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Evidence of Brønsted Acidity on Sulfided Promoted and Unpromoted Mo/Al_2O_3 Catalysts

It is uncertain what effect acidity, especially protonic (Brønsted) acidity, has on typical hydrotreating reactions over molybdenum-containing, sulfided catalysts. In particular, the possibility of a protonic mechanism taking place in some of these reactions is still an open question (*1*). For example, over a sulfided $CoMo/Al_2O_3$ catalyst, it has been found that isooctene readily undergoes cleavage to butene and that diisopropylbenzene dealkylates easily to cumene (*2*). On the other hand, dealkylation of cumene (a standard test for Brønsted acidity) was very slight under the same conditions. Since these reactions are typical of carbonium-ion reactions, it was proposed that this catalyst possessed weak Brønsted acidity. In a study of the hydrogenation of 1-hexene (*3*), small amounts of propylene were found together with the major product, hexane. The amount of the former increased with increase in the H_2S partial pressure, leading to the supposition that H_2S increased the Brønsted acidity of the sulfided catalyst. The hydrodenitrogenation of quinoline was also found to be promoted by H_2S (*4*), which was attributed to an increase in the number of Brønsted acid sites. However, no direct evidence for the presence of Brønsted acid sites was obtained in any of these studies.

Adsorption of basic molecules, especially pyridine, has been widely used to titrate the surface acid sites on catalysts. One of the advantages of using pyridine as the probe molecule for monitoring acidity is that it can adsorb both as coordinated and protonated pyridine on Lewis and Brønsted acid sites, respectively. These adsorbed pyridine species can be easily distinguished by infrared spectroscopy (*5*). Brønsted and Lewis acid sites have been detected for oxidic promoted and unpromoted Mo/Al_2O_3 catalysts (*6–10*) but only Lewis acidity has been found on the corresponding sulfided catalysts (*7, 8, 10*). Thus, no direct evidence exists for Brønsted acid sites on sulfided catalysts. Nevertheless, it has been argued that Brønsted sites may be present but that the IR band characteristic of pyridinium ion is too weak to be observed, or that the Brønsted acidity is so weak that the pyridinium ion formed readily desorbs prior to detection. Recently, some authors have considered the possibility that Brønsted acid sites are not present on the surface of the sulfided catalysts, with the result that a noncarbonium ion mechanism has to be considered for the catalysis by the sulfides (*11, 12*). It should be pointed out that most of the previous IR studies have been carried out with pyridine adsorption at relatively low temperatures (below 423 K). It occurred to us that since the Brønsted acidity, if it exists, must be weak, higher temperatures may be required to produce the pyridinium ion. The present note reports IR evidence of Brønsted acidity at elevated temperatures corresponding to those typically employed under hydroprocessing reactions.

The sample preparation and sulfiding procedure were as described previously (*13*). The unpromoted Mo/Al_2O_3, consisting of 7.6 wt% Mo, and the promoted catalysts, containing about 3 wt% Ni or Co with 10 wt% Mo, were prepared by depositing the active materials onto η-Al_2O_3 (surface area, 230 m^2 g^{-1}) via impregnation (or coim-

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pregnation in the case of the promoted catalysts), followed by drying and calcining at 773 K in air for 2 h. The samples, which were pressed into self-supporting wafers, were sulfided *in situ* in the IR cell by passing a gas mixture consisting of 1.7% H_2S in H_2 over the calcined precursors at 723 K for 2 h, followed by a N_2 flush treatment at 673 K for 16 h. The sample was then evacuated at various temperatures corresponding to those used for pyridine adsorption. Pyridine (spectroscopic grade) was purified by freeze-pump-thaw cycles. Slight excess of pyridine was adsorbed on the sample for 1 h before the more weakly held pyridine was desorbed by evacuation for at least 1 h. The adsorption and desorption processes were followed throughout by continuously recording the IR spectra. All spectra were recorded using a Digilab FTS-80 Fourier transform infrared spectrometer.

