JOURNAL OF CATALYSIS 78, 454–460 (1982)

NOTES

Mössbauer and Auger Spectroscopic Studies of Supported and Sulfided Fe–Mo Hydrodesulfurization Catalysts

The iron–molybdenum catalysts which are most widely used (*1–4*) for the oxidation of methanol to formaldehyde, epoxidation of olefins, and the isomerization and oxidation of 1-butene are now being examined (*5*) for hydrogenation of coal extracts. Numerous investigations (*6–8*) have been carried out on these catalysts to understand various structural features necessary for the proper functioning of the catalysts. Recently, Carbucicchio (*9*) studied Fe_2O_3–MoO_3 supported on SiO_2 and Al_2O_3 using Mössbauer effect and found that both Fe and Mo react with the supports. A literature survey reveals that no work on the catalytic activity and the identification of the various phases in the calcined and the sulfided Fe–Mo/Al_2O_3 catalysts has been carried out. In this study a series of Fe–Mo/Al_2O_3 catalysts with different atomic ratios, R = Mo/Mo + Fe, of 0.05, 0.25, 0.50, 0.75, 0.90, and 0.95 were prepared and characterized by X-ray diffraction and Mössbauer and Auger spectroscopic techniques. The percentge conversions of coal liquids soluble in tetrahydrofuran (THF), ethyl acetate, and pentane as a function of R values were also determined. Evidence of the interaction between the support and the active components of the catalysts is again observed. Additional evidence of the variation in the amount of different species in the catalyst with the change in the concentration of iron atoms is also found. It is observed that the activity of the Mo/Al_2O_3 catalyst is highly influenced by the presence of Fe atoms in the samples.

EXPERIMENTAL

Preparation of the catalysts. The η-Al_2O_3 support was prepared by calcining 300 g of −325-mesh boehmite (Conoco's Catapal SB) at 500°C for 16 hr. The calcined batch was cooled in a desiccator and stored in a tight plastic jar until used. The catalysts were batched to contain 8.7 mole% active component (MoO_3 + Fe_2O_3), while the atom ratio Mo to (Mo + Fe) was varied from 0.05 to 0.95.

The samples were prepared using Fisher Scientific reagent-grade ferric nitrate and ammonium heptamolybdate. The samples were impregnated using the incipient wetness technique. A double-impregnation procedure was used in which the component present in the greater amount was added first. The required amount of molybdate or nitrate was added to deionized water and the solution diluted to a volume of 20 ml. This was added to 25 g of the support. The mixture was stirred during the addition to ensure even distribution of the active components. The mixture was allowed to stand at room temperature for ½ hr and then dried overnight at 120°C. The dried mixture was heated at a furnace rate of 200°C/hr to 300°C and held for 2 hr. The minor component was then added as described above. The samples were dried overnight at 120°C and finally calcined in an air-purged furnace at 500°C for 16 hr. Calcination of the samples was also carried out between impregnations. Samples were also prepared by reversing the impregnation order to determine if this had any effect on the activity of the catalysts. The catalysts were presulfided in the autoclave runs at ambient pressure in a 10% H_2S/H_2 mixture at 350°C for 4 hr using a gas flow of 100 cm^3/min.

Mössbauer spectroscopy. ^{57}Fe transmission Mössbauer spectra of the calcined and

0021-9517/82/120454-07$02.00/0

the sulfided samples with $R = 0.05, 0.25, 0.50$, and 0.75 were recorded using a constant-acceleration microprocessor-based spectrometer (Promeda). Due to a small percentage of iron in the remaining two samples with $R = 0.90$ and 0.95, their Mössbauer spectra could not be recorded with the same spectral quality. All the spectra were computer fitted using an iterative nonlinear least-squares program. A source of 180 mCi ^{57}Co in Rh matrix was used for recording these spectra. The isomer shifts were measured with respect to α-Fe at room temperature.

X-Ray diffraction. The X-ray diffraction patterns of the $R = 0.05$ and 0.25 samples showed the presence of α-Fe_2O_3. In all other samples the only crystalline material detected was Al_2O_3. A summary of all the phases observed by X-ray diffraction and Mössbauer spectroscopy along with the batch compositions of the samples is given in Table 1.

Auger spectroscopy. Auger electron spectra of all the samples were recorded under ultrahigh vacuum (UHV) (base pressure of 2×10^{-10} Torr) conditions. Before recording the spectra all the samples (in the form of pellets) were sputtered using argon gas and an ion gun operated at 2 keV and 10 mA filament current.

