SYNTHESIS OF HYDROGENATION CATALYSTS FOR THE HYDROPROCESSING OF PETROLEUM FRACTIONS

Kh.A. Nasullaev[1], Sh.Sh. Mengliev[2], Sh.T. Gulomov[3], R.S. Khabipov[4], S.N. Suyunbaev[5], R.M. Alladinov[6]
Tashkent Institute of Chemical Technology, Tashkent, Republic of Uzbekistan
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Abstract. *Various aspects of the synthesis of catalysts for the hydroprocessing of petroleum fractions based on spent alumina adsorbent and kaolin clay are examined, and their influence on catalytic activity is discussed. The study considers the preparation of catalyst supports, their physicochemical properties, and the effect of composition and heat-treatment conditions on the performance of the resulting catalysts. The feasibility of partially replacing imported aluminum hydroxide with spent alumina adsorbent and kaolin from local raw materials is demonstrated. The obtained catalysts showed satisfactory activity and stability in the hydroprocessing of petroleum fractions and may be recommended for industrial application.*

Keywords: *catalysts, catalytic activity, hydroprocessing, aluminum oxide, dearomatization, carbonization of supports, spent adsorbent.*

Introduction

The increasing demand for ultra-clean fuels, combined with the growing share of heavy crude oils with high aromatic hydrocarbon content in petroleum feedstocks, both in Uzbekistan and worldwide, poses serious economic and technological challenges for the modern oil-refining industry. In particular, the demand for middle distillates is steadily increasing, while the quality of available feedstocks is declining. Low-quality petroleum feedstocks, as well as alternative renewable raw materials, require more intensive processing in order to meet the demand for additional ultra-clean motor fuels. Therefore, hydrocatalytic processes are becoming increasingly important in oil refining.

This paper examines various aspects of the use of non-traditional support components in the synthesis of hydrodearomatization catalysts for the processing of petroleum fractions. Aluminum hydroxide, which constitutes the major portion of catalyst mass, is not produced in Uzbekistan. One potential raw-material source of aluminum oxide is the large-scale waste product of the Shurtan Gas Chemical Complex, namely spent alumina adsorbent (OAA). Therefore, a series of studies was carried out to demonstrate the feasibility of replacing up to 60% of imported aluminum hydroxide with OAA and kaolin clay from the Angren deposit. In this system, kaolin serves as a modifier of pore structure and mechanical strength.

Materials and Methods

Catalyst supports were prepared by extrusion after peptization of mixtures of the starting powders (Table 1) with an aqueous HNO3 solution, followed by heat treatment in air or nitrogen.

The samples were characterized using the following instruments: a Carlo Erba mercury porosimeter, a JXA-8800R Superprobe electron microanalyzer (JEOL), a Dron-3 diffractometer, a Q-1500D derivatograph, a Tesla electron microscope, a Specord-75 IR spectrometer, an SP-9 PYE UNICAM atomic absorption spectrometer, and a Chrom-5 chromatograph.

Electronic spectra of the catalysts and adsorbed acid-base indicators, used for surface-property evaluation according to the method described in reference [5], were obtained using a Hitachi-330 spectrophotometer. The amount of chemisorbed O2 was determined by pulsed gas chromatography after preliminary reduction of the catalysts in H2 at 823 K.

The hydrogenation catalysts were prepared by double impregnation with analogous solutions, with intermediate heat treatment. The hydrogenation performance of the samples was evaluated on the basis of changes in the polyaromatic compound content of the feedstock. The catalysts were tested in a pilot flow unit with a catalyst loading of 150 mL. Hydroprocessing of the deasphalted residual oil fraction and crude kerosene was carried out at a hydrogen pressure of 4 MPa, whereas hydroprocessing of the diesel distillate was conducted at 5 MPa. The reactor temperature was maintained in the range of 573-593 K.

