CHARACTERIZATION OF Mo-CONTAINING SYSTEMS SUPPORTED ON $AlPO_4$-5 AND ALUMINIUM PHOSPHATE AND THEIR BEHAVIOR IN THIOPHENE CONVERSION*

Alla A. SPOJAKINA, Nina G. KOSTOVA and Ljubomir DIMITROV
Institute of Kinetics and Catalysis,
Bulgarian Academy of Science, 1113 Sofia, Bulgaria

Received September 13, 1991
Accepted October 22, 1991

The properties of $AlPO_4$-5 with zeolite-like structure and amorphous aluminium phosphate modified by nickel and/or molybdenum (1 wt. % and 10 wt. %, respectively) have been studied using ESR and IR spectroscopy and catalytic testing in hydrodesulfurization (HDS) of thiophene. The chemical interaction between all components of catalysts, with formation of polymolybdate structures is revealed. The impact of the support is reflected in the difference of composition of polymolybdates, and different interactions with the hydrogen sulfide eliminated in thiophene conversion. The selectivity of the thiophene conversion and adsorption of H_2S eliminated depend on the method of introduction of components only for $AlPO_4$-5.

Molybdenum-containing catalysts including those supported on zeolites are of great interest. The need for multifunctional catalysts has promoted research on different supports. Specific zeolite properties expand significantly the possibilities of catalysts containing them. Zeolite resistence to hydrogen sulfide and ammonia are especially attractive in such processes. For example, it is known that faujasite zeolites are used in Mo-containing catalysts for hydrodesulfurization (HDS)[1,2]. Data on molybdenum effect on the properties of other zeolite types including aluminium phosphate with zeolite-like structure are scarce[3,4]. It was shown that zeolite type affects the catalytic behaviour in thiophene HDS on catalysts containing Mo and supported on a zeolite. In contrast to faujasite, aluminium phosphate molecular sieve posesses no ion exchange capacity. Polar hydroxyl groups can appear on the external surface as a result of terminal defects of the crystallites. One can conclude that ionic species can hardly be stabilized inside the channels of a neutral framework of $AlPO_4$-5. Ion exchange of the latter gives only 0·05 wt. % Ni (ref.[5]). That is why the metals in this zeolite can be introduced only by impregnation. As far as the hydrodesulfurization reaction is concerned, phosphate molecular sieve is interesting because of the promoting effect of phosphorus on the activity of conventional Ni-Mo catalysts[6].

---

* Presented as poster at the *International Symposium "Zeolite Chemistry and Catalysis", Prague, September 8—13, 1991.*

The latter are typically prepared by means of wet impregnation of components on supports exhibiting polar terminal groups[7]. This directs the attention to comparison of the zeolite supported samples with those based on amorphous alumonophosphate (AlP) with similar composition. Amorphous phosphates are currently of considerable interest as catalysts and carriers for metals for a number of industrially important processes including hydrorefining[8].

These facts formulate the principal purpose of this paper, to investigate the effect of phosphate zeolite-like structure on the component state and catalytic behaviour in thiophene conversion in the presence of catalysts modified with Ni and/or molybdenum.

EXPERIMENTAL

Molecular sieve $AlPO_4$-5 was synthesized using a procedure based on an Europian Patent[9]. To remove the template, the sample was calcined at 873 K. The crystallinity was checked by X-ray powder diffraction (CoKα-radiation). The product exhibits an atomic Al/P ratio of 1·1 according to chemical analysis. The excess of aluminium exists presumably in the form of amorphous alumina.

Amorphous aluminium phosphate (AlP) was prepared according to ref.[10]. The sample was calcined at 873 K. Its surface area was 100 $m^2 g^{-1}$.

