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Supercritical *n*-Butane Isomerization

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Abstract—Supercritical *n*-butane isomerization over the solid acid catalysts sulfated zirconia, TiO_2-supported $H_4[Si(W_3O_{10})_4] \cdot xH_2O$ (Keggin-type heteropoly acid), and H-mordenite is studied in a flow reactor. The critical parameters of *n*-butane are calculated for a wide range of reaction conditions. Changing from gaseous *n*-butane to supercritical *n*-butane markedly extends the lifetime of the catalysts. Under supercritical conditions, the activity and selectivity of the catalysts are invariable, provided that the density of the reaction mixture is in the vicinity of the critical density of *n*-butane. After the catalysts are deactivated in the gas medium, they can be partially or completely reactivated in the supercritical fluid.

The kinetics of heterogeneous catalytic reactions, as well as the selectivity of these reactions with respect to desired products, often depends on the adsorption (desorption) and diffusion rates of the reactants. In reactions under ordinary conditions (in the gas or liquid phase), the ratio of these rates is not always optimal. Conducting reactions at supercritical temperatures and pressures, one can take advantage of the following unique properties of supercritical fluids: as compared to gases, supercritical fluids have a higher density, dissolving power, and thermal conductivity; as compared to liquids, they afford higher solute diffusion rates and are much more compressible. The beneficial effect of these properties on the reaction kinetics is due to the following facts: a more perfect mixing is attained, especially for reactants in different physical states; temperature in exothermic reactions is easier to control, because the heat capacity and thermal conductivity of the reaction mixture peak near the critical point; the condensed unsaturated by-products are extracted *in situ* and removed from the catalyst surface; and so on [1–3].

In view of the above, supercritical heterogeneous catalysis is of great interest at the moment [1–6]. Sander *et al.* [4, 5] studied supercritical *n*-butane isomerization on sulfated zirconia. Their experiments were conducted at such supercritical pressures and temperatures that the relative density of the medium (ρ_{rel}), equal to the ratio of the actual density (ρ) to the critical density (ρ_{cr}), was above, below, or equal to unity. It was demonstrated that the lifetime of the catalyst in the supercritical fluid is longer than that in the gas medium. At the same time, the *n*-butane conversion and the isobutane selectivity of the reaction under supercritical conditions were always lower than in the gas medium and, moreover, decreased as the pressure was raised. However, other conditions being equal, catalyst efficiency in the supercritical phase was much higher than in the gas phase.

There were studies of the effects of supercritical conditions on hexene-1 isomerization and isoparaffin alkylation with olefins [3, 6]. Most of the experiments were carried out with supercritical carbon dioxide as the solvent. It was demonstrated that the most appropriate temperature and pressure ranges are $(1.05–1.2) \times T_{cr}$ and $(0.9–2.0) \times P_{cr}$. These are the conditions under which strongly adsorbed coke precursors are most soluble and are rapidly removed from the catalyst surface.

Here, we report a comparative study of supercritical *n*-butane isomerization over different solid acid catalyst systems in the absence of any solvent. The catalysts in question are sulfated zirconia, the Keggin-type heteropoly acid $H_4[Si(W_3O_{10})_4] \cdot xH_2O$ (HSiWO), and H-mordenites varying in skeletal Si : Al ratio.

EXPERIMENTAL

Catalysts. Sulfated zirconia, SO_4/ZrO_2, was prepared from commercial sulfated zirconium hydroxide (MEL Chemicals). Zirconium hydroxide with a particle size of 0.5 to 1.0 mm was calcined in flowing dry air at 600°C for 3 h, the heating rate being 2.5 K/min. Because sulfated zirconia is very hygroscopic, before each run, the catalyst was activated *in situ* at 400°C in flowing dry air for 1 h with a heating rate of 2.8 K/min, and then cooled to a preset temperature in flowing helium.

TiO_2 was loaded with 20 wt % $H_4[Si(W_3O_{10})_4] \cdot xH_2O$ (Merck) by incipient-wetness impregnation to obtain an $HSiWO/TiO_2$ catalyst. The catalyst was calcined at 340°C for 2 h in flowing dry air (heating rate, 2 K/min). Before each run, the catalyst was activated *in situ* at 200°C for 1 h in flowing helium.

Commercial NH_4-mordenite (Akzo Nobel) with Si : Al = 10 and 15 was converted into the H-form by heating it to 500°C at a rate of 5 K/min in flowing helium and maintaining this temperature for 2 h.

Experimental procedure. The catalytic reaction was carried out in a flow reactor fed with liquid *n*-butane at a VHSV of 2–3 h^{-1}. Our experimental setup is schematized in Fig. 1. The reaction product was analyzed on an LKhM-80 gas chromatograph using steel columns 3 mm in diameter packed with 15% polyphenylmethylsiloxane/S-22 zeolite.