Table 1. Effect of Composition and Heat-Treatment Conditions at 823-873 K on the Specific Surface Area, Carbon Content, and Surface Properties of Supports

Support Code	Composition of Support Components (Calcination Medium)	Ssp., m^2/g	C, %	Surface pKa centers (concentration, mg-eq/g)
1	60% OAA + 40% GOA (air)	160	0.05	-5.6 (0.05); -3.3 (0.15); +1.5 (0.19); +3.8 (0.31); +9.3 (0.01)
2	GOA + 10% kaolin (air)	265	0	-8.2 (0.008); -5.6 (0.08); -3.3 (0.23); +1.5 (0.34)
3	60% OAA + 30% GOA + 10% kaolin (air)	109	0.03	+1.5 (0.01); +3.8 (0.18); +6.1 (0.37); +9.3 (0.014)
4	OAA + 30% kaolin (air)	91	0	+1.5 (0.13); +3.8 (0.23); +6.1 (0.25); +9.3 (0.01)
5	GOA (air)	275	0	-6.3 (0.01); -5.6 (0.07); -3.3 (0.24); +1.5 (0.48); +3.8 (0.50)

Results and Discussion

The GOA used for sample synthesis consisted of a mixture of boehmite and pseudoboehmite and exhibited weak acidic surface sites with pKa values ranging from +3.8 to +6.1. OAA contained 30-50% γ-Al2O3, 5-15% α-Al2O3, and 40-60% boehmite with crystal sizes ranging from 10 to 100 nm. The impurity content varied within the following ranges (%): Na2O, 1.7-2.0; Cl, 0.3-0.8; CaO, 0-0.5; TiO2, 0.3-0.5; and V2O5, 0.4-0.6. In addition to weak acidic sites, the OAA surface also contained basic sites with pKa values up to +10.3. Kaolin contained 45-70% kaolinite and 20-30% quartz. The main impurities were P2O5, SO3, K2O, CaO, FeO, and BaO. The acidity of kaolin was within the pKa range from +1.5 to +3.8.

The use of OAA has specific features related to its role in polyethylene production. Fresh adsorbent is used to purify polymer solutions from polymerization catalyst residues such as VOClx and TiClx, present in the form of chelate complexes with deactivators and associated compounds, by chemisorption at 533-583 K under high pressure. The total carbon content of the chemisorbed substances ranged from 1.5 to 4.5% of the OAA mass.

It was found that heating 100 g of OAA granules to 513 K in a reactor resulted in the desorption of 4.3 g/100 g of water and 0.6 g/100 g of unidentified organic substances, with absorption bands corresponding to -CH2 and -CH3 groups (2930, 2873-2843 $cm^{-}1$), as well as C=O, C-O-H, C-O, and O-H groups (1720, 1410, 1282, and 933 $cm^{-}1$) in the IR spectra of the gas

phase. The evolution of CO and CO2 began above 520 K, reached a maximum concentration at 833-923 K, and was completed within 18 hours at 973 K. In total, 5.9 g of CO, 4.8 g of CO2, 1.6 g of HCl, and 0.2 g of H2O were released from 100 g of OAA in the temperature range of 833-973 K.

The weight loss (ΔP) due to H2O removal from fresh adsorbent in the endothermic region at 393-453 K was less than 2%, whereas complete conversion of boehmite to Al2O3 resulted in a weight loss of 7.2% (Fig. 1, curve 1).

