

EFFECT OF PARTIAL REMOVAL OF NICKEL OR COBALT PROMOTORS FROM MOLYBDENUM SULPHIDE HYDROREFINING CATALYSTS ON THEIR ACTIVITY

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Three commercial nickel-molybdenum and cobalt-molybdenum hydrorefining catalysts were sulphided and then treated with 10% hydrochloric acid. The amount of extracted nickel or cobalt increased with time of leaching; the activity of the catalysts for hydrogenation of toluene was enhanced by short leaching but was decreased when the acid treatment was prolonged. X-ray photoelectron spectroscopy of the Ni-Mo catalyst showed that the leaching results in major changes in the surface concentrations of nickel and molybdenum.

Cobalt and nickel are well known and much studied promoters of molybdenum or tungsten sulphide catalysts for hydrotreatment of petroleum fractions. However in spite of great efforts, their precise role is not clear. In commercial catalysts, which always include alumina carrier, the promoters are distributed into various chemical species. Beside forming an active phase (*e.g.* called non-stoichiometric Co-Mo-S phase by Topsøe and coworkers¹⁻³ in case of Co-Mo catalysts) and spinels with Al_2O_3 , cobalt and nickel are present as sulphides^{4,5}. Recently, Landau and coworkers⁶ studied the system Ni-Mo (without alumina), prepared by mechanical mixing of oxides, calcination and sulphiding, and have found that the specific hydrogenation activity was maintained or even increased when a large part of nickel sulphide Ni_3S_2 was removed from the catalysts by leaching with hydrochloric acid. The remaining nickel sufficed to promote the activity of MoS_2 and could not be extracted by further treatment. This is in good agreement with some theories on promoting effects in sulphide catalysts (for reviews see^{7,8}) which assume some incorporation of the promoter into the molybdenum (or tungsten) sulphide phase.

We have been interested whether acid leaching of sulphided commercial hydrotreating catalysts would also lead to extraction of cobalt or nickel and if so, how it would affect their activity. In these catalysts, the initial concentration of the promoter is by one order of magnitude lower than in the preparations of Landau and coworkers⁶ and the components are much more dispersed than in their mechanical mixtures.

EXPERIMENTAL

Catalysts. Commercial hydrorefining catalysts Shell 324 (17.7% MoO₃, 3.3% NiO), Cyanamid HDS-20 (14.3% MoO₃, 4.9% CoO) and Cherox 36-01 (Chemical Works, Litvínov; 14.1% MoO₃, 3.6% CoO), all on alumina carriers, were crushed and fractions 0.16–0.25 mm were sieved out. The samples were sulphided in a stream of hydrogen, saturated by carbon disulphide at –78°C, for 18 hours at 350°C.

Catalysts leaching. A sample (8.6 g) of sulphided catalyst was immersed into 10% HCl (35 ml), 5% HCl (50 ml), 10% tetrasodium ethylenediaminetetraacetate (100 ml) and 10% ammonium sulphide (50 ml) solutions, respectively, and let to stand for required time at room temperature. The solid was filtered off, washed with distilled water and dried. The collected liquids were analyzed for nickel, molybdenum and aluminium.

Catalyst testing. The activity was determined by hydrogenation of a toluene–cyclohexane mixture (1 : 1 molar ratio), containing 2 mol % of CS₂ at 370°C and total pressure of 2.0 MPa in a flow reactor containing 7.00 g of the catalyst. The space velocity of toluene was 1.35 mmol . h⁻¹ g⁻¹ in all experiments, the partial pressure of toluene was varied in the range 0.060 to 0.222 MPa by changing the flow of hydrogen. The conversion was determined by gas chromatographic analysis of the liquid product which was sampled every 0.5 hour. After 6 to 8 hours, a steady-state conversion was achieved which was taken as a measure of activity.

Photoelectron spectra were recorded using the ESCA 3 MK II (VG Scientific) apparatus and X-ray radiation corresponding to the Al K_{α1,2} line. The spectra were empirically smoothed, then digitalized using the plotter Hewlett–Packard 7225A and further treated on the Hewlett–Packard 9825A calculator. The concentrations of individual elements were calculated from the integral of the spectrum in the measured range. It was assumed that the intensity I of a spectral line is proportional to the product $c\sigma\lambda(E_k)T(E_k)$ where c is the concentration of the atoms, σ the effective photoionization crosssection, $\lambda(E_k)$ mean free path of the photoelectrons and $T(E_k)$ transmission function of the analyzer (E_k is the kinetic energy of photoelectrons). The approximate relation $\lambda(E_k) \sim E_k^{1/2}$ and the relation $T(E_k) \sim E_k^{-1}$ give for the concentration

$$c \sim IE_k^{-1/2}\sigma^{-1},$$

where the kinetic energy E_k is given by the difference of the energy of the radiation (1486.6 eV) and bonding energy corresponding to the measured line. The spectra, corrected on the linear background, were fitted by Gaussian curves using the least square procedure. The bonding energies were read using the maxima of the calculated Gaussian curves and using the correction for the influence of charging of the non-conductive samples, based on the position of the Al 2p line. For the three studied samples, the lines Al 2p, Ni 2p, Mo 3p and S 2p were measured. For Al 2p, the position of the line was taken as equal to 74.5 eV, according to ref.⁹ for Al₂O₃.

