Benzyl Sulfonic Acid Siloxane as a Catalyst: Oligomerization of Isobutene

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The application of benzyl sulfonic acid siloxane (BSS) for the oligomerization of isobutene and the scission of oligomers has been investigated. Under suitable reaction conditions (130°C, normal pressure) the conversion of isobutene is quantitative and yields 52 wt% of di-, 40 wt% of tri- and 3 wt% of tetraisobutene besides a maximum of 2 wt% of odd-numbered products, consisting of 5-, 7-, 9-, 11-, 13-, and 15-C atoms. At temperatures up to 200°C the conversion of isobutene decreases to 35% due to pseudoequilibria between the initial oligomerization products and their splitting products, yielding a ratio of oligomers of di : tri : tetraisobutylene of 130 : 40 : 1. Over a period of 120 h operation at 130°C the catalyst activity decreases by 50% due to partial loss of sulfonic groups and deactivation of some of the groups which remain. © 1985 Academic Press, Inc.

INTRODUCTION

The upgrading of C_4 cracking cuts of naphtha includes the separation of isobutene from *n*-butene. Because of their similar physical properties these two compounds are preferentially separated by the chemical conversion of isobutene, e.g., (*1–4*) hydration, oligomerization, methoxylation, polymerization, esterification, or reaction with heavy metals, phenols, hydrogen chloride, or hydrogen sulfide. In addition, physical operations such as azeotropic distillation and selective absorption, can be applied.
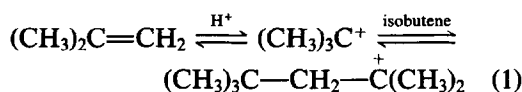
For the separation steps involving hydration, oligomerization, or methoxylation cationic ion-exchange resins based upon sulfonated styrene–divinyl benzene copolymers have proved to be satisfactory catalysts (*4, 5*). However, the thermal stability of the ion-exchange resins limits their application to about 130°C.

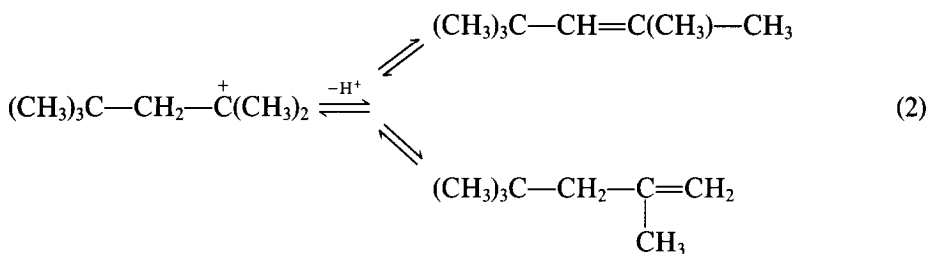The goal of our investigations is to find out whether the attachment of organic ion exchangers to silica as a support would produce a catalyst of higher temperature stability. From that point of view we decided to study benzyl sulfonic acid siloxane because the lowest dissociation energy of 440 kJ/mol given by the Si–C bond is relatively high. Zimmermann (*6*) was the first to attach benzyl sulfonic acid to silica by reacting benzyl sulfonic acid silanetriol with silica gel. The procedure is long term and yields products which are not reproducible. Good results are obtained, as we found, when trimethoxybenzyl silane, which is prepared by known methods (*7*) is reacted with previously activated silica and subsequently sulfonated.

Benzene sulfonic acid siloxane (BSS) proved to have a much higher temperature stability than ion-exchange resins (*8*). This fact opens the investigation of BSS as an acidic catalyst for reactions above 130°C.

The following contribution deals with the oligomerization of isobutene and the splitting of the oligomers on BSS as a catalyst. Both reactions proceed via the carbenium ion mechanism (*9–11*):

$$(CH_3)_2C{=}CH_2 \xrightleftharpoons{H^+} (CH_3)_3C^+ \xrightleftharpoons{\text{isobutene}}$$
$$(CH_3)_3C{-}CH_2{-}\overset{+}{C}(CH_3)_2 \quad (1)$$

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$$(CH_3)_3C—CH_2—\overset{+}{C}(CH_3)_2 \underset{}{\overset{-H^+}{\rightleftharpoons}} \begin{cases} (CH_3)_3C—CH=C(CH_3)—CH_3 \\ \\ (CH_3)_3C—CH_2—\underset{|}{C}=CH_2 \\ \qquad\qquad\qquad CH_3 \end{cases} \qquad (2)$$

The equilibria are determined by the reaction conditions and the stability of the carbenium ion (*12, 13*).

