

Surface Structure and Catalytic Activity of a Reduced Molybdenum Oxide–Alumina Catalyst. 1. The Adsorption of Pyridine in Relation with the Molybdenum Valence

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The adsorption of pyridine on a complete monolayer molybdenum oxide–Al₂O₃ catalyst was studied. Both Lewis and Brønsted acid sites are present on a catalyst with a Mo valence of ~4.1. The orientation of adsorbed pyridine was studied by means of its interaction with surface OD groups, which leads to the formation of only 2-deuteriopyridine. The fraction of molybdenum ions active for hydrogenation reactions and that for pyridine adsorption is approximately equal to the Mo⁵⁺ content, i.e., ~0.2. It is concluded that ensembles of Mo ions of higher and lower valencies (possibly Mo⁵⁺ and Mo⁴⁺) are the sites active for the chemisorption of organic molecules and hydrogen and for hydrogenation reactions.

Introduction

The nature and strength of the acid sites of surface oxides have been the subject of various investigations by means of infrared spectroscopy. To this extent the spectra of adsorbed pyridine appeared to be better interpretable than those of ammonia.^{1–4}

In a previous paper we mentioned the existence of Lewis and Brønsted acid sites on a reduced molybdena–alumina catalyst as indicated by pyridine adsorption.⁵ Kiviat and Petrakis⁶ also found such adsorption sites on a similar catalyst but they could not verify whether the adsorption takes place on the alumina or on the molybdenum oxide. We shall discuss their conclusions in this paper. We report on the investigations of a catalyst, which consists of an alumina carrier almost completely covered with a monomolecular layer of molybdenum oxide.^{7,8} The orientation of the adsorbed pyridine toward the surface was studied by observing its interaction with deuterium present on the surface. Measurements of the mean valence of Mo after reduction and of the maximum amount of pyridine adsorbed provided data for discussing the topography of the surface after reduction and the nature of sites active for hydrogenation reactions.

Experimental Section

a. *Preparation of the Catalyst.* From a stream of water vapor saturated with MoO₂(OH)₂ this compound was adsorbed on γ -Al₂O₃ at 600 °C. In most cases Degussa alumina (75 m² g⁻¹) was used as a carrier. The catalyst, which contained 10.2% MoO₃ by weight, was reduced in a stream of purified hydrogen during 16–24 h at 450 °C.⁸

b. *Valence Measurements.* The average valence of molybdenum was determined by means of a method described by Bourret.⁹ This method is based on the determination of the amount of NaIO₄ necessary to oxidize the molybdenum to Mo(VI). Oxygen was carefully excluded. The reduced samples were stirred in the oxidizing solution until the color due to reduced molybdenum ions had vanished. A blank run was always taken with pure alumina which took not more than a few percent of the periodate needed for the reduced Mo catalysts. The accuracy of the method was checked by means of

pure bulk MoO₂ tableted with pure γ -alumina. Mo valencies between 4.01 and 4.08 were found in the last case.

c. *Quantitative Adsorption Measurements.* The adsorption of pyridine was studied by using a quartz spring balance. The spring sensitivity was 1 mm/10 mg. A load of 0.5 g of catalyst was used.

d. *Infrared Measurements.* The same equipment and procedures were used as described elsewhere.⁷ Because of the strong absorption due to the relatively high amount of reduced molybdenum oxide an attenuation comb in the reference beam together with electronic transmission scale expansion always had to be used.

e. *ESR Measurements.* A Varian X-band spectrometer was used with a 100-kHz modulation unit. The measurements were carried out after reduction in situ.

f. *Materials.* Reagent grade Merck pyridine was used after having been dried and outgassed by the freezing, pumping, and thawing technique. D₂ was supplied by Baker (purity >99%), MoO₃ by Schuchardt, and bulk MoO₂ by K & K Laboratories Inc.

