Isobutane Alkylation with Butenes and the Oligomerization of C_4 Olefins in Supercritical Reagents

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Abstract—The competing reactions of isobutane alkylation with butenes and butene oligomerization under supercritical and ordinary gas–liquid conditions are studied over a variety of catalysts: sulfated zirconia, titania-supported heteropolyacids and tungstia, and chlorinated aluminum–platinum catalyst. Both reactions proceed rapidly, showing no substantial decrease in catalytic activity, under supercritical conditions at 140–165°C and 40–45 atm. By contrast, alkylation and oligomerization in the liquid phase and particularly in the gas phase are accompanied by a rapid deactivation of the catalyst. Passing from ordinary gas–liquid conditions to supercritical conditions dramatically accelerates the reaction and the regeneration of the deactivated catalyst. Reaction selectivity depends significantly on the isobutane/olefins (butenes) (I/Ol) ratio in the initial mixture. At I/Ol = 14, isobutane alkylation with butenes is the main reaction pathway, which results in the complete conversion of the butenes to C_8 alkylation products. The yield of saturated isoalkanes is as high as 70%. Reducing the I/Ol ratio to 0.5 results in the domination of butenes over alkylation.

The problem of producing antiknock motor fuels from petroleum feedstock is solved in several ways: isomerization of normal C_6–C_8 alkanes to isostructural hydrocarbons, reforming of hydrocarbons to aromatic compounds, and introduction of oxygen-containing compounds such as MTBE, ETBE, DME. However, in the United States, as in countries of the EU and of Southeast Asia, the concentration of both oxygen-containing compounds and aromatic compounds, especially benzene, are stringently restricted by state environmental standards. Therefore, the main avenue in the production of components antiknock fuel is the synthesis of isoparaffins, particularly by means of the alkylation of light isoparaffins with olefins.

At present, isobutane alkylation with butenes is industrially carried out in the liquid phase with the use of concentrated sulfuric acid or liquefied hydrogen fluoride as catalysts. The stricter legislation requires the replacement of these catalysts with those that are more environmentally friendly. For this reason, heterogeneous catalytic systems for the commercial manufacture of the C_6–C_8 isoparaffins by the alkylation of light isoparaffins with olefins have been intensively sought over the last three decades.

The main disadvantage of the solid acid–catalyzed alkylation is rapid catalyst deactivation by heavy unsaturated products. These products are formed through olefin oligomerization competing with alkylation and are strongly adsorbed on the catalyst surface. This is responsible for the low productivity of the heterogeneous catalysts per cycle between regenerations.

A possible way of reducing the poisoning of the heterogeneous alkylation catalysts by condensation products is to perform alkylation under supercritical conditions. The properties of supercritical fluids (SCF) have been actively studied in the last 10–15 years. The density, viscosity, and diffusivity of SCFs are intermediate between the corresponding properties of gases and liquids. The unlimited mutual miscibility of reagents and reaction products in the supercritical state, as well as the dissolution of deposited coke precursors in SCF, markedly lengthens the lifetime of catalysts between their regenerations.

Most supercritical catalytic reactions have been studied in CO_2 and propane as the supercritical solvents [1–4]. The critical parameters of carbon dioxide are 31.2°C and 72.8 atm, and those of propane are 96.8°C and 41.9 atm. These characteristics cover the entire region of the most important reactions of hydrocarbons. Therefore, use of these materials as supercritical solvents is quite reasonable. At the same time, use of these supercritical solvents in large-scale commercial processes is economically unfeasible. A more feasible alternative is the use of the reagents themselves, for instance, butane and butene as supercritical solvents. As was shown in our previous studies [5–8], this presents a real opportunity.

The purpose of this work is to compare isobutane alkylation with butenes over heterogeneous acid catalysts under both supercritical conditions and the same process in the gas or liquid phase. Such studies have rarely been undertaken. We found only a few works on alkylation in supercritical reagents over zeolites [9, 10],

sulfated zirconia–based catalysts [11], and heteropoly-acids [12].