In the technical process the oligomerization of isobutene is performed at about 100°C and under 20 bar pressure on an ion-exchange resin (Lewatit SC 104)[2] as a catalyst, resulting in a ratio of di- to triisobutene of 1.5 (*3, 4*). The splitting of the oligomers proceeds thermally in the temperature range 250–450°C (*1*). The reaction conditions can be reduced to 175–200°C by employing suitable catalysts (*14*). Besides the pure isobutene other olefinic compounds as well as saturated hydrocarbons are formed. In technical processes cracking catalysts of the zeolite type are used (*1*).

EXPERIMENTAL

Preparation and Characterization of BSS

Technical silica gel (e.g., 125 g) is activated by refluxing it with concd hydrochloric acid for about 4 h, filtered, washed until neutral with deionized water, and dried at 250°C. After cooling to about 100°C the silica gel is reacted with trimethoxybenzyl silane (TMBS), prepared from trichlorobenzyl silane (e.g., 25 g) and anhydrous methanol in (250 ml) anhydrous toluene.

The product is cooled to room temperature, filtered, washed with toluene/methanol (1 : 1 v/v), and dried at 120°C. The sulfonation is performed with 96% sulfuric acid at 80–90%. During sulfonation the temperature rises to about 100°C where it should remain for 3 h. The reaction mixture is cooled to room temperature, transferred

into (250 ml) 50% sulfuric acid, and diluted and washed with deionized water. The final product (BSS) is dried at 120°C.

The main and reproducible characteristic features of BSS are as follows (*15*): 0.68 mmol H^+/g (calculated from titration with NaOH to pH 6.8, and from elemental analysis, all values are in agreement within ±0.03%), moisture content 0.7 wt%, 3.0 mmol OH^-/g (calculated from the reaction with $LiAlH_4$ taking the water content into account, Hammett acidity $-6.2 > H_0 > -6.6$, indicator method), density 2.12 g/cm^3, bulk density 510–540 g/liter, pore volume 0.93 ml/g, surface (BET) 540 m^2/g, swelling behavior at room temperature: no swelling in water, methanol, benzene, toluene, alkanes, olefins, organic acids, and ethers. Thermal stability on heating under nitrogen: 240 h at 300°C gives no loss in capacity (calculated from titration and elemental analysis); 100 h at 350°C gives 5% loss of sulfonic acid groups; 70 h at 400°C completely destroys the product. A proposal for the structure of BSS (*15*) is based upon the quantitative analysis of the intermediates (Eq. (3)).

The activated silica gel (*a*) contains 3.1 ± 0.1 mmol OH^-/g. After the reaction with TMBS the product contains 1.7 ± 0.05 mmol OH^-/g which means that only 45% of the starting OH^- groups react with TMBS. From elemental analysis 6.57 ± 0.02 wt% of carbon are found; this is in agreement with 0.68 mmol benzyl groups/g (*b*), while structure *c* should contain 1.40 mmol benzyl groups/g. After hydrolysis of the intermediate a product (*d*) is obtained, which contains 2.4 ± 0.07 mmol OH^-/g. From these results it must be concluded that 1

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[2] Polystyrene sulfonic acid crosslinked with 4 wt% of divinyl benzene. (Bayer AG).