Results

1. *Determination of the Mean Valence of Mo in the Reduced Catalyst.* Reduction of the complete monolayer catalyst by means of purified hydrogen at 450 °C during 16 h or longer yields a mean Mo valence of 4.14 (standard deviation 0.13 after 10 runs). Even reduction for some weeks does not change this value. Catalysts containing less molybdenum than that corresponding to a complete molybdenum(VI) oxide monolayer, prepared by adsorption of polymolybdate anions from solutions of various acidities,⁸ however, are reduced less (Table I). They do not reach the mean valence of four under the chosen circumstances. This fact is in agreement with the results of Sondag¹⁰ and Massoth,¹¹ among others, as well as with the change of the Mo⁵⁺ content with increasing Mo percentage found by other authors.¹² Variation of the temperature of course has a great influence on the final degree of reduction.

2. *The Infrared Absorption Spectrum of Pyridine on Steam-Treated Alumina.* The alumina was treated with steam at 600 °C (*p* = 500 Torr) for a few hours, i.e., under the

TABLE I: Mo Valences of MoOx–Al₂O₃ Catalysts with Different Percentages of Mo^a after Reduction for 16 h at 450 °C in Hydrogen

% MoO ₃	Mean Mo valence	% MoO ₃	Mean Mo valence
2.8	5.7	17.8	4.6
4.9	5.2	22.0	4.4
11.7	4.6		

^a The carrier was Ketjenfine alumina ($S_g = 220 \text{ m}^2/\text{g}$). A full monolayer corresponds to about 27% MoO₃.

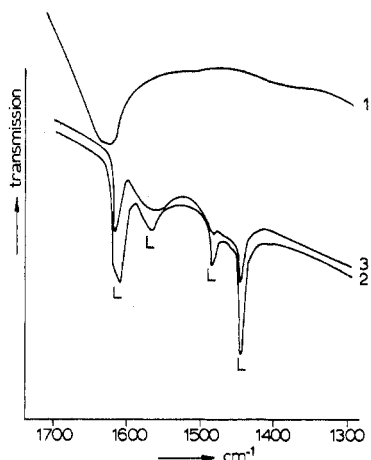


Figure 1. Spectra of pyridine adsorbed on Al₂O₃: (1) background without pumping off water; (2) after evacuation at 150 °C for 0.5 h; (3) same treatment at 250 °C; L = Lewis bound pyridine.

same conditions as the alumina used for the preparation of the catalyst. This is necessary because of some change of the OH group spectrum after this treatment, which is indicative of a change of the surface structure.⁷

The spectrum of pyridine adsorbed at room temperature at $p = 10$ Torr and pumped off at 150 °C (Figure 1) is almost identical with the spectrum measured by Parry.³ The bands around 1450 and 1620 cm⁻¹ show Lewis acidity. Even the presence of some water vapor ($p = 10$ Torr, $t = 400$ °C, see background spectrum) before the adsorption of pyridine does not create protons able to form a Brönsted adsorbed species.

3. *The Spectrum after Adsorption of Pyridine on Molybdenum Oxide–Alumina with a Mean Mo Valence Near Four.* The absence of a 1630-cm⁻¹ band before pyridine adsorption clearly shows that water has been carefully removed by evacuation at 450 °C and 10⁻⁵ Torr (Figure 2, spectrum 1).

The main changes in the spectrum of samples with pyridine adsorbed at room temperature (compare Figures 1 and 2) are due to the presence of additional bands in Figure 2 above 1600 cm⁻¹ and of a weak band at 1540 cm⁻¹. These bands reflect the existence of a pyH⁺ species on the molybdenum(IV) oxide–Al₂O₃ surface.^{3,4,6} Obviously, some water has been taken up by the disk during pyridine adsorption. The presence of more water yields more Brönsted acidity (Figure 3) as shown by the intensity of the 1540- and 1640-cm⁻¹ bands. This is in agreement with the observations made in case of silica–alumina.^{3,4}

4. *The Interaction of Adsorbed Pyridine with OD Groups.* H–D exchange was brought about by means of D₂ at 450 °C until all OH hydrogens had vanished. The disk was then evacuated at the same temperature to obtain some resolution