Autoclave runs. The coal used for this study was IL#6 (Burning Star Mine). It was crushed to pass 200 mesh. Seventy-five grams of this coal was mixed with Panasol oil in a ratio of 1 : 1 and charged to an autoclave. The mixture was loaded and heated at 430°C for 15 min in a hydrogen atmosphere at 2000 psi. About 7.5 wt% of the catalyst was used in the autoclave. For each catalyst the amounts of THF, ethyl acetate, and pentane solubles of the coal liquid products were determined.

RESULTS AND DISCUSSION

Mössbauer Measurements

The ^{57}Fe Mössbauer spectra of the calcined samples with $R = 0.05$ and 0.25 look alike and consist of the superposition of two six-line patterns and a broad central doublet. The first six-line pattern (major component) in both samples has a hyperfine field of 505 ± 6 kOe and an isomer shift (IS) of 0.36 ± 0.03 mm s^{-1}. This field is assigned to the bigger particles of α-Fe_2O_3 which could be formed by the growth of the small particles of α-Fe_2O_3, due to the calcination at 500°C. The second six-line pattern (minor component) having a hyperfine field of 470 ± 10 kOe and $IS = 0.27 \pm 0.03$ mm s^{-1} also appears in the two samples. This probably is due to the presence of a small amount of γ-Fe_2O_3 in the samples.

The broad central doublet in the two samples has $IS = 0.33 \pm 0.03$ mm s^{-1} and $QS = 0.95 \pm 0.03$ mm s^{-1} (QS = quadrupole splitting). This may be due to the presence of an iron aluminate phase (*10*) in the alumina support. The distribution of Mo in these samples cannot be determined with any certainty with the present available data but in view of the large quadrupole splitting for the central doublet it is not unreasonable to assume that some of the Mo ions are also incorporated into the iron aluminate phase.

In the remaining two samples with $R = 0.50$ and 0.75, a broad and symmetric doublet is observed. This doublet was computer fitted in terms of two superimposed doublets with $IS = 0.37 \pm 0.03$ and 0.35 ± 0.03 mm s^{-1} and $QS = 1.01 \pm 0.03$ and 0.73 ± 0.03 mm s^{-1}, respectively. The first doublet with larger value of QS appears to originate from a similar species of iron aluminate phase (*10*) in the alumina support as observed in the previous samples. The second doublet is attributed to the superparamagnetic particles of α-Fe_2O_3. No evidence of the presence of a bulk phase of α-Fe_2O_3 or γ-Fe_2O_3 was noted in the two samples, indicating that no sintering of iron oxide particles occurred at 500°C.

Figures 1A–D show the room-temperature ^{57}Fe Mössbauer spectra for the sulfided samples with $R = 0.05, 0.25, 0.50$, and 0.75, respectively. All the spectra, as shown in the figure, were fitted in terms of two super-

TABLE 1

A Summary of the Batch Compositions and Various Phases Found in Fe–Mo/Al_2O_3 Catalysts

Mo/Mo + Fe	Weight percentage Fe_2O_3	Weight percentage MoO_3	Weight percentage Al_2O_3	Phases found by:					
				X-Ray diffraction		Mössbauer spectroscopy			
				Major	Minor	Calcined sample		Sulfided sample	
						Major	Minor	Major	Minor
0.05	8.43	0.80	90.76	α-Fe_2O_3	—	Bigger particles of α-Fe_2O_3	(a) γ-Fe_2O_3 (b) Iron aluminate	Superparamagnetic particles of $Fe_{(1-x)}S$	(a) Bigger particles of $Fe_{(1-x)}S$ (b) Iron aluminate
0.25	6.57	3.96	89.48	α-Fe_2O_3	—	Bigger particles of α-Fe_2O_3	(a) γ-Fe_2O_3 (b) Iron aluminate	Superparamagnetic particles of $Fe_{(1-x)}S$	Iron aluminate
0.50	4.30	7.76	87.94	—	Al_2O_3	Superparamagnetic particles of α-Fe_2O_3	Iron aluminate	Superparamagnetic particles of $Fe_{(1-x)}S$	Iron aluminate
0.75	2.11	11.14	86.44	—	Al_2O_3	Superparamagnetic particles of α-Fe_2O_3	Iron aluminate	Superparamagnetic particles of $Fe_{(1-x)}S$	Iron aluminate
0.90	0.84	13.59	85.57	—	Al_2O_3	—	—	—	—
0.95	0.38	13.16	86.46	—	Al_2O_3	—	—	—	—

Note. $Fe_{(1-x)}S$ in an iron sulfur phase different from the commonly known pyrrhotites.