$$\text{(3)}$$
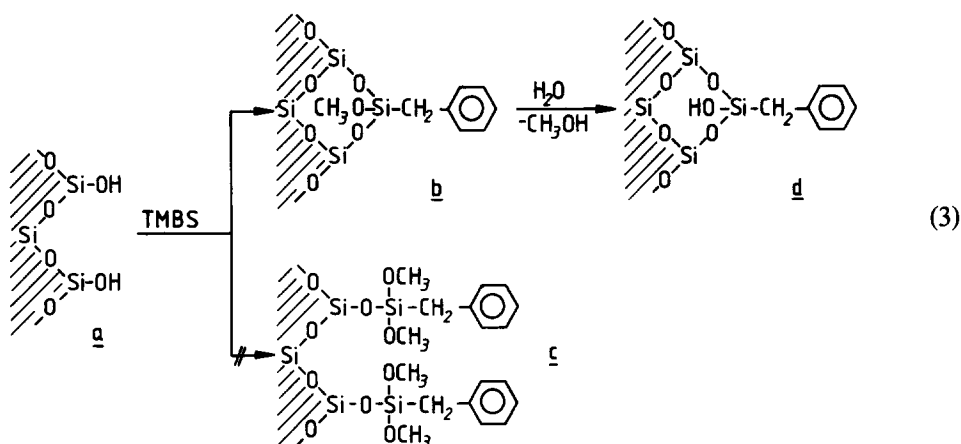
mol of TMBS reacts with two neighboring OH⁻ groups of silica gel. This is in agreement with the predictions of Peri and Hensley (16) and of Gallei (17) that the surface of silica gel predominantly contains paired silanol groups. These statements were confirmed by Unger and Gallei (18) who found that trichlorobenzyl silane is bifunctionally bound to silica gel surfaces.

Oligomerization of Isobutene

The experiments were performed with isobutene of >99.5% purity (technical grade) in a tubular fixed-bed reactor at normal pressure with variation of the temperature, residence time, and reaction time. Previously heated (preheater) isobutene from a pressure storage vessel was passed into the reactor and subsequently the reaction mixture was cooled to −60°C. The condensed phase was fractionated by distillation and the fractions were analyzed by gas chromatography and by the coupling of GC and MS. The gaseous phase was analyzed separately. All reaction products were identified by authentic samples of at least 99% purity.

Table 1 shows a typical range of the fractions and the main components of a typical oligomerization product.

Splitting of Oligomers

Method and Equipment. Diisobutylene and triisobutylene were used as starting materials. These products were obtained from the fractional distillation of the oligo-

TABLE 1

Typical Boiling Range and Main Components of Oligomers from Isobutene

Oligomer	Boiling range (°C)	Main components	Weight (%)
Diisobutylene	100–110	$CH_2{=}C(CH_3){-}CH_2{-}C(CH_3)_3$	74
		$(CH_3)_2C{=}CH{-}C(CH_3)_3$	21
Triisobutylene	175–183	$(CH_3)_3C{-}CH_2{-}\underset{\parallel}{C}{-}CH_2{-}C(CH_3)_3$ CH_2	34
		$(CH_3)_3C{-}CH{=}C(CH_3){-}CH_2{-}C(CH_3)_3$	52
Tetraisobutylene	230–235	$(CH_3)_3C{-}CH_2{-}\underset{\mid}{C}{=}CH{-}C(CH_3)_2{-}CH_2{-}C(CH_3)_3$ CH_3	38

merization products of isobutene. Each fraction had a minimum purity of 97%.

The experiments were performed in the same equipment which was used for the oligomerization reactions with the exception that a metering pump was used for filling the preheater.

Analysis. GC analysis was performed under the following conditions: Carlo Erba, Fractovap, Ser. 2150. Program: LT-Prog. Model 232, electrometer 180, integrator Spectra Physics Computing Integrator Autolab System I, recorder Leeds, and Northrup Speedomax.

Column: OV 101, 100-m capillary; temp. 70–200°C; temp. program: 70–140°C, 10-min isotherm at 70°C, heating rate 10°C/min; 140–200°C, 5-min isotherm at 140°C, heating rate 10°C/min; injector temperature 225°C, injection volume 0.5 μl, carrier gas pressure 200 kPa N_2, postaccelerator 180 kPa N_2, detector FID, 100 kPa H_2, 150 kPa air.

C_4 components were analyzed under the following conditions: column: 80/100 Carbopack C/O, 19% picric acid, 2.2-m glass capillary, temp. 30°C, injection temp. 125°C, injection vol. 50 μl gaseous, carrier gas pressure 300 kPa N_2, detector FID, 100 kPa H_2, 150 kPa air.

GC/MS analysis. Chromatograph: Varian 1400, modified for GC/MS coupling.