EXPERIMENTAL

Catalysts

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

The heteropolyacids $H_4[SiW_{12}O_{40}] \cdot xH_2O$ (HSiWO) and $H_3[PW_{12}O_{40}] \cdot xH_2O$ (HPWO) (MERCK) were supported on TiO_2 (Degussa) by incipient-wetness impregnation to the extent of 20 wt %. The catalysts were calcined at 340°C in flowing dry air for 2 h (heating rate, 2 K/min). They were activated *in situ* in flowing helium for 1 h at 200°C before each run.

The catalyst 15% WO_3/TiO_2 was prepared by incipient-wetness impregnation of TiO_2 (Degussa) with an aqueous solution of $(NH_4)_2WO_4$ followed by calcination in flowing air at 300–600°C for 10 h.

Platinum on chlorinated alumina (0.5% Pt/γ-Al_2O_3-Cl), a bifunctional catalyst, was prepared by the incipient-wetness impregnation of a chlorinated support with chloroplatinic acid and was then activated in flowing hydrogen at 450°C for 2 h. The catalytic activity of the LaCaHX catalyst prepared by ion exchange between zeolite HCaX and an aqueous solution of lanthanum(III) nitrate was also estimated.

Catalytic Measurements

Catalytic experiments were performed in a flow reactor. The liquid mixture of hydrocarbons was fed with a VHSV of 1–8 h^{-1}. A schematic of this setup is presented in an earlier publication [7].

The reaction products of isobutane alkylation with butenes and of butene oligomerization were analyzed on-line on two chromatographs. The composition of the original mixture and the conversion of the original compounds (the consumption of C_4 olefins and isobutane) were determined using a 3-m-long column packed with Celite C-22 and PPMS as the stationary phase. The original butane–butene mixtures and reaction products were simultaneously analyzed using a 50-m-long capillary column packed with SE 54. Some catalysate samples were analyzed by chromatomass spectrometry.

To study isobutane alkylation with butenes and the oligomerization of C_4 olefins, we prepared mixtures with different isobutane/butenes ratios (I/Ol). Table 1 presents the compositions of three butane–butene mixtures. The main component of mixtures **2** and **3** was

Table 1. Butane–butene mixtures of alkylation and oligomerization

Component	Composition, %		
	1	**2**	**3**
Isobutane	31.1	85.5	92.8
n-Butane	7.8	1.4	0.7
Isobutene	17.6	1.9	0.9
Butene-1	13.1	10.7	5.4
Butene-2	28.4	0.5	0.2
ΣC_5	2.0	–	–
I/Ol	0.5 : 1	6.5 : 1	14 : 1

Table 2. Critical temperatures, pressures, and densities of the components of the C_4 mixtures and some C_8 hydrocarbon isomers [13]

Hydrocarbon	T_c,°C	P_c, atm	ρ_c, g/cm^3	$\rho_{(293 K)}$
C_4				
isobutane	135.1	36.0	0.221	0.557
n-Butane	152.2	37.5	0.227	0.579
Isobutene	144.9	39.5	0.234	0.594
Butene-1	146.6	39.7	0.233	0.595
cis-Butene-2	162.6	41.5	0.239	0.621
trans-Butene-2	155.6	40.5	0.235	0.604
C_8				
n-Octane	295.8	24.5	0.232	0.703
2,2,3-Trimethylpentane	290.4	26.9	0.261	0.716
Octene-1	293.6	25.9	0.241	0.715

isobutane, whose content was 85.5 and 93 vol %, respectively. These isobutane-rich mixtures were used in the study of the alkylation reaction. Furthermore, these mixtures contained butene-1, whose amount in mixture **2** was 11%. The isobutene content was lower than 2%, and the total amount of *cis*- and *trans*-butene-2 was only 0.5%.

The component ratio in mixture **1** was different from the component ratios in mixtures **2** and **3**: the total amount of isobutane and *n*-butane in mixture **1** was 40%. This mixture was used in the study of catalytic butene oligomerization competing with alkylation. Equal volumes of the butene isomers were present in this mixture.

Reference critical parameters of the components of these mixtures are listed in Table 2.

The critical temperatures of butenes are 145–160°C, and *cis*-butene-2 has the highest critical temperature of 162.6°C. The critical temperatures of normal butane and isobutane are somewhat lower, specifically, 135 and 152°C.