Impregnation has been performed with aqueous solutions of $Ni(NO_3)_3.H_2O$ and $(NH_4)_6.Mo_7O_{24}.H_2O$. Samples containing both nickel and molybdenum have been prepared by wet simultaneous or successive (nickel as the first element) impregnation without intermediate heat treatment. The samples have been dried at 373 K and calcined for 2 h at 623 K. The samples contained 1 wt. % of Ni and 10 wt. % of Mo and are denoted as $AlPO_4$-5 or AlP (for amorphous phosphate) followed by the chemical symbol of the introduced component (Ni, Mo). For example, $AlPO_4$-5-NiMo has been prepared by coimpregnation of Ni and Mo. The sample $AlPO_4$-5-Ni — Mo has been obtained by sequential impregnation.

IR spectroscopy in the region 400—1 200 cm^{-1} using pellets in KBr (sample : KBr ratio is 1 : 150) (Specord IR 75 spectrometer) has been used for characterization of state of parent and modified phosphates.

The ESR spectra have been recorded on a Bruker ER 200D spectrometer operating at 9·7 MHz (X Band) at room temperature. Prior to registration of the spectra, the samples had been pretreated in a quartz reactor.

The catalyst samples (100 mg) have been tested for HDS of thiophene in a continuous flow reactor operating at atmospheric pressure, temperature of 623 K, with gas chromatographic analysis of products. Each sample, prior to the introduction of thiophene, had been heated 1·5 h in hydrogen flow (40 ml min^{-1}). Sulfidation has been carried out by H_2S evolved from thiophene. The catalytic activity has been evaluated by the conversion of thiophene to hydrocarbons and hydrogen sulfide.

RESULTS AND DISCUSSION

The crystallinity of the parent $AlPO_4$-5 and nickel modified $AlPO_4$-5-Ni has been confirmed by X-ray analysis. New additional lines appeared on diffractograms of molybdenum modified samples. The diffractogram of aluminium phosphate indicated its amorphous nature[11]. However, no phase of MoO_3 has been identified in the Mo-containing samples.

The characteristic bands of $AlPO_4$-5 (625, 730 and 1 100 cm^{-1}) are present in the IR spectra of the modified samples (Fig. 1). Some new bands have been revealed in the spectra of the calcined Mo-containing samples. The patterns of the catalyst samples, prepared by impregnation of both the zeolite and the amorphous phosphate, are similar. Therefore only the spectra of the zeolite-supported samples are shown.

The bands, observed in the frequency region 880 – 950 cm^{-1}, characterize vibrations of $Mo{=}O_t$ bonds of highly polymerized molybdenum compounds[12,13] as a result of interaction between the support and the impregnated components. The Mo—O—Mo bridged bands at 630 – 650 cm^{-1} additionally confirm the presence of polymolybdates (both iso and hetero)[14–16]. The correct identification of the separate species is hindered by overlapping of their characteristic bands with the bands of the zeolite. Nevertheless, the formation of aluminium heteropolymolybdate (bands at 650, 890, 910 and 950 cm^{-1}) in all Mo-containing samples could be safely recognized.

Shift of the band at 650 cm^{-1} to lower frequency at about 625 cm^{-1} and appearance of the band at about 825 cm^{-1} indicate a formation of nickel heteropolymolybdate[16].

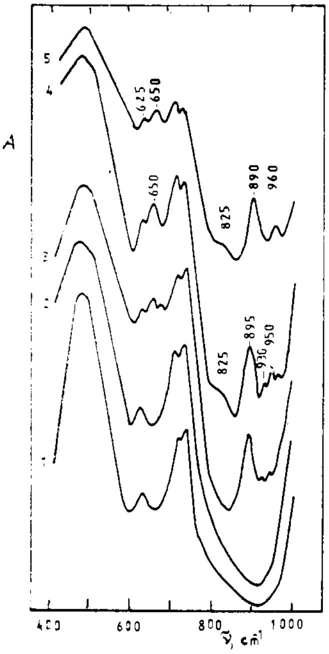

FIG. 1

IR spectra of samples, calcined at 623 K: $AlPO_4$-5; 2 $AlPO_4$-5-Ni; 3 $AlPO_4$-5-Mo; 1 $AlPO_4$-5-NiMo; 5 $AlPO_4$-5-Ni + Mo

Appearance of low intensity band at 960 cm^{-1} in the spectra of NiMo zeolite samples could indicate participation of PO_4^{3-} groups of the zeolite in the formation of phosphorus-molybdenum heteropoly compounds[15].

