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MECHANISM OF HYDRODENITROGENATION (Part 9)

H_2-D_2 EXCHANGE IN REDUCED MOLYBDENUM CATALYSTS

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contents

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ABSTRACT

Diffuse reflectance infrared spectroscopy was used to study the deuterium exchangeability of reduced molybdena catalysts supported on silica, alumina and 75% silica-alumina. It was found that silica hydroxyls react partially with deposited molybdena. The new species formed does not lead to regeneration of hydroxyls on the catalyst. On the other hand, the interaction of molybdena with alumina or silica-alumina leads to the generation of interfacial OH groups, that compensate for the hydroxyls lost to reaction.

INTRODUCTION

Efficient nitrogen removal from heterocyclic aromatics in liquid fuels calls for the development of catalysts with better HDN activity than is available with the traditional HDS catalysts, such as CoMo/gamma-Al_2O_3 and NiMo/gamma-Al_2O_3. Over these catalysts, the first step is the partial or total hydrogenation of the heterocyclic ring -- at equilibrium at normal operating conditions -- and the rate-limiting step is the scission of the C-N-C bonds. Therefore an increase in the rate of C-N-C scission should produce an overall increase in the HDN yield.

In this project it is proposed that the selectivity of the HDN reaction can be affected by an alteration of the catalyst acidity since it is possible that an acidic Hofmann-like deamination pathway is operative [1] in parallel with the hydrogenolysis of saturated C--N--C bonds. Such was the conclusion from the study done of the denitrogenation of piperidine [3], where it was demonstrated that Bronsted acid sites are active for the denitrogenation of N-heterocycles, whereas Lewis sites are not.

To understand better the role of acidic sites in the presence of hydrogenation and hydrogenolysis sites, molybdena was supported on a series of acidic aluminas, and the resulting new acidity and molybdic phases were characterized [4]. The oxidized catalysts supported on silica-aluminas showed increases from 3 to 150% of weak, medium and strong acid sites, which were produced by the molybdena phases.

The new acidity is of both Lewis and Bronsted type, the predominance of one over the other depending upon support composition, as well as on loading and state of oxidation of Mo [5]. High-alumina supports and low Mo loading favor dispersed Mo species, in particular bidentate and monodentate di-oxo Mo species. The latter is responsible for the new Bronsted acidity. Coordinative unsaturation of polymolybdates is responsible for the new Lewis acidity, which is increased upon reduction of Mo. High-silica supports favor monodentate species (high Bronsted acidity) up to 4 wt% MoO_3. Beyond that, polymolybdate species and Lewis acidity predominate.

The nature of the reduced molybdena phases is obviously affected by support composition [4,6]. The silica-rich supports favor more reducible phases, including a segregated $Al_2(MoO_4)_3$ phase, which presumably will have different hydrogenation and hydrogenolysis sites than the less reducible phases, which are favored by alumina-rich supports. It must be noticed that pure gamma-alumina does not lead to the formation of $Al_2(MoO_4)_3$. This is only formed upon calcination of Mo oxides over silica-rich silica-aluminas, and is highly reducible [6]. Pure silica supports favor the agglomeration of a definite phase of MoO_3, which is also highly reducible. In these complex catalysts, a varying number of hydrogenolysis sites will be accompanied by a varying number of acidic sites, and their combined roles will affect the activity and selectivity for HDN.