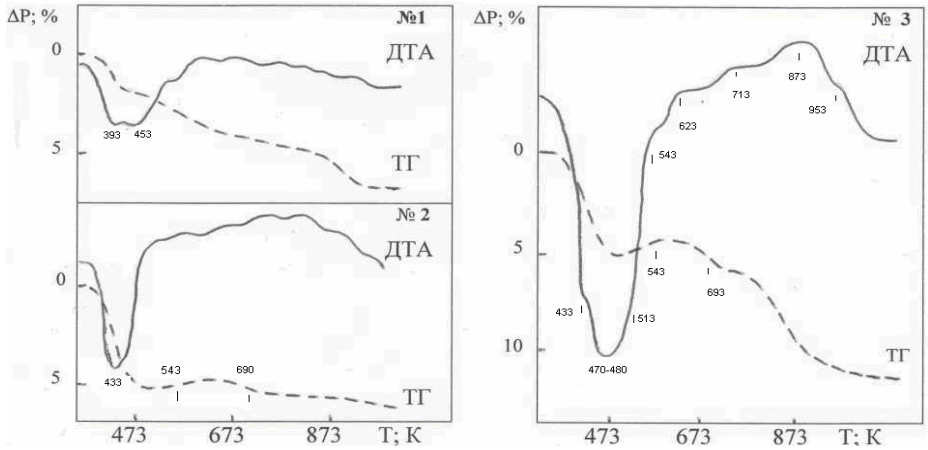


Figure 1. Thermograms of fresh adsorbent (1); OAA sample with 1.5% C (2); and OAA sample with the maximum content of chemisorbed substances, 4.5% C (3).

Under the conditions of thermogram recording using 100 mg of OAA powder, an endothermic effect accompanied by a weight loss (ΔP) of 5% was observed at 433-513 K, and the depth of this effect was proportional to the carbon content. The increase in weight by 1-2% in the exothermic region at 543-693 K can be explained by oxygen addition to chemisorbed substances, which exceeded the simultaneous desorption of carbon-containing gases and water. At a heating rate of 10 K/min, weight changes (ΔP = 7%) and thermal effects accompanied by the release of heat at 543, 623, 713, 873, and 953 K, as well as the evolution of CO, CO2, traces of H2O, and HCl, were observed for approximately one hour and ceased at 1093 K.

The calculated weight loss during complete oxidation of compounds of the CH3(-CH2-)n-COOH type and chelate complexes of V and Ti, responsible for the presence of 0.6 mg V2O5, 0.5 mg TiO2, and 0.8 mg Cl in 100 mg of OAA, was 7.2% (Fig. 1, curve 3). In this process, approximately 14 mg of O2 should be consumed, and 16.5 mg of CO2, 4.4 mg of H2O, and 0.3 mg of HCl should be released into the gas phase. Differential thermal analysis and thermogravimetry data, together with measurements of H2O, CO, and CO2 formed during heating in air, indicate a stepwise removal of chemisorbed substances from OAA, preceded by oxygen addition and characterized by strong chemical bonding to the adsorbent surface.

The mechanical strength and wide-pore structure of the dearomatization catalyst supports, achieved through the addition of OAA and kaolin, were retained after the application of active metals (Tables 1 and 2).

Table 2. Physicochemical Characteristics of Catalysts Prepared on Various Supports

Catalyst Code	TiO2, %	V2O5, %	WO3, %	NiO, %	CoO, %	MoO3, %	Support Code	Strength, kg/mm	Pore radius, nm (pore	Ssp., m²/g

									volume, cm^3/g)	
Kt-6	0	0	0	1.73	4.2	17.9	3	2.85	3-5 (0.45); 5-15 (0.060); > 90 (0.02)	295.5
Kt-8	0.01	0.03	0	1.70	4.19	17.6	4	3.15	<3 (0.12); 5-7 (0.10); 45-160 (0.32)	109.5
Kt-9	0.02	0.03	0	6.03	0	18.1	4	3.43	<3 (0.10); 5-7 (0.09); 45-160 (0.36)	105.8
Kt-10	0.02	0.02	1.4	5.92	0	17.8	4	3.27	3-4 (0.19); 10-40 (0.35); >120 (0.01)	89.5

With increasing concentrations of active components, the formation of very fine pores intensifies during the thermal decomposition of hydrated nickel (or cobalt) molybdates and tungstates aggregated within the pores of the catalyst precursor during repeated impregnation with combined solutions. Based on the results of sequential extraction with water and aqueous ammonia, it was shown that the proportion of surface Ni(Co) and Mo structures strongly bound to the support and responsible for hydrodesulfurization reactions decreased to 30-60%, depending on the support. The amount of weakly bound Ni, Co, Mo, and W structures possessing the highest hydrogenating capacity increased with the use of OAA and followed the following order: Kt-6 (4.7/24.7) ≤ Kt-8 (11.5/23.5) < Kt-9 (12.6/24.2) ≤ Kt-10 (12.7/25.2).

