

THE COMPARISON OF TWO PREPARATIONS OF A Ni-Co-Mo/Al₂O₃-SiO₂ HYDROTREATING CATALYSTS

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Received October 19th, 1987

Accepted October 23rd, 1987

Two preparations of Ni-Co-Mo/Al₂O₃-SiO₂ hydrorefining catalysts differing in the method of SiO₂ addition were investigated by the combination of several chemical and physical methods. As the result of the modification in preparation procedure, the following changes occurred simultaneously: the increase of relative surface concentrations of active metals detected by XPS, the increase of surface acidity measured by ammonia thermodesorption, the increase in porosity, the formation of larger pores, enlargement of the particles forming the texture of surface shown by SEM and the increase of the rate of hydrodesulphurization of tetrahydrothiophene. The response of other characteristics was small: surface polarity measured by reversible adsorption of benzene and heptane, the rate of hydrodesulphurization of thiophene and the rate of decomposition of tetrahydrothiophene in nitrogen. The difference in the performance of both catalysts is explained by the combination of several factors. The necessity of combination of several characterization techniques in the study of the relation between preparation procedure and performance of the catalyst is stressed.

Industrial hydrotreating Co-Mo/Al₂O₃ and Ni-Mo/Al₂O₃ catalysts have been investigated by a number of chemical and physical methods with the aim to rationalize the relations between the composition, preparation procedure, various bulk and surface properties and catalytic activity.

The first type of such studies investigated the sets of catalysts with a different metal loadings and a different Co/Mo (Ni/Mo) ratios; e.g. comparisons activity - ESCA data¹, activity - chemisorption of O₂, H₂S, and CO (ref.²), activity - Mössbauer spectroscopy data³. The present work does not fall into this category.

The second type of studies compared the sets of very similar or identical composition, which were prepared by similar or unknown, but probably very similar procedure. A frequent case of this kind was a set of commercial catalysts from various producers. The authors usually correlated the catalytic activity with only one or two physico-chemical parameters; e.g. activity - XPS data⁴, activity - chemisorption of oxygen⁵, activity - temperature programmed desorption and reduction

features^{6,7}, activity — amount of sulphhydryl groups on the surface⁸, activity — texture and hydrogen chemisorption⁹, activity — shape of extrudates¹⁰, activity — adsorption of tetrahydrothiophene¹¹. Only limited success has been achieved and the more complex approach, evaluating more various physical and chemical properties of catalysts simultaneously is clearly needed to obtain a better correlation of activity with other chemical and physical data.

The purpose of the present work was to compare two closely related Ni-Co-Mo/Al₂O₃-SiO₂ catalysts developed for the hydrotreating of vacuum distillate^{12,13}. They had identical gross composition and their preparation procedure differed only in the way of introduction of SiO₂. This small modification of preparation procedure improved catalytic activity which was tested on the whole extrudates (3 mm) by hydrodesulphurization of vacuum oil at 5 MPa and by hydrodesulphurization of thiophene at 0.35 MPa, ref.¹³.

In the present work, the previous catalytic results were completed by the activity measurements on the catalysts crushed to powder in order to determine whether the difference in activity of extrudates is due to different texture or due to different intrinsic activity of catalyst material. The testing reactions were HDS of thiophene at atmospheric pressure and parallel dehydrosulphurization (elimination of H₂S) and dehydrogenation of tetrahydrothiophene in nitrogen. The catalytic activity measurement was standardized by the simultaneous testing of standard Co-Mo/Al₂O₃ catalyst recommended by Working Party on Catalyst Reference Materials^{14,15}. The samples were further characterized by several various physico-chemical techniques in order to explain the difference in catalytic performance. The surface composition of catalysts in oxidic and presulphided state was determined by XPS. The polarity of surface, again both in oxidic and sulphide state, was characterized by reversible adsorption of easily polarizable benzene and nonpolarizable heptane. Acid-base properties were tested by thermal desorption of chemisorbed ammonia. Morphology of samples was studied by SEM and their texture was determined by porosimetry.

