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Characterization of Hydroprocessing Catalysts by Resolved Temperature-Programmed Desorption, Reduction, and Sulfiding

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A flow system is described for carrying out temperature-programmed desorption and reaction experiments with resolution of the desorbed products by on-stream gas chromatographic analysis. The apparatus has been used to characterize hydroprocessing catalysts (MoO_3, γ-Al_2O_3, MoO_3/γ-Al_2O_3 having various MoO_3 contents, Co–Mo/γ-Al_2O_3, Ni–Mo/γ-Al_2O_3, and Ni–W/γ-Al_2O_3) by temperature-programmed desorption with He, temperature-programmed sulfiding with H_2S in H_2, and temperature-programmed reduction with H_2. The results show that a decreasing temperature of appearance of H_2S peaks in the TPR spectra of sulfided Mo/Al_2O_3 catalysts corresponds to an increasing Mo content and increasing catalytic activity. TPR data provide a rapid qualitative test for the presence of incompletely sulfided MoO_3 on the catalyst surfaces. Quantitative TPR data associated with the formation of sulfur anion vacancies on the surface indicate that only a small fraction of the sulfur is removed by reaction with H_2, this fraction being higher for the promoted catalyst Co–Mo/Al_2O_3 (~0.3 molecule/nm^2) than for the less active, unpromoted catalyst Mo/Al_2O_3 (~0.06 molecule/nm^2).

INTRODUCTION

Spectroscopic techniques are the most fruitful for determining structures of species adsorbed on catalyst surfaces, and when used in combination with gravimetric or volumetric adsorption measurements, they can provide quantitative information about the surface sites. A set of techniques exemplified by temperature-programmed desorption (TPD) (*1*) and temperature-programmed reduction (TPR) (*2*) gives a kind of spectra from which complementary structural information may be inferred. The latter techniques offer the advantages of being simple and inexpensive, rapidly providing quantitative data determining numbers of surface sites.

Variations on the theme of TPD [e.g., flash desorption into a vacuum chamber equipped with a mass spectrometer (*3*)] illustrate the value of detailed analysis of the products evolved from a surface. Our objective in this research was to extend the conventional TPD and TPR flow techniques to allow resolution of the species desorbed from the surface. The application of the modified technique is demonstrated here for hydroprocessing catalysts, which exist in both oxidic and sulfidic forms and therefore give products of reduction with hydrogen including both H_2O and H_2S.

Hydroprocessing catalysts have been characterized by almost all the available surface spectroscopic methods [as reviewed by Massoth (*4*)], but there is still no consensus concerning the structures of the catalytically active forms (*4–6*). There is little doubt, however, that the original (oxidic) form of a catalyst like CoO–MoO_3/γ-Al_2O_3 undergoes drastic changes, experiencing a whole range of structures between that of the oxidic form and that of the working (sulfidic) catalyst (*4, 6, 7*). There are only a few reported studies of the sulfiding process (e.g., (*8, 9*)), and much remains to be learned about it. The results summarized here provide some new infor-

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mation about sulfiding, showing how the conventional TPD/TPR technique can be simply modified to allow rapid investigation of this process.

EXPERIMENTAL

Temperature-Programmed Desorption and Reduction

The design of the apparatus (Fig. 1) is essentially that used for conventional TPD/TPR, except that the effluent gas stream does not pass directly through the standard thermal conductivity detector, but instead is injected periodically into an on-line gas chromatograph for separation and analysis of the desorbed gases. The 150-cm-long, 0.2-cm-i.d. stainless-steel column used for separating H_2S and H_2O was packed with Porapak Q (100–200 mesh) and thermostated at 75 ± 1°C. The sample of catalyst powder (typically 0.4 g, 80–100 mesh) was held in a stainless-steel tube having a 0.32-cm i.d. The tube was 18 cm long and packed upstream and downstream of the catalyst with about 1.5 cm^3 of inert alundum powder. The tube was mounted in a stainless-steel block which could be heated at a constant rate with a Hewlett-Packard Model 240 temperature programmer. The energy was introduced through a ceramic-insulated band heater surrounding the block. A well allowed the placement of a thermocouple for monitoring the temperature at the outer tube wall and at the center of the catalyst bed. The remainder of the apparatus is described in detail elsewhere (*10*).

