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Studies of Molybdena–Alumina Catalysts

XVI. Effect of High-Temperature Sulfiding

Candia *et al.* (*1*) recently reported an increase in hydrodesulfurization (HDS) activity of $CoMo/Al_2O_3$ catalysts sulfided at 600°C. They attributed the increase in activity to a more active CoMoS phase (Type II) compared to the regular Type I CoMoS phase found in catalysts sulfided at 400°C. Breysse *et al.* (*2*) found a similar effect with NiW/Al_2O_3 catalysts. Prada Silvy *et al.* (*3*), however, reported no change in HDS activity in sulfiding $CoMo/Al_2O_3$ catalysts up to 700°C. In these studies, sintering of the support occurred due to the higher sulfiding temperatures employed compared with the original calcining temperature of the catalyst (~500°C). We decided to determine the effect of sulfiding temperature on the HDS and hydrogenation (HYD) activity of Mo and CoMo catalysts on an alumina support stabilized by calcining at a higher temperature than that used in the sulfiding treatments in order to avoid the complications due to support sintering during sulfiding.

The alumina support used was a Ketjen γ-Al_2O_3 (000–1.5E), which was crushed and sieved to 20–40 mesh and calcined in air at 750°C for 16 h. The surface area of the support dropped from an original value of 206 to 168 m^2/g due to this calcination. Catalysts containing Mo were prepared by incipient wetness impregnation with ammonium paramolybdate solution (pH 7.6) to give nominal compositions of 5 and 6% Mo, followed by drying and calcination at 500°C. A portion of the latter oven-dried catalyst was further impregnated with cobalt nitrate to give 1% Co in the final calcined catalyst (500°C). The catalysts were sulfided at 400, 550, or 700°C. Sulfided catalysts were characterized by CO_2 (*4*) and NO (*5*) chemisorption using a pulse technique. At least duplicate measurements were made on each sample. Catalytic activities for HDS of thiophene and HYD of hexene were carried out at 350°C and under atmospheric pressure in a fixed-bed reactor (*6*). Pseudo first-order rate constants were calculated from conversions.

Uptake of NO on the sulfided support increased from 0.09 mmol/g at 400°C to 0.18 mmol/g at 700°C. Apparently, the high temperature activated NO adsorption sites. Redey *et al.* (*7*) also reported an increase in NO chemisorption on an unsulfided alumina when the calcination temperature was increased from 500 to 700°C. However, for the 6% Mo catalyst, NO uptakes decreased monotonicallly from 0.27 mmol/g for 400°C sulfiding to 0.19 mmol/g for 700°C sulfiding. These data show the importance of accounting for uptake of the support in determining the net NO adsorption due to the MoS_2 phase.

Data for net NO uptake, MoS_2 coverage, and rate constants for HDS and HYD are given in Table 1. Catalyst NO uptakes for the sulfided Mo/Al_2O_3 catalysts were corrected for support contribution by accounting for the free alumina surface and actual weight of alumina present using support NO uptakes (*5*). Coverages were determined from CO_2 measurements on sulfided supports and catalysts (*4*). Values obtained for catalysts sulfided at 400 and 550°C gave values reasonably consistent with theoretical values for single-layer MoS_2 slabs (*4*), while the values at 700°C sulfiding represented an average slab size of

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TABLE 1

Results for Mo/Al_2O_3 and $CoMo/Al_2O_3$ Catalysts

Catalyst	Sulfiding T[a] (°C)	NO uptake[b] (mmol/g)	MoS_2[c] coverage	Rate const.[d]	
				k_T	k_H
A (4.9% Mo)	400	0.185	0.22	12.5	17.1
	550	0.174	0.24	10.5	18.5
	700	0.089	0.15	6.3	11.7
B (5.8% Mo)	400	0.196	0.20	12.0	
	550	0.165	0.21	8.7	
	700	0.044	0.13	3.2	
C (5.8% Mo, 1% Co)	400			128	
	550			148	
	700			140	

[a] 10% H_2S/H_2 for 2 h.

[b] Corrected for support contribution. Values are ± 0.010.

[c] From CO_2 adsorption. Theoretical for single layer ~0.22 (5.8% Mo) and ~0.18 (4.9% Mo). Values are ± 0.03.

[d] First-order constant for thiophene HDS (k_T) or hexene HYD (k_H), cm^3/g min at 350°C.

about 1.5 layers. This can be compared to an average number of 2.8 layers for a similarly sulfided catalyst reported by Candia *et al.* (*8*). The latter catalyst undoubtedly suffered some loss in surface area, which may account for the increased growth.

Table 1 shows that increase in sulfiding temperature resulted in significant decrease in net NO uptake and a corresponding decrease in HDS activity. The decrease in NO adsorption is indicative of an increase in MoS_2 slab size (*9*). The variation in k_T/NO, presented in Fig. 1, shows little effect of sulfiding temperature on intrinsic activity. (Error bars are estimated standard deviations of data.) This indicates that the site activity does not change with change in slab size. Similar data for hydrogenation show a marked increase in intrinsic activity (k_H/NO) with sulfiding temperature. This difference may be indicative of different types of site requirements for HDS and HYD (*10*).

