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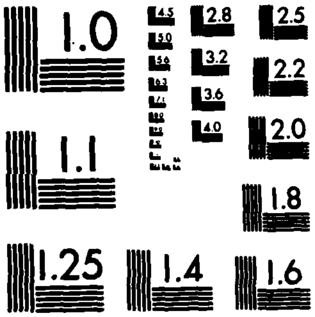

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FT-IR/PA Study of Quinoline Adsorbed on Calcined and Sulfided Mo/γ-Al_2O_3

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FT-IR/PA STUDY OF QUINOLINE ADSORBED ON CALCINED AND SULFIDED $Mo/\gamma-Al_2O_3$

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ABSTRACT

Photoacoustic infrared spectra of quinoline adsorbed on ~~γ~~ gamma-alumina and on oxide and sulfided forms of ~~$Mo/\gamma-Al_2O_3$~~ are reported. In agreement with prior studies with pyridine, both Lewis and Bronsted acidic sites are detected on the oxide catalyst, but only Lewis sites are observed on the sulfided catalyst. Certain surface hydroxyl groups and some Lewis site Al^{3+} anionic vacancies appear to participate cooperatively in the binding of quinoline to the sulfided ~~$Mo/\gamma-Al_2O_3$~~ surface. A precursor to carbonium ions that does not involve a Brønsted acid site is postulated.

Introduction

The study of catalytic hydrodenitrogenation (HDN) of nitrogen containing polyaromatic heterocycles found in fuels derived from oil shale, coal or low grade petroleum is of continuing interest. Reaction network studies of HDN have been carried out over sulfided molybdena catalysts by a number of investigators[1-6] using quinoline as the model compound. The presence of both a heterocyclic ring and a benzene ring in quinoline makes its reaction pattern representative of the benzenoid derivatives of pyridine. These studies have shown that hydrodenitrogenation proceeds via hydrogenation of either or both rings in the quinoline followed by hydrogenolysis of C-N bonds first to open the hetero-ring and subsequently to convert the resulting aliphatic amine intermediates to hydrocarbon and ammonia.

The simultaneous presence of organosulfur compounds and organonitrogen compounds under industrial conditions results in the formation of H_2S by hydrodesulfurization of the former during HDN. Studies of the effect of H_2S on HDN by Satterfield and Gültekin[7] have shown that the presence of H_2S has a slight inhibiting effect on the intermediate hydrogenation steps involved in the overall HDN of quinoline but a marked accelerating effect on the hydrogenolysis step. The latter effect has led Yang and Satterfield[8] to propose that the active site for C-N bond cleavage involves a Brønsted acid site. Massoth and Muralidhar[9] have reviewed other evidence for the possible presence of Brønsted sites on sulfided hydrotreating catalysts. It should be pointed out that these studies can only imply the presence of Bronsted acid sites by comparisons with well known carbonium ion reaction mechanisms, but do not prove their existence. Results of studies[10-16] on the surface acidity of γ-alumina and Mo/γ-Al_2O_3 both in the oxide and sulfided state may be summarized as follows: 1) γ-Alumina has only Lewis acid sites both in the oxide and sulfided state; 2) Both Lewis and Brønsted acid sites are present on calcined Mo/Al_2O_3; and 3) Sulfided Mo/Al_2O_3 has only Lewis acid sites that can be detected spectrally.

Several infrared studies[10,11,16] of pyridine adsorbed on sulfided Mo catalysts have failed to detect the presence of Brønsted acidity. If present, its acid strength must be very weak, or it may develop under hydroprocessing conditions. Since quinoline adsorbs more strongly than pyridine on these catalysts,[17] it was thought that perhaps the Brønsted acidity could be detected by use of quinoline as a probe. No infrared studies have been reported for quinoline adsorbed on calcined (oxide) or sulfided molybdenum catalysts.

The FT-IR/PA technique is well suited for the spectroscopic examination of probe molecules chemisorbed on optically opaque, supported metal catalyst samples and has been described elsewhere.[18] The FT-IR/PA spectra of quinoline adsorbed on both calcined and sulfided forms of γ-Al_2O_3 and Mo/Al_2O_3 were studied and the infrared transmisison spectra of quinoline hydrochloride and the quinoline-$AlCl_3$ adduct were obtained for the assignment of the bands due to Lewis and Brønsted sites on the catalyst surface.

EXPERIMENTAL

The catalyst samples used in this work contained 8% by weight Mo supported on γ-alumina (Ketjen 000 - 1.5 E) having a surface area of 209 m^2/g. An incipient wetness technique was used for preparing the catalyst. The catalysts were precalcined at 500°C for 12 hours. All sample pretreatments were carried out in a conventional vacuum line. The oxide catalyst was prepared by flowing air (Matheson/breathing quality) over the catalyst at 400°C for two hours followed by four hours evacuation. The sulfided samples were prepared by flowing a 9.7% H_2S/H_2 gas (Matheson) mixture over the sample at 400°C for two hours followed by four hours evacuation.

The catalysts were exposed to quinoline (Alfa, 99%) at 150°C for five hours at ~ 4 torr after the quinoline was subjected to several freeze-pump-thawing cycles to remove any traces of gaseous impurities, and then distilled through a P_2O_5 drying column. After exposure, the catalyst was purged in flowing helium for 1 hour and then evacuated for 12 hours at 150°C to remove as much physically adsorbed quinoline as possible. The sample was cooled to room temperature and stored under a positive pressure of helium before it was transferred to the photoacoustic cell in an inert atmosphere glove box.

