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Gas-Phase and Supercritical *n*-Pentane Isomerization on H-Mordenite

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Abstract—The skeletal isomerization of supercritical *n*-pentane on the H form of mordenite under flow conditions was studied for the first time. It was found that the conversion of supercritical *n*-pentane was 30–35% at 90% selectivity for isopentane at 260°C, 130 atm, and a liquid hourly space velocity of 30 h^{-1}. The catalyst was deactivated as the temperature was increased above 280°C. According to differential thermal analysis data, the deactivation was related to the deposition of condensation products on the surface. The resistance of the H form of the zeolite to poisoning in *n*-pentane isomerization in a gas phase at 1–8 atm was lower than that under supercritical conditions. It was found that H-mordenite deactivated under gas-phase reaction conditions at 260°C and 8 atm can be regenerated by passing to supercritical isomerization conditions (260°C and 130 atm).

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INTRODUCTION

The skeletal isomerization of alkanes is the key step in current petroleum processing and a source of environmentally friendly high-octane gasoline components [1]. It is well known that this isomerization is performed at temperatures to 200°C on a bifunctional platinum catalyst based on chlorinated alumina or on platinum supported on alumina with the addition of chlorine-containing compounds in small amounts to the reaction mixture [2]. Catalysts based on platinum-containing mordenite are also used in this process at a temperature higher than 250°C [3]. Another new catalytic system, sulfated zirconia modified with transition metal cations (Fe, Mn, etc.), was proposed in 1995 [4]. To eliminate the poisoning effect of condensation products and to retain a sufficient productivity of these bifunctional catalysts, in all cases, the isomerization is performed in a 4- to 10-fold excess of hydrogen with hydrogen recycling.

Supercritical fluids have been successfully used as solvents in order to solve problems arising from the poisoning of heterogeneous catalysts; they have been found highly effective for the regeneration of the initial activity of samples under these conditions [5, 6]. Some publications have been devoted to the isomerization of light alkanes in a supercritical state without solvents. Thus, Hou et al. [7] studied *n*-pentane isomerization on sulfated zirconia near the critical point of the substrate in a batch reactor.

We have accumulated a great body of experimental data on heterogeneous catalytic reactions under supercritical conditions; these data are indicative of their advantages over gas-phase reactions in terms of activity, selectivity, and longer catalyst lifetimes [8–10]. We found that a fundamental difference between the supercritical process and the gas-phase isomerization of light alkanes is an increase in the lifetime of the solid-acid catalyst in the absence of platinum from the catalyst and without the addition of hydrogen to the feed. In this case, a hydrocarbon simultaneously acts as both a reactant and a solvent, which favorably affects the activity and productivity of the catalyst.

The aim of this work was to study the skeletal isomerization of *n*-pentane in the supercritical state on H-mordenite and to compare the resulting activities, selectivities, and lifetimes of the catalyst with the corresponding gas-phase reaction parameters.

EXPERIMENTAL

Zeolite Catalyst Preparation

A solid-acid catalyst prepared from the NH_4 form of mordenite (AKZO Nobel, 2125 114) with a Si/Al ratio of 11 was used in the reaction of *n*-pentane isomerization. To prepare this catalyst from the ammonia hydrogen form, the parent zeolite was calcined in a flow of air with gradual heating to 500°C and exposed at the specified temperature for 4–5 h.

Procedures for Catalytic Tests, Reaction Product Analysis, and the Determination of Catalyst Coking

The catalytic properties of zeolites were experimentally studied using a laboratory setup based on KL-1 and KL-2 catalytic units designed at the Special Design Bureau of the Zelinskii Institute of Organic Chemistry, Russian Academy of Sciences. The inlet and outlet

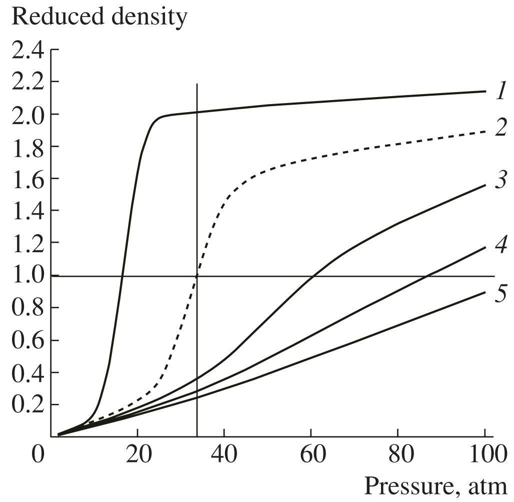

Fig. 1. Reduced density versus pressure isotherms for *n*-pentane at (*1*) 150, (*2*) 196.6, (*3*) 240, (*4*) 290, and (*5*) 340°C.