Figure 1 displays the spectra obtained from adsorption at 423 and 673 K on both the sulfided Mo/Al_2O_3 and the sulfided Al_2O_3 support. At 423 K, pyridine adsorption gives rise mainly to bands characteristic of pyridine adsorbed on Lewis acidic sites (LPY) on both Mo/Al_2O_3 and the Al_2O_3 support (Fig. 1a, 1b). The band frequencies are similar for the catalysts and the support but a more clear splitting of the band around 1600 cm^{-1} is seen for the Al_2O_3 support (1621 cm^{-1} and 1614 cm^{-1}). The Lewis sites apparently arise from adsorption on the support and the slightly lower intensity of the catalyst spectrum compared with the support indicates some coverage of Lewis sites due to the Mo sulfide phase with no adsorption of the latter. Chemisorption of pyridine at 673 K (Fig. 1c, 1d) shows a considerable difference in the spectra. The spectrum of pyridine adsorbed on the sulfided Al_2O_3 support at 673 K (Fig. 1c) shows, as expected, much lower adsorption compared with the support at 423 K and shows no evidence of pyridinium ion (BPY). In the case of Mo/Al_2O_3, in addition to an enhancement of the band intensity, the appearance of additional bands is also observed. Of special significance is the appearance of the band at 1545 cm^{-1} usually assigned to the pyridinium ion. In fact this band already starts to appear at 573 K. In addition to this band, bands at 1360, 1287, and 1112 cm^{-1} are also observed. A comparison of the relative intensity of the bands between the spectra at the different adsorption temperatures suggests overlapping band components at around 1626 and 1497 cm^{-1} in the spectrum with the higher adsorption temperature. These extra bands are likely to be due to surface α-pyridone (*14*) formed in a surface reaction on the catalyst above 573 K. The 1545 cm^{-1} band could therefore also be due to pyridonium species. In any case, the presence of Brønsted acidity is evidenced. The reaction is not observed on either the plain oxidic Al_2O_3 (as also found in (*15*)) or the plain sulfied η-Al_2O_3 (the results for sulfided Al_2O_3 is shown in Fig. 1) even at the adsorption temperature of 673 K, whereas the reaction readily occurs in the presence of

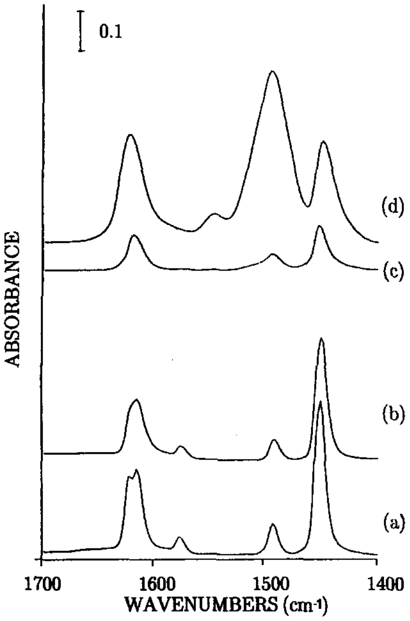


FIG. 1. IR spectra of pyridine at 423 K on (a) Al_2O_3 and (b) Mo/Al_2O_3, and at 673 K on (c) Al_2O_3 and (d) Mo/Al_2O_3. All samples were sulfided at 723 K prior to adsorption.

the Mo sulfide phase. These results therefore show that the presence of the metal sulfide is responsible for the surface reaction with pyridine.

The adsorption behavior observed for the sulfided Mo/Al_2O_3 catalyst is also seen for the Co- and Ni-promoted sulfided catalysts (Fig. 2), where the BPY band becomes evident at elevated temperature, but is not observed at the lower temperature. A weak BPY band is observed for the oxidic CoMo/Al_2O_3 catalyst (Fig. 2a), in agreement with other workers. The intensities of the bands are greater in the NiMo (Fig. 2d) than in the CoMo (Fig. 2c) catalysts. A comparison with Fig. 1d (note that the scale is one-half than that of Fig. 2) shows that the unpromoted catalyst exhibits higher band intensities than either of the promoted catalysts. The approximate relative ratio of BPY/LPY for these samples are in the order Mo > CoMo > NiMo. Thus, the unpromoted, sulfided catalyst contains more Brønsted sites at 673 K than the promoted, sulfided catalysts.