He (Matheson, 99.995% purity) and H_2 (Matheson, 99.999% purity) were used as the carrier gases for TPD and TPR, respectively. Before entering the reactor, the carrier gas (He or H_2) passed through beds of deoxo catalyst and activated zeolite to remove traces of O_2 and H_2O, respectively. The effluent gases passed through a 55-cm length of 0.05-cm-i.d. stainless-steel tubing into a Carle eight-way sampling valve with two 1-cm^3 sampling loops. The typical mean residence time of the effluent gases in the line between the catalyst bed and the sampling valve was 0.1 sec.

In a typical experiment, the catalyst was heated to 515°C in flowing He to remove adsorbed impurities, then cooled to room temperature. The catalyst was then heated to 515°C at a rate of 15°C/min in flowing H_2S in H_2 [10 vol% H_2S in H_2 flowing at 60 cm^3 (STP)/min]; sulfiding continued at this temperature for 2 hr. After sulfiding, the sample was cooled to room temperature in the H_2S/H_2 stream; it was then purged with He for several minutes, and the TPD experiment was initiated with the flow of He at a rate of 60 cm^3 (STP)/min. The catalyst heating rate was 10°C/min. After the maximum temperature (usually 515°C) was

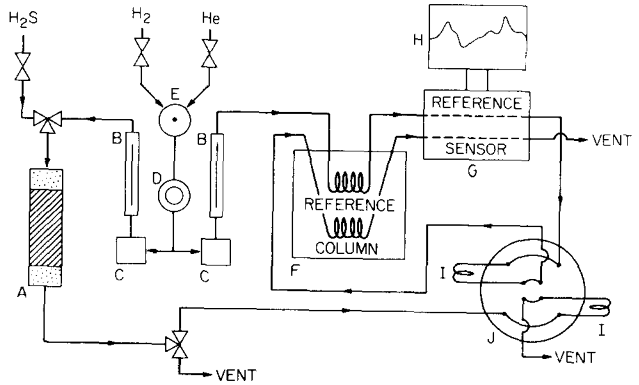

FIG. 1. Apparatus for resolved temperature-programmed desorption and reaction experiments: A, reactor; B, rotameter; C, flow controller; D, pressure controller; E, ball valve; F, gas chromatograph; G, thermal conductivity detector; H, recorder; I, sampling loop; J, eight-way Carle valve.

TABLE 1

Catalyst Properties

Catalyst	Source	Composition	Surface area (m^2/g)
Co–Mo/γ-Al_2O_3	American Cyanamid	$\left\{\begin{matrix}5.6\%\ \mathrm{CoO}\\ 11.2\%\ \mathrm{MoO_3}\end{matrix}\right\}/\gamma\text{-}\mathrm{Al_2O_3}$	176
Ni–Mo/γ-Al_2O_3	American Cyanamid	$\left\{\begin{matrix}3.1\%\ \mathrm{NiO}\\ 18.3\%\ \mathrm{MoO_3}\end{matrix}\right\}/\gamma\text{-}\mathrm{Al_2O_3}$	149
Ni–W/γ-Al_2O_3	Nalco	$\left\{\begin{matrix}5.1\%\ \mathrm{NiO}\\ 22.0\%\ \mathrm{WO_3}\end{matrix}\right\}/\gamma\text{-}\mathrm{Al_2O_3}$	250
γ-Al_2O_3	BDH Chemicals	—	~100
2.5% MoO_3/γ-Al_2O_3	Cheng and Schrader (*12*)	2.5% MoO_3/γ-Al_2O_3	~100
5% MoO_3/γ-Al_2O_3	Cheng and Schrader (*12*)	5.0% MoO_3/γ-Al_2O_3	~100
10% MoO_3/γ-Al_2O_3	Cheng and Schrader (*12*)	10.0% MoO_3/γ-Al_2O_3	~100
15% MoO_3/γ-Al_2O_3	Cheng and Schrader (*12*)	15.0% MoO_3/γ-Al_2O_3	~100
MoO_3/γ-Al_2O_3(E)	Technical University, Eindhoven	12.0% MoO_3/γ-Al_2O_3	~200
WO_3/γ-Al_2O_3(E)	Technical University, Eindhoven	19.0% WO_3/γ-Al_2O_3	~200
MoO_3	Pfaltz and Bauer	100% MoO_3	—

reached, the catalyst was cooled again to room temperature, and the TPR segment of the experiment was initiated with the start of H_2 flow; again the carrier gas flow rate was 60 cm^3 (STP)/min, and the catalyst heating rate was 10°C/min.

