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Influence of Process Variables on the Continuous Alkylation of Isobutane with 2-Butene on Superacid Sulfated Zirconia Catalysts

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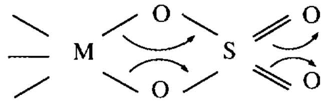
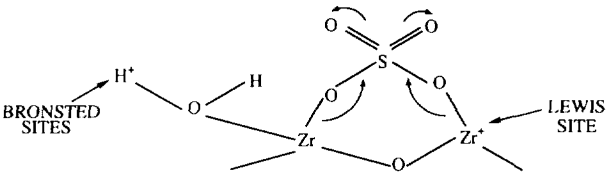
Two sulfated zirconia catalysts have been prepared by impregnation of zirconium hydroxide with H_2SO_4 0.3 *N* and 1 *N*. Both samples showed superacid sites as shown by a desorption temperature peak in the NH_3 TPD at ca. 813 K. The activity and selectivity of these catalysts have been studied for the alkylation of isobutane with *trans*-2-butene in a computer-controlled continuous fixed bed reactor coupled with a sampling system which allows to make differential analysis of the products from very short reaction times. In this way, the influence of the main process variables, i.e., time on stream, reaction temperature, olefin WHSV, and isoparaffin/olefin ratio, on the 2-butene conversion and product distribution has been investigated. Cracking of larger carbocations and alkylation of isobutane with 2-butene to give trimethylpentanes were the predominant reactions occurring on the superacid catalyst in the initial stages of the reaction. The alkylation/cracking ratio increased when decreasing reaction temperature. A fast catalyst decay with time on stream was also observed, and this was accompanied by an increase in the oligomerization of butene. © 1994 Academic Press, Inc.

INTRODUCTION

Replacement of homogeneous liquid by solid acid catalysts is highly desired, not only by the easier separation of the catalyst from the reaction products, but also from an environmental point of view. After the success of zeolites as acid catalysts with medium-strong acidity, research has been focused on the preparation and characterization of solid catalysts having a superacidic character. Superacids are considered to have an acidity higher than 100% H_2SO_4, i.e., a $H_0 \leq -12$ Hammet acidity function (1, 2) and can be prepared by several approaches (3): (1) liquid superacids supported on suitable carriers; (2) a combination of metal halides with inorganic salts (e.g., $AlCl_3$–$Ti(SO_4)_3$, $AlCl_3$–$CuCl_2$, . . .); (3) perfluorinated resin sulfonic acid (e.g., Nafion-H); and (4) sulfate-promoted metal oxides (e.g., SO_4^{2-}/ZrO_2, SO_4^{2-}/TiO_2, SO_4^{2-}/Fe_2O_3). Among these, sulfate-promoted metal oxides have been found to exhibit excellent catalytic properties for a number of acid-catalyzed hydrocarbon reactions (4). These catalysts, especially those of the sulfated zirconia type, are able to catalyze the isomerization of short linear alkanes at relatively low temperatures (below 150°C) (5–7). Even though it is accepted that the presence of sulfate species with covalent S═O bonds on the oxide surface is necessary to obtain superacidity (8), the exact nature of the catalytically active sites remains an open question in the literature. Thus, it is suggested that the superacid centers are Lewis sites associated to the metal cation (9), whose acid strength is strongly enhanced by an electron induction effect of S═O in the sulfur complex, as is shown in Scheme 1. Others (8, 10, 11) have suggested that the Lewis and Brønsted sites generated from adsorbed water molecules (Scheme 2) are responsible for the catalytic activity. These Brønsted sites are easily interconverted to Lewis sites by evacuation at temperatures above 150°C.



SCHEME 1



SCHEME 2

Consequently, the preparation and activation conditions of the SO_4^{2-}/ZrO_2 superacids greatly influence the catalytic properties of the material for the isomerization reaction (8, 10–12).

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Besides isomerization of short paraffins, alkylation of isobutane with light olefins is an important process in the refining industry to produce high-octane gasoline. Alkylation gasoline is highly desired for producing reformulated fuels owing to its high octane (both RON and MON) and its "clean" combustion. However, an increase in the alkylation capacity can only be expected if the commercially used liquid acids can be replaced by new solid noncontaminant acid catalysts. Among the different solid acids proposed as alkylation catalysts (13), zeolites have been, by far, the most studied in the past few decades (14–17). Zeolites were seen to give a high initial alkylation activity, but deactivation occurred rapidly after a few minutes time on stream (17, 18). At this later stage of the reaction, hydrogen transfer activity is very low and olefin oligomerization, giving mainly dimethylhexenes, predominates over true alkylation (17, 18).

