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EXPERIMENTAL EVIDENCE OF DIRECT INFLUENCE OF THE COMPOSITION AND PREPARED CONDITIONS ON THE ACTIVITY AND SELECTIVITY OF HYDROTREATING CATALYSTS**Kh.A.Nasullaev, Sh.T.Gulomov, U.Kh.Sayidov, Z.A.Teshabaev, M.P.Yunusov**

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Synthesis questions of oxides Ni-Mo, Co - Ni-Mo and Co-Mo catalysts for processes of hydrodesulfurization and hydrogenation of aromatic hydrocarbons in the composition of kerosene, deasphaltisate and natural gas are considered.

Keywords: *Catalysts, activity, hydro-process, aluminum oxide, adsorbent, oil, gas, model systems.*

Introduction

Processing raw hydrocarbons into different types of commercial-grade fuel and oil involves environmental, economic and quality issues. Insufficient refining of fuel from sulfur and aromatic hydrocarbon causes environmental pollution. Sour sulfur contained in natural gas causes active corrosion of pipelines and equipment to result in enormous economic losses. Compositions based on compounds of Mo, Co and Ni, applied on γ - Al_2O_3 are typical for a great number of catalysts in hydro-processing oil products to comply with up-to-date requirements of residual content of sulfur and aromatic compounds [1]. Rather promising is the single soaking with joint solutions and complexing agents, as well as the coating with nickel or cobalt in the composition of molybdenum heteropoly compounds. Noteworthy is the combination of nickel and cobalt in the composition of Co-Mo/ γ - Al_2O_3 hydro-treating catalysts [2; 3]. Nickel as (co) promoter helps

with "containment" of cobalt cations in the CoMoS phase, and the synergistic improving catalysts' activity is typical for the reactions of hydrogenation and hydrodesulphurization.

The paper focuses on various aspects of the application of non-traditional component carriers in the synthesis of elements of multilayer catalyst systems comprised of catalysts of hydro-desulphurization and hydro-dearomatization for processing fractions of highly resinous oil with the sulfur in high content, as well as for the removal of mercaptan from natural gas given the availability of CO_2 and H_2O . The paper examines the influence of additives to developed aluminum oxide adsorbent, waste of Al_2O_3 - TiO_2 carrier and kaolin clay in the process of synthesis, both physical and chemical, as well as catalyst properties of Co-Mo, Ni-Mo, Co-Mo-Fe, Ni-Fe-Mo and Co-Ni-Mo catalysts when hydro-processing liquid and gaseous raw hydrocarbons.

Experiment

Carriers and catalysts were synthesized in line with our own technology [3]. A sample (Carrier №-1) was made up of a mixture of 55% of industrial aluminum hydrate (pseudo-boehmite prepared on the basis of gibbsite by alkaline deposition; Ryazan, Russia), 10 % of kaolin ("Angren Kaolin" Ltd.) and 35 % of Al_2O_3 (developed adsorbent of the Shurtan

Gas and Chemical Complex) followed by peptization with boric acid and hydrogen nitrate as well as shaping as Raschig rings or trefoil. Carrier №-2 was prepared in the same manner as a mixture of 45% of pseudo-boehmite (Russia), 10% of kaolin, 10% waste of Al_2O_3 - TiO_2 Carrier ("Himex", Uzbekistan) and 35 % of developed adsorbent. Carrier №-3

was prepared in the same way but on the basis of a mixture of 55% of pseudo-boehmite Sasol SB alcoholate-derivative (Sasol SB Pural GmbH, Germany), 10% of kaolin and 35% of developed adsorbent.

Note that shaped carriers were calcinated at 823K, and after cooling soaked in a joint stabilized phosphoric acid solution of ("P") series or citric acid (C₁ series). Various catalysts of C₂ series were prepared on the basis of citric acid and soaked by means of consistently wet method with varied values of pH. The molybdenum was applied first out of aqueous solution of ammonium

heptamolybdate (Mo/№-1). Then the base of Mo/№-1 was soaked in a joint solution of nickel nitrate (cobalt, iron) - citric acid with an appropriate pH. An actual content of molybdenum, nickel, cobalt and iron in various catalysts is shown in the Table attached.