RESULTS AND DISCUSSION

The dependences of conversion on partial pressure of toluene in the feed showed a maximum at approximately 0.1 MPa with all catalysts; its position did not change with any treatment of the catalysts. Fig. 1 demonstrates this situation for the Ni–Mo catalyst Shell 324. In this case, the maximum is sharp but with the two Co–Mo catalysts, Cyanamid HDS-20 and Cherox 36-01, the maxima are flat (Fig. 2). Figs 1 and 2

show also the influence of 10% hydrochloric acid on catalysts activity. The unchanging position of the maximum has allowed to base the discussion on the conversions obtained only at the partial pressure of 0.106 MPa which are summarized in Table I.

The data in Table I confirm that also with the commercial catalyst containing Ni and Mo sulphides on a carrier, the leaching with 10% hydrochloric acid results in removal of substantial fractions of nickel and in an increase of activity. However, prolonged treatment leads to a decrease of activity in spite of the fact that only a small additional amount of the promotor is removed from the catalysts. Also some aluminium was extracted but only traces of molybdenum were detected in the leachate. The treatment with 5% hydrochloric acid, as well as with tetrasodium ethylenediaminetetraacetate and ammonium sulphide caused slight deactivation of the catalysts.

When the treatment of the Ni-Mo catalyst was reversed, *i.e.* when leaching preceded sulphidation, substantial loss of activity was observed. Also with the Co-Mo catalysts, partial removal of cobalt from sulphided samples with 10% hydrochloric acid increased their activity for hydrogenation as the data in the lower part of Table I demonstrate.

The observed behaviour of sulphided Ni-Mo and Co-Mo catalysts upon leaching with 10% hydrochloric acid suggests at least two forms of the promotor being present: one form which is readily dissolved in the acid and which removal benefits the activity;

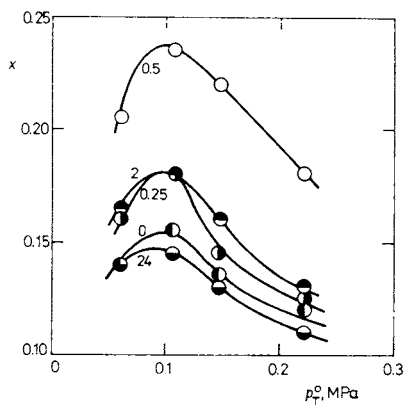


FIG. 1

Dependence of toluene conversion (x) on its partial pressure in the feed for Shell 324 (Ni-Mo) catalyst. The numbers at the curves denote time of leaching with 10% hydrochloric acid in hours

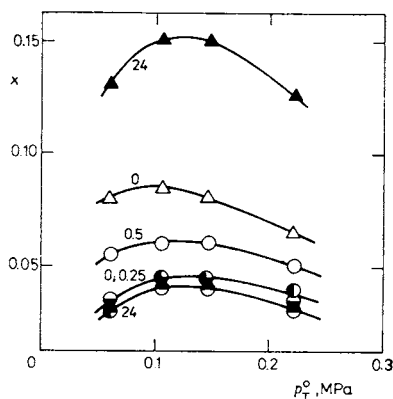


FIG. 2

Dependence of toluene conversion (x) on its partial pressure in the feed for the Co-Mo catalysts. Circular points: Cherox 36-01, triangles: Cyanamid HDS-20. The numbers at the curves denote time of leaching with 10% hydrochloric acid in hours

TABLE I
Effect of treatment of sulphided catalysts with hydrochloric acid on their properties

Catalyst Extractant concentration	Property	Duration of treatment, h						
		0	0.25	0.50	1.00	2.00	6.00	24.00
Shell 324 10%	Ni removed, %	0	32.2	34.7	—	41.0	—	42.0
	Al removed, %	0	7.8	8.6	—	11.7	—	12.4
	surface area ^a	173	163	174	—	176	—	181
Shell 324 5%	conversion, x ^b	0.155	0.180	0.235	—	0.180	—	0.145
	Ni removed, %	0	—	—	20.5	—	23.0	23.9
Cherox 36-01 10%	conversion, x ^b	0.155	—	—	0.145	—	0.135	0.140
	Co removed, %	0	29.0	42.5	—	—	—	71.8
HDS-20 10%	conversion, x ^b	0.045	0.045	0.060	—	—	—	0.40
	Co removed, %	0	—	—	—	—	—	23.0
	conversion, x ^b	0.085	—	—	—	—	—	0.150

^a After activity determination, m²/g; ^b at partial pressure of toluene in the feed $p_T^0 = 0.106$ MPa.

the second form which reacts slowly and which loss decreased the activity. On the basis of the work of Landau and coworkers⁶ on mechanically mixed and calcined sulphides of nickel and molybdenum and of the results of Topsøe and coworkers¹⁻³ who have identified a Co-Mo-S phase as the active component of Co-Mo hydro-refining catalysts, we may assume that the unnecessary form is the isolated nickel