During both TPD and TPR experiments, 1.0-cm^3 samples of the effluent gas were diverted periodically (usually at 1- to 1.5-min intervals) via the Carle valve to the gas chromatographic column for separation and analysis.

The areas under each H_2S peak were determined with a digital integrator. Using calibration data, the peak areas were converted into mole fractions. Since the H_2O peaks in the gas chromatograms were relatively broad, the areas could be estimated with a precision of only about $\pm 10\%$. The H_2S peak areas were determined with a precision of $\pm 1\%$.

With data determined in this way, TPD and TPR curves were generated for H_2S and H_2O separately. The cycle comprising sulfiding, TPD, and TPR was reproducible within experimental error for all the samples tested.

Details of the TPR experiments characterizing the oxidic catalysts are given elsewhere (*11*).

Temperature-Programmed Sulfiding

In a typical experiment, a catalyst sample (0.4 g) was placed between two beds of alundum and heated to 515°C to remove adsorbed impurities; the completion of desorption of water was indicated by the effluent gas chromatograms. The sample was then cooled to room temperature, and the temperature-programmed sulfiding was carried out as follows. A stream of 10 vol% H_2S in H_2 was allowed to flow over the catalyst at 60 cm^3 (STP)/min, and the temperature was raised to 500°C at a rate of about 15°C/min and then maintained at this value for 2 hr. The behavior of the catalyst during the sulfiding was characterized by periodic analysis of the effluent H_2S–H_2O mixture during the heat-up period.

Materials

The catalyst samples included γ-alumina and various molybdenum-on-alumina samples {some described elsewhere (*12*), some prepared by similar methods for this research, and one [designated by the symbol

(E)] prepared in Eindhoven and described elsewhere (*13*)}. Other samples, including W/γ-Al_2O_3(E) and commercial catalysts promoted with Co and with Ni, were also investigated. They are listed with sources, compositions, and approximate surface areas in Table 1.

RESULTS AND DISCUSSION

Temperature-Programmed Desorption

Figure 2 shows the TPD spectra of three commercial presulfided hydroprocessing catalysts, namely, Ni–W/Al_2O_3, Ni–Mo/Al_2O_3, and Co–Mo/Al_2O_3. The results demonstrate the differences between unresolved spectra, obtained with the conventional TPD technique (i.e., with a thermal conductivity detector but no gas chromatograph interfaced to the effluent line), and the resolved H_2S spectra obtained with the modified apparatus described above. The patterns obtained from the two techniques are similar, but the resolved spectra are evidently more fine-grained.

The relatively small differences between the pairs of curves for each catalyst are explained by the differences in thermal conductivities of the effluent gases (H_2O, H_2S, and H_2). H_2 has a slightly greater thermal conductivity than He, and H_2O and H_2S have much lower thermal conductivities. Therefore, when He is used as the carrier gas (in TPD), the sensitivity of the instrument for H_2 is low in comparison with that for H_2O and H_2S. It follows that the unresolved and resolved spectra are expected to be nearly the same when only H_2S and H_2 are evolved, and that large differences between the two spectra reflect the presence of both H_2O and H_2S. Consistent with these expectations, the amounts of water evolved during the TPD experiments characterized by Fig. 2 were found to be small. The benefit of separating H_2S from H_2O will become clear in the discussion of the temperature-programmed reduction (TPR) and sulfiding, which follows.

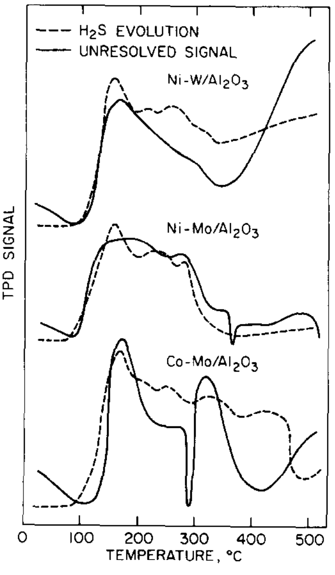

FIG. 2. Temperature-programmed desorption plots for sulfided commercial hydroprocessing catalysts. The heating rate was 10°C/min.