The behavior of the catalysts in the thiophene conversion is evidenced most convincingly by the difference in their phase compositon and state of components. This difference is most obvious during the initial period on stream (1 – 1·5 h) (Table I).

One has to keep in mind that the catalytic surface of the samples, preliminary heated at 623 K in hydrogen atmosphere (see Experimental) is changing continuously as a result of the interaction of H_2S evolved from the converted thiophene in the presence of the catalyst before reaching a steady state.

The profile of the activity change on stream presumably depends on the composition of precursors of active species and their interaction with the support. It should be noted that zeolite supported samples continue to adsorb H_2S after reaching a stationary activity (Table I). One can observe that the zeolite itself absorbs H_2S,

TABLE I

Preparation and catalytic performance of Mo(Ni) catalysts containing phsophate support in thiophene conversion

Sample	Support structure	Composition mg/g		Method of preparation	Property[a]	Conversion of thiophene after, min			
		Mo	Ni			10	50	120	200
1	$AlPO_4$-5	100	—	impregnation	a	30	12·0	11·0	10·0
					b	100	100·0	100·0	50·0
2	$AlPO_4$-5	100	10	coimpregnation	a	inactive	7·6	12·0	12·0
					b	—	100·0	95·8	58·3
3	$AlPO_4$-5	100	10	sequential impregnation	a	5	12·0	12·0	10·0
					b	100	100·0	41·6	20·0
4	amorphous	100	—	impregnation	a	9	12·0	9·0	7·0
					b	100	45·8	22·0	0·0
5	amorphous	100	10	coimpregnation	a	32	26·0	21·0	16·0
					b	94	53·8	0·0	0·0
6	amorphous	100	10	sequential impregnation	a	37	21·0	17·0	17·0
					b	100	38·0	0·0	0·0
					c	30			

[a] a Conversion of thiophene in hydrocarbons (%) (LHSV = 0·6 h^{-1}). b H_2S adsorbed by catalyst (%) from H_2S evolved during the reaction. c Conversion of thiophene in hydrocarbons (%) over catalyst performed 200 min followed by hydrogen treatment during 60 min.

in contrast to the amorphous phosphate. No adsorption of hydrogen sulfide is detected on the AlP modified samples after attaining steady-state conversion.

The initial conversion over the $AlPO_4$-5-Mo sample is almost three times higher than that during the steady state. It means that active sites for HDS are present in the reduced $AlPO_4$-5-Mo, H_2S evolved by this reaction decreases the activity of these sites. The high quantity of n-butane in the reaction products should be mentioned (Fig. 2). The activity of the AlP-Mo is quite low (Table I). The nickel loaded samples show no activity but nickel decreases the initial activity of $AlPO_4$-5-Mo and increases that of AlP-Mo (samples 1 – 3 and 4 – 6 in Table I).

Nickel shows a synergetic effect on Mo in AlP supported samples (Nos 5 and 6, Table I) similarly to conventional Mo-containing catalysts. The preparation of AlP-supported samples affects only the time interval for reaching the steady state and does not change the distribution of reaction products during the time on stream (Fig. 2).

The effect of nickel on $AlPO_4$-5-Mo is quite different. Nickel retards the process of active sites formation for HDS stationary activity and its promoting effect appears to be smaller (Table I). In the same time nickel lowers the hydrogenating function of molybdenum. In addition, nickel drastically affects the selectivity of the thiophene conversion (Fig. 2). The latter depends on the method of nickel loading. Compared to the $AlPO_4$-5-Mo sample, a decrease of isomerization and hydrogenation activity has been observed for the coimpregnated sample as a result of a secondary reaction related to hydrogenolysis of C—C bonds of C_4 hydrocarbons (about 40% of the thiophene conversion).