The diffraction patterns were obtained on the diffractometer DRON-3 using filtered CuK α , voltage - 30 kV, current -20mA. Electron spectrums were obtained using the spectrophotometer Hitachi-330 Raman- AND X.

Results and discussion

Stable joint solutions of ammonium heptamolybdate with one or two transition metal nitrates were obtained at pH=1.3-2.5 (stabilization H₃PO₄) and pH=0.5 (stabilization C₃H₈C₇H₂O). Polymeric ions of molybdenum in such conditions while in contact with ions of Co²⁺ or Ni²⁺, may form heteropolyanions [4]. As a result, hydrated molybdates of MeMoO₄ type and heteropolyanions [NiH₆Mo₆O₂₄]⁴⁻, [CoH₆Mo₆O₂₄]⁴⁻, together with appropriate cations of Co²⁺, Ni²⁺, NH⁴⁺ and anions of NO₃⁻ and PO₄⁻³ coexisted in joint solutions. X-ray studies revealed stabilized H₃PO₄, a number of amorphous and crystal phases in the composition of concentrated or dried at 393K joint solutions. Diffraction patterns of dried catalysts of "P" series, in addition to the broad lines from γ -Al₂O₃ and narrower lines of quartz have shown the halo effect in the area of d= 8.0-2.6A. Note that a diffraction pattern of the catalyst №7/H-2-P has shown lines of anatase and rutile.

Also, appearance of a wide halo was due to the overlapping of many weak lines which correspond to nickel and cobalt molybdate previously identified in the model systems as follows:

NiMoO₄H₂O -d=0.820 (23); 0.431(7); 0.401(3); 0.325 (100); 0.300(90); 0.280(5); 0.20 (12); 0.190(10) A; x- NiO MoO₃yH₂O - d=0.672(20); 0.379(18); 0.335(23); 0.326 (17) A; NiMoO₄ - d= 0.615 (5); 0.37(3); 0.34 (20); 0.307(50); 0.272(30); 0.206(10); 0.191(4) A

CoMoO₄H₂O -d = 0.633 (15); 0.383(33); 0.350 (23); 0.338 (100); 0.338(43); 0.314 (26) A; CoMoO₄ -d =0.623(13); 0.354(22); 0.313 (26) A. Note that percentage point terms are given inside brackets. Diffraction patterns of NiMo, NiCoMo and FeNiMo catalysts within "P" series against halo effects have shown lines from NiMoO₄H₂O and x NiO MoO₃ yH₂O. Lines of weaker intensity (d =11.0(3); 5.11(5); 3.03(2) A) from (NH₄)₄[Ni(OH)₆Mo₆O₁₈]·5H₂O have been revealed only through the use of XFA NiMo catalysts. XFA analysis of catalysts №2/H-1-P and №3/H-1-P (dried under 393K) also revealed several strong peaks against the halo effect. Such diffraction peaks are typical for crystal phases CoMoO₄ H₂O и (NH₄)₄[Co(OH)₆Mo₆O₁₈] 5H₂O (d =10,87(4); 11.02 (3); 5.72(7); 5.12(9); 3.73(2) A). As opposed to the «P» series, in case of dried catalysts of «C₁» and «C₂» series, the source lines were detected in the diffraction patterns only. However, Raman spectrums of all dried catalysts proved to be the same, all of them containing bands 955-952 (intense), 900 (shoulder) 570-565, 355 and 220 sm⁻¹. These bands were in keeping with poly-molybdates.