The infrared transmission spectra of quinolinium hydrochloride and quinoline-$AlC\ell_3$ adduct were obtained using a Qualimatic Digilab FT-IR spectrophotometer. In the former case $HC\ell$ gas (Matheson) was bubbled through a $CHC\ell_3$ (Fisher) solution of quinoline. The quinoline-$AlC\ell_3$ adduct was prepared by adding a stoichiometric amount of triply sublimed $AlC\ell_3$ (Fisher) to a $CHC\ell_3$ solution of quinoline.

RESULTS

Quinoline and its Complexes

Infrared spectra in the 1800 cm^{-1} to 1250 cm^{-1} region of quinoline, quinoline-$AlCl_3$ adduct and quinolinium hydrochloride are given in Figs 1a, 1b and 1c respectively. Figures 1a and 1b are practically identical and therefore one cannot assign Lewis adducts ambiguously. The spectrum of quinolinium hydrochloride is sufficiently different (appearance of new bands at 1637 cm^{-1}, 1558 cm^{-1}, 1410 cm^{-1} and enhancement of the band at 1392 cm^{-1}) to make assignment of the Brønsted bands quite certain. The spectrum of quinolinium-$AlCl_3$ adduct over the entire infrared region (4000 cm^{-1} to 1800

cm^{-1} and 1250 cm^{-1} to 400 cm^{-1} regions are not shown here) agrees well with the data of Luther et al.[19]

Oxided Catalysts

Figure 2 displays the FT-IR/PA spectrum of calcined γ-alumina before and after exposure to quinoline. In Fig. 2a, infrared absorptions in the 1620-1350 cm^{-1} region can be ascribed to the ring stretching modes of quinoline.[20] The out of plane and in plane deformational C-H modes in the 1350 to 800 cm^{-1} region are partially (1200 cm^{-1} to 800 cm^{-1}) buried under the broad Al-O framework vibration of the Al_2O_3 support which is centered around 875 cm^{-1} and extends from 1050 cm^{-1} to 600 cm^{-1}.[21]

The well established conclusion that the surface acidity of calcined γ-alumina is only attributable to Lewis sites compels one to compare the spectrum (Fig. 2a) with that of the quinoline-$AlCl_3$ complex (Fig. 1b) in assigning the vibrational bands. On comparing these two spectra it is seen that most of the vibrational bands of the quinoline-$AlCl_3$ complex appear in the spectrum of quinoline adsorbed on γ-alumina with changes in relative intensity and the expected small frequency shifts arising from the perturbation by the surface field.[22] However, the difference in infrared absorption bands in the region 1800 cm^{-1} to 1250 cm^{-1} between quinoline and quinoline-$AlCl_3$ adduct being slight, the possibility of physical adsorption or adsorption through some other kind of chemical interaction (hydrogen bonding) cannot be ruled out.

The bands to be assigned to adsorbed quinoline in the 1650 cm^{-1} to 1250 cm^{-1} region are at 1623 cm^{-1}, 1600 cm^{-1}, 1517 cm^{-1}, 1377 cm^{-1} and 1309 cm^{-1}. The bands at 1473 cm^{-1}, 1444 cm^{-1} and 1406 cm^{-1} cannot be assigned unambiguously because several bands in that region, attributable to the O-H bending mode of surface hydroxyl groups, are also present in the spectrum of calcined γ-alumina.

In Fig. 2b the series of bands in the region 3070 cm^{-1} to 2952 cm^{-1} are attributable to the C-H stretching mode of quinoline. The bands in the high frequency end are due to the α-hydrogens and the lower frequency bands are attributable to β-hydrogens of quinoline.[23] The bands at 3733 cm^{-1}, 3674 cm^{-1}, 3656 cm^{-1} and 3567 cm^{-1} in Fig 2c are due to the O-H stretching mode of the surface hydroxyl groups of the alumina support.[24]

Figure 2d is the spectrum of blank calcined γ-alumina. Sharp bands at 3768 cm^{-1}, 3735 cm^{-1}, and 3678 cm^{-1} and weak shoulders at 3700 cm^{-1} and 3657 cm^{-1} plus a very broad band centered around 2900 cm^{-1} due to hydrogen bonded surface hydroxyl groups are observed. The positions of the bands are in general agreement with previous findings.[25-27] The remarkable difference in the hydroxyl stretching region of spectra 2c and 2d is noted, an indication that a strong perturbation[27] of the surface hydroxyl groups of the support occurs on adsorption of quinoline. This observation will have important consequences as will be discussed below.

Figure 3a displays the FT-IR/PA spectrum of quinoline adsorbed on calcined Mo/Al_2O_3. In addition to the bands attributed to adsorbed quinoline on alumina (Fig. 2a), new bands are observed at 1696 cm^{-1}, 1642 cm^{-1}, 1561 cm^{-1}, 1411 cm^{-1} and 1394 cm^{-1}. The bands at 1517 cm^{-1} and 1623 cm^{-1} seem to be markedly attenuated in intensity.