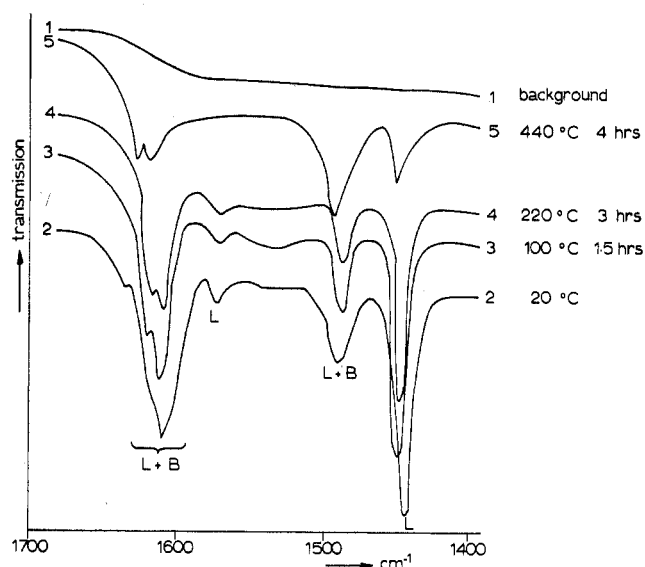


Figure 2. Spectra of pyridine adsorbed on a "dry" molybdenum oxide(IV)–Al₂O₃ catalyst: L = Lewis bound pyridine, B = Brönsted bound pyridine. (1) Background after evacuation at 450 °C for 8 h. The evacuation conditions after adsorption of pyridine are indicated.

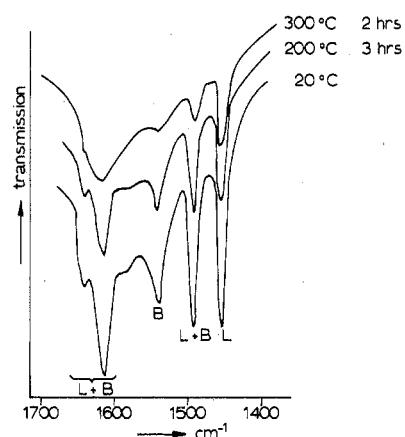


Figure 3. Spectra of pyridine adsorbed on a water containing molybdenum oxide(IV)–Al₂O₃ catalyst.

of the OD groups spectrum and to remove water and deuterium from the system. The evacuation took place for a short time to avoid elimination of too many chemisorbed deuterium atoms (Figure 4B, spectrum 1).

After adsorption of pyridine at room temperature all bands found around 1500 cm⁻¹ (see Figure 4A) may be ascribed to coordinately bound species. Neither pyD⁺ nor pyH⁺ can be detected: the 1540-cm⁻¹ pyH⁺ band is substituted by the corresponding pyD⁺ band which coincides with the 1490-cm⁻¹ band¹³ (Figures 1 and 2). The adsorption disturbs all OD groups. Upon evacuation and raising the temperature a slight restoration of the original OD groups spectrum is observed due to some desorption of pyridine (Figure 4B). At temperatures above 300 °C the OD groups tend to vanish and at the same time a band at 1435 cm⁻¹ appears. The relative increase in intensity of this band stops when the OD groups are no longer detectable. This shows that a surface reaction has taken place.

5. *Experiments Pertaining to the Adsorption Capacity of Alumina and of Molybdenum(IV) Oxide–Al₂O₃.* The quartz spring balance measurements at 350 °C reveal that on the

