React. Kinet. Catal. Lett., Vol. 22, Nos 3–4, 417–420 (1983)

# 12-MOLYBDOPHOSPHORIC ACID AS STARTING MATERIAL FOR Ni–Mo/$Al_2O_3$ HYDRODESULFURIZATION CATALYSTS

Y. Okamoto, T. Gomi, Y. Mori, T. Imanaka and S. Teranishi

Department of Chemical Engineering, Faculty of Engineering Science, Osaka University,
Toyonaka, Osaka 560, Japan

Received November 23, 1982
Accepted December 22, 1982

12-Molybdophosphoric acid was examined as starting material for NiO–$MoO_3/Al_2O_3$ HDS catalysts as well as the addition effect of phosphoric acid. Optimum activities were found to be attained at a lower NiO content, suggesting the effective formation of Ni–Mo interaction species on the addition of P.

12-Молибдофосфорная кислота была испробована в качестве исходного вещества при получении HDS катализаторов NiO–$MoO_3/Al_2O_3$, а также эффект присоединения фосфорной кислоты. Оптимальная активность достигается при низком содержании NiO, что свидетельствует об эффективном образовании Ni–Mo взаимодействующих частиц при присоединении P.

The promoting nature of Co or Ni in $MoO_3$ or $WO_3/Al_2O_3$ HDS catalysts is still controversial /1/. Recently, several models have been proposed for the active species in promoted catalysts /2–4/. All the models presented previously are consistent in the point that the promotive effect of Co or Ni is induced by the intimate contact between the Co or Ni and the Mo or W sulfide phases. One of the possible preparation methods to obtain improved catalysts is to use directly a Ni or Co salt of a Mo compound. It is reported in patent works /5/ that the addition of phosphoric acid into HDS catalysts improves the catalytic performances. However, the promoting nature of P is not yet clear. In this work, in order to obtain efficient NiO–$MoO_3/Al_2O_3$ HDS catalysts, 1,2-molybdophosphoric acid (MPA) and its Ni salt were examined as starting materials, as well as the addition effects of phosphoric acid.

## EXPERIMENTAL

Conventional NiO–$MoO_3/Al_2O_3$ catalysts having various NiO contents and 15 wt. % $MoO_3$ were prepared by an incipient wetness impregnation method using aqueous solutions of ammonium paramolybdate (APM) and Ni nitrate (Ni–Mo/Al).

$Al_2O_3$ was supplied by the Catalysis Society of Japan (JRC-ALO-2, 267 $m^2/g$). A required amount of APM was first impregnated then dried at 393 K for 16 h, followed by a $Ni(NO_3)_2$ impregnation. After drying again, the catalyst was calcined at 773 K for 2 h. Ni–MPA/Al was prepared by using MPA instead of APM. An appropriate amount of phosphoric acid was added to the Ni–Mo/Al catalyst before calcination. After drying, P–Ni–Mo/Al was calcined at 773 K for 2 h.

The HDS reaction of thiophene was carried out over the catalyst at 673 K under atmospheric pressure of the mixture: thiophene/benzene/$H_2$ (1/0.8/43, $H_2$ flow rate; 135 ml/min) using a fixed-bed flow reactor /6/. The catalyst was presulfided with $CS_2/H_2$ at 673 K for 1 h. The reproducibility of thiophene conversion was better than ±2%.

## RESULTS AND DISCUSSION

Figure 1-A shows thiophene conversions over the three series of $NiO-MoO_3/$ $/Al_2O_3$ catalysts in the function of the NiO content. At a low NiO content ($\leq$ 3 wt. %), the Ni–MPA/Al catalyst exhibited a significantly higher HDS activity than the Ni–Mo/Al catalyst, whereas the activity of the catalyst containing more than 5 wt. % NiO was lower. Consequently, it is evident that the Ni–MPA/Al catalyst is superior to the Ni–Mo/Al catalyst both in higher maximum activity and in lower NiO content required to show it.