The data of Fig. 2 show that for all the promoted catalysts, there is a peak at about 160°C, which is always the most intense, followed by a fingerprint region of the spectrum at higher temperatures. The low-temperature peak is attributed to H_2S which had adsorbed on the catalyst during cooling under H_2S. Similar behavior was also found to be characteristic of γ-alumina, W/Al_2O_3, and a series of Mo/Al_2O_3 catalysts, all in the sulfided form. Typically, all the TPD spectra showed the onset of desorption at about 80°C, and in most cases desorption was virtually completed at temperatures between 350 and 450°C.

Temperature-Programmed Reduction

TPR studies may be carried out either by measuring the consumption of H_2 by the catalyst when the carrier gas contains H_2 in low concentration (say, 5% H_2 in He) or by measuring the desorption of a species (say, H_2S) formed in the surface reaction with H_2. We have used both methods, the first in the TPR of the three promoted catalysts in the oxidic form (Fig. 3) and the second in the TPR of the same catalysts in the sulfided form (Fig. 4).

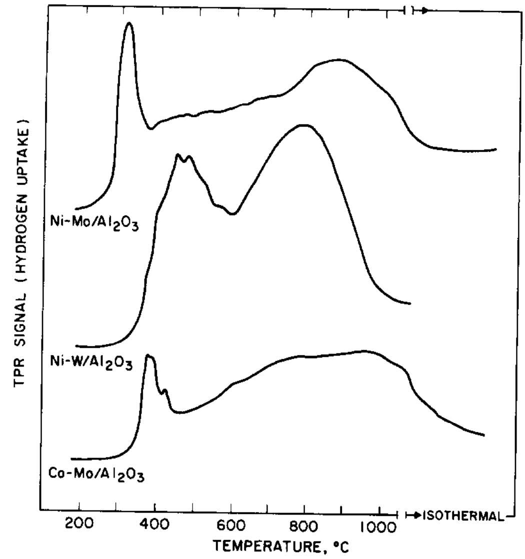

FIG. 3. Temperature-programmed reduction plots for commercial hydroprocessing catalysts in the oxidic state. The heating rate was 5°C/min.

The results of Fig. 3 show the H_2 consumption as a function of temperature. The experiments were carried out with an apparatus different from that described here and allowing programming of the temperature up to 1050°C (*11*). This procedure apparently led to complete reduction of each catalyst. Reduction of each started at about 350°C and was completed around 1050°C. The spectra can be divided into two regions, a low-temperature peak (at 380, 320, and 460°C, for Co–Mo/Al_2O_3, Ni–Mo/Al_2O_3, and Ni–W/Al_2O_3, respectively) and a broad band at higher temperatures (centered at about 800°C for each of the three samples). Results of recent TPR experiments (*11*) show that W/Al_2O_3 has a peak roughly coinciding with the broad high-temperature peak of the Ni–W/Al_2O_3 catalyst. This comparison suggests that the low-temperature peak is associated with Ni and the high-temperature peak with W. Similar results were found with Mo/Al_2O_3 (*11*), suggesting that for Ni–Mo/Al_2O_3 (and Co–Mo/Al_2O_3), the low-temperature peaks are associated with Ni (and Co) and the high-temperature peaks with Mo. We speculate that the fine structure of the lower-temperature peak may be characteristic of the particular catalyst and the degree of dispersion, reflecting the presence of different oxidic species on the surface.