As mentioned previously, it is well established that Brønsted sites are present on the $Mo/\gamma\text{-}Al_2O_3$ surface; thus, one of the ways to assign the bands attributable to Brønsted acid sites on this surface would be to compare this spectrum with the spectrum of quinolinium ion (Fig. 1c) and identify similarities in the ring vibrations of quinoline in the 1700 cm^{-1} - 1350

cm^{-1} region as was done by Parry[28] in a pyridine adsorption study. By comparing the two spectra, Fig. 1c and Fig. 3a, we assign the bands at 1642 cm^{-1}, 1561 cm^{-1}, 1411 cm^{-1} and a distinct shoulder at 1394 cm^{-1} to quinoline adsorbed on Brønsted acid (BQ) sites on the oxide Mo/γ-Al_2O_3 catalyst. The appearance of the strong band at 1696 cm^{-1} is noted. Since a similar band was not found in the complex quinolinium hydrochloride spectrum (Fig. 1c), we cannot attribute this band to Lewis or Bronsted sites on the catalyst surface. Assignment of this band is deferred until later. The change in the relative intensities of the bands at 1623 cm^{-1} and 1518 cm^{-1} compared to that of Fig. 2a is noted; a possible implication of this will also be discussed.

On incorporation of Mo the hydroxyl region of the spectrum of γ-alumina shows, (Fig. 3b) the expected changes[29-31], namely the bands at 3733 cm^{-1} and 3674 cm^{-1} are attenuated and replaced by a broad peak. However, the 3567 cm^{-1} band is unaffected by incorporation of Mo in the γ-alumina support. The 3070 cm^{-1} band and the bands around 2950 cm^{-1} are also relatively unaffected by addition of Mo.

Sulfided Catalyst

Figure 4 displays the FT-IR/PA spectrum of quinoline adsorbed on sulfided Mo/γ-Al_2O_3 catalyst. The bands at 1641 cm^{-1}, 1560 cm^{-1}, 1411 cm^{-1} and 1394 cm^{-1} attributed to Bronsted sites on the oxide catalyst (Fig. 3a) are absent in this case as in previous pyridine adsorption studies.[16,32] Other bands due to adsorbed quinoline in this region (Fig. 4a) although unshifted in frequency (with 4 cm^{-1} resolution) have been altered remarkably in relative intensities, compared to the oxide state (Fig. 3a). The intensities are comparable to those found in the γ-alumina spectrum (Fig. 2a). The intensities of the bands at 1623 cm^{-1} and 1516 cm^{-1} for the sulfided Mo/Al_2O_3

catalyst (Fig. 4a) are markedly enhanced compared to the calcined catalyst (Fig. 3a). This observation is important in interpreting the results.

The broadening of the 1598 cm^{-1} band and the appearance of a distinct shoulder at 1365 cm^{-1} on the 1375 cm^{-1} band, could be associated with the 1570 cm^{-1} and 1341 cm^{-1} bands found in infrared studies[21,33] of H_2S adsorbed on alumina, which we have also observed (spectrum not shown) in the present study. The 3567 cm^{-1} band remained unshifted on sulfiding; however, there is a noticeable broadening of the H-bonded band superimposed on the sharp 3567 cm^{-1} band, indicative of an increase in hydrogen bonding on sulfiding, in line with previous observations.[29]

Finally, the strong band at 1696 cm^{-1} found in the oxide Mo/Al_2O_3 catalyst persists (within 4 cm^{-1} resolution) on the sulfided catalyst. This observation will have an important bearing on the proposed model of quinoline adsorption on the Mo/Al_2O_3 catalyst.

Discussion

Assignment of the 3567 cm^{-1} band.

As mentioned previously, on comparing Figs. 2c and 2d a remarkable difference in the O-H stretching region of γ-alumina is noticed. The highest frequency band at 3768 cm^{-1} is sharply attenuated. The bands at 3674 cm^{-1}, 3656 cm^{-1} and 3733 cm^{-1} remain relatively unaffected and a strong band peaking at 3567 cm^{-1} has appeared in the former.

The appearance of this 3567 cm^{-1} band may indicate a selective type of interaction of the quinoline molecule with the O-H groups largely responsible for the high frequency 3788 cm^{-1} band. Kiselev and Uvarov,[27] in their infrared study of adsorbed benzene on γ-alumina have observed a similar selective shift (110 cm^{-1}) of the high frequency O-H band towards the longer wavelength region. They have attributed this to a specific and selective interaction of the benzene molecule with the surface hydroxyl groups responsible for the high frequency band. Studies of methyl benzenes adsorbed on a silica surface[34] have shown a shift of ~ 20% of the high frequency bands towards longer wavelengths indicating a strong and selective interaction. This together with the observation that pyridine adsorption on alumina does not perturb the OH frequencies[35,36] leads us to infer that adsorbed quinoline on a γ-alumina surface, in addition to the possible formation of a Lewis type adduct through the nitrogen lone pair, interacts (hydrogen bonds) strongly and selectively with the surface hydroxyl groups. This occurs through the Π-electron system of the non-nitrogen containing aromatic ring[37-39] (as observed by an approximately 8% shift of the high frequency O-H stretching bands towards the long wavelength region, giving rise to the strong band at 3567 cm^{-1} on adsorption of quinoline). This type of interaction may be partly responsible for the observation that quinoline adsorbs more strongly than pyridine,[17] although the pK_a values (pyridine = 5.16 and quinoline = 4.87)[40] indicate that the reverse should be the case if purely acid-base type interactions are considered on acidic surfaces.

Assignment of the 1696 cm^{-1} band.

The strong band at 1696 cm^{-1} found in the oxide Mo/Al_2O_3 catalyst (Fig. 3a) persists in the sulfided catalyst (Fig. 4a) and is also present as a weak, somewhat shifted but distinct shoulder (1689 cm^{-1}) in the spectrum of quinoline adsorbed on γ-alumina (Fig 2a). Because of the absence of any band in this region in the spectra of both QHCl and the Q-$AlCl_3$ adduct, this band cannot be attributed to a simple Brønsted or a Lewis type adduct of quinoline. We assign the 1696 cm^{-1} band from the following considerations.