The HDN reaction of pyridine was utilized to assess the variation in activity and selectivity produced by the nature of the support [7]. The results revealed that for silica-alumina supports (>50 wt% silica) the optimum loading of molybdena is 4 wt%. At this low loading the activity and selectivity towards HDN were maximum. The main parameters affecting the activity and selectivity are here postulated to be Mo reduction state and surface acidity. Thus low-temperature oxygen chemisorption was utilized to investigate surface reducibility of near-surface Mo, and effect of catalyst loading and support composition on such reducibility [8]. It was determined that for supports with compositions under 50% silica, the optimum loading producing maximum surface reducibility is 8 wt% MoO_3, while for supports with more than 50% silica, the optimum loading is 4 wt% MoO_3. At this loading, a substantial portion of the support (containing acidic sites) is also exposed. The role of Lewis sites produced on the molybdena surface by coordinative unsaturation is the strong adsorption of aromatic or unsaturated amines, and the destabilization of C-C and C-N bonds. Hydrogenation and hydrogenolysis can then occur by H addition. The highly acidic Bronsted sites, present on the support as well as on the molybdena, strongly chemisorb the hydrogenated amines. The acidic sites probably contribute to the denitrogenation, as shown by the abundance of unsaturated hydrocarbons produced, and are also active for cracking and cyclization, as shown by the selectivity towards methane and cyclopentene.

The mechanism postulated for this acid-catalyzed denitrogenation must involve the Bronsted acid sites present on the support and molybdena-support interface, since strong Bronsted sites on the molybdena phase itself are unlikely to be formed. In fact, earlier results showed that Bronsted acidity amount diminished with increased molybdena loading. Therefore, the approach to be taken in this work to show the participation of Bronsted acid sites in the mechanism of HDN of pyridine involves the exchange of surface hydroxyl hydrogen with deuterium. During the past quarter [9] we showed it is possible to exchange deuterium with surface OH in silica, alumina and silica-alumina, at temperatures under 400°C, and using D_2O and D_2 as deuterium sources. A question remains of whether the loading of molybdenum followed by its reduction will affect the exchangeability of surface OH.

Therefore, during this quarter we studied the effect of loading of molybdena on exchangeability of surface OH. In particular we searched for qualitative evidence of the presence of OH coordinated to Mo, in distinction from OH coordinated to support.

EXPERIMENTAL

Synthesis of Supports and Supported Molybdena

Silica-aluminas were prepared with a range of composition from 10-90 wt% silica. Separately, pure silica and gamma-alumina were also synthesized from the same precursors as the silica-aluminas. The supports were characterized by BET surface area, ammonia chemisorption and TPD, and IR of adsorbed pyridine. Details of the preparation and characterization results were given before [2].

Supported molybdena was prepared by incipient impregnation method from ammonium heptamolybdate, and were dried and calcined according to the technique described previously [4]. Three loadings were generated: 4, 8 and 12 wt% molybdena. The oxidic catalysts were prereduced in 50 ml/min H_2 at 400°C for 4 hours in a fixed-bed microreactor. Subsequently the powder was lightly compressed into a 13 mm pellet and rereduced in situ in the DRIFT cell, by flowing H2 at 400°C for 1 hour.

Deuterium Exchange

The exchange was effected with D_2 inside the DRIFTS cell equipped with environmental chamber and described before [5]. A catalyst pellet was made with 100 mg of powder compressed at about 200-500 psig for about 5 min. No additive was used in these pellets. The pellet was rereduced as described above. Finally, the sample was evacuated at 400°C during 1 hour (10^{-5} Torr) to remove gas phase hydrogen.

For the exchange using D_2, 2 atm of gas was kept in the cell maintained at 400°C during 1 hour. The temperature was reduced to 150°C under pressure, followed by evacuation at 150°C during 1 hour. DRIFT spectra were then recorded under vacuum at 150°C.

Exchange of deuterium using D_2O was not an option in these experiments due to the high oxidability of the reduced molybdena.

RESULTS AND DISCUSSION

Figure 1 shows two series of spectra, the first (top four) corresponding to reduced supported molybdena catalysts, and the second (bottom four) corresponding to deuterium-exchanged catalysts. Each series consists of spectra for pure silica support, and for supported molybdena at different loadings: 4, 8 and 12 wt%. The bands observed for the supported molybdena catalysts match exactly those for the pure silica support. Thus the assignment given before [9] still prevails. Following Baumgarten et al. [10] the band at 3744 cm^{-1} belongs to the terminal silanol groups Si-OH on the surface of grains; these silanols are sufficiently isolated to not interact (via H-bond) with neighboring silanols. The broad band between 3700 and 3300 cm^{-1} belongs to the H-bonded silanols on the silica surface. After exchange, new bands at 2757 cm^{-1} and 2720-2400 cm^{-1} appear, and they correspond to the isolated and deuterium-bonded OD groups, respectively.