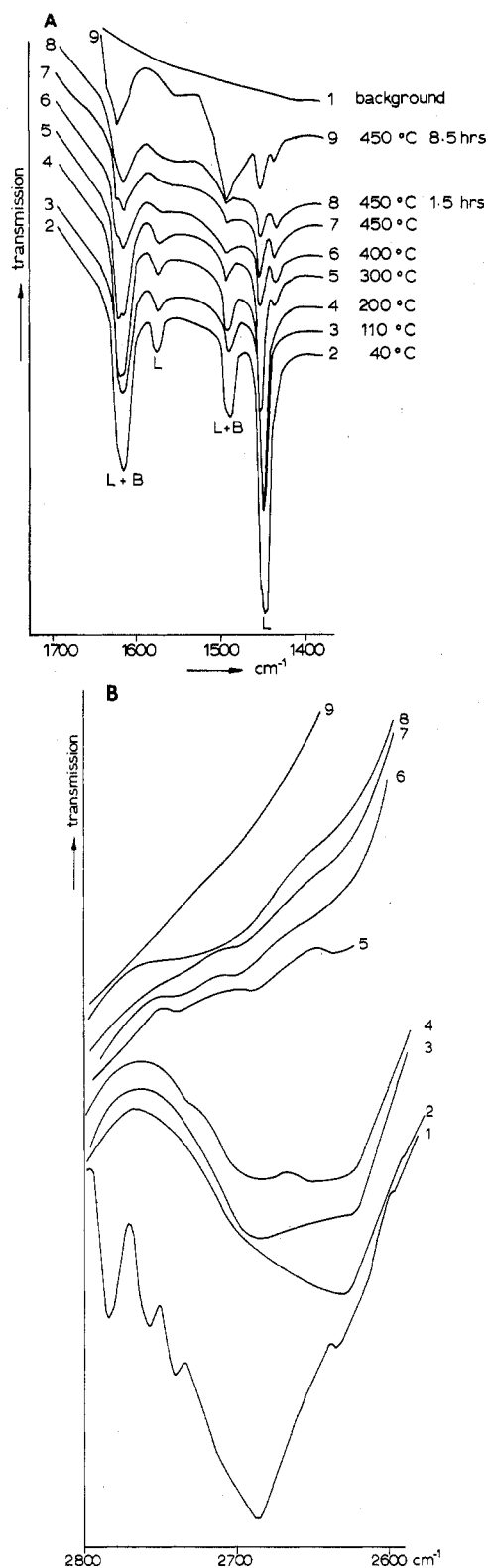


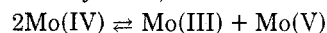
Figure 4. (A and B) Spectra during the reaction of adsorbed pyridine with OD groups after evacuation for 0.5 h unless otherwise indicated. The numbers in Figure 4A correspond with those in Figure 4B: (4A) spectra of pyridine; (4B) spectra of OD groups.

reduced moly-alumina the maximum concentration of pyridine (reached at $p = 8$ Torr) is about twice that on pure alumina, i.e., 2.5×10^{-3} and 1.3×10^{-3} mmol m $^{-2}$, respectively. Nearly the same ratio was found in our laboratory at 300 °C when using the dynamic adsorption method.¹⁴

Discussion

The Molybdenum Valence. As shown, the average valence of the Mo ions is 4.1 after reduction at 450 °C for 16 h. This value is hardly time dependent. Also, the presence of water ($p = 15$ Torr) during the reaction does not cause a remarkable change in the valence state,¹⁵ which is in contrast with what was found by Sondag¹⁰ and Massoth.¹¹ The fact, reported in the literature,¹¹ that a lower coverage of the alumina by molybdenum(VI) oxide yields a higher mean valence is established by our measurements (see Table I). This supports the conclusion that those parts of the alumina which strongly bind the molybdenum(VI) ions stabilize the higher valences.^{11,12}

Many authors have reported the detection by ESR of Mo(V) ions having reduced the catalyst with hydrogen.^{12,16} Qualitative ESR measurements in our laboratory revealed the presence of Mo(V) ions even after reduction at 450 °C for 1 week (providing a valence of four). Recently, Seshadri and Petrakis,¹⁶ studying a catalyst with a Mo percentage comparable with that of a complete monomolecular molybdenum(VI) oxide layer, found that after reduction at 450 °C for some hours, at least 10% of the Mo ions had a valence of five, which is in accordance with the measurements performed by Masson and Nechtschein.¹² The inaccuracy in the determination of the valence (i.e., 4.1 ± 0.1) does not allow us to ascribe this fact to the stabilizing influence of the carrier. Also a disproportionation reaction may occur, viz.