From the correlation chart[41] of infrared spectroscopy, absorptions in this region could be due to a $-\overset{|}{C}=N-$ stretching mode. Fabian et al.[42], in their review of the $-\overset{|}{C}=N-$ stretching mode have noted the difficulty in identifying bands in this region due to considerable change in intensity and frequency of these absorptions with changing environment. The $-\overset{|}{C}=N-$ absorptions in non-conjugated ring systems occur within the 1690-1640 cm^{-1} region. The absorptions in the high frequency end of this region are mainly due to compounds like oxazines, and oximes (1674 - 1665 cm^{-1}), in which one or more NH groups are attached to the carbon atom of the C = N link; in guanidine and related compounds, a variation between 1718 and 1530 cm^{-1} is found.[43] Because of the lack of resemblance between these compounds and quinoline, it is not logical to assign the 1696 cm^{-1} band to a specific structure yet. However, "...when the nitrogen atom of the C = N bond is so substituted that it is able to take on a more polar character, the characteristic frequency alters considerably......The direction of frequency shift in such cases depends in part on the nature of the charge on the nitrogen atom. In N = C compounds, for example, the frequencies are raised a little above the normal,....".[43] Leonard et al.[44] found that a shift of 10-50 cm^{-1} toward higher frequency is observed in going from $-\overset{|}{C}=\overset{|}{C}-\overset{|}{N}-$ to $-\overset{|}{C}H-\overset{|}{C}=\overset{+}{N}<$. For example, in going from 1-n-butyl-2-methyl- Δ^2-tetrahydro pyridine to its perchlorate salt, a shift of 34 cm^{-1} is observed giving rise to a band at 1684 cm^{-1}. In the case of the perchlorate salt of 1,2-dimethyl- Δ^2-pyroline, a band at 1699 cm^{-1} is observed. Leonard et al.[44] have assigned these high frequency bands to $-\overset{|}{C}=\overset{+}{N}<$ stretching modes. The closer resemblance of quinoline to these compounds makes it possible to speculate on slightly better grounds that the 1696 cm^{-1} band is due to the formation of a bond that resembles a $-\overset{|}{C}=\overset{+}{N}<$ species. However, for adsorbed quinoline to give rise to a band at 1696 cm^{-1}, because of formation of a $-\overset{|}{C}=\overset{+}{N}<$ type of bond as assigned above, a mechanism that causes the loss of conjugation of the ring system must exist. We propose that the O-H... Π-cloud interaction that gives rise to the 3567 cm^{-1} band causes the loss of conjugation of quinoline.

As mentioned previously, the bands probably attributable to the N - H bending modes of quinolinium ion are absent in the spectrum of the sulfided catalyst. The 1696 cm^{-1} band persists with similar intensity as in the oxide Mo/Al_2O_3 catalyst, which rules out the possibility that nitrogen lone pairs coordinate with protons giving rise to the 1696 cm^{-1} band through an unconjugated $-\overset{|}{C}=\underset{|}{\overset{+}{N}}-H$ type of species. The most probable situation would be the coordination of the nitrogen lone pairs to Al^{3+} anionic vacancies, where the Lewis acidity is enhanced on incorporation of Mo. However, the direct coordination to Mo anionic vacancies on the surface cannot be ruled out. The question of lone pair coordination is discussed in greater detail below.

Proposed Models

The evidence presented points strongly to a cooperative phenomenon operative on the catalyst surface. We propose an interaction involving the high frequency O-H groups and the Lewis acid sites in the catalyst surface. It should be mentioned that Knözinger et al.[45] have invoked the concept of cooperative effects in their IR-study of adsorbed organic molecules on alumina surfaces.

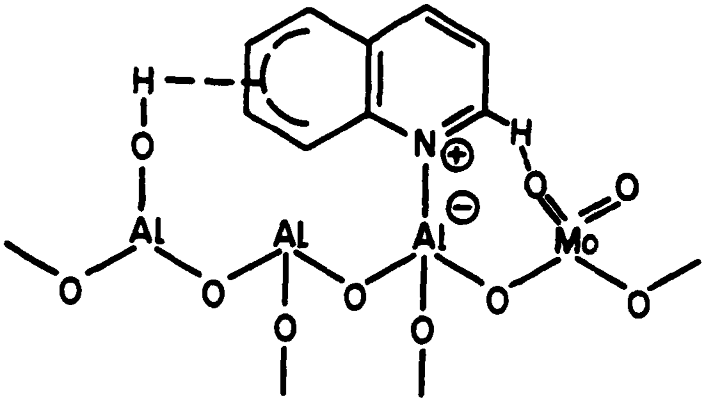
A crude model that emerges from the results of this study would be as follows: Quinoline adsorbed on calcined γ-alumina interacts with the surface mainly through a strong O-H...Π-cloud interaction. The Π-electron cloud of the quinoline ring system interacts (hydrogen bonds) specifically with the high frequency (3780 cm^{-1}) O-H groups on the alumina surface. This causes a loss of conjugation of the aromatic quinoline. A weak Lewis type adduct is formed by coordination of the nitrogen lone pairs to Al^{3+} anionic vacancies, resulting in a shoulder at 1696 cm^{-1} attributable to an unconjugated $-\overset{|}{C}=\overset{+}{\underset{|}{N}}$---$-Al^{-}$ type of species as assigned above. Chemisorbed quinoline on the oxide Mo/γ-Al_2O_3 surface exists mainly in two forms: Brønsted type adducts and a Lewis type adduct which is different from that found on a pure γ-alumina surface. The Brønsted adduct is evidenced by the appearance of the bands due to N-H bending modes present in the spectrum of quinolinium ion. The appearance of the intense band at 1696 cm^{-1} and the sharp attenuation of the bands at 1622 cm^{-1} and 1518 cm^{-1} is attributed to quinoline adsorbed on a Lewis site of the γ-alumina modified by the presence of Mo in the Al_2O_3 lattice.