In order to check whether the previously quoted increase in HDS activity with sulfiding temperature observed for CoMo catalysts might have been due to support surface area changes, HDS activities were determined on the CoMo catalysts. The results of Table 1 show that HDS activities increased and then slightly decreased with increase in sulfiding temperature, confirming earlier studies. The HDS data, calculated in terms of reaction rates, are compared in Fig. 2 to data of Candia *et al.* (*1*) for a similar catalyst containing the same Co/Mo ratio. It is seen that our data are in

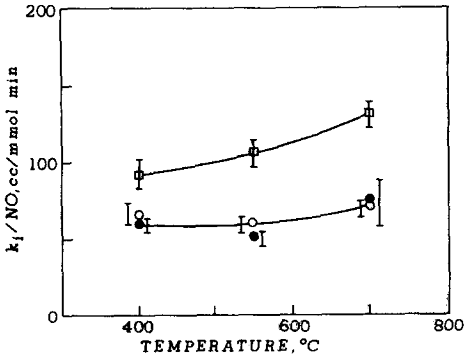

FIG. 1. Variation in specific activity for HDS (○) and HYD (□) versus sulfiding temperature. Open circles for catalyst A, solid circles for catalyst B.

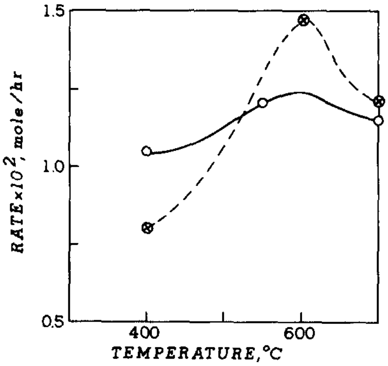

FIG. 2. Comparison of rate data versus sulfiding temperature for CoMo/Al_2O_3 catalysts. (○) Catalyst C, (⊗) Ref. (1).

general agreement with Candia *et al.*, but show a somewhat lower activity profile with sulfiding temperature. Chemisorption measurements were not done on the CoMo catalysts, as it has been shown that total NO uptake on these catalysts does not correlate with HDS activity (*11*).

In summary, high-temperature sulfiding of Mo/Al_2O_3 catalysts was found to decrease NO chemisorption (increase MoS_2 particle size) and decrease HDS activity. Intrinsic HDS activity (per NO), however, was hardly affected by sulfiding temperature (up to 700°C), whereas intrinsic HYD activity increased. For a CoMo/Al_2O_3 catalyst, a maximum in HDS activity was observed at an intermediate sulfiding temperature.

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REFERENCES

1. Candia, R., Topsøe, T., and Clausen, B. S., *in* "Proceedings, 9th Iberoamerican Symposium, Lisbon, Portugal, 1984," p. 211.
2. Breysse, M., Bachelier, J., Bonnelle, J. P., Cattenot, M., Cornet, D., Decamp, T., Duchet, J. C., Durand, R., Englehard, P., Frety, R., Gachet, C., Geneste, P., Grimblot, J., Gueguen, C., Kasztelan, S., Lacroix, M., Lavalley, J. C., Leclercq, C., Moreau, C., de Mourgues, L., Olive, J. L., Payen, E., Portefaix, J. L., Toulhoat, H., and Vrinat, M., *Bull. Soc. Chim. Belg.* **96,** 829 (1987).
3. Prada Silvy, R., Delannay, F., Grange, P., and Delmon, B., *Polyhedron* **5,** 195 (1986).
4. Zmierczak, W., Qader, Q., and Massoth, F. E., *J. Catal.* **106,** 65 (1987).
5. Miciukiewicz, J., Zmierczak, W., and Massoth, F. E., *Bull. Soc. Chim. Belg.* **96,** 915 (1987).
6. Cable, T. L., Massoth, F. E., and Thomas, M. G., *Fuel Process. Technol. 4,* 265 (1981).
7. Redey, A., Goldwasser, J., and Hall, W. K., *J. Catal.* **113,** 82 (1988).
8. Candia, R., Sørensen, O., Villadsen, J., Topsøe, N.-Y., Clausen, B. S., and Topsøe, H., *Bull. Soc. Chim. Belg.* **93,** 763 (1984).
9. Topsøe, H., and Clausen, B. S., *Appl. Catal.* **25,** 273 (1986).
10. Massoth, F. E., and Mualidhar, G., *in* "Fourth Climax Intern. Conf. Chemistry and Uses of Molybdem" (B. F. Barry and P. C. H. Mitchell, Eds.), p. 343. Climax Molybdenum Co., Ann Arbor, MI, 1984.
11. Topsøe, N.-Y., and Topsøe, H., *J. Catal.* **84,** 386 (1983).