Reduced density of isobutane
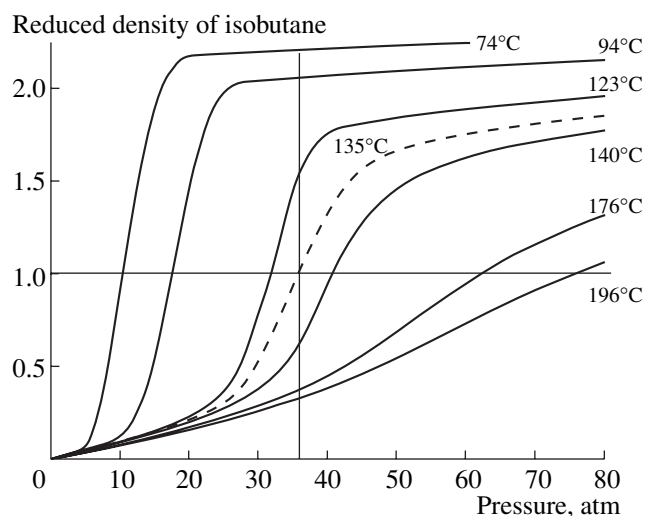
Fig. 1. Pressure-dependent isotherms of the reduced density of isobutane.

Isobutane alkylation and the oligomerization of C_4 olefins in mixtures **2** and **3** proceed in excess isobutane at any conversion. Therefore, alkylation conditions should be primarily chosen with regard for the critical parameters of isobutane. The isotherms of the reduced density of isobutane, $\rho_r = \rho/\rho_c$, calculated from the three-parameter Pitzer correlation [13] are listed in Fig. 1. As was shown in [3–9], the temperatures and pressures most appropriate for supercritical substrates are those at which the density of the medium is equal to or approaches its critical value. In Fig. 1, these conditions are defined by the intersection of the $\rho_r = 1$ line with the above-critical (>135°C) isotherms of the reduced densities of isobutane (dotted line). For this reason, we examined isobutane-rich mixtures (**2, 3**) at a fixed temperature (140°C) and pressure (40 atm). These reaction parameters differ only slightly from the critical parameters of isobutane (135.1°C, 36 atm).

The pseudocritical characteristics of the original mixture **1** (Table 1) calculated from the three-parameter state equation for mixtures [13] are 139°C and 38 atm. However, when choosing experimental conditions, it is necessary to take into account that considerable amounts of oligomerization products of C_5–C_{12} butenes are formed at high conversions of C_4 hydrocarbons. Simple calculations show that the volume of the mixture will be reduced at most by one-fourth at 60–80% butene conversion. The mole fraction of reaction products can reach 20%. From the highest critical temperature of butenes (162.6°C for *cis*-butene-2) and the critical parameters of the reaction products (Table 2), it is clear that the supercritical process involving mixture **1** can be carried out at a temperature of at least 165°C and a pressure of 45 atm, and it is these parameters that were set in our experiments.

When the isobutane/butenes ratio is 14, mixture **3** is alkylated rapidly over sulphated zirconia and supported HSiWO and HPWO (Fig. 2) and the conversion of initial butenes is close to 100%. By contrast, the conversion of butenes over WO_3/TiO_2 does not exceed 20% under comparable conditions. Under supercritical conditions (140°C and 40 atm), the butene conversion in the alkylation and oligomerization reactions over all catalysts did not decrease for 5–10 h.