On incorporation of Mo, the Lewis acidity of the Al^{3+} anionic vacancy is increased, resulting in a strong coordination of the nitrogen lone pairs to these sites. This almost complete charge transfer from nitrogen together with the deconjugative effect of the O-H... Π-system interaction forms the unconjugated $-\overset{|}{C}=\overset{+}{\underset{|}{N}}-$ type of species. The enhancement of the Lewis acidity of the Al^{3+} ion may be attributable to a combination of electronic and steric effects.[46]

The electronic part may be an electron withdrawing inductive effect of Mo species on an adjacent Al^{3+} ion. This inductive effect could be similar to the one that gives rise to Brønsted acidity on the γ-alumina surface with incorporation of Mo, an effect that makes the hydroxyl protons more labile.

The steric effect could be attributed to the presence of Mo, inducing a certain degree of disorder in the alumina surface. The ions of a disordered surface may undergo at least a local reorganization under dynamic conditions (viz. high temperature). Thus, the access and consequent coordination to a Al^{3+} ion may be facilitated by a displacement towards the surface. Similar reasoning has been presented before to explain the bonding of sterically hindered 2,6-dimethyl pyridine to Al^{3+} sites on an alumina surface.[46]

In the infrared study of monosubstituted quinoline[47] it has been observed that an electron withdrawing substituent at the 2- or 6-position causes approximately an order of magnitude attenuation of the 1622 cm^{-1} and 1508 cm^{-1} bands. Hence, most probably an electron withdrawing mesomeric effect, operative through hydrogen bonding at the 2-position of quinoline with the reactive oxygen atoms of the molybdenum oxide, causes the sharp decrease of the 1622 cm^{-1} and 1518 cm^{-1} bands. However, a similar type of effect at the 6-position cannot be ruled out. The model may be schematically represented as

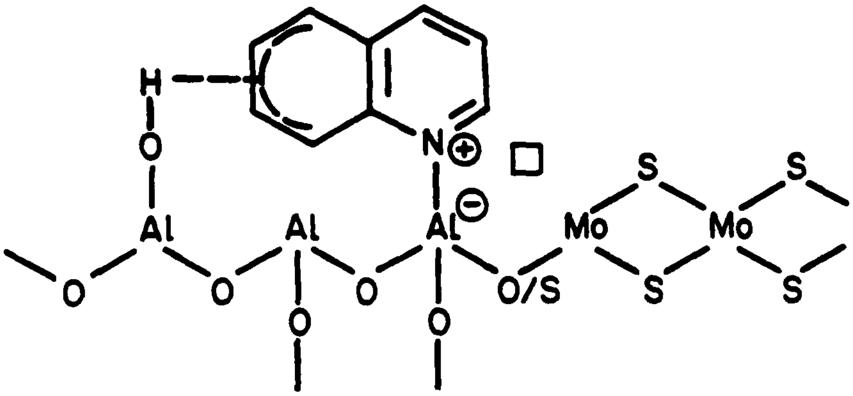


I

On sulfiding, the terminal oxygens associated with the molybdena are first replaced by sulfur,[48] followed by rupture of the interaction bonds with the support to form a monomolecular two-dimensional MoS_2 cluster.[49] Sulfur anion vacancies are likely present at the edges of the clusters.[9]

The persistence of the 1696 cm^{-1} band (Fig. 4a) indicates the presence of a $-\overset{|}{C} = \overset{+}{\underset{|}{N}}-$ type of species on the surface of the sulfided catalyst and also indicates that the electronic and steric effects mainly responsible for the almost complete charge transfer from nitrogen to Al^{3+} vacancies are still operative in the sulfided catalyst. The reappearance of the bands at 1623 cm^{-1} and 1516 cm^{-1} indicates the absence of a strong electron withdrawing effect at the 2-position of adsorbed quinoline. This may be a consequence of replacement of the terminal oxygen atoms, associated with molybdena by sulfur or anionic vacancies. The enhanced intensity of the bands in the 1700 cm^{-1} to 1300 cm^{-1} region (Fig. 4a) compared to the oxide catalyst spectrum (Fig. 3a) is probably due to the increased acidity[50] and hence greater adsorption on the sulfided catalyst. The slight broadening of the 1696 cm^{-1} band with the appearance of a shoulder at 1684 cm^{-1} may indicate that the environment of the Al^{3+} ion is altered (i.e. the C = N stretching vibrations are very sensitive to the environment). However, direct coordination of the nitrogen lone pairs with Mo anionic vacancies (generated on sulfiding) cannot be ruled out.

A schematic representation of the model for adsorbed quinoline on the sulfided catalyst is shown below.



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The symbol □ denotes an anionic vacancy and the O/S signifies a partial attachment of the MoS_2 phase to the Al_2O_3 surface through an O or S atom.