EXPERIMENTAL

Both samples compared are designed as G-5/P and 798 K, in consistency with previous reports on the development of these catalysts¹³. Catalyst G-5/P was a pilot plant product and 798K was prepared on a laboratory scale. The precursor of the carrier of G-5/P was precipitated by the addition of the mixture of sulphuric and nitric acid to the slurry of sodium aluminate and silicic acid hydrogel, i.e. at pH changing from 14 to 6.5. In the case of carrier of 798K, the solutions of sodium silicate, sodium aluminate, and nitric acid were added simultaneously to a precipitation vessel in such a way that precipitation occurred at constant pH 6.5. Further procedure was the same for both catalysts. The precipitates were dried at 120°C, kneaded with a solution of ammonium molybdate, extruded, dried, calcined, impregnated with a solution of cobalt and nickel nitrates and again calcined. The gross composition of catalysts was 3% NiO, 3.5% CoO, 16% MoO₃, 2% SiO₂, the balance being alumina. Extrudates had diameter 3 mm and were

crushed to the 0.16–0.25 mm particle size. Part of the powder was presulphided by the mixture H_2S/H_2 by the method described elsewhere¹⁶; presulphided samples were passivated by slow contacting them with air and stored at ambient atmosphere.

The standard Co–Mo/ Al_2O_3 catalyst of the Working Party on Catalyst Reference Materials^{14,15} was provided as 0.25–0.45 mm particles by National Physical Laboratory, Great Britain*. It is designed further as NPL.

XPS spectra were measured on ESCA 3 MK II VG Scientific apparatus using radiation energy corresponding to the line $Al K_{21,2}$. The positions of the lines were corrected using line $Al 2p$ (74.5 eV). The experimental spectra were smoothed by the computation procedure used already in our previous study of another hydrotreating catalysts¹⁷. The positions of lines of Mo, Ni, Co, Si, and S were very similar as in our previous study on another catalysts¹⁷ and were in good agreement with the literature referred there. The samples were measured both in oxidic and sulphide form. The sulphided samples were partially oxidized during storage on air and exhibited two forms of sulphur, S^{2-} and SO_4^{2-} , and two forms of molybdenum; the position of lines of these species were again very similar as found previously for another commercial catalysts¹⁷.

The adsorption of heptane and benzene was measured by the standard chromatographic technique, for refs. see literature¹⁸. The adsorption was evaluated in terms of chemical potentials of adsorbed hydrocarbons and the whole procedure was identical as used in our previous study of a set of commercial Co–Mo/ Al_2O_3 hydrotreating catalysts¹⁹.

Surface acidity measurements by ammonia thermodesorption were made by the standard chromatographic technique^{20,21}. The samples of catalysts were in oxidic form. They were saturated by gaseous ammonia at 180°C and physically adsorbed ammonia was removed by purging with nitrogen. The chemically bound ammonia was desorbed by a stepwise ($\Delta t = 50^\circ C$) increase of temperature up to 550°C and detected by a thermal conductivity detector. The samples were heated 3 h at 550°C in argon before the measurement.

The morphology of samples (in oxidic form) was measured by Stereoscan 180 scanning electron microscope. Pore size distribution was measured in the range 1.5–10 nm by benzene adsorption²² and in 10–7 500 nm range by mercury porosimetry.

Reactions of model compounds were studied in integral tubular flow microreactor at atmospheric pressure. The analysis of products was made by gas chromatography.

RESULTS AND DISCUSSION

The XPS spectra were measured on both oxidic and sulphide samples. The energies of lines for Mo, Co, Ni, S, and Si were the same for both catalysts and do not indicate any difference in quality of species present on the surface. They were also indistinguishable from energies found by us previously for the set of other commercial and model hydrorefining catalysts¹⁷.

The intensities of lines provided the relative atomic concentrations which are shown in Table I. Values of them fall into the limits observed by us for the set of hydrotreating catalysts in our previous paper¹⁷. In that paper we had not found any correlation between concentrations and activity. However, the two samples of Co–Ni–Mo/ Al_2O_3 – SiO_2 catalysts studied here are as for preparation very closely related, which makes the comparison of relative concentrations more reasonable.

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It is seen in Table I that the relative concentrations are within the limits of error of the measurement, the same for oxidic and sulphide samples. This shows that the distribution of metals on the surface is not significantly changed by sulphidation in agreement with the fact that industrial hydrotreating catalysts preserve their catalytic properties even after several cycles sulphidation – regeneration by oxidation.