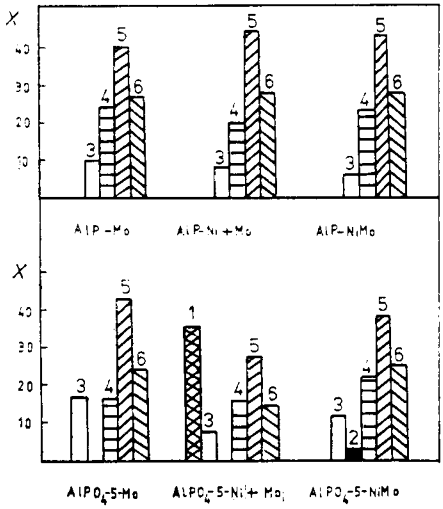

FIG. 2

Product distribution in thiophene HDS for $AlPO_4$-5 supported samples at 11·5% conversion and AlP supported samples at 17% conversion (conversion for AlP-Mo sample was 7%) 1 $C_1 - C_3$ hydrocarbons; 2 isobutane; 3 n-butane; 4 1-butene; 5 *trans*-2-butene; 6 *cis*-2-butene. X moles per 100 moles of converted thiophene

It is difficult to develop a concept of the actual mechanism of formation of C_1—C_3 hydrocarbons on $AlPO_4$-5-NiMo. They originate most probably from the bifunctional action of metallic nickel and acidic centres. The latter seem to be formed as a result of the hydrogen sulfide adsorption by zeolite. In contrast to coimpregnated $AlPO_4$-5-NiMo sample, the products of C_4 hydrogenolysis do not appear over the sequentially impregnated sample. Only a small yield of isobutane has been detected. This type of active sites appears upon loading with nickel and indicates the formation of new strong acidic sites[17]. Probably they appear as a result of the reduction of nickel species introduced by a partial ion exchange with outer external OH groups of zeolite[18].

A number of factors can affect the state of components (particularly their reducibility[19,20]) in the catalysts investigated: the support nature, the component composition and activity, the method of preparation and the following treatment.

Some more information about the correlation between the activity and state of components has been obtained using ESR measurements. The catalysts dried on air and calcined at 623 K gave a low-intensive signal characteristic of Mo^{5+} ion with $g_\perp = 1{\cdot}94$ and $g_\parallel = 1{\cdot}89$ (Fig. 3*a*). Subsequent reduction of Mo-containing samples at 623 K significantly increases the signal of Mo^{5+} ion (Fig. 3*b*). The low anisotropy $(g_\perp - g_\parallel = 0{\cdot}05)$ of Mo^{5+} signal shows that Mo^{5+} ion is observed in octahedral ligand surrounding, distorted tetragonally[21]. The polymolybdate phase observed in the oxidized state of the catalysts could be the precursor of this state of molybdenum. The changes of the ESR patterns of the samples after different

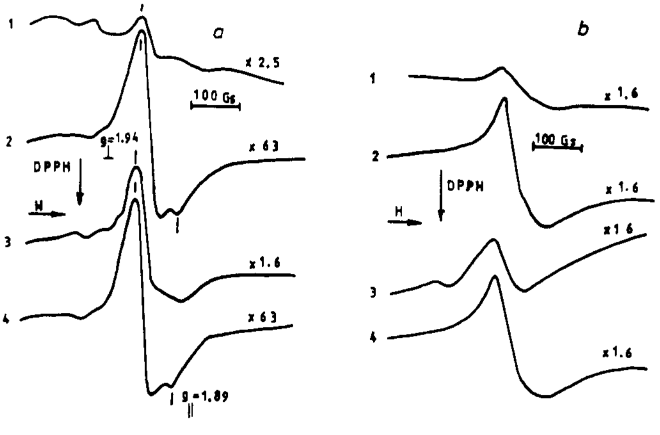

FIG. 3

ESR spectra of AlP-Ni + Mo (*a*) and $AlPO_4$-5-Ni + Mo (*b*). Samples treated successiely at 623 K by 1 air (2 h); 2 hydrogen (1·5 h); 3 hydrogen and thiophene mixture (3·5 h); 4 hydrogen (1 h) treatments are similar and therefore only one NiMo containing sample for each support is shown in Fig. 3. It should be noted that the different intensity of Mo^{5+} signal in the individual catalyst samples is observed and points to their different reducibility. The latter corresponds more or less with the activity of the samples in the thiophene conversion presented in Table I. This suggests that the reduction of the molybdenum species is a substantial step in the transformation of the oxidic precursor into the sulfide state.

