as with molybdena-alumina. Data for two tungsta-alumina catalysts are collected in Table 1, together with related data for molybdena-alumina, chromia-alumina, and rhenia-alumina made by the same equilibrium adsorption method with the same Ketjen CK-300 alumina. These data show that the ratio of Lewis to Brønsted acidity can be varied both by changing the loading and the reduction temperature, as well as controlling the amount of H_2O present. Interestingly, all of these catalysts behaved in the same general way. An apparent contradiction exists with the work of Olsthoorn and Boelhouever (*17*) with rhenia-alumina catalysts. They reported that pyridinium ion was evident in spectra from adsorbed pyridine when the catalysts had been very slightly reduced by contact with alkenes at room temperature, but was absent when pyridine was adsorbed under the same cir-

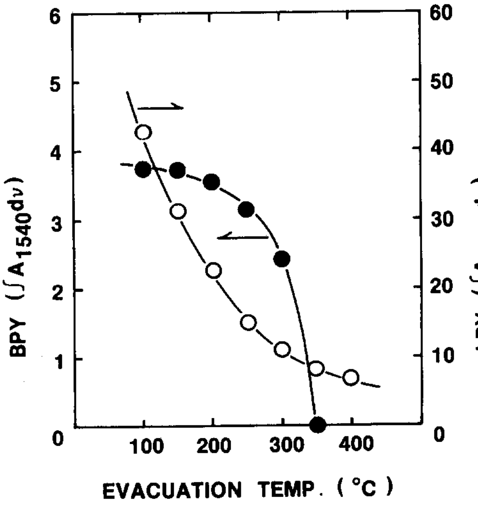

FIG. 8. Desorption of pyridine from the oxidized form of a molybdena-alumina catalyst (8% Mo), made by incipient wetness method with increasing evacuation temperature.

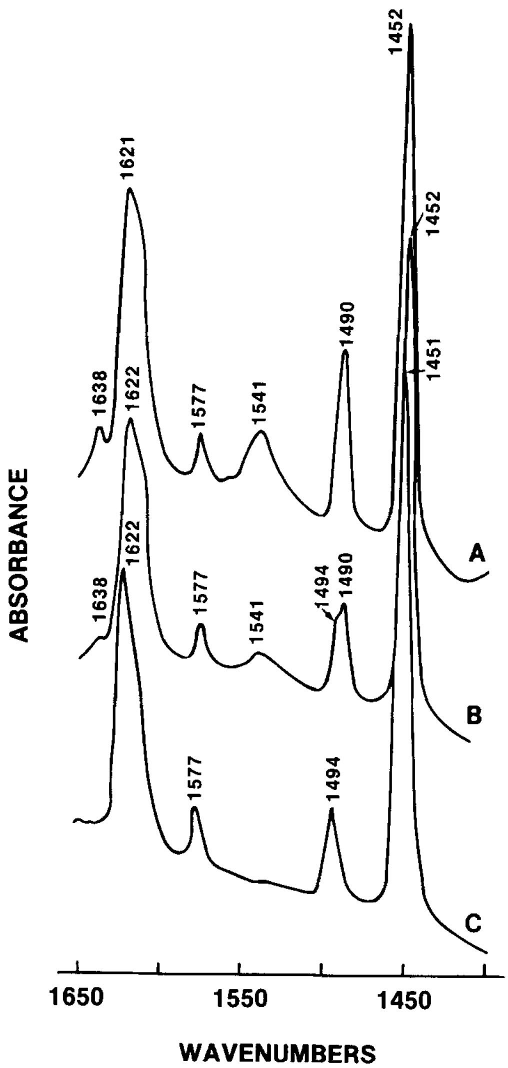

FIG. 9. Spectra from pyridine adsorbed on a tungsta-alumina catalyst (5.6 × 10^{20} W/g). Spectrum A is for the oxidized catalyst after exposure to 4 Torr of pyridine vapor at 200°C for 1 hr and then evacuated at this temperature for 2 hr; Spectrum B was obtained after evacuation of pyridine at 450°C followed by reoxidation at 500°C and reduction in flowing purified H_2 [100 cm^3 (NTP)/min] for 20 hr at 550°C; pyridine was then adsorbed as for Spectrum A. Spectrum C was obtained in the manner used for Spectrum B, but after a 4-hr reduction at 700°C.

cumstances on an unreduced catalyst. The addition of a small amount of water to the latter, however, effected formation of pyridinium ion.

DISCUSSION

Although the picture developed must be viewed with some caution, it is tempting to interpret the results as follows. The surface of the raw catalyst after calcining with O_2 above 450° contains patches of a polymolybdate species (*11*). These may be a couple of layers thick and are bonded to the surface by replacement of alumina hydroxyl groups forming Mo–O–Al bonds [Fig. 6 and (*3*, *4*)]. These bonds may be broken by reduction and the lost alumina hydroxyl groups (partially) regenerated (*16*). In this case the molybdena is reduced and ceases to be a site for Brønsted acid formation even in the presence of H_2O, which now functions as a catalyst poison by filling the CUS. The Mo–O–Al bond of the oxidized catalyst may also be cleaved by H_2O and forms a Brønsted acid in this process. Presumably this reaction may be represented by a process analogous to that for rhenia (*17*), i.e.,

$$\mathrm{Al{-}O{-}ReO_3} + \mathrm{H_2O} \rightarrow \mathrm{Al{-}OH} + \mathrm{HOReO_3} \quad (1)$$

where it is understood that the acidic center is located on the partially hydrolyzed molybdena-cluster. This reaction is not possible after reduction because the Mo–O–Al bond has already been broken. The effects of evacuation temperature (Fig. 3) and the effects of loading are also understandable in these terms. On unreduced catalysts the Brønsted acidity increases with loading whereas the Lewis acidity falls (Fig. 5), particularly as the alumina surface becomes completely covered as evidenced by the nearly complete elimination of surface hydroxyl groups (Fig. 6). The nearly linear increase in Brønsted acidity may reflect a nearly linear increase in surface coverage with paramolybdate clusters. The invarience of the Lewis acidity with loading for reduced catalysts suggests that Lewis sites are available on molybdena-covered as well as on the alumina surface. This is of interest because the concept of CUS would lead one