The relative surface concentrations of active metals Mo/Al, Co/Al, and Ni/Al obtained by XPS are lower than those calculated from gross composition which are Mo/Al = 0.075, Co/Al = 0.031, and Ni/Al = 0.026. We have obtained similar results also with other industrial hydrotreating catalysts previously¹⁷. It shows that oxides and sulphides of active metals are present in relatively large particles, the bulk of which does not contribute to XPS signal.

The XPS spectra indicate the different distributions of metals on compared catalysts. The value of atomic ratios Mo/Al, Co/Al, and Ni/Al in Table I are distinctly higher for 798K catalyst than for G-5P sample. This higher content of metals in surface layers of 798K catalyst is also confirmed by higher S/Al ratio. (A part of sulphur in sulphidic G-5/P catalyst might originate from the sulphuric acid used in preparation procedure but this fact does not weaken the above argument.)

The reversible adsorption of aliphatic nonpolarizable heptane and aromatic polarizable benzene has been previously used to characterize the surface of a set of commercial and model hydrotreating catalysts¹⁹. The present results summarized in Table II should be discussed in connection with these previous data.

The adsorption of heptane (evaluated as $\Delta\mu^a(\text{H, I/CH-3601, S})$) is, in comparison with previously measured catalysts¹⁹, exceptionally large. This is easily interpreted

TABLE I
Relative atomic concentrations in surface layers determined by XPS spectroscopy

Catalyst	Mo/Al	Co/Al	Ni/Al	S/Al	$\text{SO}_4^{2-}/\sum\text{S}^a$
G-5/P oxidic	0.051 (± 0.004)	0.008 (± 0.007)	0.016 (± 0.003)	— ^b	— ^b
G-5/P sulphidic	0.053 (± 0.006)	0.004 (± 0.005)	0.010 (± 0.003)	0.127 (± 0.014)	0.53
798K oxidic	0.069 (± 0.005)	0.033 (± 0.003)	0.022 (± 0.002)	— ^b	— ^b
798K sulphidic	0.072 (± 0.006)	0.027 (± 0.040)	0.016 (± 0.003)	0.191 (± 0.023)	0.42

^a $\sum\text{S} = \text{SO}_4^{2-} + \text{S}^{2-}$; ^b not determined.

as the result of relatively high content of metals in the present catalysts. However, we have no simple explanation for the observation that the response of this adsorption to sulphidation (evaluated as $\Delta\mu^a(\text{H, I(s)}/\text{I(o), S})$) is rather different on both samples.

The difference in adsorption of benzene and heptane (evaluated as $\Delta\mu^a(\text{B}/\text{H, I, S})$) is a measure of the polarity of liquids used in gas-liquid chromatography which has been later applied also to gas-solid chromatography and to characterization of catalysts, for related literature see ref.¹⁸. This difference was rather similar for both studied catalysts both in oxidic and sulphidic form and fell into the range of values found for other hydrotreating catalysts previously¹⁹. The method thus does not indicate any important difference in polarity of the surface of catalysts being compared.

The previous study¹⁹ showed that coprecipitated and impregnated catalysts differ distinctly in the response of adsorption of hydrocarbons to sulphidation (evaluated as $\Delta\mu^a(\text{H, I(s)}/\text{I(o), S})$ and $\Delta\mu^a(\text{B, I(s)}/\text{I(o), S})$). The response of coprecipitated catalysts was low (similar to alumina alone) and of impregnated catalysts high (similar to MoO_3). The response of both present catalysts G-5/P and 798K was low, so that they behave like coprecipitated catalysts. This is consistent with the method of preparation of them. The molybdenum salt was added to the support precursor before calcination and the contact of Mo with alumina is thus similar as in coprecipitated catalysts.

The results of acidity measurements by ammonia chemisorption are shown in Fig. 1. The total amount of ammonia desorbed in the interval 250–550°C was

TABLE II

Relative chemical potentials $\Delta\mu^a$ of adsorbed hydrocarbons measured by chromatographic method. Details of method, evaluation and symbols in refs^{18,19}; H — heptane, B — benzene, I(o), I(s) — oxidic and sulphidic sample, resp., S — adsorbed amount, CH-3601 — standard catalyst.

