

2. A. G. Akhmadullina et al., in: Improvement in Sulfur Purification of Hydrocarbon Raw Material and Gas Fractionation [in Russian], TsNIITneftekhim, Moscow (1980), pp. 158-162.
3. M. B. Mick, Hydrocarb. Proc., 55, No. 7, 137-142 (1976).

AROMATIZATION OF GASOLINE ON ZINC-MODIFIED ZEOLITE-CONTAINING CATALYSTS

T. M. Gairbekov, M. I. Takaeva,
A. K. Manovyan, and I. L. Aleksandrova

UDC 665.664.4.097:3.665.663

Modification of ultrahigh-silicon (UHS) zeolites of the ZSM type [1] and UHS zeolite-containing catalysts [2] with gallium and zinc significantly improves their catalytic properties in aromatization of hydrocarbons. However, the effect of the amount of modifying metal has been inadequately studied.

The activity and selectivity of granulated catalysts synthesized by addition of 30% decationized UHS zeolite (Si:Al = 16) to an amorphous aluminosilicate matrix were investigated in the present study. The concentration of zinc was varied within the limits of 0-10 wt.% in the catalyst. Low-octane (65 points, MM) gasoline from thermal cracking (TCG) containing 40% unsaturated hydrocarbons was used as the raw material for aromatization (cycloreforming). The experiment was conducted on a flow-type laboratory setup. The characteristics of the starting TCG and the experimental method are reported in [2].

As the data in Fig. 1 indicate, at moderate temperature (425°C), the maximum changes in the catalytic properties of the samples are observed on addition of the first 0.5 wt.% of zinc: the cracking activity decreases sharply (the yield of gas decreases by ~8%) and the yield of liquid catalyzate increases while coke formation does not change (~3.5%). The concentration of aromatic hydrocarbons in the liquid catalyzate decreases by 10% (Fig. 2), which causes a 3-4-point decrease in its octane number, determined by the calculation method in [3]. The paraffins:olefins ratio decreases sharply in the cracking gases (Fig. 3).

A further increase in the concentration of zinc to 10 wt.% virtually does not alter the properties of the catalysts with respect to the indicated indexes except for the yield of hydrogen, which increases by almost three times (see Fig. 1). The concentration of xylenes increases and the concentration of C₉₊ components decreases while the concentration of benzene and toluene remain almost constant in the aromatic compounds formed (Table 1) with an increase in the concentration of zinc in the catalyst. The concentration of unsaturated hydrocarbons in the catalyzate does not exceed 5-8 wt.% in all cases.

The changes in the catalytic properties of the samples established at moderate temperatures of aromatization correlate with the data from IR spectroscopic analysis, which indicate that addition of the first 0.5 wt.% of zinc to UHS zeolite sharply decreases the intensity of the lines at 3600 cm⁻¹. These lines characterize the strongly acid hydroxyl groups [4] active in low-temperature transformations of hydrocarbons. An increase in the intensity of the lines at 1455 cm⁻¹, assigned to groups with Lewis acidity [5], is simultaneously observed in the IR spectra of pyridine adsorbed on the surface of the zeolite-containing catalyst. When the concentration of zinc is increased to 10 wt. %, the acidity of the catalysts does not change significantly.

When the temperature is increased to 500°C, modification of the catalysts with zinc has almost no effect on the yield of cracking gases and liquid catalyzate (see Fig. 1), but the selectivity of the reactions of aromatization of TCG increases significantly (see Fig. 2). The maximum concentration of aromatic compounds in the catalyzate (~82%) and its octane number (~92) are attained when 5 wt.% zinc is added to the catalyst. The concentration of unsaturated hydrocarbons in the catalyzate does not exceed 3%.

M. D. Millionshchikov Institute of Petroleum. Scientific-Research Institute of Petroleum, Grozny. Translated from Khimiya i Tekhnologiya Topliv i Masel, No. 10, pp. 6-7, October, 1989.

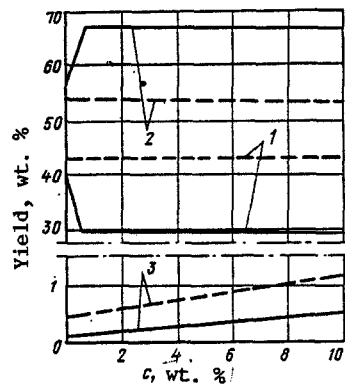


Fig. 1. Effect of the concentration c of zinc in the catalyst on the yield of products of cycloreforming at different temperatures (2 h^{-1}): —) 425°C ; ---) 500°C ; 1) gas; 2) liquid catalysate; 3) hydrogen.

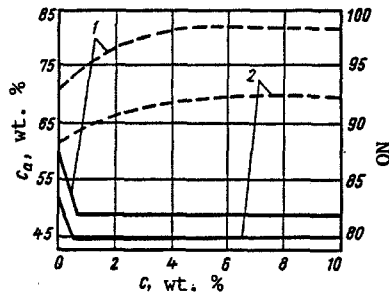


Fig. 2. Effect of the concentration c of zinc in the catalyst on the concentration c_a of aromatic hydrocarbons (1) in the catalyst at different temperatures and its octane number ON (2): —) 425°C ; ---) 500°C .