The same three promoted catalysts, after sulfiding followed by TPD under He, underwent programmed heating up to 500°C while experiencing flow of pure H_2. The results (Fig. 4) show the resolved H_2S and H_2O spectra. For each catalyst, the low-temperature pattern in the H_2S curve, starting at about 200°C, was followed by a steep rise beginning at a temperature between 400 and 500°C. The deconvolution of the curves suggested in Fig. 4 indicates the presence of two principal low-temperature peaks appearing before the rate of evolution of H_2S starts to rise sharply and monotonically. These peaks (observed at 290 and 390°C for Co–Mo/Al_2O_3, 300 and 350°C for Ni–Mo/Al_2O_3, and 250 and 350°C for Ni–W/Al_2O_3) are attributed to the transition metal species on the surface, since with pure alumina (Fig. 5) only a monotonic increase in the H_2S evolution rate was found. This latter part of the TPR spectrum

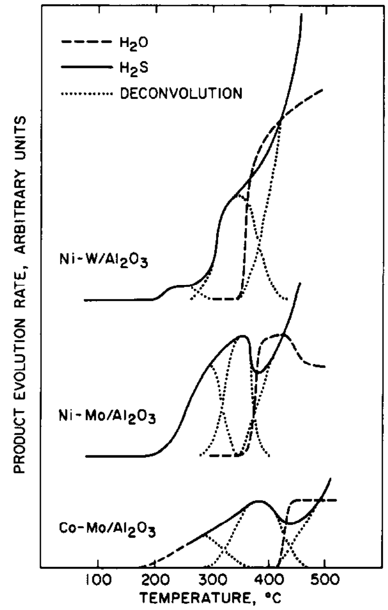

FIG. 4. Temperature-programmed reduction plots for sulfided commercial hydroprocessing catalysts. The heating rate was 10°C/min.

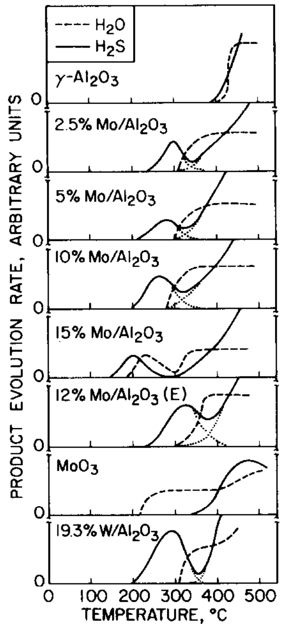

FIG. 5. Temperature-programmed reduction plots for sulfided catalysts. The heating rate was 10°C/min.

for H_2S evolution typically starts at a temperature greater than 350°C, always being associated with the commencement of water evolution, which rapidly attains a nearly constant rate. The foregoing results lead to the suggestion that water observed during TPR of the sulfided catalysts was evolved at least partially from the alumina support, as a product of H_2 reduction.

This suggestion is supported by TPR results obtained with sulfided, unpromoted Mo/Al_2O_3 and W/Al_2O_3 catalysts, as shown in Fig. 5. These data establish the trend for various loadings of MoO_3 between 2.5 and 15%. Although with these catalysts the desorbed H_2S associated with the Al_2O_3 support started to appear at a somewhat lower temperature (~300°C) than observed for the promoted catalysts and pure alumina (>350°C), the initiation of this desorption was always accompanied by the initiation of water evolution.

The data of Fig. 5 also show that the low-temperature H_2S desorption peak indicative of Mo species on the surface shifted to lower temperatures with increasing Mo loading on Al_2O_3; with the highest Mo loading (15% MoO_3/Al_2O_3), the peak was observed at 200°C. This catalyst, in contrast to those just mentioned, gave evidence of a low-temperature peak in the H_2O spectrum centered at 230°C, which preceded the evolution of the water associated with the alumina support.

Raman spectra obtained with the same samples (i.e., those containing 2.5 to 15% MoO_3 on Al_2O_3, Fig. 5) in oxidic form (*12*) (and changes in color from white to yellow) indicate that a full molybdenum monolayer was formed at a MoO_3 content of about 8%; the samples containing 10 and 15% MoO_3 incorporated MoO_3 crystallites (*12*). We therefore associate the first water peak evolved from the sulfided 15% MoO_3/Al_2O_3 sample with the presence of crystallites of MoO_3 in the oxidic form of the catalyst. Consistent with this suggestion, the data of Fig. 5 show that pure (unsupported) sulfided MoO_3 started to evolve H_2O at 220°C. But with this latter sample, H_2S desorption started at 350°C, showing a maximum at 470°C. Consequently, we conclude that the low-temperature H_2S peak characterizing the sample containing 15% MoO_3 (as well as other samples) is not associated with MoS_2 crystallites formed from some of the MoO_3 crystallites during sulfiding, but instead with the molybdenum monolayer, whereas the low-temperature H_2O peak is associated with these MoS_2 crystallites. Evidently, some surface oxygen was still present in these samples, and it is easily removed by reduction with H_2 (*14*). The TPR method, therefore, is suggested as a rapid, preliminary test for the presence of incompletely sulfided products of crystalline MoO_3.

