Conversion of Lower Alkanes in the Presence of Metal Nanoparticles Supported on a Zeolite Matrix

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Abstract—It is shown that pentasil-type zeolites involving Zn and Pt nanoparticles display a high aromatizing activity in the conversion of lower alkanes. The effects of the zeolite matrix composition and the concentration and nature of a modifying additive on the activity, selectivity, and stability of the obtained catalysts are studied. It is found that upon the addition of Pt nanopowder, the duration of the stable operation of gallium-containing zeolite increases.

INTRODUCTION

Interest in the study of the catalytic properties of nanomaterials synthesized under unsteady-state conditions by mechanochemical activation (MCA), electric explosion (EE) of conductors, and the gas-phase method (GP) has increased recently. MCA was very efficient in obtaining nickel-based catalysts for hydrocarbon decomposition [1] and allowed one to improve the performance of catalysts and supports [2, 3]. The selectivity of benzene hydroxylation in the presence of a catalyst based on platinum nanopowder, which was produced by the electric explosion of nanopowder (EENP) is higher than 90% [4]. The comparative studies of various platinum catalysts showed that the yield of phenol in alkane conversion in the presence of the platinum EENP–based catalyst is 4–5 times higher than that for the conventional Pt/SiO_2 catalyst. In CH_4 oxidation over nanodispersed Pt catalysts, the selectivity to CH_3OH and CH_2O was as high as 92–94% at a methane conversion of 2% [4]. Replacement of conventional silver powders with EENP allowed one to extend the temperature range of ethanol oxidation to acetaldehyde with a selectivity of ~100% [5]. Nickel and iron EENP obtained in an argon atmosphere were more selective toward olefins in CO hydrogenation than the analogous samples prepared by traditional methods [6, 7]. Correlation between the catalytic properties of nickel powders with the same size of particles that were produced by the EE and GP methods showed a higher specific catalytic activity in CO hydrogenation of GP-nanopowders, especially in the case of medium-sized particles (20 nm) [6, 8]. Furthermore, on GP-nanopowders, only saturated hydrocarbons were formed with a selectivity that was independent of particle sizes. Unusual catalytic properties of platinum and silver EENP in ethylene epoxidation and partial oxidation of the C–H bond by molecular oxygen was noted in [4, 9]. These properties were explained by a large energy excess, the existence of metal–microstructure interface, and by the rigid spatial localization of the active states. Thus, the peculiarities of microgeometry and a high specific surface area of the nanosystems create new opportunities for the development of highly selective and active catalysts [10]. At the same time, pentasil-type zeolite catalysts are widely used in various processes due to their combination of a unique molecular-sieve and physicochemical properties [11–14]. The efficiency of zeolite catalysts in hydrocarbon conversions can be improved by their modification with various metals. The promoting effect of metals is especially pronounced if materials are used that have a particle size of not larger than several tens of nanometers [15, 16]. In this connection, the aim of this study was to examine the effects of Zn and Pt additives, obtained by the EE method, on the catalytic properties of pentasils in C_3–C_4 alkane conversion.

EXPERIMENTAL

Nanosized powders (NSP) of zinc and platinum were produced by the EE of 0.1–0.2 mm wire in an argon atmosphere. This method is based on a sharp change in the physical state of a metal owing to intense energy release, when a high-density current pulse is passed. Pulse bulk heating of a metal in a vacuum or in an inert medium leads to high temperatures and rates of scattering and cooling for the material. The particles thus formed bear size, phase, defect and other energetically unsaturated states. In the condensation in a flow of rapidly expanding vapor, metal powders are formed with an average particle size of ~70 nm.