Diffraction patterns of all catalysts (series «P», «C₁» and «C₂») calcinated under 823K have shown the line of quartz strongly extended by moderate intensity as per line Al₂O₃ and corresponded to the metal molybdate against the halo effect in the area d=6.4-2.3 A. No oxide phases have been

detected (FeMoO_4 , MoO_3 or CoAl_2O_4 , NiAl_2O_4 , FeAl_2O_4). The XFA analysis has revealed the presence of crystallite mixture γ - and $\langle x\text{-Fe}_2\text{O}_3$ ($d = 4.81; 2.94; 2.69; 2.48; 2.31; 2.22$ Å) in the content of catalyst agents №1/H-1-P and №2/H-1-P. The great intensity of halo in case of catalyst within the "P" series has shown their lower dispersion.

Results of the XFA analysis in regard to a greater catalyst dispersity of "C₁" and "C₂" series coincided with the data of the Raman spectroscopy. A degree of polymerization of molybdate structures decreased in a row as follows: №9/H-1-C₁ > №10/H-1-C₁ > №13/H-1-C₂ ≥ №14/H-1-C₂ > №6/H-1-P > №4/H-1-P ≥ №7/H-2-P > №12/H-1-C₂.

As a consequence, an edge of a broad sheet of charge transfer in the oxygenated complexes Mo^{6+} within the electron spectrums appr. 270-285 nm showed a joint presence of MoO_4^{2+} and polymerized molybdate-ions within the structure of catalysts № 3-5, 7 of series «P». An exact location of such bands displays a local symmetry of Mo^{6+} environment which depends on factors of coordination and physical form. Isolated (particles) of molybdates within the tetrahedral site (Mo_{Td}) found characteristic band of absorption about 250 nm, whereas a signal from poly-molybdates within the octahedral state (Mo_{Oh}) is observed in the area between 260 and 330 nm depending on the degree of agglomeration of these particles. In addition, both types of particles Mo^{6+} show two strong bands of absorption of approx. 200-220 nm. The deconvolution Spectrum Ni-Mo of the catalyst clearly indicates the presence of molybdenum particles within the octahedral and tetrahedral states [4]. The ratio of intensity of Mo_{Oh} (275-330 nm) and Mo_{Td} (200-275 nm) can provide qualitative information about poly-molybdate MoO_x centers on the surface of various catalysts. From this it follows that when transiting to higher percent catalysts the band's edge shifted to 300 nm (№8/H-3-P, №11/H-1-C₂, №12/H-1-C₂) and further to 330 nm (№9/H-1-C₁, №13/H-1-C₂) due to the increase in polymerization level of molybdate-anions.

The UV-visible electron spectrums of cobalt solutions were received following the

dissolution of ammonium heptamolybdate and cobaltous nitrate in sour aqua solutions to demonstrate the same cobalt varieties in the aqueous solution with bands having been formed under 460-465, 513-520 and 615-619 nm.

These bands are typical for Co(II) d-d of electron transitions in the hexaqua complexes $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$. Meanwhile, bands which were localized within 645-658, 730-735 and 1065 nm and classified as structures with nickel ions [3]. A comparison of relationship (respective) between d-d transitions of nickel and cobalt in treating solutions and Ni (Co) Mo samples of "P" series showed their stability. It was indicative of the persistence of hydrated ion $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ while drying, and the interaction of metals with the carrying base caused by electrostatic adsorption. On the contrary, d-d transitions of Ni^{2+} in dried samples of «C₂» series have shown a red shift Ni^{2+} : 653 nm → 660 nm, 395 nm → 400 nm; Co^{2+} : 653 nm → 660 nm, 395 nm → 400 nm) caused by the increase in bond strength of ligands. According to a spectrochemical row, this bathochromic shift was related to the replacement of water ligands in hydrated ion of nickel with weaker surface ligands that form complexes with nickel ions in the inner coordination sphere, AlO-Ni-Citrate. A predominant complex formation of about pH 3-8 manifested itself under maximum mol fraction at pH 3.3 and pH 5.8, respectively $[\text{Ni}(\text{HCit})(\text{Cit})(\text{H}_2\text{O})_4]^{3-}$ and $[\text{Ni}(\text{Cit})_2(\text{H}_2\text{O}(\text{H}_2\text{O})_4)]^{4-}$ respectively [5]. A simple pale green nickel nitrate solution in the water (pH 3.7) consisted only of hexahydrate nickel $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$. At pH 0.3 and mol fraction of $[\text{Ni}^{2+}] = 0.63\text{M}$ as well as mol ratio $\text{Cit}^{3-}/\text{Ni}^{2+} = 2$, the solution color remained pale green. On the contrary, at pH 3.4, the mol fraction $[\text{Ni}^{2+}] = 0.63\text{M}$ and mol ratio $\text{Cit}^{3-}/\text{Ni}^{2+} = 2$, the solution color turned to be green-blue. In accordance with the article [5] and due to the increase in pH, the replacement of citrate ligand in the complex $[\text{Ni}(\text{Cit})_2(\text{H}_2\text{O}(\text{H}_2\text{O})_4)]^{4-}$ ammonium and the rise in the mol fraction of uncoordinated citric acid has occurred.