The proposed cooperative effect on the catalyst surface is consistent with the concept of dual sites involved in the HDN of quinoline on sulfided molybdenum catalysts postulated by Yang and Satterfield.[8] Their postulated dual sites are sulfur anionic vacancies associated with the molybdenum and Brønsted acid sites. The present study suggests a somewhat different picture of the role and nature of these sites. The absence of infrared spectral evidence for the Brønsted sites on the sulfided catalyst suggests that structure II above is the precursor to the carbonium ion and the subsequent cleavage (hydrogenolysis) of the C-N bond. On the sulfided catalyst, the formation of a carbonium ion at the 2-position of quinoline is facilitated by the elimination of the reactive oxygens associated with the molybdenum. As noted above, an electron withdrawing effect is operative through hydrogen bonding at the 2-position on the oxide catalyst. This is consistent with the observation that increased sulfiding enhances HDN of quinoline.

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Figure Captions

1. FT-IR transmission spectra of the following solutions (a) quinoline/$CHCl_3$ (b) quinoline/$AlCl_3$/$CHCl_3$ and (c) quinoline/HCl/$CHCl_3$

2. (a), (b) and (c) are different regions of the FT-IR/PA spectrum of quinoline adsorbed on calcined γ-alumina. (d) FT-IR/PA spectrum of blank calcined γ-alumina. The ordinate represents normalized photoacoustic response. Each region of the spectra (a), (b), (c) and (d) is individually autoscaled.

3. (a) and (b) are different regions of the FT-IR/PA spectrum of quinoline adsorbed on calcined Mo/γ-alumina. The ordinate represents normalized photoacoustic response and (a) and (b) are individually autoscaled.

4. (a) and (b) are different regions of the FT-IR/PA spectrum of quinoline adsorbed on sulfided Mo/γ-alumina. The ordinate represents normalized photoacoustic response. (a) and (b) are individually autoscaled.

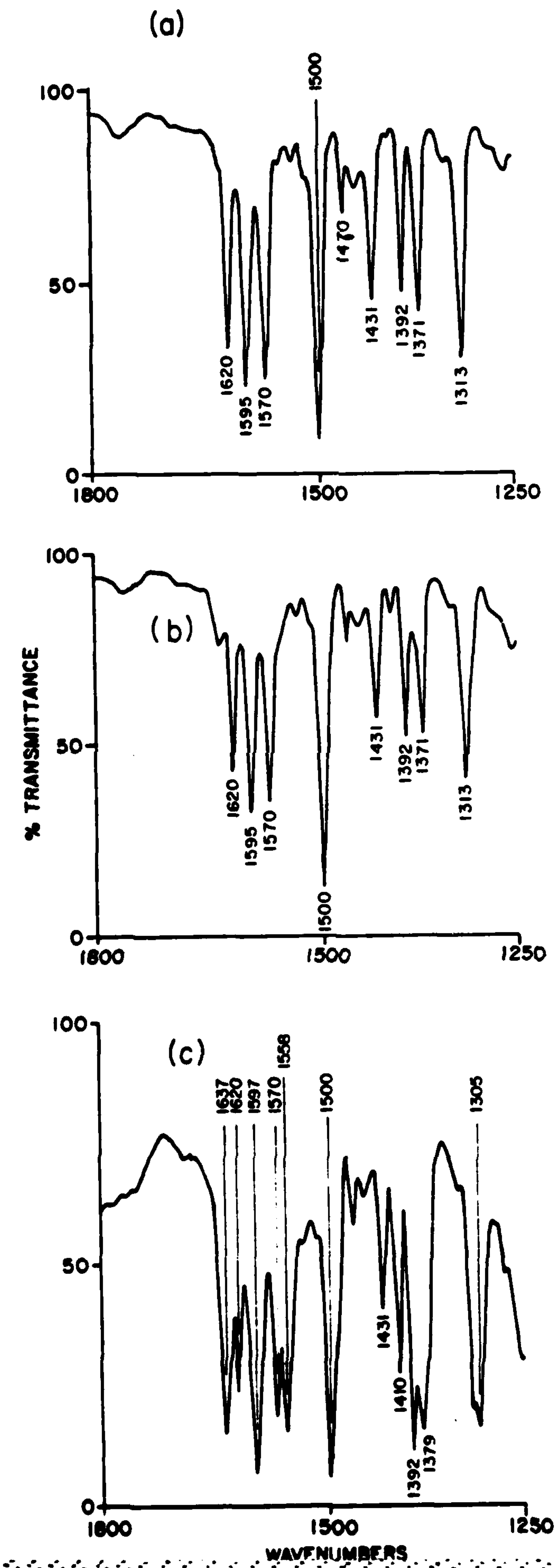
(a)
100
50
0
1500
1620
1595
1570
1470
1431
1392
1371
1313
1800
1500
1250
(b)
100
50
0
1620
1595
1570
1500
1431
1392
1371
1313
1800
1500
1250
% TRANSMITTANCE
(c)
100
50
0
1637
1620
1597
1570
1558
1500
1305
1431
1410
1392
1379
1800
1500
1250
WAVENUMBERS