The sample from Eindhoven containing 12% MoO_3 behaved similarly to the abovementioned monolayer samples, i.e., those containing 2.5 to 10% MoO_3. We infer that the Eindhoven sample, because of its greater surface area (Table 1), lacked MoO_3 (or, in the sulfided state, MoS_2) crystallites.

Replacing Mo by W had no apparent

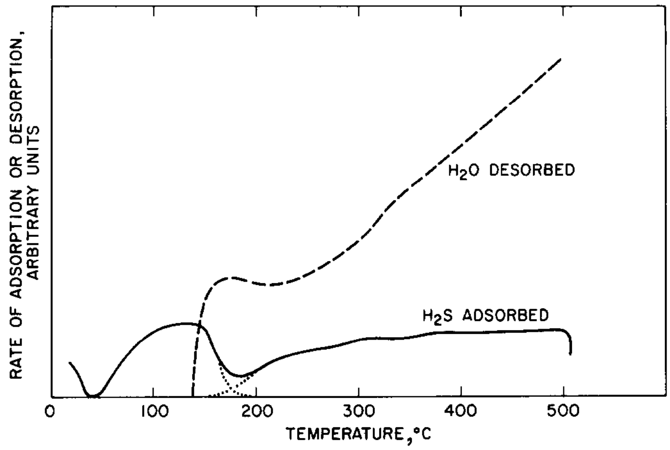

FIG. 6. Temperature-programmed sulfiding of Co–Mo/Al_2O_3. The heating rate was 10°C/min. Prior to the experiment, the sample had been heated to 500°C and held until water evolution ceased.

effect on the resolved TPR curves, as indicated by the results obtained with the 19.3% WO_3/Al_2O_3 sample (Fig. 5).

The analysis of data to this point has been qualitative, and attempts to obtain quantitative data (indicative of activation energies of desorption and reaction) by variation of the rates of heating were not fruitful. In contrast to the commonly observed behavior in TPD experiments, the TPD and TPR peaks barely shifted as the rate of heating was varied in the range 5 to 15°C/min. These results would at first suggest high activation energies of desorption and reaction, but we infer that the situation is more complex, since the "fine structure" of the whole TPD and TPR patterns varied—and not reproducibly—as a function of the rate of heating, and new peaks were observed at the lower rates of heating. We attribute these complications to the complex nature of the catalysts; different surface species and varying states of dispersion are believed to be involved, changing during heating and presumably being sensitive to the rate of heating. It seems likely that the exact composition of the surface prior to the start of the TPD/TPR experiment might be sensitive to the sulfiding procedure.

Temperature-Programmed Sulfiding

In an attempt to clarify the role of sulfiding, some preliminary experiments were done with variations in sulfiding conditions: (1) preheating the catalyst in He or in air before sulfiding; (2) changing the sulfiding temperature from 500 to 400°C; (3) changing the duration of sulfiding from 2 to 12 hr; and (4) changing the rate of heating in the sulfiding step from 5 to 15°C/min all failed to produce any significant change in the results of the subsequent TPD/TPR experiments.