Relative chemical potential ^a kJ mol ⁻¹	Catalyst I	
	G-5/P	798K
$\Delta\mu^a(\text{H, I(o)}/\text{CH-3601(o), S})$	-4.45	-4.45
$\Delta\mu^a(\text{B}/\text{H, I(o), S})$	-0.80	-0.50
$\Delta\mu^a(\text{B}/\text{H, I(s), S})$	-0.40	-0.80
$\Delta\mu^a(\text{H, I(s)}/\text{I(o), S})$	-0.24	0.97
$\Delta\mu^a(\text{B, I(s)}/\text{I(o), S})$	0.16	0.58

^a Example: $\Delta\mu^a(\text{B}/\text{H, I(o), S})$ is the difference in chemical potentials of adsorbed benzene and heptane on catalyst I in oxidic form at the same adsorbed amount S.

0.875 for G-5/P and 0.934 mol NH₃ kg(cat)⁻¹ for 798K. As should be expected, these values are higher than 0.150 mol NH₃ kg(cat)⁻¹ found by other authors²³ for silica supported catalysts. On the other hand, they are rather lower than those found by Surin et al.²¹ for Ni-Mo/Al₂O₃ catalyst - 2.4, and alumina support alone - 1.7 mol NH₃ kg(cat)⁻¹. In conclusion the catalyst 798K was found to be more acidic than G-5/P, the difference being highest in the region of weakly bound ammonia.

The pore size distribution results are shown in Fig. 2 and scanning electron micrographs of both catalysts are in Fig. 3. The catalyst 798K exhibited higher overall porosity, 0.55 vs 0.49 cm³ g⁻¹ and contained more of large pores. Scanning electron micrographs of it show higher particle sizes which agrees with porosity measurements.

The results obtained on the reactions of model compounds are summarized in Fig. 4 and Table III. The level of activity of studied samples was compared with NPL standard catalyst. This NPL sample was chosen as a reference material by Working Party on Catalyst Reference Materials several years ago^{14,15} but up to now only one paper used this catalyst as a reference point²⁴. However, it is expected that it will be used more extensively in future studies. The results in Fig. 4 and Table III show that our Co-N.-N_o/Al₂O₃-SiO₂ catalysts were almost twice more active than NPL standard.

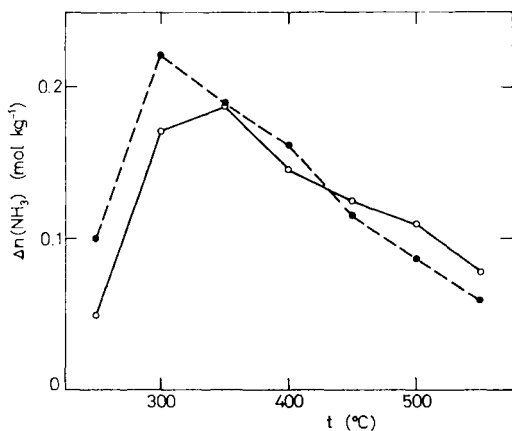


FIG. 1

Temperature desorption of ammonia on catalysts G-5/P and 798K. $\Delta n(\text{NH}_3)$ is the amount of ammonia desorbed in the temperature interval $\Delta t = t - 50$; — G-5/P, - - - 798 K

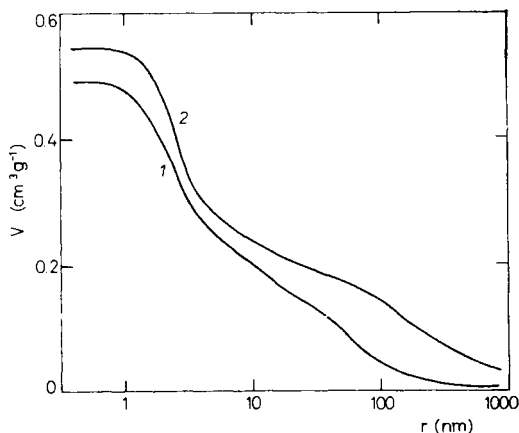


FIG. 2

Cumulative pore size distribution of catalysts G-5/P and 798K; r is pore diameter, V is pore volume, 1 G-5/P, 2 798K