Initial supports were pentasils with a $SiO_2/Al_2O_3 = 60$ ratio: aluminosilicate (AS) and galloaluminosilicate (GAS). These were prepared by hydrothermal synthesis from alkaline alumina–silica gels. Hexamethylene diamine was used as an organic additive. The concentration of gallium oxide introduced into a zeolite at the
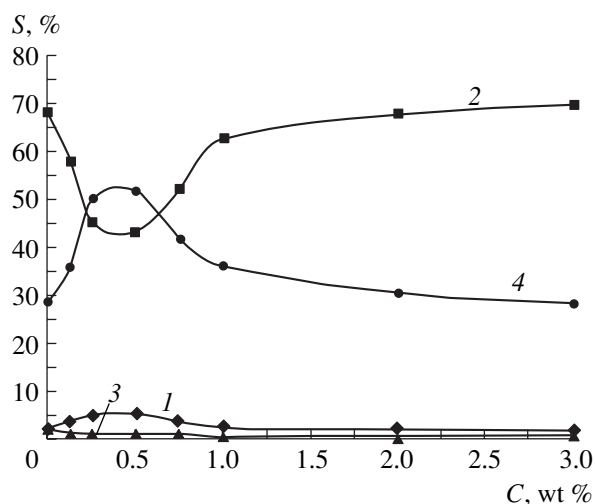
Fig. 1. Dependence of the selectivities (S) to (*1*) hydrogen, (*2*) C_1–C_2 alkanes, (*3*) C_2–C_3 alkenes, and (*4*) aromatic hydrocarbons on the concentration (C) of Zn NSP in AS at $T = 550°C$ and $v_0 = 100$ h^{-1}.

Fig. 2. Conversion (X) of C_3–C_4 alkanes and the selectivity (S) of product formation on AS, GAS, and on the samples, containing 0.5% NSP of Zn and Pt ($T = 500°C$, $v_0 = 100$ h^{-1}).

stage of hydrothermal synthesis was 2.2 wt %. According to IR spectroscopic and X-ray diffraction analysis, the obtained samples exhibited a high degree of crystallinity, contained no admixture of the amorphous phase, and are categorized as ZSM-5-type pentasils. Zeolites were transformed to the H form by double decationation using a 25% solution of NH_4Cl with subsequent calcination at 540°C for 6 h (the concentration of Na_2O in the samples was lower than 0.05%). Catalysts containing Zn and Pt were prepared by dry mixing of metal NSP with AS or GAS powders in a ball mill in air for 2 h. To compare the catalytic properties, we also prepared samples with the same amounts of zinc, which was introduced by various methods: by ion exchange from a solution of zinc nitrate followed by additional impregnation with mother liquor, by mixing with a conventional powder of zinc and zinc oxide (ZnO).

Catalytic runs were performed in a flow-type system with a quartz reactor of volume 5 cm^3 at atmospheric pressure, a temperature of 450–600°C, and space velocities of 100–400 h^{-1}. Pressed samples (the 0.25–0.50 mm fraction) without a binder were used. The reaction products were analyzed by gas chromatography. According to preliminary estimates of the catalytic activity of Pt and Zn NSP without a support, no conversion of the mixture of lower alkanes (2.2% C_2H_6, 73.7% C_3H_8, and 24.1% C_4H_{10}) occurred under the above conditions.

RESULTS AND DISCUSSION

The results of the study of the effect of Zn NSP on the catalytic properties of AS are presented in Fig. 1. As can bee seen, the Zn additive results in a substantial increase in the selectivity of alkane aromatization. Thus, at a zinc concentration of 0.5%, the selectivity attains a maximum value of 51.3%. With an increase in
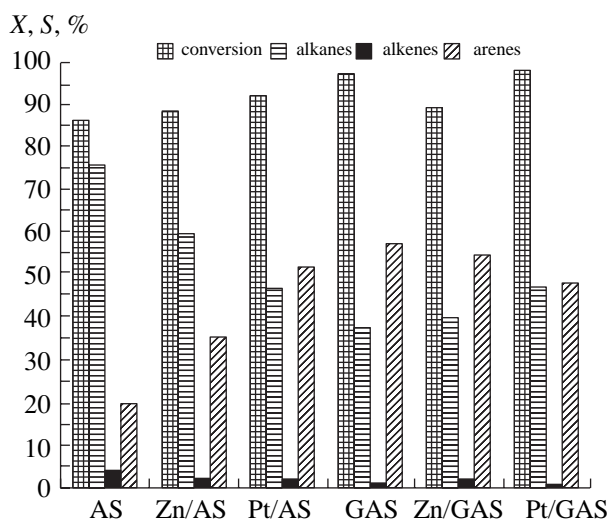
the Zn NSP content of AS, the selectivity of aromatization decreases, and the cracking activity of the catalysts grows.