Some new information was derived, however, from plots of the resolved temperature-programmed sulfiding data showing H_2S consumption and H_2O evolution for Co–Mo/Al_2O_3 (Fig. 6). The H_2S curve shows one peak in the 50–180°C region and a second at a temperature >200°C. Water evolution started at 140°C and was apparently related to the second H_2S peak. At least part of the H_2O desorbed at temperatures >300°C was not associated with the H_2S consumed. Since the spectrum for pure alumina showed virtually no deviation from the baseline for either H_2S or H_2O over the entire temperature range, the temperature-programmed sulfiding pattern of Fig. 6 may

TABLE 2

Summary of Quantitative TPD and TPR Results

Sulfided catalyst	Onset temperature for H_2S desorption (°C)		H_2S desorbed (molecules/nm^2)				S^a/M^b, atomic ratio (Peak I, TPR)
			TPD		TPR		
	TPD	TPR	Peak I	Remainder	Peak I	Remainder	
Co–Mo/Al_2O_3	80	200	0.24	0.23	0.28	0.11	0.05[c]
Ni–Mo/Al_2O_3	80	200	0.29	0.29	0.40	1.20	0.04[d]
Ni–W/Al_2O_3	80	200	0.14	0.40	0.22	0.67	0.06[e]
γ-Al_2O_3	80	400	0.19	0.38	—	0.30	—
2.5% MoO_3/Al_2O_3	80	250	0.20	0.48	0.05	0.24	0.07[f]
5.0% MoO_3/Al_2O_3	80	220	0.10	0.20	0.07	0.80	0.05[f]
10% MoO_3/Al_2O_3	80	200	0.15	0.25	0.06	0.45	0.02[f]
15% MoO_3/Al_2O_3	80	170	0.08	0.13	0.04	0.60	0.01[f]
12% MoO_3/Al_2O_3(E)	85	230	0.10	0.40	0.10	0.25	0.06[f]
19% WO_3/Al_2O_3(E)	85	200	0.17	0.14	0.14	0.80	0.06[g]

[a] S refers to sulfur desorbed as H_2S in the first peak in TPR.

[b] M refers to transition metal atom.

[c] S/(Mo + Co)/2; [d] S/(Mo + Ni)/2; [e] S/(Ni + W)/2; [f] S/Mo; [g] S/W.

be explained as follows: alumina sites are presumed to be readily saturated with H_2S at room temperature before the onset of heating. On the other hand, Mo-containing surface species are presumably less reactive with H_2S, and the first H_2S consumption peak may be identified with dissociative adsorption of H_2S, which does not lead to H_2O formation. The second peak is suggested to result from a water-forming reaction between H_2S and surface Mo species. Some of the H_2O evolved in the high-temperature region (>300°C) may be a product of reduction by H_2 introduced in the sulfiding gas mixture.

Relations between Spectra and Catalyst Structure and Activity

The TPD experiments suggest the removal of weakly bound H_2S associated with the Al_2O_3 support. This suggestion is confirmed by data (not shown) indicating the similarity of TPD spectra of H_2S evolved from γ-Al_2O_3 and from the sulfided Mo/Al_2O_3 and promoted Mo/Al_2O_3 catalysts. The H_2S might be coordinated at Lewis acid sites (Al^{3+} ions) (*15*) or coordinated to these sites while also being hydrogen bonded to neighboring oxygen atoms (*16*).

A fraction of the surface-bound sulfur could not be removed by the TPD experiments but could be removed by reduction with H_2. As discussed above, the two H_2S peaks in the TPR spectrum appearing at temperatures ≤390°C (depending on the catalyst composition) are associated with Co, Ni, and Mo ions on the catalyst surface. The surface reaction may involve a surface sulfur anion and H_2, forming H_2S and a surface anion vacancy (*17, 18*):

$$\underset{|\,|\,|\,|}{\mathrm{SSSS}} + H_2 \rightleftarrows \underset{|\,|\,|\,|}{\mathrm{S\square SS}} + H_2S \qquad (1)$$

Sulfur anion vacancies have been frequently suggested as catalytic sites for hydrodesulfurization and other hydroprocessing reactions (*5*), and it is possible that the TPR reaction created catalytic sites. This suggestion is consistent with the results of low-pressure pulse-microreactor studies of the hydrodesulfurization of thiophenic compounds (*18, 19*), which show a rough agreement between the onset temperature of the first TPR peak of sulfided Co–Mo/Al_2O_3 and the lowest temperature at which this catalyst demonstrated hydrodesulfurization activity.

Further, the onset temperature of H_2S evolution during TPR of the Mo/Al_2O_3 catalysts decreased with increasing Mo content and therefore with increasing catalytic activity for thiophene hydrodesulfurization at low pressure (*20*). Therefore, the ease of formation of sulfur anion vacancies indicated by TPR appears to give a measure of the relative hydrodesulfurization activity of the catalysts.