Mass spectrometer: Varian MAT 311 A. Conditions for GC: column OV 101, 100-m capillary, temp. 60–200°C, heating rate 4°C/min, injection temp. 215°C, injection volume 1.0 μl, carrier gas pressure 200 kPa He, detector FID, electron energy 20 eV. Conditions for MS: electron emission 1000 μA, electron energy 70 eV.

RESULTS AND DISCUSSION

Product Distribution of Oligomers Dependent on the Reaction Temperature and the Residence Time

In a preliminary investigation we observed that, because of the exothermic reaction (54 kJ/mol) and the high activity of BSS, the oligomerization of isobutene in the tubular fixed-bed reactor proceeds to a maximum pseudoequilibrium at 120–140°C without any addition of energy, when the space velocity equals 4 liters/g · h. For further experiments concerning the variation of the reaction temperature and the space velocity, instead of cooling the reactor the catalyst was homogenously mixed with silica, which is known to be catalytically inactive in the oligomerization of isobutene within the temperature under investigation (*19*). By this procedure the conversion of isobutene is reduced but local overheating is avoided.

TABLE 2

Temperature Dependence of the Oligomerization Products of Isobutene[a]

Temp. (°C)	Conversion (wt%)	Product distribution[b] (wt%)						
		C_4	C_{5-7}	C_8	C_{9-11}	C_{12}	C_{13-15}	C_{16}
50	20	80.0	—	0.4	—	17.1	—	2.5
80	68	32.0	0.2	12.1	—	50.7	—	4.6
110	95	5.0	0.3	38.9	0.5	50.6	0.5	3.4
130	97	3.0	0.8	52.1	0.7	39.6	1.0	2.8
150	85	15.0	1.6	41.7	1.1	32.4	2.6	2.4
200	35	65.0	0.2	26.2	—	7.6	0.1	0.2
250	3.8	96.2	—	3.6	—	0.2	—	—

[a] Conditions: Reaction temperature, 50–250°C; 1 g of catalyst + 1 g of silica; isobutene (>99.5% purity); normal pressure.
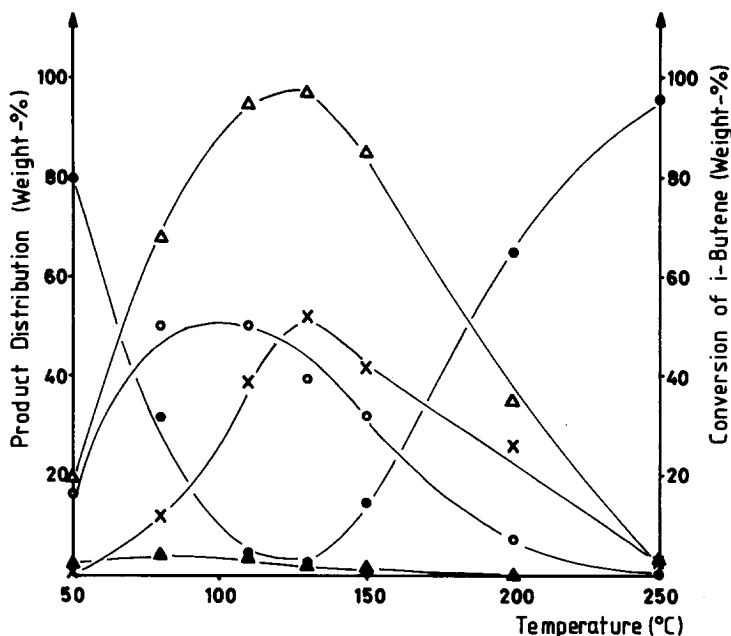[b] Calculated for isobutene input.

FIG. 1. Conversion of isobutene and product distribution of the oligomerization of isobutene as a function of temperature. ($\triangle$) Conversion, ($\bullet$) isobutene, ($\times$) di-, ($\bigcirc$) tri-, ($\blacktriangle$) tetraisobutylene.

The temperature-dependent results of the oligomerization of isobutene at a constant space velocity are summarized in Table 2. This dependence is graphically shown in Fig. 1. The maximum conversion of 97% is obtained at 130°C, yielding a mass ratio of di : tri : tetraisobutylene = 20 : 15 : 1.