The density of supercritical butane as a function of temperature was calculated using a three-parameter Pitzer's correlation [7]. In Fig. 2, we plot the pressure dependence of the relative density ρ_{rel} of pure *n*-butane for four different temperatures. Here, relative density is the ratio of density under the given conditions to density at the critical point. The relative density–pressure isotherm at the critical temperature of *n*-butane, 152.2°C, is shown as a dashed line. The critical pressure, 37.5 atm, is marked with a vertical line. The area to the right of this line under the dashed isotherm represents supercritical conditions. The catalytic reaction was conducted at the temperatures specified in the caption to Fig. 2 and pressures such that the relative density of the reaction mixture was nearly equal to unity; that is, butane density in the reaction was equal to its critical value. To find out how the reaction depends on the type of reaction medium, we carried out the reaction with gaseous *n*-butane at atmospheric pressure and 20 atm and with supercritical *n*-butane at 60 and 110 atm over the $HSiWO/TiO_2$ catalyst at a fixed temperature of 260°C.

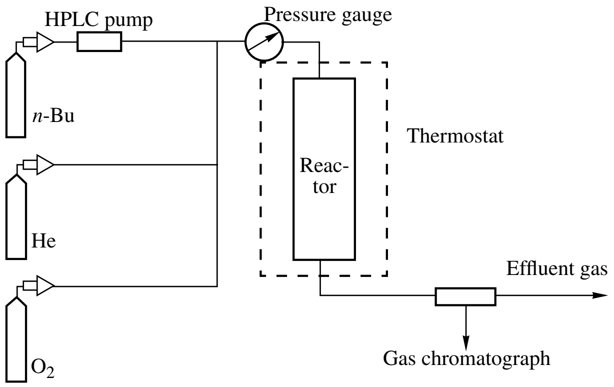

Fig. 1. Experimental setup for catalytic tests in the gas and supercritical media.

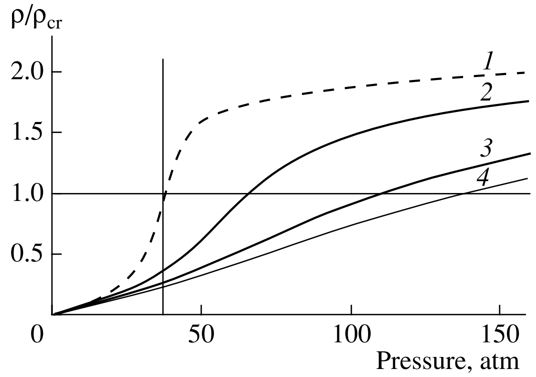

Fig. 2. Pressure dependence of the relative density of pure *n*-butane calculated using a three-parameter Pitzer's correlation for *T* = (*1*) 152.2, (*2*) 190, (*3*) 260, and (*4*) 300°C.

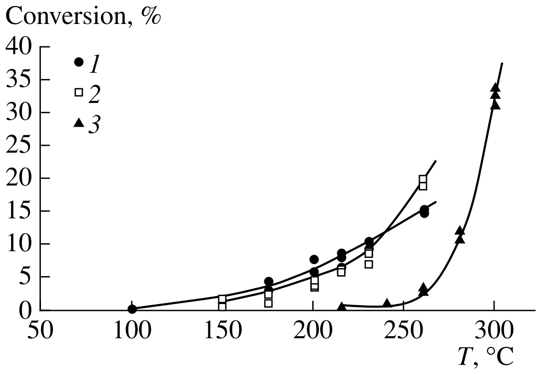

Fig. 3. Temperature dependence of *n*-butane conversion over (*1*) SO_4/ZrO_2, (*2*) $HSiWO/TiO_2$, and (*3*) H-mordenite at 60 atm.

RESULTS AND DISCUSSION

The critical temperature and pressure of *n*-butane are 152.2°C and 37.5 atm, respectively. Therefore, it is possible to use *n*-butane as a reaction medium without adding a solvent. The desired product, isobutane, has similar critical parameters of 135.1°C and 36.0 atm, so the critical state of the reaction mixture will not change greatly during the reaction.

The effect of supercritical conditions on *n*-butane isomerization was studied with sulfated zirconia, supported HSiWO, and H-mordenite as catalysts. Considering the purposes of this work, the basic requirement for the catalyst was that it provide a high isobutane yield in the vicinity of critical *n*-butane parameters. This constraint arises from the fact that the density of a supercritical fluid at a fixed temperature can be increased only by raising the pressure. Obviously, the lower the reaction temperature, the lower the pressure needed to attain a required density of the medium.