When solid superacids were tried as alkylation catalysts, those of the sulfated zirconia type were seen to give the most promising results (19). Unfortunately, despite its potential interest, the data available in the open literature concerning the catalytic behavior of these materials in the alkylation reaction are very scarce (20, 21).

In this paper we report the influence of the main process variables, i.e., time on stream, reaction temperature, olefin space velocity, and isoparaffin/olefin ratio, on the activity and selectivity of sulfated zirconia superacids for the continuous alkylation of isobutane with 2-butene.

EXPERIMENTAL

Catalyst Preparation and Characterization

Sulfated zirconia (SZ) catalysts were prepared by impregnation of zirconium hydroxide with an aqueous solution (5 cm^3 per 1 g of zirconium hydroxide) of H_2SO_4 during 1 h, followed by filtration, drying at 393 K, and calcination at 823 K. This calcination was performed *in situ*, before the reaction, under 20 cm^3 min^{-1} of air during heating at 8 K min^{-1} until 823 K. This temperature was maintained for a period of 3 h, and then the air flow was shifted to nitrogen (50 cm^3 min^{-1}) while cooling the catalyst at the desired reaction temperature. In this way, two SZ samples were prepared using 0.3 *N* (sample SZ-I) and 1 *N* (sample SZ-II) H_2SO_4 solutions. The zirconium hydroxide was obtained by hydrolysis of $ZrOCl_2$ $8H_2O$ (Aldrich) with ammonium hydroxide (25 wt%, 5 cm^3 min^{-1}) by vigorous stirring at room temperature until the pH reached a value of 8.3. Then, the product was filtered, carefully washed until no Cl^- were detected, and finally calcined at 433 K overnight.

The X-ray diffraction (XRD) (40 KV, 40 mA, nickel filtered Cu*Kα* radiation) pattern of the zirconium oxide, obtained by calcination of the hydroxide at 823 K for 3 h, showed the presence of a nearly pure tetragonal crystalline phase.

The surface area of the catalysts was measured from the adsorption isotherms of N_2 at 77 K using the BET method in an ASAP 2000 (Micromeritics) equipment.

The sulfur content of the final catalysts was obtained by X-ray fluorescence (XRF) in an Outokumpu X-MET 840.

The acidity of the samples was measured by TPD of NH_3 on a 2900 TPD/TPR apparatus (Micrometritics). In a typical experiment, 200 mg of sample was pretreated first in O_2 flow at 823 K during 3 h, and finally in N_2 flow during 30 min. Then, the sample was saturated with NH_3 at 373 K and heated from 373 to 873 K in He flow, at a heating rate of 10 K min^{-1}. The amount of NH_3 desorbed was monitored with a TCD. Blank runs were performed under the same conditions but without any NH_3 adsorbed on the sample. The TPD diagrams of the two SZ samples, after substraction of the blank run, are shown in Fig. 1.

The physicochemical properties of the SZ catalysts are reported in Table 1.

Reaction System and Experimental Procedure

The alkylation experiments were carried out by feeding a mixture of isobutane (>99% purity) and *trans*-2-butene (>99% purity) to a fixed bed stainless steel reactor. The reactants were maintained in liquid phase in two separate vessels under nitrogen pressure, and fed to the reactor at the desired liquid feed rate by means of two piston-type pumps. All the experiments were performed at a total pressure of 2.5 MPa, and reaction temperatures ranging from 263 to 323 K. Under these reaction conditions reactants and products were in liquid phase. The stream coming out from the reactor was depressurized by means of a pressure controller needle valve, diluted with a nitro-

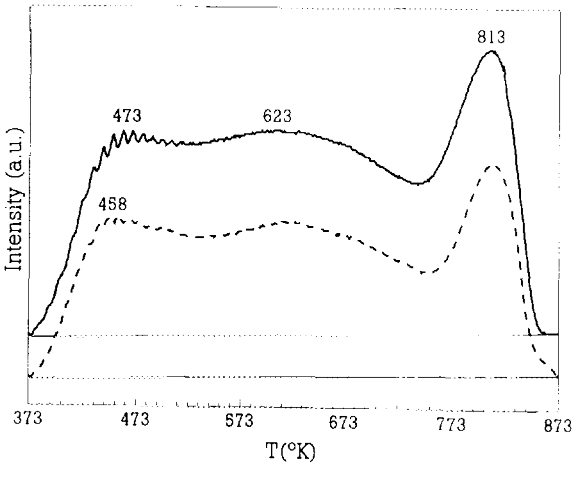

FIG. 1. TPD diagrams of desorbed NH_3 for the two superacid SO_4^{2-}/ZrO_2 samples treated with different H_2SO_4 concentrations: (—) 0.3 *N*; (---) 1 *N*.