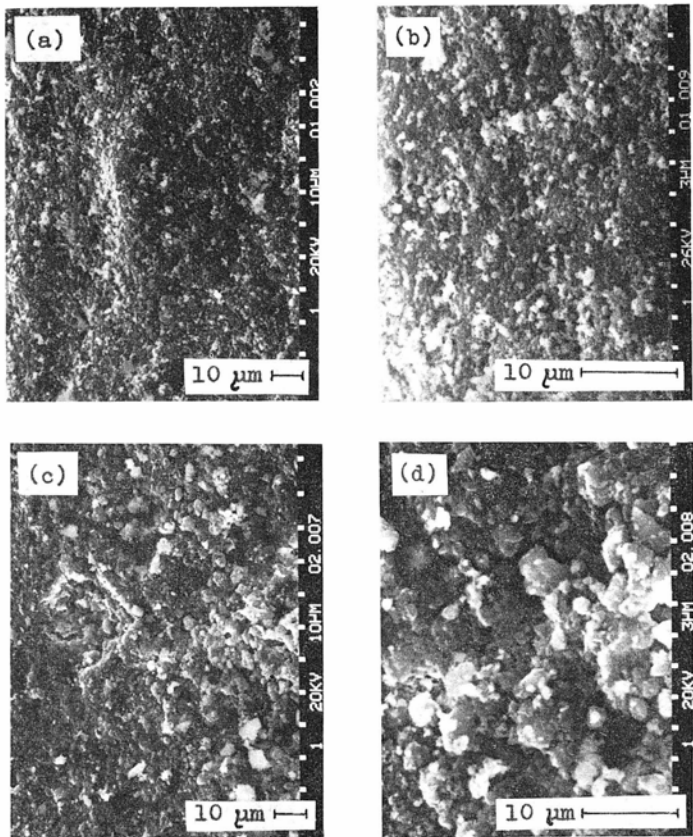


FIG. 3
SEM micrographs of catalysts: a, b — G-5/P,
c, d — 798K

In tetrahydrothiophene hydrodesulphurization the catalyst 798K was more active than G-5/P sample (Fig. 4). For thiophene hydrodesulphurization and tetrahydrothiophene decomposition in nitrogen, both catalysts exhibited the same activity

TABLE III

Catalysts activities in hydrodesulphurization (HDS) of thiophene (TH) and in parallel dehydrogenation and desulphurization of tetrahydrothiophene (THT) in nitrogen

Catalyst ^a	Conversion, %		
	HDS of TH ^b	Reaction of THT in N ₂ ^c	
		Dehydrogenation	Desulphurization
G-5/P	28	30	30
798K	28	30	30
NPL standard	14	—	—

^a Catalysts tested in non-presulphided form. ^b 0.1 g cat., H₂ 0.27, TH 0.002 mol h⁻¹, 350°C, atm. pressure. ^c 1.3 g cat., N₂ 0.39, THT 0.009, toluene (solvent) 0.009 mol h⁻¹, 400°C, atm. pressure.

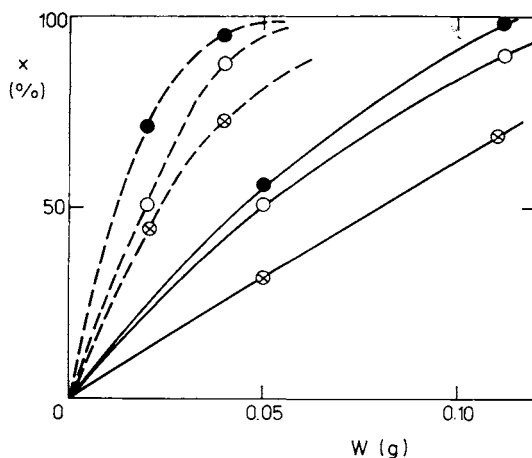


FIG. 4

Hydrodesulphurization of tetrahydrothiophene at atmospheric pressure and temperature 400°C. W is catalyst charge, x is conversion, feed rates: hydrogen 0.39, tetrahydrothiophene 0.009, and toluene (as solvent) 0.044 mol h⁻¹; ----- non-presulphided, ----- presulphided samples, ○ G-5/P, ● 798K, ⊗ NPL standard

(Table III). Also the selectivity dehydrogenation/desulphurization of tetrahydrothiophene reaction in nitrogen was indistinguishable. According these activity evaluations obtained here with 0.16–0.25 mm particle size, the difference between both catalysts seems to be less pronounced as compared with previous testing in vacuum oil hydrodesulphurization and thiophene hydrodesulphurization on original 3 mm extrudates¹³. This might be connected with intraparticle diffusion effects. The proper texture of catalyst 798K is responsible for higher difference in activity observed on 3 mm particles.