All the catalysts in question appeared to be active in *n*-butane isomerization into isobutane. Figure 3 plots *n*-butane conversion as a function of temperature for these catalysts in the region of supercritical *n*-butane.

n-Butane isomerization over sulfated zirconia occurs starting at a temperature as low as 150°C, so this reaction can be investigated with *n*-butane in all its states, including gas, liquid, and supercritical fluid. We studied this reaction at 190 and 215°C. It is impossible to employ this catalyst at higher temperatures: at 250°C, it loses activity because of the irreversible sulfate reduction to hydrogen sulfide.

n-Butane isomerization over $HSiWO/TiO_2$ affords a rather high isobutane yield at 260°C.

Maximum *n*-butane-to-isobutane conversion and isobutane selectivity under supercritical conditions

Catalyst	*T*, °C	*P*, atm	Maximum conversion, %	Equilibrium conversion, %	Isobutane selectivity, %
SO_4/ZrO_2	190	65	20–22	50	80
$HSiWO/TiO_2$	260	110	18–20	43	78
H-mordenite	300	138	25–27	40	40

n-Butane isomerization over H-mordenite does not occur up to 250°C (Fig. 3). As the temperature is further increased to 300°C, *n*-butane conversion grows sharply, being almost independent of the silica modulus.

The table lists maximum *n*-butane conversion data for the catalyst system in question at pressures such that the density of supercritical *n*-butane is equal to its critical density, as well as equilibrium conversion data calculated for the specified conditions. The working temperatures and pressures necessary to achieve the critical density of *n*-butane were determined from the calculated data presented in Fig. 2.

Clearly, in no case does the maximum *n*-butane conversion reach the equilibrium value. The highest selectivity, about 80%, is attained with sulfated zirconia and supported heteropoly acid. These catalysts afford equal maximum *n*-butane conversions. With H-mordenite, isobutane selectivity is much lower and does not exceed 40% at the specified conversion. This observation is explained by the fact that H-mordenite, at elevated temperatures, much accelerates cracking and disproportionation reactions, yielding considerable amounts of propane, pentane, and hexane. This variation of the reaction outcome is further evidence of the bimolecular mechanism of *n*-butane isomerization [8, 9].

Note that both overall *n*-butane conversion and isobutane selectivity under supercritical conditions are constant in time, as distinct from those in the reaction involving gaseous *n*-butane.

The isomerization of gaseous *n*-butane over the catalyst systems has been studied by a number of researchers [8–12]. Here, we compare the gas-phase and supercritical *n*-butane isomerization reactions. Figure 4 shows the time dependence of the conversion of gaseous *n*-butane over $HSiWO/TiO_2$ at atmospheric pressure and 20 atm. Evidently, the activity of the catalyst decreases over time. Similar time dependencies of conversion were observed for the other catalysts. Raising the pressure of gaseous *n*-butane increases the maximum conversion of the reactant without suppressing catalyst deactivation.

Figure 5 plots the time dependence of the conversion of gaseous and supercritical *n*-butane over $HSiWO/TiO_2$ at 60 ($\rho < \rho_{cr}$) and 110 atm ($\rho = \rho_{cr}$), respectively. At a near-critical density of the medium, the activity of the catalyst does not decrease, but even grows slightly with time. The supercritical medium readily dissolves the strongly adsorbed densification products, which could deactivate the catalyst, and removes them from the catalyst surface. Thus, conducting the reaction under supercritical conditions markedly extends the lifetime of the catalyst. At 60 atm and 260°C, when the density of the medium is below critical, the activity of the catalyst decreases over time (Fig. 5), as in the case of gaseous *n*-butane. Apparently, supercritical *n*-butane has a limited dissolving power at $\rho_{rel} < 1$. Somewhat different data were reported by Sander *et al.* [4, 5], who did not observe catalyst deac-

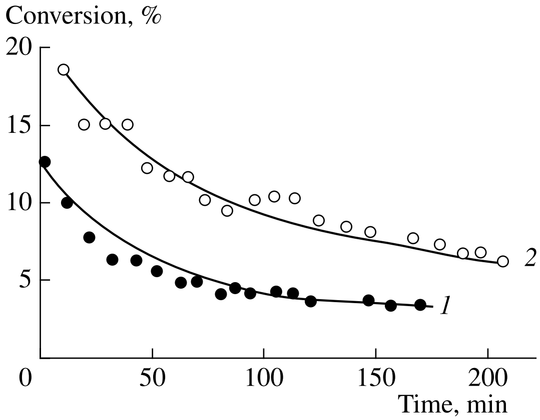

Fig. 4. Time dependence of the conversion of gaseous *n*-butane over the $HSiWO/TiO_2$ catalyst. T = 260°C; VHSV = 2 h^{-1}; P = (*1*) 1 and (*2*) 20 atm.