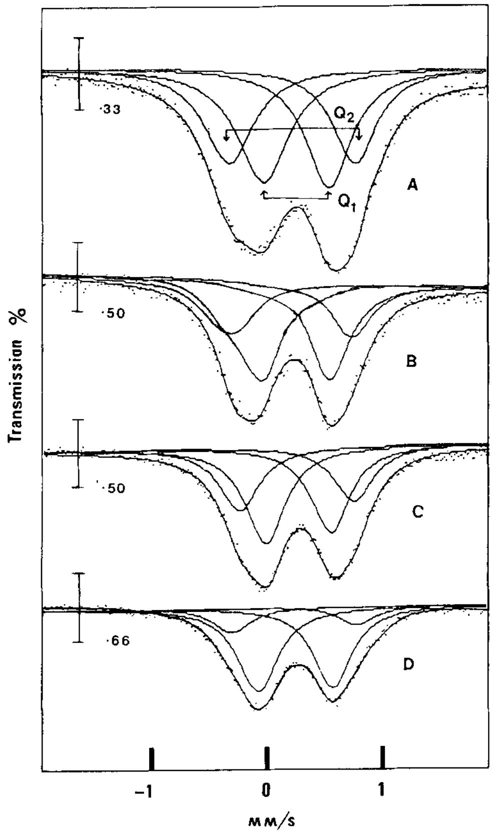

FIG. 1. Room-temperature ^{57}Fe Mössbauer spectra of sulfided Fe–Mo/Al_2O_3 catalysts with (A) $R = 0.05$, (B) $R = 0.25$, (C) $R = 0.50$, and (D) $R = 0.75$. The solid lines in all spectra are the result of the computer fit using an iterative nonlinear least-squares program.

imposed quadrupole doublets. The inner doublet (Q_1) has IS = 0.36 ± 0.03 mm s^{-1} and QS = 0.65 ± 0.03 mm s^{-1} and the outer doublet (Q_2) has IS = 0.37 ± 0.03 mm s^{-1} and QS = 1.07 ± 0.03 mm s^{-1}. It is interesting to note that the doublet Q_2 has Mössbauer parameters similar to those for the first doublet (with large QS) for the calcined samples. This doublet, therefore, is assigned to the iron aluminate phase in the alumina support. Apparently, this phase remains unaffected by sulfidation in all the samples.

In order to identify the phase with the doublet Q_1 the Mössbauer spectra of all the samples were recorded with a large velocity. Such a spectrum for the $R = 0.05$ sample at room temperature is shown in Fig. 2(top). It consists of a central doublet (superposition of Q_1 and Q_2) and a minor component in the form of a six-line pattern. In the remaining three samples only a central doublet (superposition of Q_1 and Q_2) is observed. No six-line pattern was observed for these samples. The values of the hyperfine field and the IS for the six-line pattern observed for the $R = 0.05$ sample were found to be 248 ± 15 kOe and 0.68 ± 0.14 mm s^{-1}, respectively. These parameters are compatible with (*11–13*) the presence of a bulk phase of a nonstoichiometric compound of iron and sulfur ($Fe_{(1-x)}S$) which can be formed due to the reaction between the iron oxide and H_2S during sulfidation. Such species can also be observed in the form of superparamagnetic particles. Therefore, the doublet Q_1 in all four samples has been assigned to the presence of superparamagnetic particles of an iron sulfur phase.

In order to confirm the above assignments, the low-temperature spectra of the

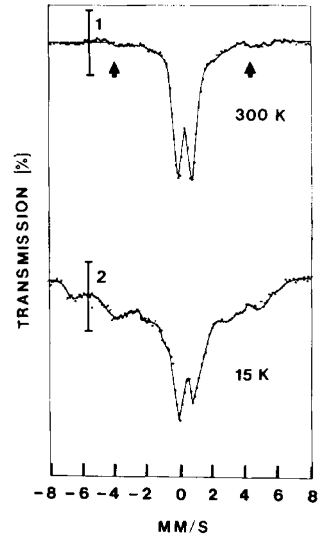

FIG. 2. ^{57}Fe Mössbauer spectra for the sulfided Fe–Mo/Al_2O_3 catalyst for the $R = 0.05$ sample at 300 and 15 K. The solid lines in both spectra are the result of the computer fit using an iterative nonlinear least-squares program.

samples were also recorded. One such spectrum for the $R = 0.05$ sample is shown in Fig. 2(bottom). The spectrum shows some relaxation effects along with the broadening of the lines. This shows that the relaxation time for flipping of spins of the superparamagnetic particles is still faster than the Larmor precession period of the nucleus. This further suggests that the particle size of the $Fe_{(1-x)}S$ phase is very small. The hyperfine field of 340 ± 7 kOe observed at this temperature is in good agreement with the reported values (*12, 13*) of the hyperfine field for such compounds.