The Adsorption of Pyridine on Alumina. The absence of Brønsted acidity when pyridine is adsorbed (Figure 1) is in agreement with the conclusions of Parry,³ among others.

The maximum amount of pyridine to be adsorbed, i.e., 1.3×10^{-3} mmol m $^{-2}$, corresponds to a surface occupation of the same order of magnitude found by Knözinger and Stolz on this oxide.¹⁷

Pyridine Adsorbed on Reduced Moly-Alumina. The spectra observed are in accordance with those of Kiviat and Petrakis.⁶ Even after careful elimination of water the weak band at 1540 cm $^{-1}$ reveals the existence of some Brønsted acidity.

Previously⁷ we showed that reduction of a complete molybdenum(VI) oxide monolayer on alumina involves a shrinkage of this layer so that the reduced molybdenum oxides covers the alumina only partly (for about 80%). Part of the pyridine may therefore be adsorbed on the bare alumina. The intensities and the positions of the OH absorption bands of the free alumina in molybdenum(IV) oxide-alumina are almost identical with those of pure alumina. This gives evidence that the adsorption capacity of the alumina as such will not differ much from that of the pure carrier, i.e., 1.3×10^{-3} mmol m $^{-2}$ of alumina. From this and the adsorption capacity of molybdenum(IV) oxide-alumina observed (twice as much as that of the carrier) the conclusion arises that pyridine is mostly adsorbed on the molybdenum oxide. The maximum pyridine-Mo ratio is about 0.20 mol atom $^{-1}$, assuming 80% coverage of the carrier by molybdenum(IV) oxide. Kiviat and Petrakis,⁶ working with the KBr technique, did not obtain spectroscopic evidence for the adsorption of pyridine on pure molybdenum oxide. As it is difficult to make unsupported molybdenum oxides with a reasonable surface area, it seems likely that their experimental technique was not sensitive enough.

The rather strong adsorption of pyridine on supported molybdenum(IV) oxide is sustained by the observation that the hydrogenation of xylene and of olefins on this oxide is poisoned by pyridine and other amines.^{14,19} The amine-Mo

ratio necessary for complete suppression of these reactions is about 0.20 mol atom⁻¹, and thus equals the pyridine adsorption capacity we found.

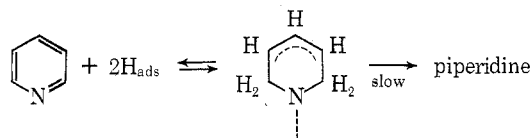
In contrast to the observations of pyridine adsorbed on a dry catalyst much Brønsted acidity was detected when water was present. The absence of this water effect when working with pure alumina shows that this proton acidity must be connected with the molybdenum. Upon increasing the temperature of evacuation the Brønsted bound pyridine disappears. We may therefore assume that this type of acidity cannot play a role in catalytic hydrogenation reactions at higher temperatures.

Above 400 °C even the spectrum of the "Lewis" pyridine changes (Figure 2, spectrum 5). Possibly under these circumstances some adsorbed pyridine is decomposed.

The Interaction of Adsorbed Pyridine with Adsorbed Hydrogen on Reduced Moly-Alumina. Similar to the literature^{4,17,18} we found that the intensities of the bands due to CH (CD) vibrations of pyridines are very weak after adsorption, especially when evacuation has taken place at temperatures above 200 °C. Moreover, the interpretation of these bands is hindered as they show complicated shifts in comparison with the spectrum of unadsorbed pyridine.¹⁸ These facts indicate that the CH and CD stretching region is not very suitable in this case for H-D exchange studies. The 2000–1000-cm⁻¹ region, however, is as shown in Figure 4. On heating, pyridine reacts with the alumina OD groups: all OD groups vanish and at the same time a new band (1435 cm⁻¹) appears. This band must be attributed to adsorbed 2-deuteriopyridine: a shift of 11 cm⁻¹ by Lewis adsorption (original ν_{19b} vibration absorbs at 1424 cm⁻¹²⁰) is in agreement with the shift we measured of the corresponding ν_{19b} band of nondeuterated pyridine (at 1439 cm⁻¹),²¹ 4-deuteriopyridine (at 1413 cm⁻¹),²⁰ and pyridine-d₃^{20,21} (at 1301 cm⁻¹). These facts inspire us to assume that, whatever deuterated pyridine species is concerned the ν_{19b} band will always show a similar shift by Lewis chemisorption.