With increasing temperature the conversion slows down as is to be expected from the exothermic oligomerization reaction. At 200°C the conversion of isobutene is 35% with a ratio of oligomers of di : tri : tetraisobutylene = 130 : 40 : 1. The amount of diisobutylene is essentially increased by the splitting of the higher oligomers at this temperature.

The fact that up to 100°C the formation of triisobutylene exceeds the formation of diisobutylene is in agreement with observations made by Güterbock (1). It should be mentioned that at normal pressure and up to 100°C the oligomers are in the liquid state. This favors the solubility of isobutene in the reaction mixture and thus the oligomerization reaction is accelerated. Beyond the boiling temperature of diisobutylene

(>110°C) this effect is reversed and the formation of higher oligomers is complicated. It must be stated that the results reflect the degree of approach to each of a large number of pseudoequilibria between the monomer, dimers, trimers, etc.

At the maximum conversion of isobutene the oligomerization product consists of 95% of the sum of di- and triisobutylene with a ratio of 1.3.

With decreasing residence time the conversion of isobutene is significantly reduced (Table 3); the increased formation of diisobutylene conforms to what is to be expected. Moreover, the portions of the splitting products such as $C_{5,7}$, $C_{9,11}$, and $C_{13,15}$ are diminished (Table 2).

Catalyst Lifetime

Data concerning the lifetime of the BSS catalyst in the oligomerization of isobutene were taken from a series of experiments at 130°C under normal pressure with 0.5 g of the catalyst mixed with 3 g of silica.

The time-dependent results are summarized in Table 4. For each run the reactor

TABLE 3

Oligomerization Products of the Isobutene Oligomerization as a Function
of the Residence Time[a]

ghsv[b] (liters/g · h)	Conversion[c] (wt%)	Product distribution[c,d] (wt%)						
		C_4	C_{5-7}	C_8	C_{9-11}	C_{12}	C_{13-15}	C_{16}
3	97	3.2	1.0	52.4	0.6	39.4	0.8	2.5
7	63	37.0	0.3	43.0	0.1	19.5	<0.1	<0.1

[a] Conditions: Reaction temperature 130°C; 1 g of catalyst + 1 g of silica; space
velocity, variable; isobutene (>99.5% purity); normal pressure.
[b] Calculated for 1 g of BSS.
[c] Calculated for isobutene input.
[d] Values from GC/MS analysis.

was filled with fresh catalyst. At the starting point the catalyst activity was 0.86 mol/g · h. By extending the time of operation a nonlinear loss of activity was observed. At the beginning the activity decreases by 50%

TABLE 4

Dependence of Catalyst Activity and Capacity on
Reaction Time[a]

Reaction time (h)	Activity (mol/g · h)	Capacity (mmol/g) from	
		Titration	S Analysis
1	0.86	0.62	0.63
19	0.86		
54	0.78	0.59	0.61
69	0.61		
74	0.57		
94	0.54		
120	0.43	0.49	0.54
165	0.39		
190	0.36		
216	0.32		
240	0.29		
260	0.32	0.34	0.39
332	0.29		
427	0.25		
457	0.21		
481	0.21		
592	0.18		
617	0.18		
761	0.14	0.10	0.16

[a] Conditions: Reaction temperature, 130°C; 0.5 g
catalyst + 3 g silica; ghsv 10 l/g · h; input, isobutene
(>99.5% purity); normal pressure.

during 120 h time of operation. Beyond this initial reaction time the catalytic activity is reduced with a half-life of about 350 h.

The catalyst activity does not exactly correlate with the ion-exchange capacity. This might be due to partial blocking of the sulfonic acid groups of the catalyst by esterification with isobutene. This assumption is confirmed by the fact that the acid–base titration yields a reproducible but lower value of capacity than would be expected from sulfur elemental analysis (Table 4). From these results it must be concluded that part of the sulfonic groups is lost from the catalyst phase and that part of the remaining anchor groups is deactivated, presumably by esterification, the esterification products being in a temperature-dependent equilibrium with the remaining reaction components. This effect is already known from the literature (20).