TABLE 1

Pyridine Adsorption Data on MoO_3/Al_2O_3 and Related Catalysts

	Loading $\times 10^{20}$ Me/g	Reduction[a] temperature (°C)	LPy[b] $\int A_{1451} d\nu$	BPy[b] $\int A_{1541} d\nu$	$\frac{1}{1 + C_L/C_B}$[c]
Unreduced Cr_2O_3/Al_2O_3	3.2	—	28.5	1.0	0.09
Unreduced $Cr_2O_3/Al_2O_3(H_2O)$[d]	3.2	—	28.8	2.4	0.18
Reduced Cr_2O_3/Al_2O_3	3.2	500	31.9	—	—
Unreduced MoO_3/Al_2O_3	2.8	—	24.6	3.0	0.25
Reduced MoO_3/Al_2O_3	2.8	500	31.0	—	—
Unreduced MoO_3/Al_2O_3[e]	5.0	—	32.5	4.0	0.25
Unreduced $MoO_3/Al_2O_3(H_2O)$[d,e]	5.0	—	17.85	11.5	0.64
Reduced MoO_3/Al_2O_3[e]	5.0	500	44.6	—	—
Unreduced MoO_3/Al_2O_3	7.3	—	9.7	8.8	0.71
Unreduced $MoO_3/Al_2O_3(H_2O)$[d]	7.3	—	1.6	13.6	0.96
Reduced MoO_3/Al_2O_3	7.3	500	31.4	—	—
Unreduced WO_3/Al_2O_3	2.1	—	33.1	2.4	0.16
Reduced WO_3/Al_2O_3	2.1	550[f]	34.5	2.4	0.15
Unreduced WO_3/Al_2O_3	5.6	—	18.2	5.5	0.45
Reduced WO_3/Al_2O_3	5.6	550[f]	27.7	3.9	0.28
Reduced WO_3/Al_2O_3	5.6	700[g]	30.0	—	—
Unreduced Re_2O_7/Al_2O_3	2.9	—	36.8	1.5	0.10
Unreduced $Re_2O_7/Al_2O_3(H_2O)$[d]	2.9	—	13.8	21.6	0.81
Reduced Re_2O_7/Al_2O_3	2.9	270	44.4	—	—

[a] Reduction time was 1 hr in flowing H_2 except as otherwise noted.

[b] Sample was exposed to 4 Torr of pyridine for 1 hr at 200°C and evacuated for 2 hr at the same temperature.

[c] $C_L/C_B = 0.37 \times (\int A_{1451} d\nu / \int A_{1541} d\nu)$. Determinations of the coefficient made by the method of Basilla (*12*).

[d] 0.2 mmol/g H_2O added at room temperature.

[e] Catalyst prepared by the usual incipient wetness method.

[f] Twenty hours.

[g] Four hours.

to think of such sites as basic, rather than acidic.

In contradiction to the report of Kiviat and Petrakis (*1*), the present work shows clearly that all detectable Brønsted acidity could be eliminated by reduction of the catalyst. This is in agreement with chemical intuition. But, then why should catalyst hydroxyl groups *increase* as a catalyst is reduced, a process which should make it more basic? Another question is if the Brønsted acidity is removed by reduction why should the activity for cyclopropane isomerization over molybdena-alumina increase with reduction (*5*)? These apparently contradictory results suggest that either the facile cyclopropane reaction is catalyzed by some unknown, undetected form of Brønsted acidity, which is present in only a very small amount, or else the isomerization occurs by some as yet unknown chemistry.

The situation may be assessed as follows. If Brønsted acid sites are effective, tracer experiments suggest that no more than about 5×10^{18}/g or $2 \times 10^{12}/cm^2$ are active (*9*). Moreover, these need not be introduced by the H_2 used for reduction; catalysts reduced with CO were found to be about as active as those reduced in H_2. The lethal dose of NH_3 required to deactivate the catalyst was not much higher, viz. $1 \times 10^{13}/cm^2$, an amount equivalent to about 3% of the Mo present. As shown in Table 1, the amount of adsorbed pyridine being observed in the ir measurements was about an order of magnitude higher (1 to 2×10^{20}/g). It is possible, although unlikely, that we could have missed detecting this small amount of acidity as a pyridinium ion.

The chemistry of cyclopropane is centered around its behavior in acid media. If the ring is being opened by some other mechanism, what are the possibilities? Haller *et al.* (*14*) recently suggested that over chromia catalysts a proton is removed from the cyclopropane ring which is then opened concomitantly to form the same allylic intermediate which they had characterized for the isomerization of deuterated propylene (*14*). We have presented evidence (*5, 9*) for the formation of metallocyclobutanes by insertion of molybdenum ions into the cyclopropane ring according to the chemistry described by Gasman and Johnson (*8*). Conceivably isomerization could occur via this intermediate. Finally, although there is no known chemical precedent for this, the cyclopropane ring might be opened by hydride insertion to form an alkyl intermediate. Evidence has been presented that the double bond isomerization of butenes occurs via this process (*15*) over reduced molybdena-alumina and over a $H_2Os_3(CO)_9PPh_2C_2H_4$–silica catalyst. The results presented herein suggest that one of the above possibilities may be actually occurring. The dilemma presented suggests a promising area for further research.

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