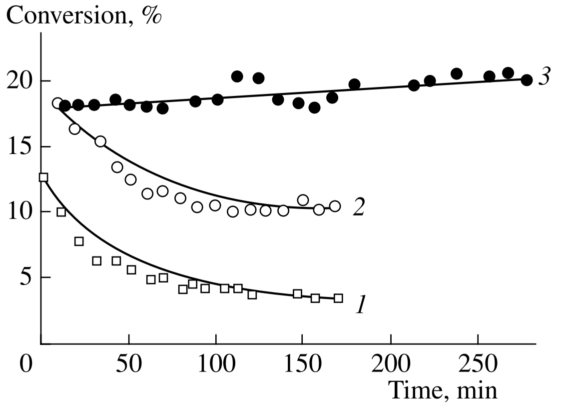

Fig. 5. Time dependence of the conversion of (*1*) gaseous *n*-butane at atmospheric pressure and (*2, 3*) supercritical *n*-butane at P = (*2*) 60 and (*3*) 110 atm over the $HSiWO/TiO_2$ catalyst. T = 260°C; VHSV = 2 h^{-1}.

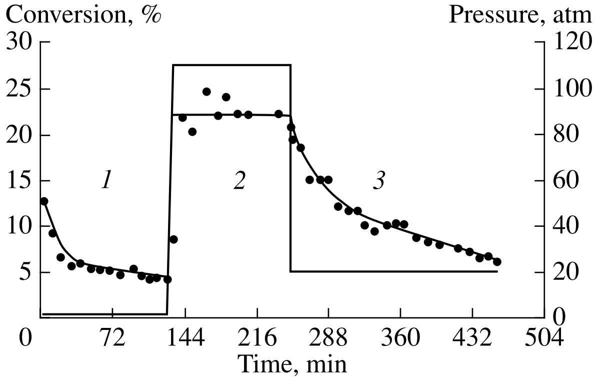

Fig. 6. Variations in *n*-butane conversion over HSiWO/TiO_2 caused by phase transitions of the reactants: (*1*) gas phase at 1 atm, (*2*) supercritical fluid at 110 atm, and (*3*) gas phase at 20 atm.

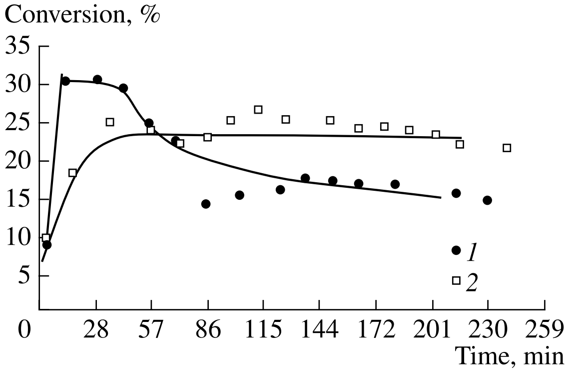

Fig. 7. Time dependence of the conversion of (*1*) gaseous *n*-butane at 20 atm and (*2*) supercritical *n*-butane at 138 atm over H-mordenite at 300°C.

tivation at any density of the supercritical medium. This discrepancy is possibly due to the very low conversion in their experiments.

If, after the HSiWO/TiO_2 catalyst is deactivated in the gas medium, the reaction is carried out under supercritical conditions at the critical density of the medium, the catalyst shows a much higher activity (Fig. 6). Again, this behavior of the catalyst is apparently due to the fact that the supercritical fluid dissolves the densification products that have resulted from the reaction in the gas medium, and removes them from the surface. Note that repeated changeovers between gaseous and supercritical *n*-butane gradually deactivate the catalyst. This can be due to the multiplicity of densification products adsorbed on the catalyst surface and the different solubilities of these products in the supercritical fluid.

Complicated behaviors are also shown by the isomerization of gaseous *n*-butane at 20 atm and supercritical *n*-butane over H-mordenite (Fig. 7). The region of stable performance of this catalyst under supercritical conditions is less pronounced than that of HSiWO/TiO_2. Raising the reaction temperature to 300°C reduces the isobutane selectivity through acceleration of cracking reactions.

CONCLUSIONS

The results of this work point out the marked difference between heterogeneous catalytic *n*-butane isomerization reactions under ordinary and supercritical conditions.

Hydrocarbon dehydrogenation on the catalyst surface and the oligomerization of the resulting unsaturated compound deactivate the catalyst. The extended lifetime of the catalyst under supercritical conditions is due to the unique capability of the medium to dissolve coke precursors and, thereby, prevent surface carbonization. A catalyst deactivated in a gas medium is reactivated in a supercritical medium owing to the mutual effect of the supercritical reactant and the catalyst in the acid-catalyzed reaction. The most effective removal of densification products takes place when the fluid density is equal to the critical density. Under these conditions, catalysts can be reactivated to a considerable or even full extent. This finding is of particular importance for catalysts that do not tolerate standard regeneration in flowing air at 550–650°C, undergoing destruction.

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