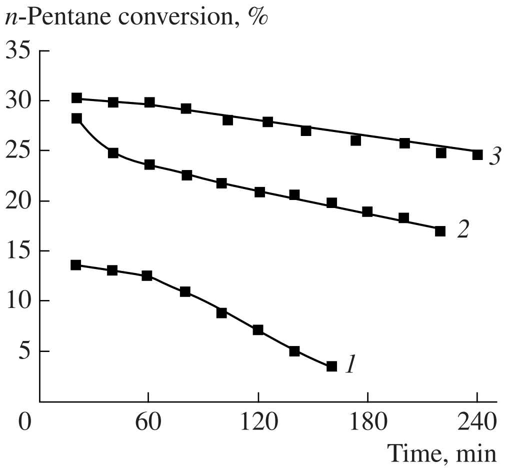

Fig. 2. Kinetics of the isomerization of *n*-pentane on H-mordenite (260°C; 30 h^{-1}) at (*1*) 25, (*2*) 75, and (*3*) 130 atm.

lines could be thermostatically controlled at temperatures to 300°C.

Under gas-phase reaction conditions at an elevated pressure, pentane was supplied using a liquid pump. Catalysts were loaded into a stainless-steel flow tubular reactor 5 mm in diameter or a quartz reactor 4 mm in diameter. The temperature was controlled to within ±0.4 K, and the furnace was heated with a Miniterm 400.31 temperature regulator (OAO MZTA). The catalyst was heated to the required temperature in a flow of helium.

To perform catalytic experiments under supercritical conditions, the catalysts were loaded into stainless-steel flow reactors rated at a maximum pressure of 300 atm; the reactors were 3–10 mm in diameter depending on the weight of the catalyst sample. The pressure in the system was produced by supplying liquid *n*-pentane with the use of an HPP 5001 liquid piston pump (Laboratorni pristroje, Prague, Czech Republic). Precise pressure adjustment at the reactor outlet was performed with a high-pressure membrane valve. The pressure in the system to 150 atm was measured with a standard pressure gage. The chromatographic analysis of products at the reactor outlet was performed on an OV-101 capillary column 100 m in length. In particular cases, the reaction products were identified by chromatography–mass spectrometry.

The quantitative determination of the degree of coking of deactivated catalysts was performed by combined thermogravimetry and differential thermal analysis (TG–DTG–DTA) using a MOM derivatograph under conditions of linear heating to 600–800°C at a rate of 10 K/min in an atmosphere of air. Catalyst samples of 40–60 mg were placed in platinum crucibles. γ-Al_2O_3 was used as the reference.

RESULTS AND DISCUSSION

To determine the conditions of *n*-pentane isomerization in the supercritical state, we calculated the parameters of state for pentane based on three-parameter correlations developed by Pitzer [11].

Figure 1 shows the pressure dependence of the reduced density of pure *n*-pentane at five temperatures. The relative density is the ratio of the density under given conditions to the density at a critical point. The isotherm corresponding to the critical temperature of *n*-pentane (196.6°C) is shown by a dashed line. The critical pressure of 33.3 atm is shown by a vertical solid line. The catalytic experiments were performed under supercritical conditions based on the isotherms of relative densities, when the density of the reaction system was close to or higher than a critical value. The critical parameters of *n*-pentane and isopentane (the main isomerization product) are similar: 196.6°C and 33.3 atm and 187.4°C and 33.4 atm, respectively. This circumstance is responsible for the homogeneity of supercritical hydrocarbon mixtures formed in the course of the reaction at any degree of *n*-pentane conversion. To perform *n*-pentane isomerization under supercritical conditions, we used temperatures and pressures higher than 220°C and 50 atm, respectively, in our experiments.