The mere creation of 2-deuteriopyridine indicates that the adsorbed molecules are orientated toward the surface in such a way that they interact with it only through their nitrogen atoms and through the hydrogen atoms at the ortho positions.

The questions arises whether the reacting pyridine is adsorbed on the alumina and/or on the molybdenum oxide. A separate experiment on pure alumina also showed the generation of 2-deuteriopyridine. On the other hand, we know that molybdenum(IV) oxide on alumina is able to chemisorb hydrogen above 300 °C, possibly in the form of hydroxyl groups.^{22,23} Perhaps the 2755-cm⁻¹ band, due to an extra OD group next to those of Al₂O₃,⁷ reflects this chemisorption (see also Figure 4). Because hydrogenation takes place only on molybdenum oxide and not on alumina, the interaction of adsorbed pyridine with chemisorbed hydrogen has to occur on the former species too. Because of these facts we may suppose that during the hydrogenation of pyridine the first and relatively rapid addition of hydrogens will occur at the ortho positions. Further hydrogenation will proceed more slowly because the chemisorbed dihydropyridine must bend toward the surface in order to pick up adsorbed hydrogen atoms.²⁴ Such a proposal for the reaction mechanism, viz.



corresponds with the kinetics determined by Sonnemans, van den Berg, and Mars,¹⁴ who found that between 300 and 375 °C the reaction rate is proportional to $p_{\text{H}_2}^{1.5}$. These kinetics suggest different chemisorption sites for pyridine and hydrogen, as is in agreement with our findings which will be reported in the future.²³

A Model for the Surface of Reduced Moly-Alumina. Our observations that the Al-OH groups of the reduced, originally complete, monolayer molybdenum(IV) oxide-Al₂O₃ catalyst are not disturbed indicate that a rather large area of the carrier is bare. This implies that the molybdenum oxide units may form monomolecular platelets.⁷

We may wonder what are the sites on these "islands" active for (de)hydrogenation reactions. From our results and those from the literature it is striking that about 10–20% of the Mo ions behave differently.

First, pyridine adsorption preferentially takes place on the latter fraction. Secondly, the hydrogenation of pyridine occurs on the same part of the surface. Some investigators^{12,16} also found via ESR measurements that at least 10% of the Mo ions have a valence of five after reduction with hydrogen. The amount of Mo⁵⁺ ions parallels the Mo content up to maximum monolayer coverage,¹² similar to catalytic activities for hydrogenation.²⁵ These facts induce us to state that Mo⁵⁺ ions are involved in the catalytic reactivity. These ions, being more or less bare (C_{4v} symmetry^{16,26,27}), are exclusively able to react with gas-phase molecules and may be protected against further reduction due to stabilization by the carrier or may be formed by disproportionation of Mo⁴⁺.

The relative amount of active sites, about 10–20%, points to the existence of ensembles of Mo with a higher valence (5 or even 6) with surrounding molybdenum with a lower valence (4 or even 3). This combination will be able to chemisorb organic molecules and hydrogen on neighboring atoms and to facilitate hydrogenation.

Conclusion

(1) Reduction of a completely covered molybdenum(VI) oxide-Al₂O₃ monolayer catalyst yields Mo ions with a mean valence of nearly four. Reduction of a moly-alumina catalyst with a lower Mo content proceeds more difficultly.