A larger reducibility of the sample $AlPO_4$-5-Mo in comparison with AlP-Mois observed and correlates with its higher activity (Table I, samples 1 and 4). It is most likely caused by the fact that Mo-species are strongly bonded with the amorphous support. In the reaction between Mo and Ni in NiMo samples supported on amorphous phosphate reduces this bond and increases activity and intensity of Mo^{5+} signal.

The treatment of the samples with hydrogen and thiophene mixture leads to the stady-state conversion followed by adsorption of hydrogen sulfide (Table I) and to the appearance of less intensive signal of Mo^{5+} ion (Fig. 3). Further, a lower decrease in intensity is observed for NiMo zeolite (not Mo zeolite) supported samples compared to those of AlP supported on. The difference obviously lies in disparate state of nickel on investigated supports. The decrease in intensity of the signal of Mo^{5+} is accompanied by the appearance of the new low-intensive signal with $g = 1{\cdot}98$. The shift of the $g_{\parallel}$ component of the signal of Mo^{5+} from 1·879 to 1·906 is related to the introduction of sulfur in Mo-ligand surrounding[22].

These results show that quantitative correlation between HDS and intensity of signal characteristic of Mo^{5+} ion cannot be expected. At least two types of Mo^{5+} states can be active in the HDS on investigated samples.

This was confirmed by the treatment of the samples in hydrogen stream. The H_2S desorption (revealed in desorbed products along with butenes) has increased the

TABLE II

ESR signals of nickel observed in zeolite-supported samples

Sample	Treatment at 623 K	ΔH(Gs)	g
$AlPO_4$-5-Ni	hydrogen	1 370	2·56
$AlPO_4$-5-Ni	hydrogen + thiophene	740	2·27
$AlPO_4$-5-NiMo	hydrogen	no signal	
$AlPO_4$-5-NiMo	hydrogen + thiophene	485	2·27
$AlPO_4$-5-Ni + Mo	hydrogen	no signal	
$AlPO_4$-5-Ni + Mo	hydrogen + thiophene	no signal	

activity (Table I, samples 3 and 6) and intensity of the signal characteristic for Mo^{5+}. The intensity is close to the initial value (Fig. 3, spectrum 4).

No signal of nickel was observed in the ESR spectra both of air-calcined and at 623 K reduced NiMo samples. This could be the result of high dispersion of nickel and interaction with the support and/or with molybdenum[23-25]. High surface of AlP and location of components inside the zeolite channels entrance this dispersion. Only $AlPO_4$-5-Ni sample, reduced at 623 K, exhibits a signal characteristic of ferromagnetic Ni^0 with g value of 2·56 (Table II). This shows that the zeolite facilitates the reduction of Ni and sintering of metal particles[26], presumably, owing to their migration from the inner part of zeolite to the outer layers. The presence of Mo in zeolite supported samples suppresses this process.

Admission of a H_2 + thiophene mixture to the $AlPO_4$-5-Ni sample results in a narrowing of the signal and a decrease of the value to 2·27 (Table II). This means increasing degree of dispersion and number of metallic nickel particles[26].

Appearance of a narrow signal of nickel in the ESR spectra of $AlPO_4$-5-Ni + Mo sample sequentially impregnated ($g = 2{\cdot}27$) under treatment by the H_2 + thiophene mixture is detected as a result of change in the nickel coordination and dispersion. Probably a partial sulfidation of nickel and the formation of sulfides of non-stoichiometric composition take place. This effect of thiophene is in agreement with data for conventional hydrotreating catalysts[25-27].