Blue shift (701 → 676 nm) of the band of d-d nickel that followed in the spectrum of

samples №9/H-1-C₁, and №14/H-1-C₂ in comparison with spectrums of other catalysts of "C₂" series showed a greater strength of coordination bonds with the ligand.

These observations showed that applied nickel in the complex NiMo-Citr (pH≥3.4) is subject to be retained wholly or partly together with the citrate of complexes $[\text{Ni}(\text{H Citr})(\text{Citr})(\text{H}_2\text{O})_4]^{3-}$ or $[\text{Ni}(\text{Citr})_2(\text{H}_2\text{O})_4]^{4-}$. Whereas in case of №9/H-1-C₁, and №14/H-1-C₂ catalysts, no surface ligands can be water ones and weaker than citrates. In order to study the coordination of citric acid upon drying (393K), infrared spectrums of «C₂» series catalysts have been obtained. The type of coordination of citric acid showed that it spectroscopically coincided with the results of the UV-visible spectrography. Infrared spectrum of the Ni-Citr solution at pH=0.5 has shown bands identical to the ones in samples (citric acid and nickel nitrate) which indicate that carboxylic acid in the residue of citric acid is neither dissociated, nor connected. However, the rise of pH in the solution resulted in the deprotonation of carboxylic groups while reducing the intensity of absorption bands of carboxylic acid. The intensity of marked unsymmetrical (γ_{as} - absorption bands at 1602 and 1567 cm^{-1}) and quite strong symmetrical oscillations of carboxylates (vs-absorption band at 1413 cm^{-1}) rose simultaneously which led to the coordination of deprotonated carboxylic groups with metal. An intense broad band 1500-1700 cm^{-1} appeared in the spectrum which was related to the adsorbed water on the basis of aluminum oxide as a part of the structure, the latter can be overlapped with signals from the carboxylate, for the band 1335 cm^{-1} came to be associated with the bands of δ (C-H) and 1401 cm^{-1} γ_{s} due to the oscillations of carboxylate. The preservation of absorption bands went to show the coordination of carboxyl groups. In accordance with the results of UV-VIS DR, the adsorbed nickel in hard №14/H-1-C₂ fails to form citrates as γ_{s} absorption from carboxylates and does not manifest itself in the

infrared spectrum as distinct from other NiMo-Citr (pH=3.4→8.7) samples.

The UV-VIS DR -spectra of all catalysts of similar composition ("P", "C₁" and "C₂" series calcinated at 823 K proved to be similar. A degree of interaction of the carrier with cobalt ions on calcination was determined through the bands triplet intensity of 555; 602 and 667 nm from $\text{Co}_{\text{Td}}^{2+}$ ions. Note that appearance of the diffuse reflection of the characteristic doublet of 595 and 633 nm from $\text{Ni}_{\text{Td}}^{2+}$ ions after calcination at 823K in the electron spectra clearly indicates the formation of a nickel-aluminum spinel. The wide absorption band at 510 nm with a shoulder around 469 nm corresponds to $\text{Co}_{\text{Td}}^{2+}$ ions in the cobalt molybdate structure. The cobalt-molybdenum and nickel-molybdenum associates were identified by the presence of absorption bands in the zone of 312-345 nm [3]. Note that bands of 417-435 nm and approx. 735-758 nm [3] are in keeping with $\text{Ni}_{\text{Td}}^{2+}$ nickel ions in the structure closer to NiMoO_4 . The number of non-active spinel structures changed in a row as follows: "P"series > "C₂"series > "C₂" series ≥