(2) Both Lewis and Brønsted acid sites are present on a reduced catalyst; perhaps only the former plays a role in catalytic reactions at higher temperatures.

(3) Adsorbed pyridine interacts via its ortho hydrogen with hydrogen chemisorbed on the molybdenum(IV) oxide-alumina surface. Pyridine adsorbed on this catalyst has the same orientation as when it is adsorbed on pure Al₂O₃. Most of the adsorbed pyridine is associated with the molybdenum part of the catalyst.

(4) Only 10–20% of the Mo ions are active for pyridine adsorption and play a role in catalytic reactions. These ions are characterized by a valence of five and are surrounded by oxygens in a C_{4v} symmetry.

(5) The sites active for (de)hydrogenation reactions consist of ensembles of molybdenum oxide units. Pyridine adsorption, poisoning, and valence measurements indicate that in these ensembles the higher (five) valent ions adsorb the compound to be (de)hydrogenated. The lower (four) valent Mo ions play a role in the adsorption of hydrogen.

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Surface Structure and Catalytic Activity of a Reduced Molybdenum Oxide-Alumina Catalyst. 2. The Mechanism of Pyridine Hydrogenation and Piperidine Dehydrogenation

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The dehydrogenation of piperidine has been studied and found to have an order of -1.5 with respect to the hydrogen partial pressure. By combining these results with those obtained for pyridine hydrogenation on the same catalyst a complete rate equation for piperidine dehydrogenation together with the stoichiometric number of the rate-determining step of these reactions could be derived. This number appeared to be one. A mechanism for pyridine hydrogenation is presented on the basis of these results and those from adsorption studies using the infrared spectroscopic technique. The rate-determining step is found to be the formation of adsorbed trihydropyridine.

Introduction

Hydrogenation of aromatic nitrogen containing compounds is the first step for their denitrogenation on metal oxide or sulfide catalysts, such as $\text{CoO-MoO}_3\text{-Al}_2\text{O}_3$.¹⁻⁴ The kinetics of this hydrogenation has been studied with the aid of model compounds such as quinoline² and pyridine.^{3,5} Only little information is available regarding the mechanism of this hydrogenation, the active sites, and the rate-determining step.

The kinetics of the hydrogenation of pyridine has been studied by varying the temperature, the reaction time, the pyridine partial pressure, and the hydrogen pressure. The conversion as a function of the reaction time shows a first-order process.^{3,6} However, the rate constant is found to be inversely proportional to the initial pyridine partial pressure.^{3,5} An explanation for these results, also observed for other nitrogen containing compounds,⁷ can be given by considering the rate equation⁵

$$\frac{dP_{\text{py}}}{dt} = k_1 \theta_{\text{py}} P_{\text{H}_2}^a = \frac{k_1 b_{\text{py}} P_{\text{py}} P_{\text{H}_2}^a}{1 + b_{\text{py}} P_{\text{py}} + \sum b_{\text{prod}} P_{\text{prod}}} \quad (1)$$

where θ_i is the degree of occupation, b_i the adsorption constant of compound i , P , the partial pressure, and k_1 , the rate constant.

A Langmuir type of adsorption of the nitrogen bases has been assumed. The adsorption of hydrogen and nitrogen bases occur on different sites⁵ and experiments with the volumetric technique confirmed that the presence of nitrogen bases does not influence the rate of hydrogen chemisorption.⁸

Because the adsorption constants of the nitrogen bases appear to be almost equal and $b_{\text{py}} P_{\text{N}_0} \gg 1$ (P_{N_0} = total pressure of the nitrogen base), this equation can be simplified as

$$\frac{dP_{\text{py}}}{dt} = k_1 \frac{P_{\text{py}}}{P_{\text{N}_0}} P_{\text{H}_2}^a \quad (2)$$

The influence of hydrogen pressure has been studied by varying this pressure from 15 to 75 atm.⁵ The results obtained at 300 and 375 °C show the order with respect to hydrogen to be 1.5–1.6 (Figure 1). A discussion on details of the mechanism

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