Data presented in the table show that samples 2 and 3, with the same activity, differ in the selectivity of aromatization (the higher value was obtained for 0.5% Zn NSP/AC). In the presence of catalyst 3, a greater amount of C_1–C_2 alkanes is formed, suggesting that this sample is more efficient in the cracking and hydrogenation of intermediate compounds. Zeolite, in which Zn was introduced by ion exchange and the impregnation method (sample 5), exhibited a lower selectivity toward aromatization than the sample containing Zn NSP.

Figure 2 shows data on the catalytic activity and selectivity of AS and GAS containing 0.5 wt % of NSP of Zn and Pt. The additives Zn and Pt substantially improve the catalytic properties of AS, as distinct from those of GAS. After modifying the latter, the yield of aromatic hydrocarbons decreased, and the selectivity to by-products (C_1–C_2 alkanes) increased.

According to the current understanding of the mechanism of catalysis by pentasils [11, 14, 17, 18], the different influence of Zn and Pt NSP on the catalytic properties of AS and GAS is attributable to the different compositions of the framework of the zeolites and different acidic properties. In the presence of aluminosilicate pentasil, olefins are mainly formed by the cracking of initial C_3–C_4 paraffins. The ability of decationated pentasil to activate the molecules of lower alkanes with subsequent dehydrocyclization of the intermediates formed is due to the presence of strong proton acid sites. These sites are responsible for the cracking of initial paraffins, oligomerization of olefins, and their partial decomposition, as well as for cyclization of unsaturated hydrocarbons [17]. In addition to the proton

Comparison of the catalytic properties of zinc-containing zeolite catalysts in the aromatization of C_3–C_4 alkanes

Sample	Catalyst	v_0, h^{-1}	T, °C	X, %	S_1, %	S_2, %	S_3, %	A, %
1	AC	100	450	60	76.6	7.4	14.7	8.8
		100	500	86	75.5	3.3	19.4	16.7
		100	550	96	67.4	2.1	28.5	27.4
		100	600	99	68.1	1.4	28.3	28.0
		200	600	92	66.1	2.4	29.7	27.3
2	0.5% Zn(NRP)/AC	100	450	61	78.5	3.2	14.5	8.8
		100	500	88	59.2	1.7	34.8	30.6
		100	550	99	42.9	1.1	51.3	50.8
		200	550	95	44.7	3.3	45.4	43.1
3	0.5% Zn/AC	100	450	62	80.0	2.9	15.1	9.4
		100	500	90	62.2	0.9	33.3	30.0
		100	550	98	50.0	0.9	43.3	42.4
		200	550	97	49.6	1.5	42.7	41.4
4	0.5% ZnO/AC	100	450	59	85.5	3.0	7.6	4.5
		100	500	89	57.5	1.6	36.5	32.5
		100	550	99	62.8	1.3	29.7	29.4
		200	550	98	59.7	1.7	31.3	30.7
5	0.5% Zn/AC	100	450	61	70.6	4.5	22.6	13.8
		100	500	88	54.8	2.7	40.0	35.2
		100	550	99	50.0	1.6	43.7	43.3
		200	550	99	50.0	2.2	43.0	42.6

Note: v_0 is the space velocity; T is the reaction temperature; X is the conversion; S_1, S_2, and S_3 are the selectivities to C_1–C_2 alkanes, C_2–C_3 alkenes, and aromatic hydrocarbons, respectively; A is the yield of aromatic hydrocarbons.