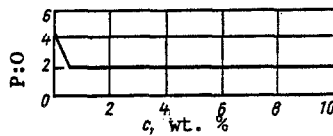


Fig. 3. Effect of the concentration c of zinc in the catalyst on the paraffins:olefins P:O ratio in gas obtained at the temperature of: —) 425°C ; ---) 500°C .

TABLE 1

Component	Composition of aromatic compounds ^{*k} (in %) for a concentration of zinc in the catalyst					
	0 %	0.5 %	2 %	5 %	7 %	10 %
Benzene	6,5	6,1	5,7	5,5	6,6	5,6
Toluene	25,3	24,9	25,1	23,3	22,9	25,5
Xylenes	43,5	45,0	45,5	49,1	47,0	51,3
C ₉₊	24,7	24,0	23,7	22,0	23,5	17,5

* 425°C , 2 h^{-1} .

The composition of the aromatic compounds formed is identical to the composition reported in Table 1. The paraffins:olefins ratio in the cracking gases is not a function of the amount of zinc in the catalyst (see Fig. 3); the yield of hydrogen increases continuously, attaining 1.2% in the initial raw material. The yield of coke remains constant: ~3.5%.

The results obtained are in agreement with the scheme of formation of aromatic hydrocarbons from low-molecular-weight olefin products of cracking proposed in [6] for UHS zeolites. The modification of the catalysts with zinc probably causes transformation of the products of cracking into aromatic components, as in addition of gallium to type ZSM zeolites [7] and the occurrence of reactions of dehydrogenation of hydrocarbons, indicated by the continuous increase in the yield of hydrogen.

LITERATURE CITED

1. H. Kitagawa, Y. Sendoda, and Y. Ono, *J. Catal.*, 101, No. 1, 12-18 (1986).
2. M. I. Takaeva, T. M. Gairbekov, A. K. Manovyan et al., *Neftepererab. Neftekhim.*, No. 1, 11-13 (1987).
3. L. F. Ovsyannikov, O. E. Pletkova, and V. B. Chizhov, *ibid.*, No. 8, 8-9 (1985).
4. I. Datka and E. Tuznik, *Proc. Int. Symp. Zeolite Catal. Siofok.*, May 13-16, 1985, Szeged (1985), pp. 173-179.
5. S. E. Spiridonov, S. N. Khadzhev, N. Ya. Yaralov, et al., *Kinet. Katal.*, 27, 201-204 (1986).
6. O. V. Bragin, B. K. Nefedov, T. V. Basina, et al., *Dokl. Akad. Nauk SSSR*, No. 1, 103-106 (1980).
7. G. Sirockman, Y. Sendoda, and Y. Ono, *Zeolites*, 6, No. 4, 299-303 (1986).

INFLUENCE OF PROCESS VARIABLES ON OXIDATION OF VACUUM RESID TO CARBOGENIC OXY-ACIDS

V. I. Antonishin, V. I. Gaivanovich,
and A. A. Sidoruk

UDC 665.652.86

It was shown previously [1, 2] that, when vacuum resid is subjected to exhaustive oxidation in benzene solution in an acidic medium (pH 1.5-2) at elevated pressure and temperature, a solid, powdery product is formed, containing large amounts of carboxyl, hydroxyl, and ester groups, i.e., carbogenic oxy-acids. The product is insoluble in water, alcohol, pyridine, and carbon disulfide; partially soluble in dioxane, N-methylpyrrolidone, dimethylformamide, and dimethyl sulfoxide; and insoluble in mineral and organic acids, with which the product does not interact at room temperature or upon heating.

Carbogenic oxy-acids have weakly acidic properties, interact readily with alkalis (undergo saponification), are quite high in thermal stability, and are reactive with respect to their functional groups [3]. They may find applications as curing agents for epoxy resins in the production of heat-resistant polymeric composites [4] and as a component of greases for heavily loaded mechanisms [5]. In view of these potential applications, it has become necessary to study the conditions under which carbogenic oxy-acids are formed in the oxidation of vacuum resid, as well as the influence of process variables on the product yield and quality.

The laboratory unit used in the present work for the oxidation of vacuum resid by atmospheric oxygen in benzene solution as well as the procedures used to perform the oxidation, separate the oxidized product, and analyze the carbogenic oxy-acids, have been described in [2, 6]. The physicochemical characteristics of the vacuum resid were as follows: density $d_4^{20} = 0.9724$; molecular weight 623; content of oils 76.4%, resins, 16.8%, asphaltenes 6.8% by weight. The conversions taking place when the vacuum resid was oxidized in benzene solution were judged from the yield of oxidized product and its content of oils, resins, asphaltenes, and carbogenic oxy-acids.

When vacuum resids are oxidized by atmospheric oxygen without a solvent, asphalts are formed. The use of more severe oxidation conditions in this case is accompanied by the

L'vov Polytechnic Institute. Translated from *Khimiya i Tekhnologiya Topliv i Masel*, No. 10, pp. 7-10, October, 1989.