We caution, however, that in comparing the promoted and unpromoted catalysts, the effect of promoter (Co or Ni) ions in increasing the catalytic activity is not indicated by the temperature of the TPR peak. Nonetheless, in comparing just the promoted catalysts with each other, the suggestion that the TPR spectra provide an indication of relative activity is consistent with the results that all three promoted catalysts showed almost the same TPR behavior, and all three had approximately the same activity for dibenzothiophene hydrodesulfurization at high pressure (*21*).

The foregoing suggestions take on added weight when the data are interpreted quantitatively (Table 2). Proceeding under the assumption that the aforementioned H_2S evolution in TPR indicates the formation of anion vacancies, we estimate the concentration of the anion vacancies on the basis of the surface areas of the original oxidic catalysts.

The estimates given in Table 2 indicate that there is about one anion vacancy/3–5 nm^2 in the promoted catalysts. The unpromoted catalysts have about an order of magnitude lower concentration of these vacancies, which is consistent with their lower activities.

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REFERENCES

1. Cvetanović, R. J., and Amenomiya, Y., *Advan. Catal.* **17**, 103 (1967); *Catal. Rev.* **6**, 21 (1972).
2. Jenkins, J. W., McNicol, B. D., and Robertson, S. D., *Chem. Tech. (Amsterdam)* **7**, 316 (1977).
3. Ehrlich, G., *Advan. Catal.* **14**, 256 (1963).
4. Massoth, F. E., *Advan. Catal.* **27**, 265 (1978).
5. de Beer, V. H. J., and Schuit, G. C. A., *Ann. N.Y. Acad. Sci.* **272**, 61 (1976).
6. Delmon, B., *in* "Proceedings of the International Conference on the Chemistry and Uses of Molybdenum," Ann Arbor, Michigan, 1979, in press.
7. Broderick, D. H., Schuit, G. C. A., and Gates, B. C., *J. Catal.* **54**, 94 (1978).
8. Massoth, F. E., *J. Catal.* **36**, 164 (1975); **50**, 190 (1977).
9. Kabe, T., Yamada, S., Oba, M., and Miki, Y., *Int. Chem. Eng.* **12**, 366 (1972).
10. Eliezer, K. F., Bhinde, M., Houalla, M., Broderick, D., Gates, B. C., Katzer, J. R., and Olson, J. H., *Ind. Eng. Chem. Fundam.* **16**, 380 (1977).
11. Thomas, R., Mittelmeijer-Hazeleger, M. C., Kerkhof, F. P. J. M., Moulijn, J. A., Medema, J., and de Beer, V. H. J., *in* "Proceedings of the International Conference on the Chemistry and Uses of Molybdenum," Ann Arbor, Michigan, 1979, in press.
12. Cheng, C. P., and Schrader, G. L., *J. Catal.* **60**, 276 (1979).
13. Konings, A. J. A., Van Dooren, A. M., Koningsberger, D. C., de Beer, V. H. J., Farragher, A. L., and Schuit, G. C. A., *J. Catal.* **54**, 1 (1978).
14. Massoth, F. E., *J. Catal.* **30**, 204 (1973).
15. Lunsford, J. H., Zingery, L. W., and Rosynek, M. P., *J. Catal.* **38**, 179 (1975).
16. Slager, T. L., and Amberg, C. H., *Canad. J. Chem.* **50**, 3416 (1972).
17. Amberg, C. H., *J. Less Common Metals* **36**, 339 (1974).
18. Kilanowski, D. R., Teeuwen, H., de Beer, V. H. J., Gates, B. C., Schuit, G. C. A., and Kwart, H., *J. Catal.* **55**, 120 (1978).
19. Kilanowski, D. R., Ph.D. dissertation, University of Delaware, 1979.
20. de Beer, V. H. J., van der Aalst, M. J. M., Michiels, C. J., and Schuit, G. C. A., *J. Catal.* **43**, 78 (1976).
21. Houalla, M., Nag, N. K., Sapre, A. V., Broderick, D. H., and Gates, B. C., *Amer. Inst. Chem. Eng. J.* **24**, 1015 (1978).