It is worth observing that the 3744 cm^{-1} band has reduced intensity at increased molybdena loading, a fact that could signify the effect of coverage of support surface by deposited molybdena. However, when combined with previous reducibility results [4,8], the present IR results indicate certain degree of reaction of deposited molybdena with surface hydroxyl groups. This reactivity and interaction is responsible for the less than maximum bulk reducibility exhibited by the silica-supported catalysts. It is also worth observing that the H-bonded silanol bands (3300-3700 cm^{-1}) are not reduced by Mo loading in the same ratio as the isolated silanol bands, which indicates that the molybdena coverage is not uniform. This lack of uniformity is caused by the different reactivity of isolated OH groups when compared to H-bonded groups. Similar conclusions can be derived from the exchanged catalyst series. Furthermore, it is observed that the band positions do not shift as a function of molybdena loading, and this is a strong indication that no Mo-OH or Si-OH-Mo are present or that they do not contribute significant absorbance to the spectrum.

Figure 2 refers to spectra of reduced and D-exchanged molybdena catalysts supported on gamma-alumina. Again the top four spectra belong to reduced catalysts and the bottom four to exchanged catalysts. The broadness of the bands caused by these catalysts is due to the existence of several types of surface hydroxyl groups on alumina. Knozinger and Ratnasamy [13], and others [11-12], indicated that five different types of OH groups can be identified on alumina: (1) isolated OH on single octahedral Al, (2) isolated OH on single tetrahedral Al, (3) isolated OH on bridge-bonded octahedral and tetrahedral Al, (4) isolated OH on triple-bridge-bonded octahedral Al, and (5) H-bonded OH. The isolated OH bands lie in the region of about 3700 to 3800 cm^{-1}, while the H-bonded bands lie between 3200 to 3600 cm^{-1}. In the present experiments both isolated and H-bonded bands are apparent before and after exchange (Fig. 2). The deposition of molybdena on alumina seems to affect the amount of isolated and H-bonded OH groups to a lesser extent than in the case of silica, even when data from bulk reducibility studies [4] showed that interaction of molybdena with alumina was very strong. The conclusion is that new OH groups are generated upon deposition of molybdena. Those OH groups may be of the form Mo-OH or Mo-OH-Al, whose stretching frequency would be red-shifted with respect to Al-OH. Careful observation shows in fact a red shift of the band corresponding to isolated OH, with no decrease in its intensity. This is most obvious for the exchanged catalysts.

Figure 3 depicts the 75% silica-alumina-supported molybdena catalysts, before and after exchange with D_2. The bare support appears to contain isolated silanol groups, as revealed by the sharp 3744 cm^{-1}, as well as aluminum-bound hydroxyls. The Bronsted acid OH^+ groups are associated with Si-O-Al groups, and also appear in the 3400-3700 cm^{-1} region, but are not readily distinguishable in these IR spectra. All groups are readily exchanged, as observed by the appearance of the new bands in the 2400-2800 cm^{-1} region. In opposition to silica (Fig. 1), and more in agreement with alumina (Fig. 2), there is an apparent increase in the amount of OH groups on silica-alumina-supported molybdena when 4 wt% molybdena is loaded. Again, this is most evident in the deuterated catalysts. Such increase may be associated with the generation of new OH groups at the interface with the support. Higher loading of molybdena provokes the decrease in interface sites, thus a net decrease in the amount of OH groups.