The amount of the phases corresponding to the doublets Q_1 and Q_2 was estimated from their spectral area (Fig. 1). It is interesting to note that the amount of $Fe_{(1-x)}S$ phase increases slightly from 60 to 64% in going from the $R = 0.05$ sample to the 0.50 sample. A dramatic increase in the amount of this species to 80% is observed for the $R = 0.75$ sample. This shows that even for a small loading of iron in the Mo/Al_2O_3 catalyst a large amount of $Fe_{(1-x)}S$ phase is produced when the sample is sulfided. It is important to point out that the process of sulfidation is primarily a solid–gas interaction, mostly taking place near or on the surface of the catalyst. Therefore, we can say that the phase $Fe_{(1-x)}S$ is, most probably, located near or on the surface of the catalysts.

From the relative spectral area of the doublet Q_2 due to an iron aluminate phase it is estimated that the amount of iron in this phase decreases slightly from 40 to 36% in going from the $R = 0.05$ sample to the 0.50 sample. Once again a dramatic decrease to 20% is observed for the $R = 0.75$ sample. These observations clearly indicate that the amount of Q_1 and Q_2 phases is composition dependent.

Auger Spectroscopy

Figure 3 shows the Auger spectrum for the $R = 0.05$ sample. The spectra for the other samples look similar to this spectrum. From Fig. 3, the presence of Al, S, C, Fe, and oxygen can be seen easily. The presence of all these elements shows that probably the surface is not rich in any one kind of species and all the species are inhomogeneously distributed on the surface.

Catalytic Measurements

In Fig. 4 the percentage conversion of coal liquids soluble in THF, ethyl acetate,

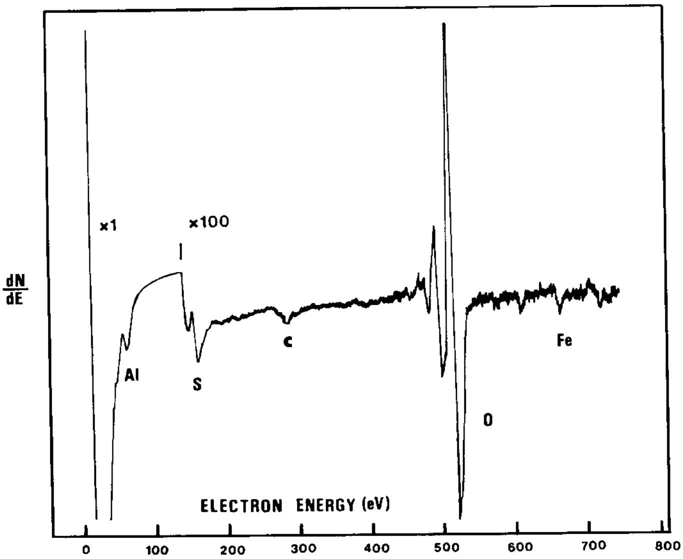

FIG. 3. Auger spectrum of the sulfided $Fe–Mo/Al_2O_3$ catalyst for $R = 0.05$.