TABLE 1

Physicochemical Properties of Sulfated Zirconia Catalysts

Sample	BET surface area (m^2 g^{-1})	Sulfur (wt%)	Tetragonal phase[a] (%)	Acidity (cm^3 NH_3 g^{-1})[b]			
				W	M-ST	VS	Total
SZ-I	148	2.6	99	2.1	8.9	2.3	13.3
SZ-II	132	2.5	99	1.4	8.4	1.6	11.4

[a] From XRD analysis.

[b] From TPD of NH_3 measurements. W, M-ST, and VS stand for acid sites of weak acidity, medium-strong acidity, and superacidity, respectively, calculated from deconvoluted TPD diagrams.

gen stream (50 cm^3 min^{-1}), and vaporized before going to a computer-controlled heated valve sampling system connected to a GC. In this way samples could be taken form very short (1 min) to longer times on stream at desired intervals, being automatically analyzed in the GC after the experiment was completed. Reactants and products were quantitatively analyzed in the GC using a FID detector after separation of the individual compounds in a 100-m capillary column (Fused Silica, Supelco). Individual C_1–C_8 hydrocarbons were identified by GC–MS and available standards. A more detailed description of the reaction system and experimental procedure can be found elsewhere (18).

The SZ catalysts were used "fresh" in all the experiments. Catalyst particles 0.59–0.84 mm in size, for which the process is not controlled by internal diffusion, were used. The catalysts were diluted with inert silica (50/50 w/w) before being introduced into the reactor. The influence of reaction temperature was studied using an isobutane/2-butene molar ratio of 15 (225 cm^3 h^{-1} isobutane and 13 cm^3 h^{-1} 2-butene) and an olefin WHSV of 2 h^{-1} (4 g SZ catalyst). The isobutane/2-butene ratio was changed between 2.6 and 15 by changing the isobutane flow rate, and the olefin WHSV was varied between 2 and 4 h^{-1} by changing the amount of catalyst in the reactor.

RESULTS AND DISCUSSION

Solid acid catalysts, such as zeolites (17, 18) and superacids (21, 22), undergo a fast deactivation with time on stream during the alkylation reaction. Thus, most of the results reported in the literature, and which were carried out in batch or semibatch reactors, are time-averaged, and are therefore masked by catalyst deactivation, making it quite difficult to discuss the intrinsic activity and selectivity of the catalysts. In addition, a direct comparison of catalysts showing different deactivation behavior can hardly be done when using averaged data. These problems can be solved by using a reaction-sampling system as the one used in this work, and which allows differential analysis of reactants and products from very short times on stream (TOS). On the other hand, analysis of the products at longer TOS allows a detailed study of the deactivation phenomena occurring during the alkylation process.

Following this methodology the catalytic performance of sulfated zirconia superacids will be discussed in the alkylation of isobutane with 2-butene under different reaction conditions.

The 2-butene conversion and product distribution obtained at 275 K on the two SZ samples treated with different acid concentration is reported in Table 2. It can be seen that sample SZ-II, obtained from the more concentrated H_2SO_4 solution, gives a slightly higher initial olefin conversion and cracking activity (C_5–C_7 products), and a lower oligomerization (C_{9+}). If one looks to the acidity results presented in Fig. 1 and Table 1, one can see that both catalysts have a similar TPD pattern. They show an intense high temperature TPD peak at ca. 813 K, which is associated to NH_3 adsorbed on superacid sites, and

TABLE 2

Influence of H_2SO_4 Concentration during the Preparation of SO_4^{2-}/ZrO_2 Catalysts on 2-Butene Conversion and Product Distribution at 275 K, Olefin WHSV = 2 h^{-1}, and i-C_4/2-$C_4^=$ Molar Ratio of 15 (TOS = 1 min)