CONCLUSIONS

Diffuse reflectance infrared spectroscopy was used to assess the deuterium exchangeability of reduced molybdena catalysts supported on silica, alumina and 75% silica-alumina. It was found that silica hydroxyls react partially with deposited molybdena. Such interaction does not lead to hydroxyl regeneration on the catalyst. On the other hand, the interaction of molybdena with alumina or silica-alumina leads to the generation of interfacial OH groups. The Si-OH-Mo groups in silica-alumina in principle should generate Bronsted acidic characteristics. This, in fact, has been shown previously for 2 and 4%-loaded 75%-silica-aluminas [5], which are more Bronsted-acidic than the support itself. On the other hand, the Al-OH-Mo groups formed on alumina do not generate new Bronsted acidity [5].

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Personnel

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REFERENCES

1. N. Nelson and R. B. Levy, J. Catal. 58(1979)485

2. R. Miranda, "Mechanism of Hydrodenitrogenation. Part I: Preparation and Characterization of Acidic Supports", DOE Report DOE/PC/89771-1, January 1990.

3. R. Miranda, "Mechanism of Hydrodenitrogenation. Part II: Piperidine Denitrogenation over Silica-Aluminas", DOE Report DOE/PC/89771-2, April 1990.

4. R. Miranda, "Mechanism of Hydrodenitrogenation. Part III: Preparation and Characterization of Acidic Molybdena Catalysts", DOE Report DOE/PC/89771-3, July 1990.

5. R. Miranda, "Mechanism of Hydrodenitrogenation. Part IV: Infrared Spectroscopy of Acidic Molybdena Catalysts", DOE Report DOE/PC/89771-4, October 1990.

6. R. Miranda, "Mechanism of Hydrodenitrogenation. Part V: X-Ray Diffraction of Supported Molybdena Catalysts", DOE Report DOE/PC/89771-5, January 1991.

7. R. Miranda, "Mechanism of Hydrodenitrogenation. Part VI: HDN of Pyridine over Acidic Molybdena Catalysts", DOE Report DOE/PC/89771-6, April 1991.

8. R. Miranda, "Mechanism of Hydrodenitrogenation. Part VII: Low Temperature Oxygen Chemisorption of Acidic Molybdena Catalysts", DOE Report DOE/PC/89771-7, June 1991.

9. R. Miranda, "Mechanism of Hydrodenitrogenation. Part VIII: H2-D2 Exchange in Non-Acidic and Acidic Supports", DOE Report DOE/PC/89771-8, September 1991.

