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Effect of Thermal Treatment on the Concentration and Distribution Profiles of Molybdenum, Cobalt, and Nickel in Co-Mo/Al_2O_3 and Ni-Mo/Al_2O_3 Catalysts

Catalysts consisting of molybdenum supported on γ-alumina with promoters such as Co or Ni are used extensively in the hydrotreating of petroleum fractions and resids (*1–3*). In view of their industrial importance, considerable attention has been paid to understanding the form in which molybdenum and other promoter atoms are present and their role in the reaction (*4–7*). Great effort has also been devoted to understanding the deactivation of these catalysts (*8, 9*). Depending on the conditions of reaction and the nature of feedstock, deactivation may result from poisoning, coking, fouling by metals, sintering, and phase transformations which occur either during use or during regeneration of the catalysts.

The thermal stability of such catalysts has been the subject of a number of studies in recent years (*10–12*). All authors report a loss of surface area. Interaction between different components of the catalysts as well as phase changes in the alumina have also been noted (*12, 13*). Very little work appears to have been done on the effect of temperature on the changes in the composition of the catalyst, and the available information is often incomplete and conflicting. For example, Dale *et al.* (*12*) reported that heating to 1000°C causes no loss of molybdenum or cobalt from a commercial Co-Mo/Al_2O_3 catalyst. In contrast, Srinivasan *et al.* (*14*) noted volatilization of MoO_3 from molybdena/alumina catalysts at temperatures of >900°C, but gave no data on the amount of molybdenum lost at different temperatures. This present study is intended to investigate the effect of thermal treatment on the concentration of active components and their distribution within the pellet in oxidic Co-Mo/Al_2O_3 and Ni-Mo/Al_2O_3 systems.

METHODS

Studies have been carried out using two catalysts obtained from the same manufacturer. The first of these was found to contain 4.5 wt% CoO, 16.2 wt% MoO_3, and the balance Al_2O_3 when fresh and to have a surface area of 248 m^2g^{-1}. The second contained 3.8 wt% NiO, 19.5 wt% MoO_3, and the balance Al_2O_3 and to have a surface area of 193 m^2g^{-1} when untreated. No phosphorus was detected in the analysis of either catalyst. Six portions of each of the catalysts were heated for 16 h in air at 200, 500, 600, 700, 800, and 900°C and then cooled to room temperature for subsequent chemical analysis. X-Ray fluorescence (Philips PW 1410) was used to determine the bulk concentrations of Co, Mo, and Ni in different heat-treated catalysts. The distribution profile of the metals within the catalyst pellet was measured by electron microprobe analysis using a scanning electron X-ray microscope analyser (Camebax) equipped with an energy dispersive X-ray analyser (EDAX).

RESULTS AND DISCUSSION

The concentrations of Co, Mo, and Ni oxides in fresh and treated catalysts are shown in Fig. 1. It may be seen that temperatures up to 700°C have no significant effect on the composition of either type of catalyst, but a substantial loss of molybdenum is noticed when they are heated above 800°C. Cobalt and nickel levels are not sig-

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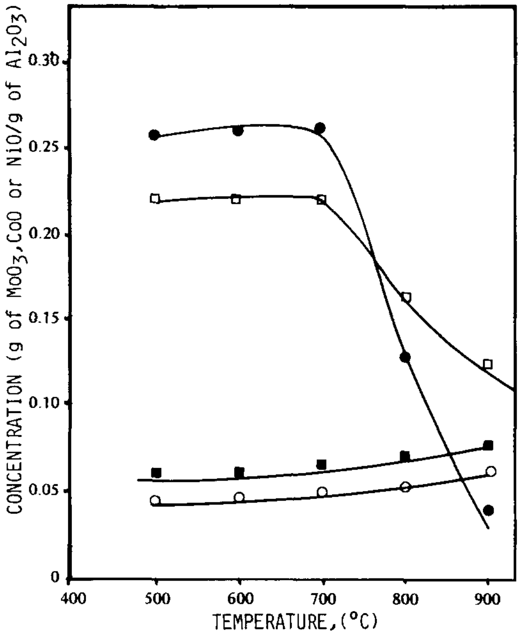

FIG. 1. Effect of temperature on Mo, Co, and Ni concentrations in Co-Mo/Al_2O_3 and Ni-Mo/Al_2O_3 catalysts. (●) MoO_3 in the heat-treated Ni-Mo/Al_2O_3 catalyst. (□) MoO_3 in the heat-treated Co-Mo/Al_2O_3 catalyst. (■) CoO in the heat-treated Co-Mo/Al_2O_3 catalyst. (○) NiO in the heat-treated Ni-Mo/Al_2O_3 catalyst.

nificantly affected. A small increase in their concentrations noticed at higher temperatures can be attributed to a small loss of weight in heating the pellets. This result is in contrast with the findings of Dale *et al.* (*12*), who reported no loss of molybdenum on heating to 1000°C. Thermogravimetric analysis (Fig. 2) confirmed our finding; a large weight loss was observed between 800 and 900°C for Ni-Mo/Al_2O_3 and between 900 and 1000°C for Co-Mo/Al_2O_3.