Before testing their activity, the "F" series catalysts were calcinated at 823 K and the "C₁" and "C₂" series dried catalysts sulphided ex situ in a tube reactor at 400°C for 4 hours in a stream of 10 vol. % H₂S in H₂ of atmospheric pressure.

Hydrogenating and desulphuring function of samples were evaluated through comparing changes in the content of total sulphur (Σ Sulphur as shown in the Table), polycyclic aromatic hydrocarbons (PAC), and mercaptan (RSH) in hydrogenation product with a flowing unit obtained due to the feed stock process.

Activity in hydrodesulphurization and hydrogenation of polyaromatic compounds in the composition of deasphaltizate and kerosene fraction has been examined on the flowing unit under a pressure of 4.0-4.5 MPa and temperature of 573-593 K while the natural gas under a pressure of 2.5-3.0 MPa and at a temperature of 573 K.

Table. Influence of composition and preparation method on activity and selectivity of catalysts

	pH of solutions			The actual content; in oxides equivalent (after calcination at 823K)				PAH and sulfur compounds concentration in the hydrogenation products of various hydrocarbons, %						
	H ₃ PO ₄ or S ₇ H ₈ O ₇ Mo + Co (Ni, Fe)	H ₂ O, Mo	C ₇ H ₈ O ₇ Co, Ni	Mo	Ni	Co	Fe	Kerosene			Deasphaltisate		Natural gas	
								PAC	ΣSulfur	PAC	ΣSulfur	Original	Dried	
Concentration of sulfur, PAH and mercaptans in the feed stock:														
№1/H-1-P	1.6			12.3	3.1		0.9	16.9	0.25	32.4	1.32	0.005	0.004	
№2/H-1-P	1.7			12.1	0	3.2	1.0	14.7	0.068	30.8	0.370	0.00023	0.00021	
№3/H-1-P	2.5			11.8		3.8		14.7	0.066	31.0	0.361	0.00020	0.00019	
№4/H-1-P	2.4			12.1	3.9			14.8	0.070	30.5	0.372	0.00021	0.00020	
№5/H-1-P	2.4			12.2	0.9	3.2		14.4	0.072	27.7	0.381	0.00025	0.00024	
№6/H-1-P	1.3			16.4	4.6			14.5	0.070	27.9	0.378	0.00024	0.00023	
№7/H-2-P	2.4			12.1	3.8			8.0	0.056	25.1	0.362	0.00021	0.00020	
№8/H-3-P	1.4			16.5	4.7			14.4	0.064	26.8	0.373	0.00023	0.00020	
№9/H-1-C ₁	0.5			16.6	4.5			7.8	0.054	25.5	0.340	0.00020	0.00019	
№10/H-1-C ₂	0.6			16.1	0.9	3.2		6.8	0.042	23.8	0.263	0.00018	0.00017	
№11/H-1-C ₂		5.5	3.5	16.1	4.3			7.0	0.035	24.2	0.252	0.00017	0.00017	
№12/H-1-C ₂		5.5	3.6	16.2	1.1	3.3		5.8	0.032	23.3	0.234	0.00014	0.00013	
№13/H-1-C ₂		5.5	3.4	16.0	0	4.5		5.9	0.030	23.6	0.203	0.00012	0.00011	
№14/H-1-C ₂		0.5	3.5	16.4	4.1			5.9	0.025	23.5	0.200	0.00012	0.00012	
								6.2	0.034	23.7	0.272	0.00015	0.00014	

Raw natural gas contained (vol.%) mercaptan - 0.005 (in S equivalent), hydrogen sulphide - 0.06 vol. carbon dioxide - 3.99, nitrogen 0.043 and water vapor. In order to evaluate the influence of water and CO₂, activity of catalysts in natural gas hydrodemercaptanization before and after passing through the adsorbent dryer has been tested in parallel. Results obtained are marked in italics in the Table.