10. E. Baumgarten, C. Lentes-Wagner, R. Wagner, J. Molec. Catal. 50, 153-65 (1989)

11. J.L. Carter, P.J. Lucchesi, P. Corneil, D.J.C. Yates, J.H. Sinfelt, J. Phys. Chem. 69, 3070-4 (1965)

12. Y. Amenomiya, J. Catal. 22, 109-22 (1971)

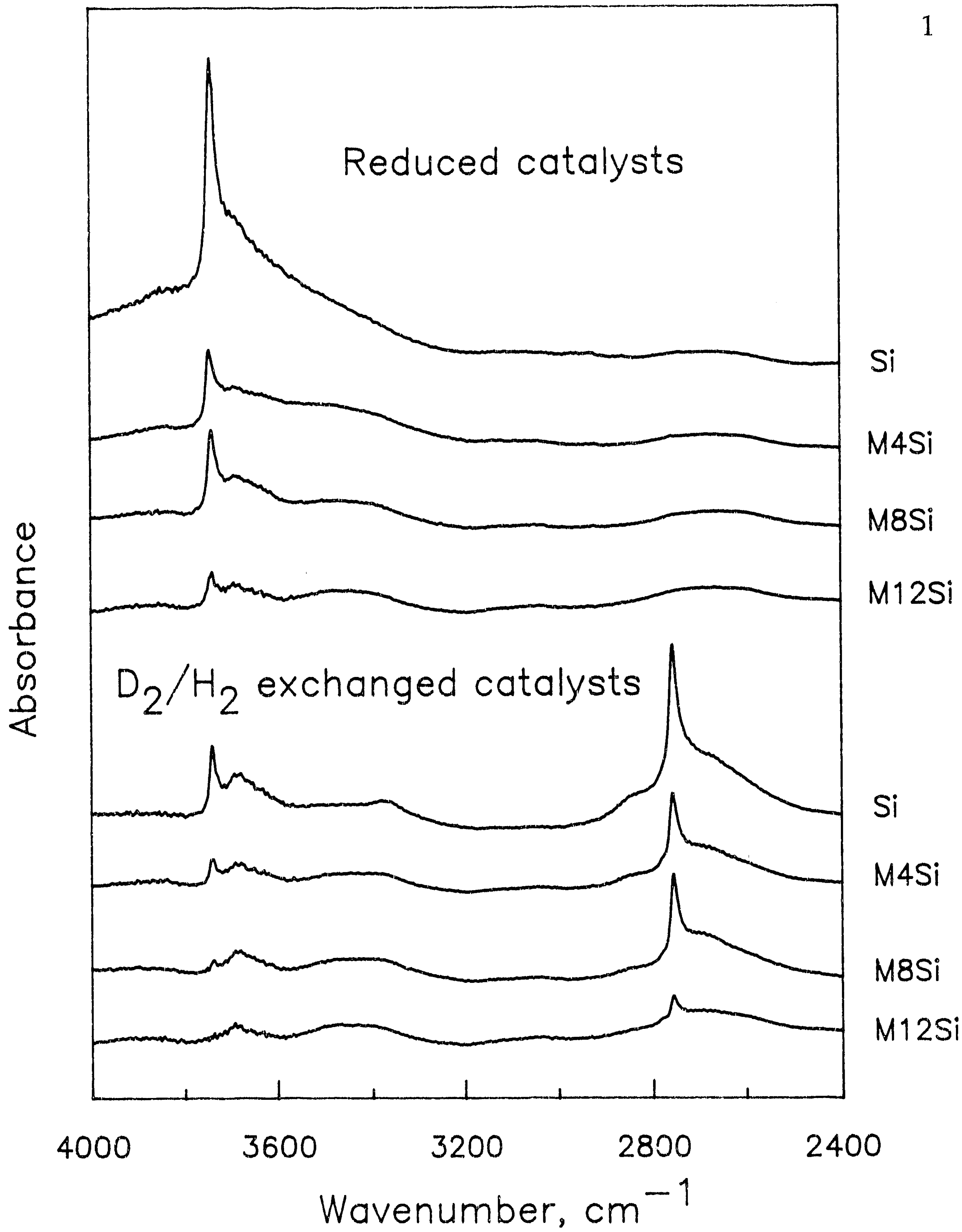
13. H. Knozinger, P. Ratnasamy, Catal. Rev. Sci. Eng. 17, 31 (1978)

FIGURES

Fig. 1 Diffuse reflectance IR spectra of reduced and deuterium-exchanged molybdena catalysts supported on silica.
Code: Si: silica, M4Si: 4% molybdena/silica, M8Si: 8% molybdena/silica, etc.

Fig. 2 Diffuse reflectance IR spectra of reduced and deuterium-exchanged molybdena catalysts supported on alumina.
Code: Al: alumina, M4Al: 4% molybdena/alumina, M8Al: 8% molybdena/alumina, etc.

Fig. 3 Diffuse reflectance IR spectra of reduced and deuterium-exchanged molybdena catalysts supported on 75%-silica silica-alumina.
Code: SA75: 75% silica-alumina, M4SA75: 4% molybdena/75%silica-alumina,etc.