In fresh catalysts after calcining, Mo and Co (or Ni) are present in their oxidic form in a bilayer comprising a monolayer of CoO or NiO superimposed on a monolayer of MoO_3 on the alumina surface (*15, 16*). Part of the Co or Ni also enters the alumina lattice, forming inactive $CoAl_2O_4$ or $NiAl_2O_4$. At higher temperatures, it is possible that the molybdena melts (m.p. 795°C) and breaks down the intimate dispersions of Ni or Co oxide with MoO_3. The molten MoO_3 diffuses through the pores to the exterior of the pellet and sublimes, causing molybdenum loss. Distribution profiles of Mo across the pellet cross section after treatment at various temperatures were measured to examine molybdenum distribution. The results, shown in Fig. 3, indicate that in fresh Ni-Mo/Al_2O_3 catalyst, Mo is uniformly distributed within the pellet and there is no appreciable change in distribution on heating it to 500°C. At 700°C or more the Mo moves toward the exterior of the pellet. However, the concentration at the pellet exterior did not increase significantly, suggesting that the excess molybdenum had volatilized from the pellet surface. Similar observations were also made for the

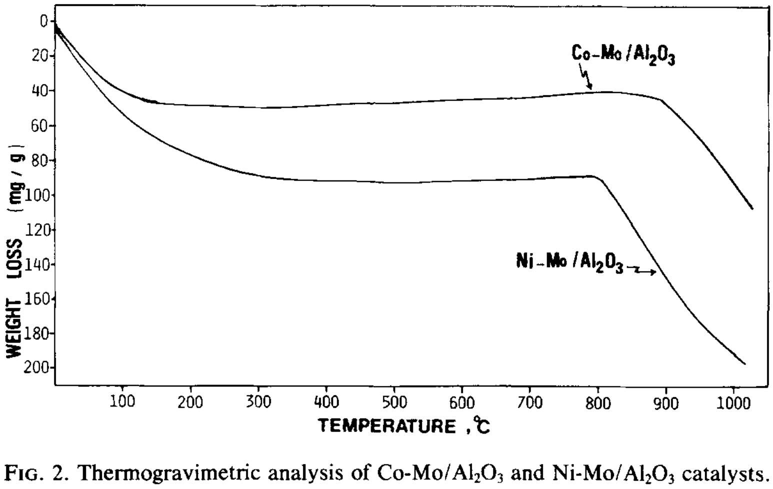

FIG. 2. Thermogravimetric analysis of Co-Mo/Al_2O_3 and Ni-Mo/Al_2O_3 catalysts.

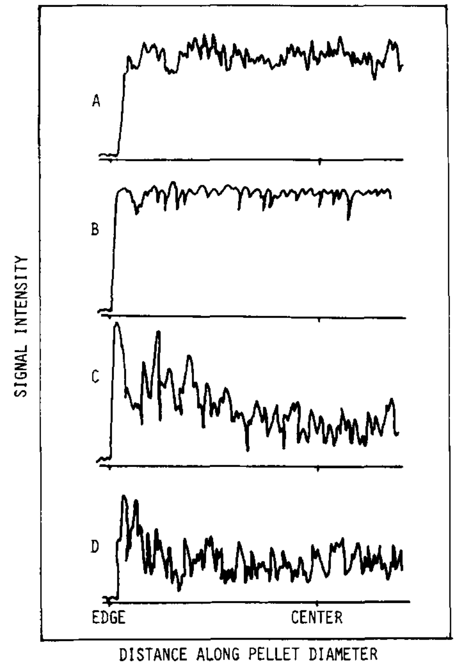

FIG. 3. Distribution line profiles for Mo in Ni-Mo/Al_2O_3 catalyst (A, fresh; B, 500°C; C, 700°C; D, 900°C).

Co-Mo/Al_2O_3 catalyst. Distributions of Co and Ni were not changed to any appreciable extent even after severe heat treatment.