In order to assess the effect of P in MPA, the effect of phosphoric acid addition was also examined with the P–Ni–Mo/Al catalyst containing 3 wt. % NiO. Figure 1-B illustrates the dependency of the activity upon the amount of doping P expressed by the $P/Mo_{12}$ atomic ratio. It is revealed that a promoting effect of P is observed, the maximum activity being found at $P/Mo_{12} = 1$ which is in excellent agreement with that of MPA. In Fig. 1-A, the HDS activity of the P–Ni–Mo/Al catalyst with $P/Mo_{12} = 1$ is shown as a function of the NiO content. They showed maximum activity at 3 wt. % NiO as with the Ni–MPA/Al catalyst. Accordingly, it is concluded that there is no essential difference in the nature of the promoting effect of P in the P–Ni–Mo/Al and Ni–MPA/Al catalysts, though the latter catalyst showed a slightly higher optimum activity. The Ni salt of MPA, $Ni_3-(PMo_{12}O_{40})_2$, supported over $Al_2O_3$ (1 wt. % NiO, 15 wt. % $MoO_3$) showed a conversion of 18%, which was higher than that of the Ni–Mo/Al catalyst with the same composition (12%) and comparable with those of the catalysts containing P. This supports the above conclusions.

On the addition of P, irrespective of the modes of addition, a "heteropolymolybdate (HPM)" structure is considered to be formed over the $Al_2O_3$ surface and,

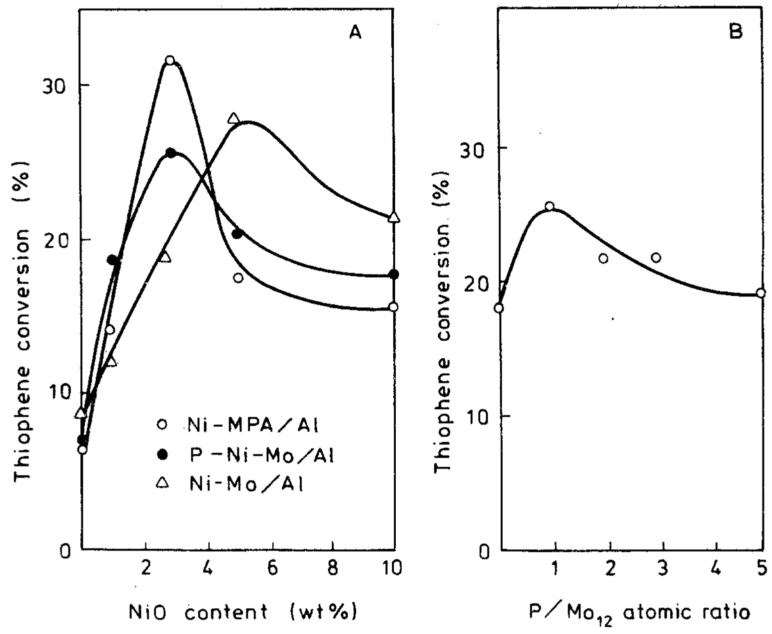

Fig. 1. A: Activity dependences of NiO–MoO$_3$/Al$_2$O$_3$ catalysts on the NiO content for thiophene HDS at 673 K. – B: Effect of phosphoric acid on the HDS activity of the Ni–Mo/Al catalyst (NiO; 3 wt. % and MoO$_3$; 15 wt. %). The amount of catalyst used was 0.15 g in A and B

accordingly, Ni salts of "HPM" when Ni is added. After calcination, the Ni salts may induce more abundant Ni cations in the vicinity of Mo or Ni–O–MO interaction species, compared to the catalyst without P. A similar model has been suggested by Knözinger et al. /7/. Both the promoting and retarding effects of P at low low and high NiO contents, respectively, would be explainable in terms of the shift in the optimum content of NiO by the more efficient formation of Ni–O–Mo, and, subsequently, of active Ni–S–Mo species. The fact that the maximum activity is not modified so strongly could be interpreted by assuming no appreciable change in the Mo sulfide dispersity with the addition of P, due to strong MoO$_3$–Al$_2$O$_3$ interactions.

## REFERENCES

1. F. E. Massoth: Adv. Catal., *27,* 265 (1978).
2. H. Topsøe et al.: J. Catal., *68,* 433, 453 (1981).
3. K. S. Chung, F. E. Massoth: J. Catal., *64,* 332 (1980).
4. Y. Okamoto, T. Imanaka, S. Teranishi: J. Catal., *65,* 448 (1980).
5. E.g. in "Molybdenum Catalyst Bibliography" Climax Molybdenum Comp. Michigan, Suppl. 6 (1977–1978).
6. Y. Okamoto, H. Tomioka, Y. Katoh, T. Imanaka, S. Teranishi: J. Phys. Chem., *84,* 1833 (1980).
7. H. Knözinger et al.: Proc. 7th Intern. Congr. Catal., p. 604. Kodansha, Tokyo, (1981).