It can be concluded that the better performance of 798K catalyst is caused by the combination of several factors. The most important is probably the better dispersion of active metals which is indicated by ratios Mo/Al, Co/Al, and Ni/Al provided by XPS spectroscopy. The higher acidity measured by ammonia desorption is another positive property of 798K. Lastly, this catalyst exhibited larger pores and porosity which affects its activity especially in the form of uncrushed extrudates.

The authors are indebted to Mrs E. Hillerová and Mrs A. Drahorádová from the Institute of Chemical Process Fundamentals, Czechoslovak Academy of Sciences, for their contributions to the experimental work.

REFERENCES

1. Gajardo P., Declerck-Grimee R. I., Delvaux G., Olodo P., Zabala J. M., Canesson P., Grange P., Delmon B.: *J. Less-Common Met.* 54, 311 (1977).
2. Burch R., Collins A.: *Appl. Catal.* 17, 273 (1985).
3. Wivel C., Candia R., Clausen B. S., Mørup S., Topsøe H.: *J. Catal.* 68, 453 (1981).
4. Declerck-Grimee R. I., Canesson P., Friedman R. M., Fripiat J. J.: *J. Phys. Chem.* 82, 889 (1978).
5. Uchytíl J., Beránek L., Zahradníková H., Kraus M.: *Appl. Catal.* 4, 233 (1982).
6. Burch R., Collins A.: *Appl. Catal.* 18, 373 (1985).
7. Burch R., Collins A.: *Appl. Catal.* 18, 389 (1985).
8. Maternová J.: *Appl. Catal.* 6, 61 (1983).
9. Dick A. L., Ensell R. L., Phillips T. R., Szczepura A. K., Thorley M., Williams A., Wragg R. D.: *J. Catal.* 72, 266 (1981).
10. de Bruijn A., Naka I., Sonnemans J. W. M.: *Ind. Eng. Chem., Process Des. Dev.* 20, 40 (1981).
11. Pitkethley R. C., Ford J. F., Goble A. G.: *Brit.* 1 026 723 (1966).
12. Grzechowiak J. R., Myszka E.: *Nafta* 40, 64 (1984).
13. Grzechowiak J. R.: *Sb. Vys. Sk. Chem.-Technol. Praze, Technol. Paliv, D* 51, 305 (1985).
14. Bond G. C., Moss R. L., Pitkethley R. C., Sing K. S. W., Wilson R. in the book: *Studies in Surface Science and Catalysis* (B. Delmon, P. Grange, P. Jacobs and G. Poncelet, Eds), Vol. 3, p. 175. Elsevier, Amsterdam 1979.
15. Mitchell P. C. H.: *Appl. Catal.* 14, 394 (1985).
16. Zdražil M.: *J. Catal.* 58, 436 (1979).
17. Drahorádová A., Hillerová E., Janáček L., Jonáš J., Sedláček J., Šafařová M., Zdražil M.: *Chem. Prum.* 36, 304 (1986).
18. Zdražil M., Scott K. F.: *Chromatographia* 13, 85 (1980).

19. Hillerová E., Zdražil M.: *Collect. Czech. Chem. Commun.* **49**, 410 (1984).
20. Popowicz M., Berak J. M., Bazarnik A.: *Przem. Chem.* **51**, 92 (1972).
21. Surin S. A., Aliev R. R., Nefedov B. K., Sidelkovskaya V. G., Turovskaya L. V., Guliev T.: *Kinet. Katal.* **22**, 1327 (1981).
22. Kankare J., Jöntti O.: *Suom. Kemistilehti B-4G*, 1967 51.
23. Janowski F., Sofianos A., Wolf F.: *React. Kinet. Catal. Lett.* **12**, 157 (1979).
24. Dobrowolski M., Nagy Z., Paál Z., Tétényi P.: *Bull. Soc. Chim. Belg.* **93**, 659 (1984).

Translated by the author (M.Z.).