Catalyst [H_2SO_4]	SZ-I [0.3 *N*]	SZ-II [1.0 *N*]
2-Butene conversion (wt%)	72.8	85.9
Distribution of C_{5+} (wt%):		
C_5–C_7	40.5	44.0
C_8	50.2	52.7
C_{9+}	9.3	3.3
Distribution of C_8s (wt%):		
TMP	92.0	92.8
DMH	6.0	4.7
Octenes	2.0	2.5
Distribution of TMPs (wt%):		
2,2,4-	49.8	52.2
2,2,3-	17.8	22.5
2,3,4-	13.1	10.2
2,3,3-	19.3	15.1

two broad less intense peaks at ca. 473 and 623 K corresponding to sites of weak and medium-strong acidity, respectively. However, we did not analyze the product desorbed at 813 K, and it may be that at this temperature decomposition of NH_3 already takes place (23). In any case, the results would indicate that on these samples part of the NH_3 was strongly retained at temperatures higher than mordenite (748 K), Beta (630 K), and ZSM-5 (683 K), which are the most acidic zeolites known. Then, it can be seen that sample SZ-I adsorbs a slightly higher amount of NH_3 and also has more superacid sites (Table 1). Indeed, this sample was seen to give a higher activity for the isomerization of *n*-butane as compared to the sample treated with H_2SO_4 1 *N* (12). The higher number of acid sites in sample SZ-I can be, in principle, attributed to a higher surface area of the zirconium oxide, as can be observed in Table 1. However, the results obtained here for the alkylation reaction indicate that the superacid sites of the sulfated zirconia catalysts are not the only active sites contributing to the observed olefin conversion (Table 1 and 2). This may be due to the different distributions in acid strength and type of acidity (Brønsted and Lewis), as well as to the broad range of reactions with different demands in acidity occurring during isobutane alkylation. Therefore, the fact that a direct relationship between the concentration of superacid sites (Brønsted plus Lewis), as measured by NH_3 TPD, and alkylation activity has not been observed is not surprising.

Table 2 also shows that very large amounts of cracked C_5–C_7 compounds are initially obtained on the two SZ catalysts even at the low reaction temperature used (275 K), while heavier C_{9+} products appear as a minority at this initial stage of the reaction. These results are in contrast with those recently reported by Liang and Anthony (20), in which cracked products are practically absent from the initial C_{5+} alkylate obtained from isobutane and 1-butene at 373 K reaction temperature on a sulfate-promoted zirconia catalyst. The authors also reported a higher initial yield of C_{9+} hydrocarbons than C_8 alkylated compounds. These results can be explained considering that the "initial" values reported by Liang and Anthony have already been taken when the catalyst has lost most of its alkylation activity, and consequently oligomerization of the olefin is the main process occurring on the partially deactivated catalyst.

From the results presented in Table 2 it can also be observed that the C_8 fraction is mainly formed by trimethylpentanes (TMPs), which are the primary products in the alkylation of isobutane with 2-butene, according to

$$\text{t-}C_4^+ + \text{2-}C_4 = \xrightarrow{\text{ALKYL}} [\text{2,2,3-TMP}]^+ \xrightarrow{\text{ISOM}} [\text{TMPs}]^+ \xrightarrow{\text{H TRANSFER}} \text{TMPs}. \quad [1]$$

Diemethylhexanes and octenes, which are obtained by dimerization of the olefin as described in Eqs. [2] and [3], are formed in very little amounts:

$$\text{sec-}C_4^+ + \text{2-}C_4 = \xrightarrow{\text{DIMER.}} [\text{3,4-DMH}]^+ \xrightarrow{\text{ISOM.}}$$

$$[\text{DMHs}]^+ \longrightarrow \text{DMHs} \quad [2]$$

$$[\text{DMHs}]^+ \longrightarrow \text{Octenes} \quad [3]$$

Furthermore, it can be seen in Table 2 that 2,2,4-TMP, which is the preferred isomer from the octane point of view, is predominantly formed on the two SZ catalysts. Since according to Eq. [1] 2,2,3-TMP should be the primary product from isobutane/2-butene alkylation, formation of 2,2,4- and the other TMPs is explained by a fast isomerization of the primary isomer on the acid sites. Nevertheless, formation of 2,2,4-TMP from self-alkylation of isobutane can also occur, although in this case the presence of olefin is necessary, since no reaction occurred when pure isobutane was fed to the reactor.