The treatment with hydrogen and thiophene mixture of simultaneously impregnated $AlPO_4$-5 NiMo and both Al-supported samples have revealed no nickel signal in the ESR spectra.

This could mean a more difficult reduction of nickel in these samples and/or an easy formation of nickel sulfides[27]. Simultaneous introduction of components in zeolite results in a higher dispersion of Ni species or in the formation of NiMo mixed phase.

REFERENCES

1. U.S. 3 730 878 (1973).
2. Visotskii A. V., Chuikova N. A., Lipoich V. G.: Kinet. Katal. *18*, 1106 (1977).
3. Visotskii A. V., Yaskina V. A., Psavko P. B.: Neftekhimiya *28*, 844 (1988).
4. Spojakina A. A., Kostova N. G. in: *Zeolites for the Nineties* (J. C. Jansen, H. Moscou and M. T. M. Post, Eds). Elsevier, Amsterdam 1989.
5. Kraushaar-Czarnetzki B., van Hooff J. H. C. in: *Stud. Surf. Sci. Catal.* (P. A. Jacobs and R. A. van Santen, Eds), Vol. 49, Part B, p. 1063. Elsevier, Amsterdam 1989.
6. Ripperger W., Saum W.: J. Less-Common Met. *54*, 353 (1977).
7. Massoth F. E.: Adv. Catal. *27*, 265 (1978).
8. Moffat J. B.: Catal. Rev.-Sci. Eng. *18*, 199 (1978).
9. Eur. 0161490 (1985).
10. Cheung T. T. P., Willcox K. W., McDaniel M. P., Johnson M. M., Bronnimann C., Frye J. J. Catal. *102*, 10 (1986).

11. Campello J. M., Garcia A., Luna D., Marinas J. M.: J. Catal. *114*, 106 (1988).
12. Jeziorowski H., Knözinger H.: J. Phys. Chem. *83*, 1166 (1979).
13. Kazanski L. P., Golubev A. M. in: *Khimiya Soedeninii Molybdena i Wolframa*. Nauka, Novosibirsk 1979.
14. Goncharova O. I., Davydov A. A., Yurieva T. M.: Kinet. Katal. *25*, 152 (1984).
15. Buckley R. I., Clark R. J. H.: Coord. Chem. Rev. *65*, 167 (1985).
16. Kazanski L. P., Olgin-Kinionis S., Ivanov-Emin B. N., Filatenko L.: Koord. Khim. *4*, 1673 (1978).
17. Misono M., Saito Y., Yoneda Y. in: *Proc. First Inter. Congr. Catal. 1*, 408 (1964).
18. Bremer H., Reschetilowski W. P., Vogtand F., Wendlandt K. P. in: *Stud. Surf. Sci. Catal.* (P. A. Jacobs, N. I. Jaeger, P. Jírů, V. B. Kazanski and G. Schulz-Ekloff, Eds), Vol. 18, p. 321. Elsevier, Amsterdam 1984.
19. Jacobs P. A. in: *Stud. Surf. Sci. Catal.* (B. Gates, L. Guczi and H. Knözinger, Eds), p. 357. Elsevier, Amsterdam 1986.
20. Thomas R., van Oers E. M., de Beer V. H. J., Medema J., Moulijn J. A.: J. Catal. *76*, 241 (1982).
21. Razi Seyedmanir S., Howe R. F.: J. Catal. *110*, 216 (1988).
22. Bray R. C., Swann J. C.: Struct. Bonding *11*, 107 (1972).
23. Surin S., Aliev P., Radchenko E., Shostakovski M., Kaliko M., Chuliev Ch.: Dokl. Akad. Nauk SSSR *242*, 649 (1978).
24. Zielinski J.: J. Catal. *76*, 157 (1982).
25. Damyanova S., Spojakina A. A., Shopov D. M.: Appl. Catal. *48*, 177 (1989).
26. Slinkin A.: Usp. Khim. *37*, 1521 (1969).
27. Sivasanker S., Ramaswamy A. V., Vishnoi S., Ratnasamy P.: J. Appl. Chem. Biotechnol. *28*, 387 (1978).