By contrast, these catalysts are rapidly deactivated and exhibit a low steady-state activity when the reac-
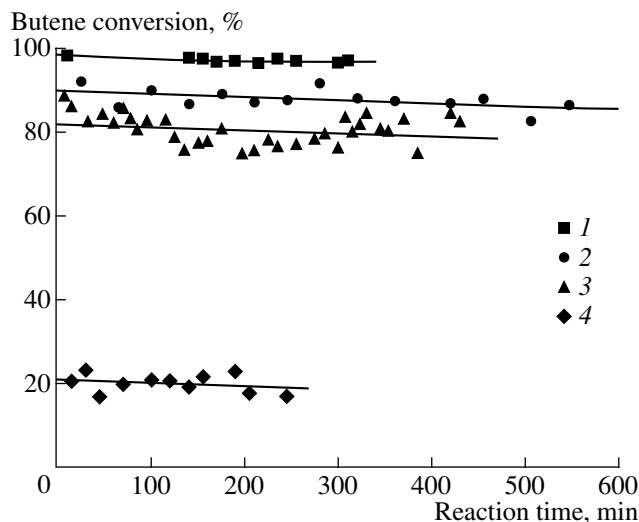
Fig. 2. Conversion of butenes in isobutane alkylation with butenes under supercritical conditions (140°C, 40 atm, VHSV = 3 h^{-1}, and I/Ol = 14) over (*1*) SO_4^{-2}/ZrO_2, (*2*) HSiWO/TiO$_2$, (*3*) HPWO/TiO$_2$, and (*4*) WO$_3$/TiO$_2$.
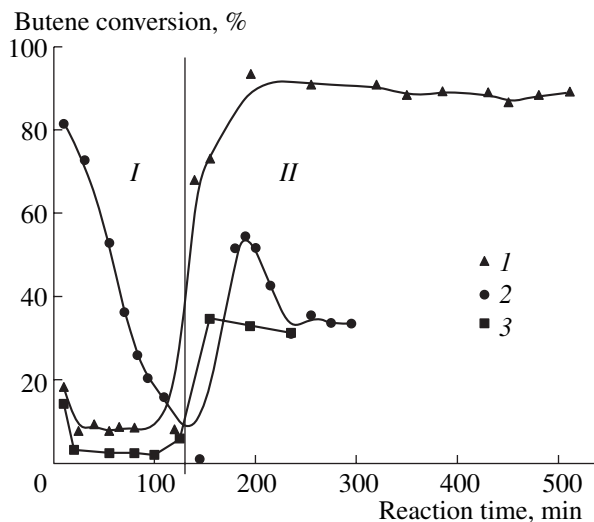
Fig. 3. Conversion of butenes in isobutane alkylation with butenes at I/Ol = 6.5 and a liquid VHSV of 2 h^{-1} (*I*) in the liquid phase at 80°C and 40 atm and (*II*) under supercritical conditions at 140°C and 40 atm over the catalysts (*1*) HSiWO/TiO$_2$, (*2*) LaCaX, and (*3*) Pt/γ-Al$_2$O$_3$-Cl.

tion is performed in the liquid phase at 80°C and an I/Ol ratio of 6.5 (Fig. 3). Passing to supercritical conditions enhances the activity and performance stability of the catalysts. The activity of the supported heteropolyacid-based catalyst is higher than that of the zeolite catalyst and the bifunctional system of platinated chlorinated alumina. Moreover, as is seen in Fig. 3, in the case of the HSiWO/TiO$_2$ catalyst, raising the temperature from 80 to 140°C at a constant pressure of 40 atm results in a liquid-to-supercritical phase transition in the reaction system. This transition favors the regeneration of the deactivated catalyst. Under supercritical conditions, the activity of the catalyst is much higher its initial activity and persists for a long time.

A similar effect was observed for the olefin-rich mixture **1**, in which the trimers, tetramers, and heavier unsaturated oligomerization products formed, at reduced pressures of 2 and 20 atm and 165°C, and rapidly poisoned the WO$_3$/TiO$_2$ catalyst (Fig. 4). On passing to supercritical conditions, the catalyst was regenerated and its activity was stabilized at a high level for a long time.

Table 3 lists experimental product composition data for alkylation and oligomerization under the supercritical conditions, illustrating their dependence on reaction conditions and the isobutane/butenes ratio. Note that the conversion of butenes over all catalysts under the above supercritical conditions is higher than 90%. Isomeric paraffins and olefins also contribute to the total yield of C$_{5+}$ products. The proportions of saturated and unsaturated hydrocarbons depend essentially on the isobutane/butenes ratio.

It is this ratio that determines the process pathway. At I/Ol = 14, the total isomeric alkane content of the product is 65–72%. This indicates the domination of the isobutane alkylation with butenes. The selectivities of sulfated zirconia and heteropolyacid catalysts toward C$_8$ alkylation products are 69 and 75% at a butene conversion of 98 and 90%, respectively.