Another interesting point to note in the results presented in Figs. 1 and 2 is that molybdenum volatilization differs in amount and temperature between the Co-Mo and Ni-Mo catalysts. The loss of molybdenum from Ni-Mo/Al_2O_3 is substantially larger and occurs at a lower temperature than from the Co-Mo/Al_2O_3. This is probably due to the differences in the diffusivity of Co and Ni ions. At higher temperatures, a large portion of the Co or Ni ions may diffuse along the surface and into the bulk of alumina forming nickel aluminate and cobalt aluminate spinels. It is possible that nickel diffuses into the bulk of alumina more rapidly than cobalt because nickel occupies octahedral sites in a spinel rather than the tetrahedral sites chosen by cobalt (*1, 17, 18*). The rapid migration of Ni into the alumina leaves MoO_3 on the alumina surface, the molybdena being free to migrate and eventually to volatilize. Since the diffusion of cobalt is slow, the liberation of free molybdena on the alumina surface will be more difficult. As a result, molybdena volatilization will be less and will occur at higher temperatures in Co-Mo/Al_2O_3 catalysts.

Detailed study of the phases present and of their effect on the catalyst characteristics and activity is currently in progress. However, the present results show that care must be exercised during any regeneration process for these catalysts as a result of the fact that significant molybdenum trioxide loss can be observed at temperatures as low as 700°C.

In conclusion, heating at very high temperatures causes substantial loss of Mo from both Co-Mo and Ni-Mo catalysts. The molybdenum volatilization is substantially larger and occurs at a lower temperature for the Ni-Mo/Al_2O_3 catalyst than for the Co-Mo/Al_2O_3 catalyst. Although difficult to prove clearly, it seems that molybdena volatization results from a breakdown of the intimate dispersions of Ni or Co oxides with Mo oxide on the alumina surface as a result of the melting of MoO_3 and the migration of the Ni and Co into the bulk of the alumina to form spinels.

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REFERENCES

1. Gates, B. C., Katzer, J. R., and Schuit, G. C. A., "Chemistry of Catalytic Processes." McGraw-Hill, New York, 1979.
2. Ohtsuka, T., *Catal. Rev. Sci. Eng.* **16,** 291 (1977).
3. McCulloch, D. C., *in* "Applied Industrial Catalysis" (B. E. Leach, Ed.), Vol. 1, p. 69. Academic Press, New York, 1983.
4. Grange, P., *Catal. Rev. Sci. Eng.* **21,** 135 (1980).
5. Ratnasamy, P., and Sivasanker, S., *Catal. Rev. Sci. Eng.* **20,** 401 (1980).

6. Topsøe, H., and Clausen, B. S., *Catal. Rev. Sci. Eng.* **26,** 395 (1984).
7. Gajardo, P., Mathieus, A., Grange, P., and Delmon, B., *Appl. Catal.* **3,** 347 (1982).
8. Delmon, B., and Grange, P., *in* "Progress in Catalyst Deactivation" (J. L. Figuereido, Ed.), p. 231. Nijhoff, The Hague, 1982.
9. Tamm, P. W., Harnsberger, H. F., and Bridge, A. G., *Ind. Eng. Chem. Process. Des. Dev.* **20,** 262 (1981).
10. Parekh, B. S., and Weller, S. W., *J. Catal.* **55,** 58 (1978).
11. Hopkins, P. D., and Meyers, B. L., *Ind. Eng. Chem. Prod. Res. Dev.* **22,** 421 (1983).
12. Dale, J. M., Hulett, L. D., Fuller, E. L., Richards, H. L., and Sherman, R. L., *J. Catal.* **61,** 66 (1980).
13. Ratnasamy, P., Mehrotra, R. P., and Ramaswamy, A. V., *J. Catal.* **32,** 63 (1974).
14. Srinivasan, R., Liu, H. C., and Weller, S. W., *J. Catal.* **57,** 87 (1979).
15. Delmon, B., Grange, P., Gajardo, P., and Delannay, F., *Hebd. Seances Acad., Sci. Ser. C* **288,** 391 (1979).
16. Apecetche, M. A., and Delmon, B., *React. Kinet. Catal. Lett.* **12,** 385 (1979).
17. Moné, R., *in* "Preparation of Catalysts" (B. Delmon, P. A. Jacobs, and G. Poncelet, Eds.), p. 381. Elsevier, Amsterdam, 1976.
18. Greegor, R. B., Little, F. N., Chin, R., and Hercules, D. M., *J. Phys. Chem.* **85,** 1232 (1981).

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