If the composition of the alkylate obtained with the superacid catalyst is compared with that obtained with the commercial liquid acids (Table 3), a much higher cracking activity can be observed for the superacid solid catalyst, especially at very short times on stream, resulting in a lower selectivity toward C_8 alkylated products. However, at 4 min TOS the product distribution obtained on the SZ catalyst approaches that of liquid acids. This occurs because at this TOS cracking reactions are strongly suppressed while the catalyst still preserves its alkylation activity. However, as we will see below, the alkylation

TABLE 3

Composition of Alkylates from Isobutane and 2-Butene with Liquid Acids (H_2SO_4 and HF) and Solid Superacid (SO_4^{2-}/ZrO_2) Catalysts

Catalyst	H_2SO_4[a]	HF[a]	SO_4^{2-}/ZrO_2[b]	
Reaction Temperature (K)	283	—	275	
i-C_4/2-$C_4^=$ molar ratio	7.2	—	15.0	
Time on stream (min)	—	—	1	4
Component (wt%):				
i-C_5	2.2	0.3	24.0	7.3
C_6s	2.6	0.9	10.3	4.6
C_7s	2.7	1.5	9.7	6.2
C_8s	88.1	93.2	52.7	74.5
C_{9+}	4.4	4.1	3.3	7.4
Trimethylpentanes/C_8s	90.8	91.8	92.8	94.5
Dimethylhexanes/C_8s	9.2	8.2	4.7	3.6
Octenes/C_8s	—	—	2.5	1.9
TMP/DMH ratio	9.9	11.2	19.7	26.2

[a] Taken from Ref. (13).

[b] Sample SZ-II.

activity strongly decreases at longer TOS. Nevertheless, when the composition of the C_8 fraction is compared, the solid superacid catalyst gives more TMPs and less DMHs at the initial reaction stages, which results in a much higher TMP/DMH ratio, and consequently in a higher octane of the alkylate.