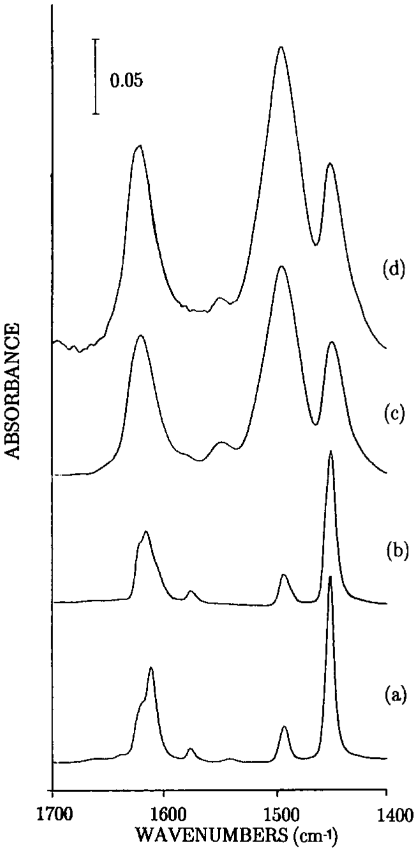
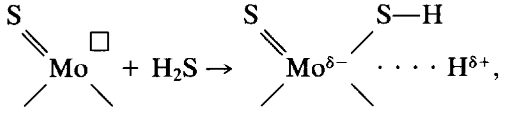


FIG. 2. IR spectra of pyridine adsorbed at 423 K on (a) calcined CoMo/Al_2O_3 and (b) sulfided CoMo/Al_2O_3, and at 673 K on (c) sulfided CoMo/Al_2O_3 and (d) sulfided NiMo/Al_2O_3.

It is seen that most, if not all, of the pyridine adsorbed on the sulfided catalysts at 423 K is on the Al_2O_3 support. This does not seem to be the case for higher temperature adsorption, where an increase in adsorbed pyridine accompanied by surface reaction and appearance of pyridinium and/or pyridonium ions occur. The former is in agreement with pyridine poisoning studies on a CoMo/Al_2O_3 catalyst at 673 K (*16*), where only about one-fifth of the adsorption was found on the support alone. Since neither the increased adsorption nor the presence of Brønsted sites was observed with the support at elevated temperature, these phenomena must be associated with the active metal sulfide phase present. The fact that the pyridine adsorption is lower on the promoted catalysts than on the unpromoted catalyst suggests that pyridine is preferentially adsorbed on the unpromoted sites.

We may rationalize these results as follows. Sulfiding at 723 K produces protonic acidity. This acidity is considerably weaker than that which exists on typical cracking catalysts. One possibility for generation of weak acidity is via dissociative H_2S reactions, viz.,



where □ represents an anion vacancy. Exposure to pyridine at high temperature activates transfer of the proton to form adsorbed pyridinium ion, whereas sufficient energy is not available at low temperature for this proton transfer to occur.

The present results provide evidence for the existence of Brønsted acid sites in sulfided promoted and unpromoted Mo catalysts at temperatures relevant to hydrotreating reactions. It is likely that Brønsted acid sites play an important role in carbonium-ion type reactions over these catalysts, such as hydrocracking or isomerization. Furthermore, in the case of hydrodenitrogenation, it is possible that pyridone or pyridonium species, which are shown to form readily, must be considered in the reaction mechanism. On the other hand, hydrodesulfurization or hydrogenation reactions do not appear to depend on Brønsted acidity, since these reactions are promoted by Co or Ni, which in fact were found to reduce Brønsted acidity. The catalytic significance of the present results is currently under investigation.

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