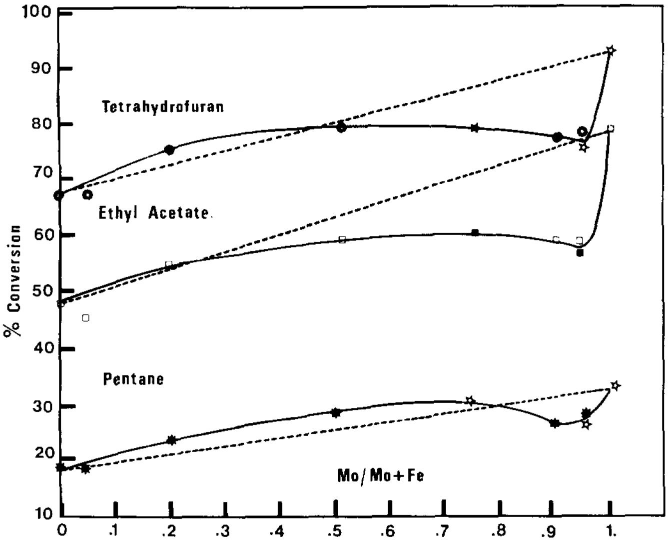

FIG. 4. Diagram showing the percentage conversion of liquefaction products in various solvents for Fe–Mo/Al_2O_3 catalysts with different Mo/Mo + Fe ratios. The open symbols are due to the samples obtained by impregnation in which the component present in greater amount was added first and the solid symbols were obtained when the order of impregnation was reversed.

and pentane as a function of *R* values are shown. The conversion evidently is maximum for Mo/Al_2O_3 catalyst. It drops to a minimum value when about 5% iron is added to this catalyst. After adding more of the iron, the percentage conversion almost remains the same (close to the minimum value). All these facts indicate that at 95% Mo and 5% Fe a strong modification in the catalytic behavior of Mo/Al_2O_3 occurs.

The above-mentioned dramatic decrease in the activity of the sulfided Mo/Al_2O_3 catalysts on adding a small amount of iron could be due to several reasons. It could be due to the interaction between Fe–Mo oxides. According to this hypothesis during the sulfiding process Fe and Mo interact strongly, resulting in the change in the structure and the activity of the catalysts. The possibility of such an interaction during calcination cannot be ruled out. However, the Mössbauer results do not indicate the presence of any known Fe–Mo mixed oxides either in the calcined or in the sulfided samples. Another reason for the decrease in the activity may be associated with the physical blocking or covering of the active center of the catalyst (Mo) by $Fe_{(1-x)}S$ particles. As mentioned before, the evidence for the presence of such particles was noted by Mössbauer spectroscopy. Also it was mentioned before that the amount of this phase is about 80% of the total iron in the sample. Therefore, even for a small loading of iron the catalyst surface would behave like that of $Fe_{(1-x)}S$. This probably is the reason for the sudden decrease in the activity of the catalyst for a small loading of iron. The same reason could be given for the low activity of all the other catalysts in the present series.

Finally, the interaction of the deposited metals or mineral matter from coal or formed intractable carbonaceous material (coke) with the catalyst can also cause the decrease in the activity of the catalyst. However, if this were true the decrease would have been the same for all the samples.

ACKNOWLEDGMENT

This work was supported by the U.S. Department of Energy and the West Virginia University E.R.C. (P.P.V. and P.A.M.).

REFERENCES

1. Adkins, H., and Peterson, W. R., *J. Amer. Chem. Soc.* **53,** 1512 (1931).
2. Trifirò, F., Notarbartolo, S., and Pasquon, I., *J. Catal.* **22,** 324 (1971).
3. Pasquon, I., Trifirò, F., and Caputo, G., *Chim. Ind.* **55,** 168 (1973).
4. Trifirò, F., De Vecchi, V., and Pasquon, I., *J. Catal.* **15,** 8 (1969).
5. Massoth, F. E., *in* "Advances in Catalysis and Related Subjects," Vol. 27, p. 265. Academic Press, New York/London, 1978.
6. Carbucicchio, M., and Trifirò, F., *J. Catal.* **45,** 77 (1976).
7. Ai, M., *J. Catal.* **52,** 16 (1978).
8. Mørup, S., Clausen, B. S., and Topsøe, H., *J. Phys. Colloq. C* **2,** C2-88 (1979).
9. Carbucicchio, M., *J. Chem. Phys.* **70,** 784 (1979).
10. Clausen, B. S., Mørup, S., Topsøe, H., and Candia, R., *J. Phys. Colloq. C* **6,** C6-249 (1976).
11. Vaughan, D. J., and Ridout, M. S., *J. Inorg. Nucl. Chem.* **33,** 741 (1971).
12. Hafner, S. S., and Kalvius, M., *Z. Kristallogr.* **123,** 443 (1966).
13. Vaghan, D. J., and Craig, J. R., "Mineral Chemistry of Metal Sulfides," p. 141. Cambridge Univ. Press, London, 1978.

P. P. Vaishnava
P. A. Montano

Department of Physics
West Virginia University
Morgantown, West Virginia 26506

R. E. Tischer
S. S. Pollack

Pittsburgh Energy Technology Center
Box 10940
Pittsburgh, Pennsylvania 15236

Received September 28, 1981; revised June 15, 1982