Fig. 1

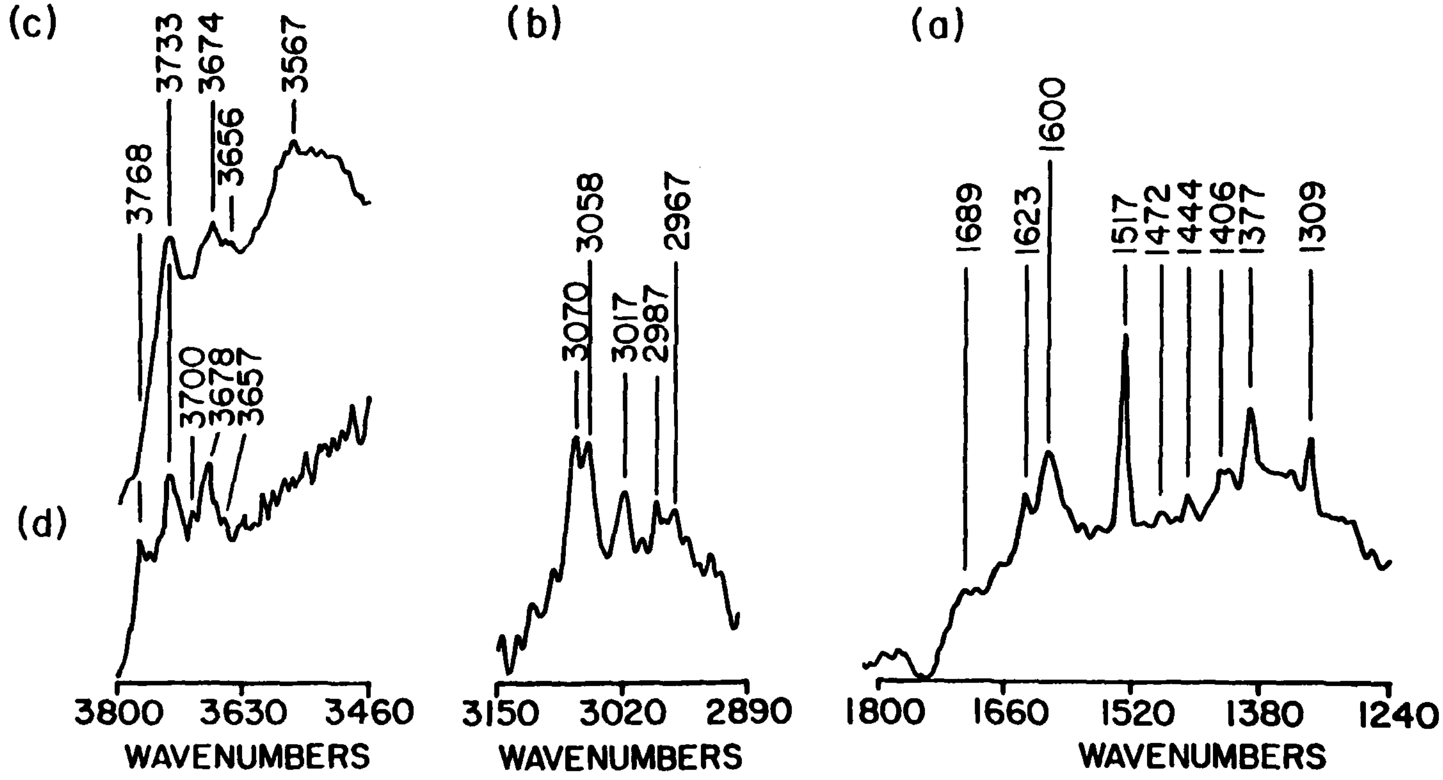
(c)
3768
3733
3674
3656
3567
(d)
3700
3678
3657
3800
3630
3460
WAVENUMBERS
(b)
3070
3058
3017
2987
2967
3150
3020
2890
WAVENUMBERS
(a)
1689
1623
1600
1517
1472
1444
1406
1377
1309
1800
1660
1520
1380
1240
WAVENUMBERS

Fig. 2

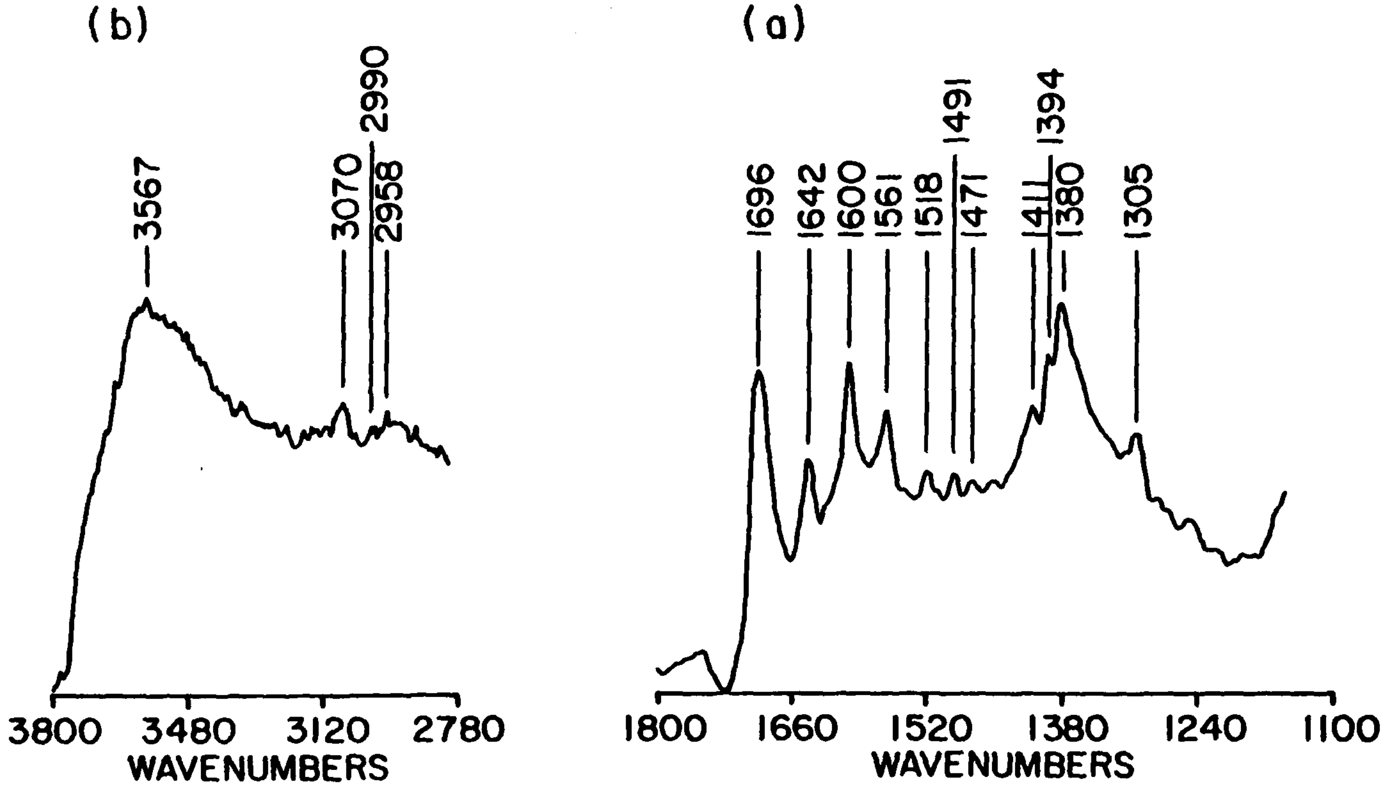
(b)
3567
3070
2990
2958
3800
3480
3120
2780
WAVENUMBERS
(a)
1696
1642
1600
1561
1518
1491
1471
1411
1394
1380
1305
1800
1660
1520
1380
1240
1100
WAVENUMBERS