Figure 2 shows the time dependence of *n*-pentane conversion at 260°C and various pressures in the presence of the hydrogen form of mordenite. It can be seen in Fig. 2 that, in the isomerization of *n*-pentane under supercritical conditions at reaction pressures of 75 and 130 atm, the catalyst activity and stability in the operation increased with time, as compared with those in the gas-phase reaction at 25 atm. The lowest rate of deactivation of the zeolite catalyst was observed as the pressure was increased to 130 atm. A 25–30% conversion at high selectivity to 90% for isopentane was retained for

Table 1. Conversion and selectivity in the reaction of *n*-pentane on H-mordenite under supercritical conditions depending on the reaction temperature (130 atm; 30 h^{-1})

Temperature, °C	Time, min	Conversion, %	Selectivity, %		
			C_3–C_4	isopentane	C_{6+}
220	40	2.2	5.8	88.1	6.2
240	40	5.9	6.0	87.7	6.3
260	40	29.9	6.9	86.9	6.3
270	40	37.9	16.0	71.7	12.3
280	25	42.4	15.5	73.5	11.1
300	20	49.5	25.2	60.6	14.2

5–8 h at a very high *n*-pentane liquid hourly space velocity (LHSV) of 30 h^{-1}, which is uncharacteristic of gas-phase conditions.

As the reaction temperature under supercritical conditions was increased from 220 to 300°C, the total conversion of *n*-pentane increased from 2 to 50%; however, the selectivity for the target product (isopentane) noticeably decreased (from 90 to 60%) in this case (Table 1). However, gaseous C_1–C_2 products of deeper cracking were not detected under these conditions. At 300°C, the selectivity of isopentane formation was 60% and the total selectivity for isomeric C_3–C_4 hydrocarbons was as high as 40%.

As follows from the data shown in Fig. 3, the stability of mordenite operation in the conversion of *n*-pentane in a supercritical state decreased with temperature. At 220–260°C, the catalyst practically did not undergo deactivation with time. At the same time, at an isomerization temperature of 280°C or higher, the zeolite completely lost its activity from an initial conversion of 40–50% in 3–5 h of operation.

This behavior of the catalyst can be due to the fact that unsaturated by-products formed in the course of reaction can undergo oligomerization and strong adsorption on the catalyst surface and result in catalyst deactivation. This can be supported by the results of the determination of light olefins in the products of catalysis (Table 2). Indeed, as the temperature of *n*-pentane isomerization was increased from 200 to 300°C, the weight concentration of C_4–C_5 olefins (dehydrogenation products) increased by a factor of tens. A portion of them was polymerized and deposited on the catalyst surface, as evidenced by DTA data for the catalyst after the reaction. These data indicate that the total amount of condensation products considerably increased with the reaction temperature.

In addition to the quantitative change, a qualitative change in the condensation products was observed as the temperature was increased. Based on published data [12], we can correlate the composition of condensation products with their combustion temperatures. The removal of surface-bound aliphatic hydrocarbons occurred at 100–350°C. At temperatures higher than 350°C, the combustion of aromatic condensed structures, which were formed both in the channels and at the outer surface of the catalyst, came into play. The bar diagram in Fig. 4 indicates that both the total amount and the fraction of high-molecular-weight condensation products increased with temperature.

Therefore, pentane cannot dissolve all of the condensation products formed at temperatures higher than 280°C even in a supercritical state, and the activity of the catalyst noticeably decreased. However, at temperatures to 260°C, supercritical pentane effectively removed low-molecular-weight condensation products to prolong zeolite operation. Thus, H-mordenite deactivated under gas-phase reaction conditions at 260°C, 8 atm, and an LHSV of 30 h^{-1} not only restored its initial high activity but also stably operated for a long time