An increase in the relative intensity of absorption bands corresponding to nickel and/or cobalt molybdates with octahedral cation coordination was observed. NiTd2+ and CoTd2+ ions in spinel structures, as well as NiWO4 in the composition of Kt-10, were not detected spectrally (Fig. 2, curves 8 and 9). Laboratory rig testing of the comparative stability of catalysts prepared on supports calcined in air and nitrogen during hydrotreating of the residual fraction boiling above 773 K revealed no trend toward progressive activity loss after 500 hours of testing and three experimental regenerations of catalysts on a carbonized support.

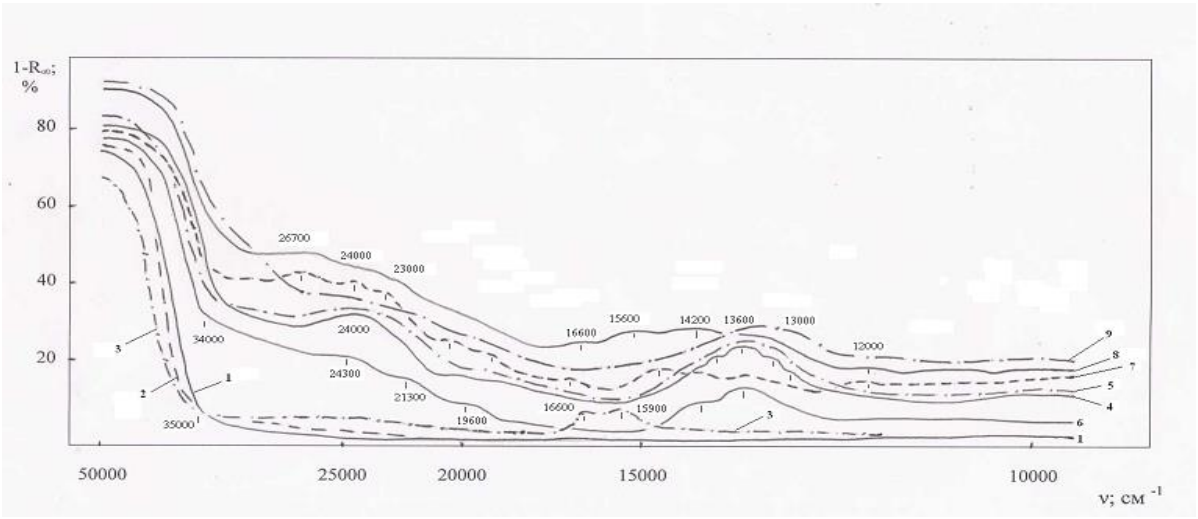


Figure 2. ***Electronic spectra of catalysts: 1 - Kt-1; 2 - Kt-3*; 3 - Kt-17; 4 - Kt-14; 5 - Kt-16*; 6 - Kt-13*; 7 - Kt-7; 8 - Kt-8; 9 - Kt-10.***

These scientific approaches made it possible to develop and implement a number of catalysts based on OAA and kaolin. Since 2012, a pilot run of a dearomatization catalyst has been carried out at the Fergana Oil Refinery on the G-24 unit as part of a multilayer catalytic system based on an industrial AKM catalyst. No increase in pressure drop was observed. The quality of the resulting base oils fully complied with enterprise standards. Full-scale loading of the catalyst into the reactors of the Fergana Oil Refinery is planned.

Conclusions

1. A combination of physicochemical methods showed that catalysts prepared using OAA and kaolin are comparable in activity and stability to catalysts based on aluminum hydroxide and can be recommended for use in industrial reactors.
2. Although the technology for producing supports containing OAA is somewhat more complex, it makes it possible to obtain catalysts with enhanced activity in the removal of sulfur compounds and impurity metals.
3. Pilot batches of the developed catalysts showed positive results under industrial conditions at the G-24 unit during the production of base oils.

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