Fig. 3

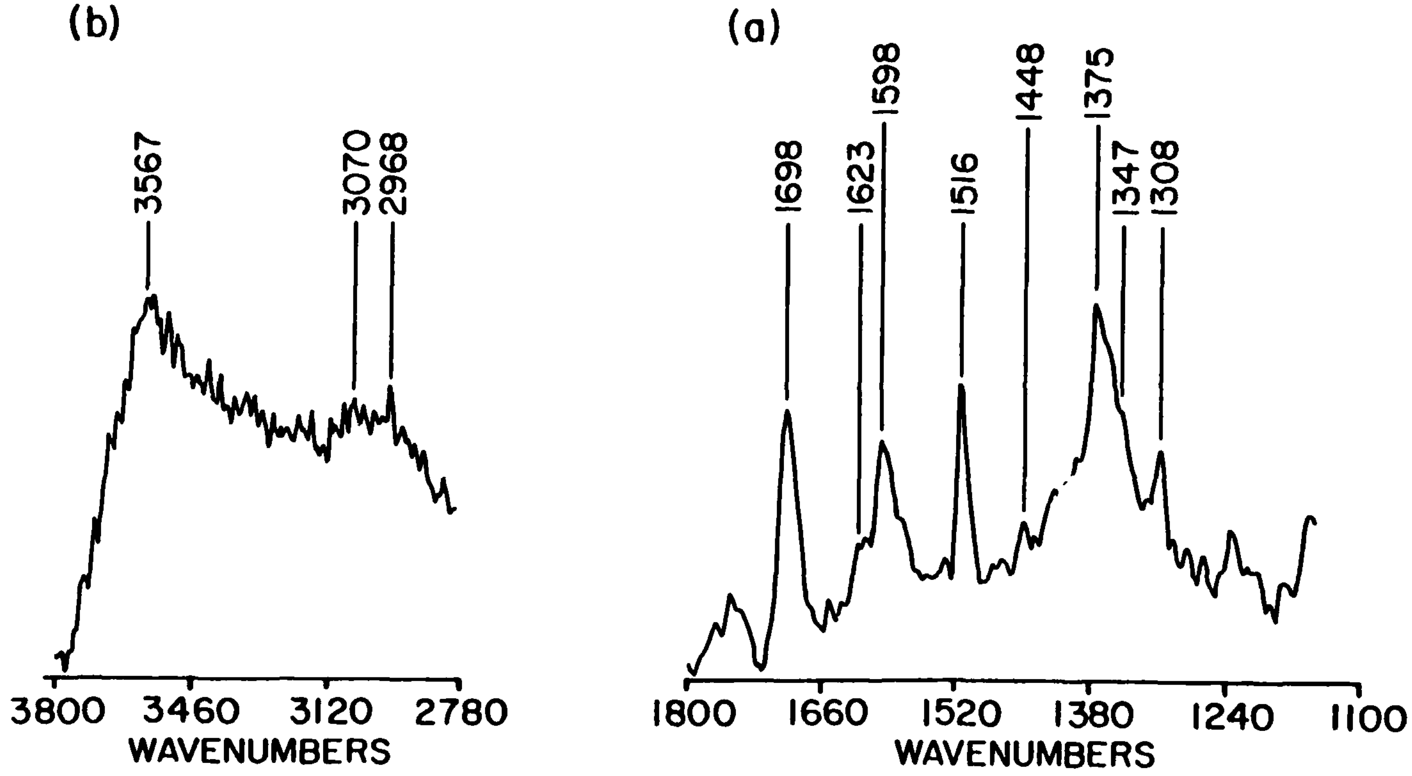
(b)
3567
3070
2968
3800
3460
3120
2780
WAVENUMBERS
(a)
1698
1623
1598
1516
1448
1375
1347
1308
1800
1660
1520
1380
1240
1100
WAVENUMBERS

Fig. 4