DRIFTS of D_2/H_2 exchanged Mo/SiO_2

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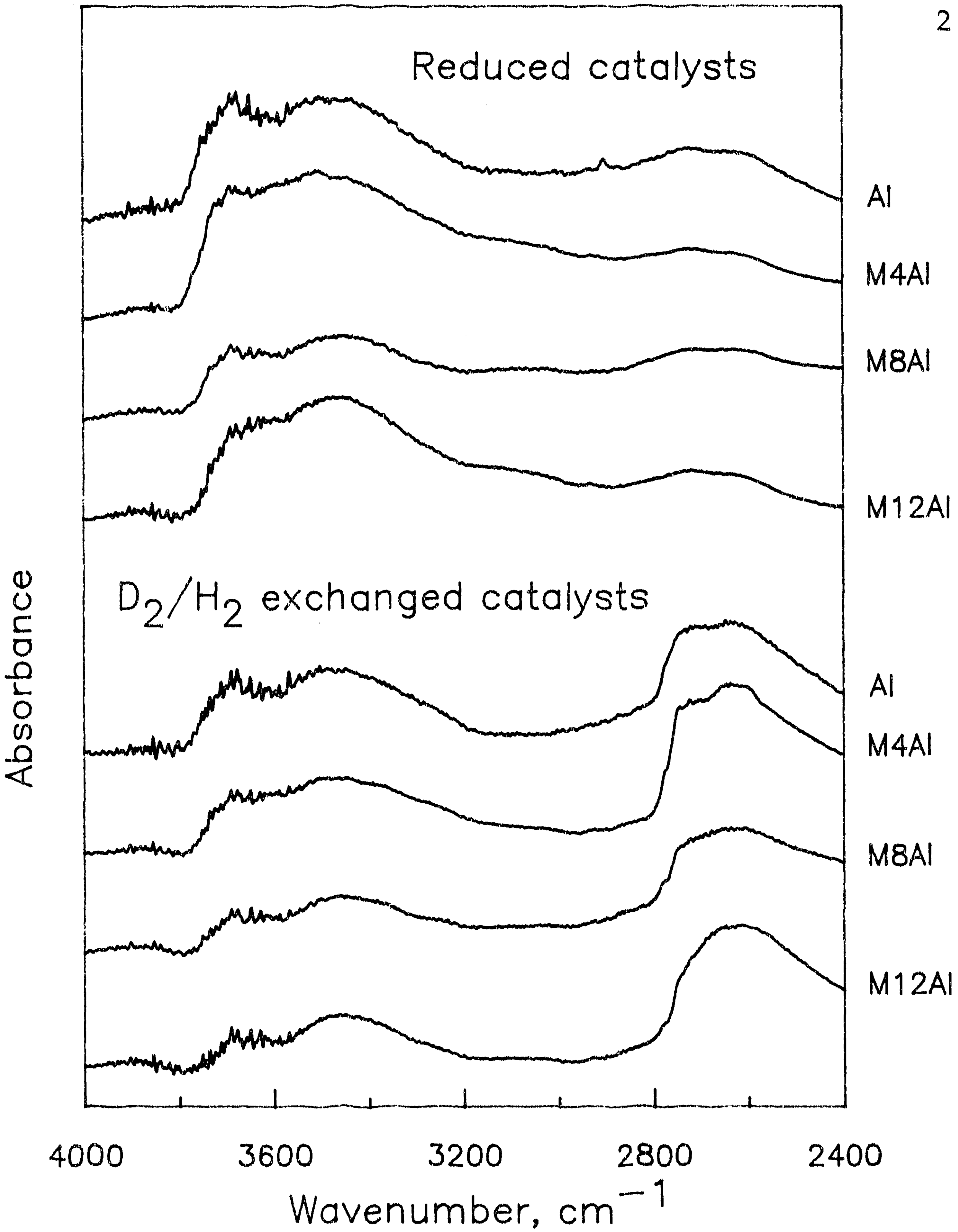