Product Distribution (Selectivity)
Dependent on the Catalyst Activity

From the reaction compositions which were obtained from the lifetime measurements (Table 4) it is possible to calculate the selectivity of oligomerization products as a function of the catalytic activity of the catalyst. Several values which correspond to significant activities are given in Table 5. The results show that with decreasing activity the splitting processes are obviously

TABLE 5

Product Distribution as a Function of the Catalyst Activity[a]

Activity (mol/g · h)	Conversion (wt%)	Product distribution (wt%)						
		C_4	C_{5-7}	C_8	C_{9-11}	C_{12}	C_{13-15}	C_{16}
0.86	97	3.0	0.3	22.3	0.8	64.4	0.4	8.8
0.42	63	37.0	0.2	21.8	0.1	38.0	0.3	2.4
0.24	30	70.0	<0.1	16.3	<0.1	13.3	<0.1	0.2
0.16	18	82.0	—	11.0	—	6.8	—	0.1

[a] Conditions and activity values from Table 4.

reduced. At the same time the amount of diisobutylene is increased in relation to the formation of triisobutylene. The total conversion of isobutene is diminished, as is to be expected.

Splitting of Diisobutylene Dependent on the Temperature

Although the splitting of the oligomer, indicated by the formation of isobutene monomer, becomes obvious above 50°C (Table 6), the amount of diisobutylene is already significantly reduced at room temperature. This loss is due to the formation

of tetraisobutylene which is formed by the dimerization of diisobutylene. Above about 75°C tetraisobutylene is split. Within the range 75–100°C a significant increase of triisobutylene is observed. This effect can be explained by the fact that triisobutylene is formed by the scission of tetraisobutylene to triisobutylene and isobutene; isobutene also reacts readily with diisobutylene to give triisobutylene. Above 100°C the triisobutylene is split into diisobutylene in growing amounts. Thus a decrease of conversion of the starting material is simulated. A significant increase of isobutene formation is observed at temperatures higher than 150°C.

TABLE 6

Temperature Dependence of the Product Distribution from the Splitting of Diisobutylene[a]

Temperature (°C)	Conversion[b] (wt%)	Product distribution[c] (wt%)			
		C_4	C_8	C_{12}	C_{16}
20	12	—	86	2	12
35	19	—	79	2	19
50	24	1	74	2	23
75	33	3	65	4	28
100	54	7	44	33	16
125	45	13	53	27	5
150	41	18	57	23	2
200	43	37	56	7	—
250	61	63	37	<1	—

[a] Conditions: Reaction temperature, 20–250°C; 3 g catalyst; lhsv 3.5 g/g · h. Starting material: mixture of >97% diisobutylene and 2% triisobutylene, normal pressure.
[b] Calculated for the input of diisobutylene.
[c] Calculated for the sum of C_4–C_{16} products.

TABLE 7

Temperature Dependence of the Product Distribution from the Splitting of Triisobutylene[a]

Temperature (°C)	Conversion[b] (wt%)	Product distribution[c] (wt%)			
		C_4	C_8	C_{12}	C_{16}
25	<2	—	1	98	—
50	3	1	2	97	—
80	23	4	7	77	12
100	29	7	15	71	7
150	71	30	39	29	2
200	79	34	45	21	—
250	84	44	40	16	—
300	87	70	17	13	—

[a] Conditions: Reaction temperature, 25–300°C; 3 g catalyst; lhsv 3.5 g/g · h. Starting material: >99% triisobutylene, normal pressure.
[b] Calculated for the input of triisobutylene.
[c] Calculated for the sum of C_4–C_{16} products.

Within the range 150–200°C a mixture of monomers of C_3 and C_4 hydrocarbons is obtained which contains 99.5% isobutene.

Splitting of Triisobutylene Dependent on the Temperature

Table 7 summarizes the results obtained by the splitting of triisobutylene. The observations are close to what is observed with diisobutylene as a starting material. Within the range 50–200°C a trivial formation of diisobutylene takes place. The conversion increases, as is to be expected, with increasing temperature. The formation of C_{16} hydrocarbons, which is observed at 80–150°C, disappears at higher temperatures in favor of a temperature-dependent equilibrium of isobutene, di-, and triisobutylene.

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