TABLE II

Surface atom concentrations estimated from intensities of the photoelectron spectrum lines in sulphided Ni-Mo catalyst Shell 324

Sample	Concentration (arbitrary units)			[Mo]/[Ni]
	Ni ^a	Mo ^b	S ^c	
Untreated	13	73	95	5.6
0.5 h in 10% HCl	8	96	173	12.0
24 h in 10% HCl	8	100	141	12.5

Used lines: ^a Ni 2p_{3/2} (856.1 eV, corresponds to chemical shift of 3.3 eV for Ni(II), *cf.*⁹; a satellite line appears at 862.2 eV); ^b Mo 3p_{1/2} and Mo 3p_{3/2} (415.3 and 398.0 eV, in agreement with lines found for MoO₃ on alumina¹⁰); ^c S 2p (162.3 eV corresponding to sulphidic sulphur, 169.2 eV corresponding to sulphate sulphur; *cf.*⁹).

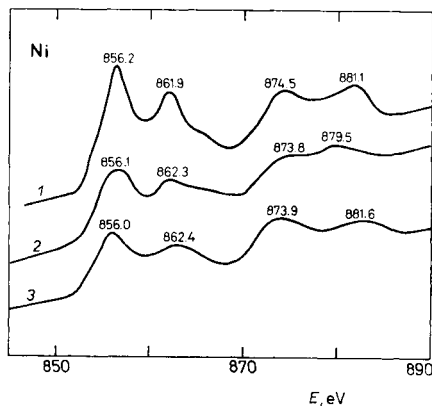


FIG. 3

Nickel lines in photoelectron spectra of the sulphided Ni-Mo catalyst. 1 Untreated, 2 0.5 h in 10% HCl, 3 24 h in 10% HCl

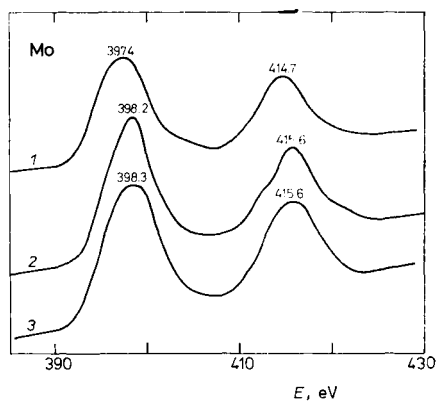


FIG. 4

Molybdenum lines in photoelectron spectra of the sulphided Ni-Mo catalyst. Denotation of curves as in Fig. 3

(or cobalt) sulphide phase and the second form constitutes the promotor in close contact with molybdenum atoms.

Then the observed increase of activity in consequence of removing part of nickel or cobalt sulphide phase can be explained by exposing more of the active molybdenum phase to reactant molecules. In order to support this hypothesis, three samples of the sulphided Ni-Mo catalysts, one untreated, two treated with 10% hydrochloric acid for 0.5 and 24 hours, respectively, were subjected to analysis by X-ray photoelectron spectroscopy (Figs 3, 4). Table II summarizes the results. The surface concentration of nickel is decreased by about forty per cent in 0.5 hour and remains unchanged during further treatment. In the same way, molybdenum surface concentration increases in the initial period of the leaching and further changes only little. However, prolonged leaching seems to destroy partially also the active phase because the activity decreased under the original value (Table I).

Although a practical application of hydrochloric acid treatment of sulphide catalysts can be hardly envisaged for improving their activity, the present results confirm that only a relatively minor part of cobalt or nickel is needed for promotion. If the way of introducing the promotor into the molybdenum phase could be improved, more active catalysts would be obtained with lesser amounts of the promotor.

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REFERENCES

1. Topsøe H., Clausen B. S., Candia R., Wiwel C., Mørup S.: *J. Catal.* **68**, 433 (1981).
2. Wiwel C., Candia R., Clausen B. S., Mørup S., Topsøe H.: *J. Catal.* **68**, 453 (1981).
3. Topsøe H., Clausen B. S., Candia R., Wiwel C., Mørup S.: *Bull. Soc. Chim. Belg.* **90**, 1189 (1981).
4. Pratt K. C., Sanders V. J., Tamp N.: *J. Catal.* **66**, 82 (1980).
5. Delmon B., Grange P., Gajardo P., Dellanoy F.: *C. R. Acad. Sci, Paris* **1979**, 288.
6. Landau M. V., Agievskii D. A., Slinkin A. A., Kipins N. A., Alekseyenko L. N., Fedorovskaya E. A., Pavlova L. I., Kucheroва T. N.: *Kinet. Katal.* **23**, 963 (1982).
7. Massoth F. E.: *Advan. Catal. Relat. Subj.* **27**, 298 (1978).
8. Grange P.: *Catal. Rev.-Sci. Eng.* **21**, 135 (1980).
9. Carlson T. A.: *Photoelectron and Auger Spectroscopy*, p. 355, 356, 361. Plenum Press, New York 1975.
10. Brinen J. C.: *J. Electron Spectr. Relat. Phenom.* **5**, 377 (1974).

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