Within each series, the desulphurization of liquid and gaseous hydrocarbons proved to be higher on Co-Mo catalysts, and upon hydrogenation of PAH in the composition of fuels and oils on Ni-Mo. Tri-metallic catalysts occupied an intermediate position. It revealed that the catalyst activity increases with the addition of citric acid due to the activity of catalysts of the same composition together with phosphoric acid added.

Conclusion

Given the results above, one can conclude as follows:

1. Carriers obtained through the use of kaolin clay, developed alumina adsorbent and waste of Al₂O₃ -TiO₂ carrier together with pseudoboehmite of varied origin may be used for preparation of active catalysts.

2. Activity and stability of any catalysts in question are commensurable to the best commercial catalysts for oil products with low sulfur content.

3. Maximum desulfurizing effect was achieved on a catalyst №13/H-1-C₂, where the complex of [Ni(Citr)₂(H₂O)₄]⁴⁺ is detected spectrally.

References

1. Tomina N.N., Nikulshin P.A., Pimerzin A.I.A. Influence of compounds of molybdenum on the activity of Mo/ γ -Al₂O₃ and NiMo/ γ -Al₂O₃ hydrofining of catalysts. *Kinetika i kataliz -Kinetics and catalysis*. 2008, vol.49, no №5, pp. 684-693. (In Russian).
2. Mozhaev A.V., Nikulshin P.A., Pimerzin A.A., Konovalov V.V. Activity of CO (Ni) MoS/Al₂O₃ catalysts obtained on base salts Co (Ni) H₆[Co₂Mo₁₀O₃₈H₄] in hydrogenolysis of thiophen and hydrofining of diesel fraction. // *Neftehimiya – Petroleum Chemistry*. 2012, vol.52, no.1, pp. 45-53. In Russian).
3. Yunusov M.P., Saidahmedov Sh.M., Jalalova Sh.B., Nasullaev Kh.A. Synthesis and study of Ni-Mo-Co catalysts for hydro-processing of oil fractions. *Catal. Sustain. Energy*. 2015, no.2, pp. 43-56.
4. Mohan S.Rana, S.K. Maity, J. Ancheyta, G. Murali Dhar. MoCo(Ni)/ZrO₂-SiO₂ hydrotreating catalysts: physico-chemical characterization and activities studies. *Applied catalysis A: General*. 2004, vol.268, issues 1-2, pp.89-97.
5. Suarez-Toriello V.A., Santolalla-Vargas C.E., J.A. de los Reyes, Vazquez-Zavala A., Vrinat M, Geantet C. Influence of pH solution on impregnation of citric acid and activity of Ni/W/Al₂O₃ catalysts. *Journal of Molecular Catalysis A: Chemical*. 2015, vol. 404, pp.36-46.

ЭКСПЕРИМЕНТАЛЬНОЕ ДОКАЗАТЕЛЬСТВО ВЛИЯНИЯ СОСТАВА И УСЛОВИЙ ПРИГОТОВЛЕНИЯ НА АКТИВНОСТЬ И СЕЛЕКТИВНОСТЬ КАТАЛИЗАТОРОВ ГИДРОПРОЦЕССОВ

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Рассматриваются вопросы синтеза оксидов Ni-Mo, Co-Ni-Mo и Co-Mo-катализаторов для процессов гидродесульфуризации и гидрирования ароматических углеводородов в составе керосина, деасфальтизата и природного газа.

Ключевые слова: *катализатор, активность, гидрообработка, оксид алюминия, адсорбент, нефть, газ, модельные системы.*

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