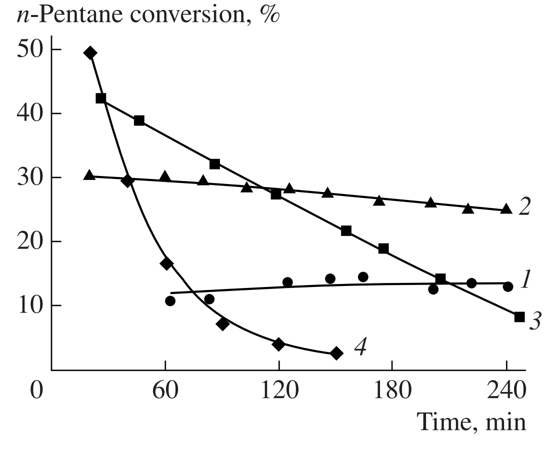

Fig. 3. Kinetics of the isomerization of *n*-pentane on H-mordenite under supercritical conditions (130 atm; 30 h^{-1}) at (*1*) 240, (*2*) 260, (*3*) 280, and (*4*) 300°C.

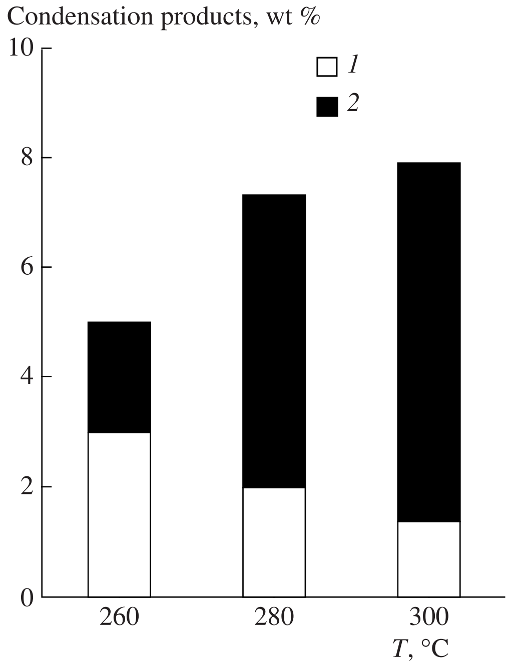

Fig. 4. Total amounts of condensation products in a catalyst sample after *n*-pentane isomerization (130 atm; 30 h^{-1}) and product distributions at oxidation temperatures of (*1*) 100–350 and (*2*) >350°C.

on going to supercritical isomerization conditions (260°C, 130 atm, and 30 h^{-1}) (Fig. 5).

Thus, the H form of mordenite is less active and prone to rapid poisoning with condensation products under gas-phase isomerization conditions. On the contrary, the isomerization of *n*-pentane under supercritical conditions at temperatures higher than 220°C and pressures higher than 100 atm is characterized by higher conversions and selectivity of isopentane formation, as well as by a higher stability of the catalyst to deactivation.

Table 2. Amounts of C_4–C_5 olefins and condensation products formed on the catalyst surface at various reaction temperatures (130 atm; 30 h^{-1})

Temperature, °C	Concentration of olefins,* wt %		Total condensation products, wt % (DTA data)
	butene	pentene	
220	0.005	0	–
240	0.04	0.001	–
260	0.05	0.005	5.0
270	0.08	0.015	–
280	0.18	0.030	7.3
300	0.35	0.035	8.0

* Analysis of the products of catalysis after 30 min of reaction.

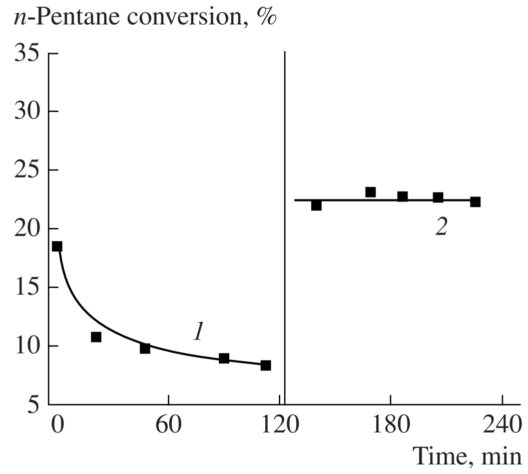

Fig. 5. Isomerization of *n*-pentane on H-mordenite at 260°C and an LHSV of 30 h^{-1} (*1*) in the gas phase at 8 atm and (*2*) in the subsequent reaction under supercritical conditions at 130 atm.

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