sites, GASs contain strong aprotic acid sites, involving gallium atoms located out of the framework, which are capable of dehydrogenating low-molecular paraffins (to give olefins) and abstracting hydride ions from unsaturated molecules; the latter reaction results in highly reactive allyl intermediates [18]. The oligomerization of olefins occurs over proton acid sites. Introducing active dehydrogenating metals (NSP of Pt or Zn) into GAS leads to the following phenomenon. The metals in the form of very small-sized particles occupy some portion of the outer surface of the zeolite crystals, making proton acid sites less accessible for reactant molecules. As a result of partial isomorphic displacement of Al atoms by Ga atoms, the efficiency of proton acid sites decreases. Moreover, when added to GAS, elements/promoters, especially Pt, increase the yield of alkanes owing to the hydrogenation of intermediate unsaturated hydrocarbons.

To determine the duration of severce cycle in aromatization of the propane–butane fraction, experiments were performed with GAS modified by NSP of Pt and Zn. Introducing gallium into the zeolite in the course of the hydrothermal synthesis leads to a substantial increase in the duration of its efficient operation along with a significant growth in the catalytic activity in aromatization (Fig. 3). The yield of aromatic hydrocarbons in the presence of the initial GAS (without its modification) is equal to 50% for ~144 h. Upon introducing 0.5% Zn NSP into the GAS, the period of stable catalyst operation is shortened. The Zn additive had an especially strong effect on the total activity of GAS and on the yield of aromatic hydrocarbons, whereas the selectivity of their formation depended on the Zn additives to a lesser degree. Platinum caused a slight decrease in the aromatization activity and a substantial increase in the duration of stable GAS operation. In
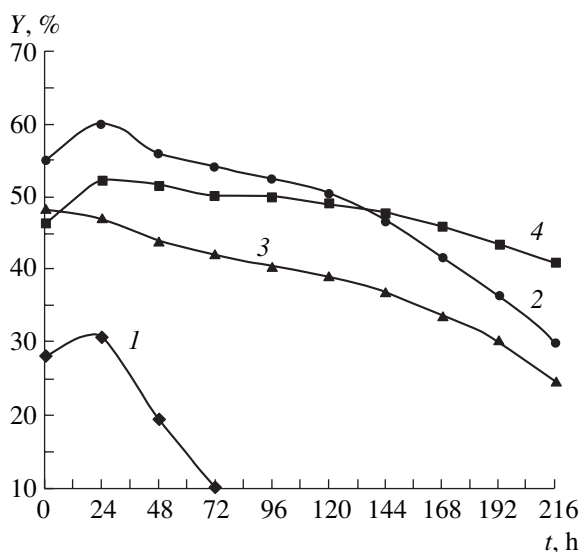
Fig. 3. Dependence of the yield (Y) of aromatic hydrocarbons on the time-on-stream (t) of (*1*) AS at $T = 600°C$, (*2*) GAS, (*3*) 0.5% Zn NSP/GAS, (*4*) 0.5% Pt NSP/GAS at $T = 500°C$ and $v_0 = 100$ h^{-1}.

contrast to Zn NSP/GAS, the 0.5% Pt/GAS sample successfully operated at 500°C and 100 h^{-1} for more than 200 h, the yield of aromatic hydrocarbons being higher than 40%.

Thus, the conclusion is that the modification of pentasil with an aluminosilicate framework by Zn and Pt nanopowders leads to an increase in its activity and selectivity toward aromatic hydrocarbons formed from lower alkanes (C$_3$–C$_4$). The introduction of Pt NSP into GAS leads to an increase in the duration of the efficient operation of the catalyst. The amount of the desired product obtained in the conversion of a propane–butane mixture heavily depends on the concentration and nature of a metal-modifier, as well as on the composition of the zeolite matrix. A nanosized powder of Zn added to a high-silica zeolite has a more appreciable effect on its catalytic properties in the conversion of lower alkanes than zinc introduced by the conventional methods.

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