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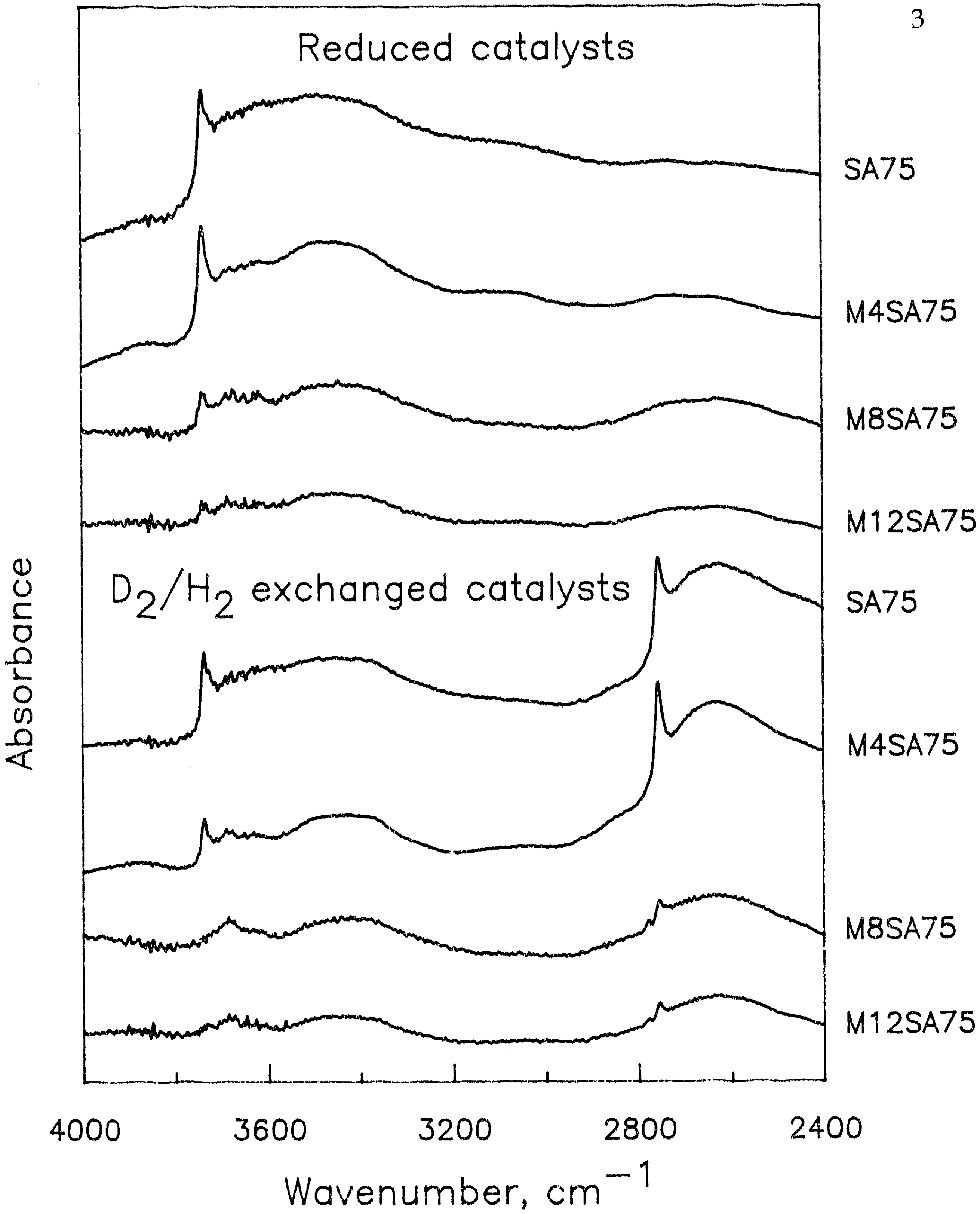

DRIFTS of D_2/H_2 exchanged Mo/75% $SiO_2-Al_2O_3$

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