A decrease in the isobutane concentration in mixture **2** (I/Ol = 6.5) results in a decrease in the rate of isobutane alkylation with butenes and in an increase in the yield of butene oligomerization products. The total yield of unsaturated olefin isomers exceeds 50%. The
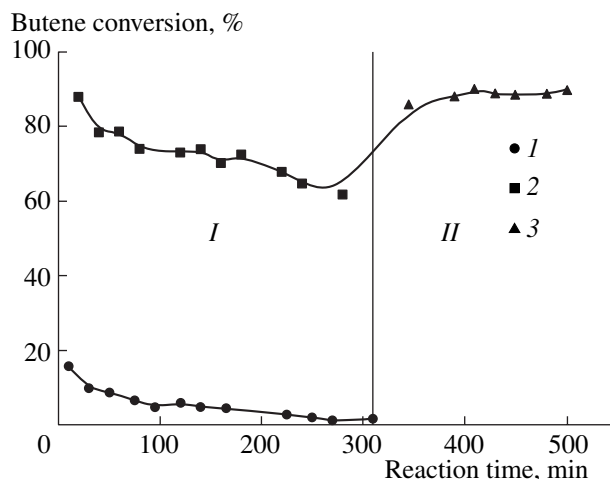
Fig. 4. Oligomerization of butenes under (*I*) gas-phase and (*II*) supercritical conditions over WO$_3$/TiO$_2$ at I/Ol = 0.5, a liquid VHSV of 2 h^{-1}, 165°C, and pressures of (*1*) 2, (*2*) 20, and (*3*) 45 atm.

yield of the dimerization products also decreases substantially. At a butene conversion of 89%, selectivity to C$_8$ dimers is slightly above 50% (56.4%). By contrast, selectivity to C$_{9+}$ oligomers increases to 36.8%.

As I/Ol is decreased from 6.5 or 14 to 0.5, the oligomerization of butenes to isomeric octenes and C$_{9+}$ olefins at 165°C and 45 atm becomes the prevailing reaction. The amount of saturated hydrocarbons do not exceed 10%. Butene conversion over the heteropolyacid catalyst reaches 96–100%, producing equal amounts of dimeric and C$_{9+}$ olefins. As the VHSV of the liquid feedstock is increased, other conditions being equal, the yield of the products of cracking of C$_{5–7}$ oligomers decreases. The catalyst WO$_3$/TiO$_2$ is less active as compared to the supported system HSiWO/TiO$_2$. The C$_4$ olefin conversion over this catalyst is 85% at the minimum space velocity (2 h^{-1}), but the selectivity to isomeric octenes is higher than 50%.

The process can be optimized to enhance the selectivity towards either the alkylation or the oligomerization of C$_4$ hydrocarbons, depending on the preference.

Table 3. Proportions of alkylation and oligomerization products under supercritical conditions

Catalyst	VHSV, h^{-1}	I/Ol	T, °C	P, atm	Conversion C$_4^=$, %	Selectivity, wt %			C$_n$H$_{2n+2}$ content of the product, %
						C$_{5–7}$	C$_8$	C$_{9+}$	
SO$_4^{-2}$/ZrO$_2$	3	14 : 1	140	40	98	6.3	68.8	24.9	65.4
HSiWO/TiO$_2$	3	14 : 1	140	40	90	5.1	75.3	19.6	72.2
HSiWO/TiO$_2$	3	6.5 : 1	140	40	89	6.8	56.4	36.8	42.8
HSiWO/TiO$_2$	6	0.5 : 1	165	45	96	8.3	45.4	46.3	8.4
HSiWO/TiO$_2$	3	0.5 : 1	165	45	100	10.1	38.7	51.2	9.2
WO$_3$/TiO$_2$	2	0.5 : 1	165	45	85	8.5	52.3	39.2	5.8

Hence, this study of isobutane alkylation with butenes accompanied by butene oligomerization has demonstrated that supercritical conditions are superior to conventional gas-phase and liquid-phase conditions. In supercritical reagents, the heterogeneous catalysts studied are characterized by a high activity and stability. Moreover, passing from gas-phase or liquid-phase to supercritical conditions allows one to regenerate *in situ* deactivated catalytic systems and to achieve conversion levels typical of fresh catalysts.

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