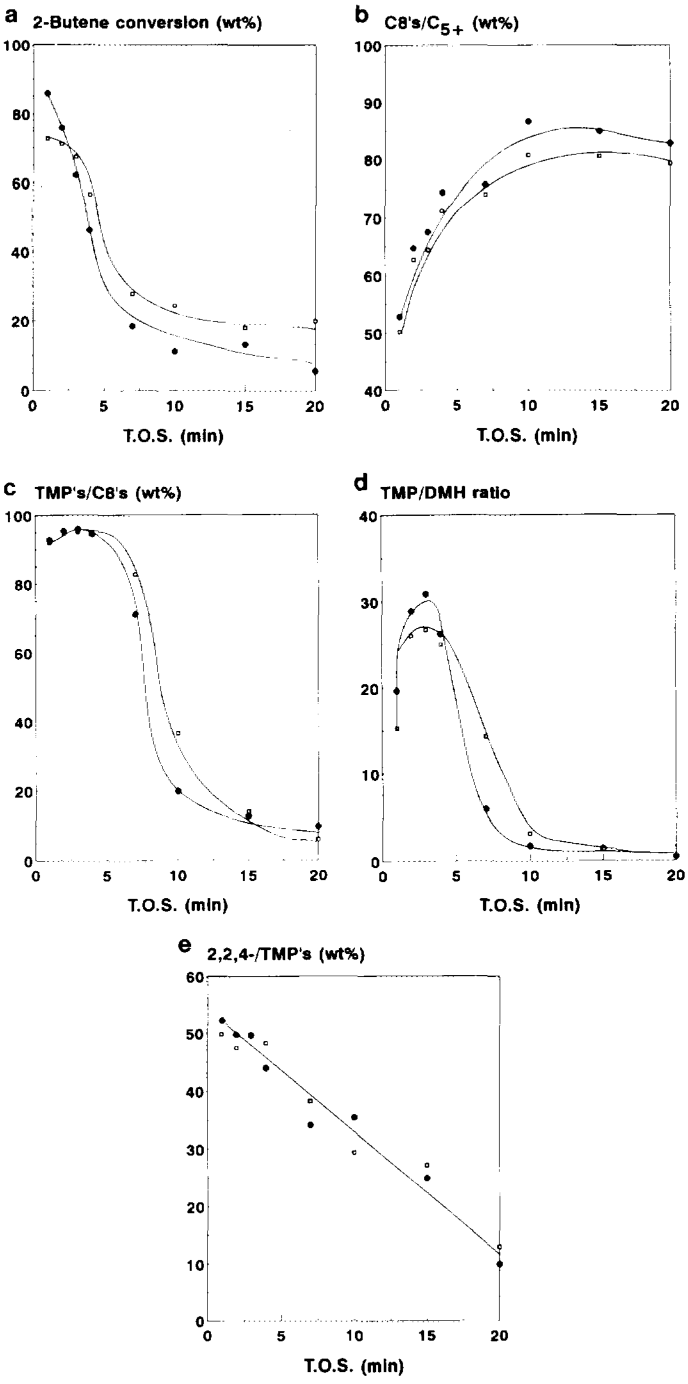

FIG. 2. Influence of time on stream (TOS) on olefin conversion and product distribution for the two SZ samples: (■) SZ-I; (●) SZ-II. Reaction conditions: T = 275 K; olefin WHSV = 2 h^{-1}; i/o ratio = 15 mol/mol.

Influence of Reaction Conditions on Activity and Selectivity

1. *Time on stream.* The decay behavior of the two SZ samples is compared in Fig. 2. In both cases, the olefin conversion sharply decreases during the first minutes, and reaches a steady state after 10–15 min TOS. The deactivation rate seems to be very similar for both catalysts despite their different initial conversion. Moreover, the change in product distribution as the catalyst ages is very similar for the two samples: there is an initial sharp increase of C_8s in C_{5+} as a consequence of cracking suppression, and a rapid decrease of TMPs in the C_8 fraction after a few minutes TOS, which is accompanied by a relative increase in octenes. A continuous decrease in the concentration of 2,2,4-TMP with TOS can also be observed in Fig. 2.

These results can be explained by assuming that the active sites responsible for catalytic cracking are the first to be poisoned. After that, decay occurs on the sites active for alkylation, in such a way that after some time only those responsible for butene oligomerization remain active. If this is so, it would appear that the acid strength needed to carry out the reactions is cracking > alkylation > oligomerization. Thus, an optimum catalyst design would involve the adequate acidity to perform the isobutane alkylation instead of the two other competing reactions.

2. *Reaction temperature.* The 2-butene conversion and a detailed product distribution obtained at 1 min TOS on the most active SZ-II catalyst are shown in Table 3 at different reaction temperatures. It can be observed that the olefin conversion decreases when decreasing the reaction temperature, the decrease being more pronounced at temperatures below 275 K. However, this decrease is much lower than that observed for zeolites under the same experimental conditions (21), indicating that the apparent activation energy is lower on the superacid catalysts than on the zeolite catalysts.

In regard to the product distribution detailed in Table 4, it is worth noting the very high cracking activity of this catalyst at the initial stages of the reaction, even at the lowest temperature used, for which ca. 22 wt% of the C_{5+} produced at 1 min TOS are cracked products. The amount of C_{9+} hydrocarbons initially formed by consecutive alkylations is relatively low, and increases at very low reaction temperatures. This could be an indication that, at higher temperatures, cracked C_5–C_7 products, and also some of the C_8s, are formed by β-scission of larger C_{12}^+ or C_{16}^+ carbocations, according to equations [4]–[7]:

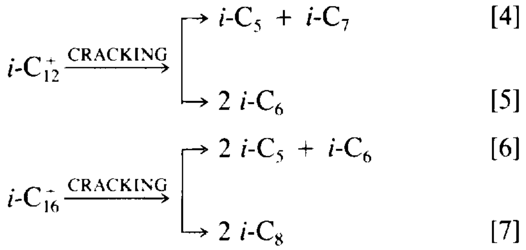

Table 4 also shows that isopentane is produced in very large amounts, even at the lowest temperature, indicating that reactions [4] and [6] occur in a higher extent than reactions [5] and [7].

With respect to the C_8 fraction, TPMs are the most abundant products initially formed in the full range of temperatures studied (Fig. 3). The concentration of TMPs in this fraction slightly decreases with increasing reaction temperature in favor of DMHs, while the initial concentration of octenes remains low and practically constant with temperature. Nevertheless, the amount of TMPs in the C_{5+} alkylate product sharply increases when decreasing reaction temperature as a consequence of the increase in C_8s. These results indicate that superacid SO_4^{2-}/ZrO_2 catalysts are very selective for the alkylation of isobutane with butene (Eq. [1]), especially at low reaction temperatures for which cracking reactions are diminished. On the contrary, when the reaction is carried out on zeolites, reactions [2] and [3] giving DMHs and octenes are the most favored at low reaction temperatures [22]. Figure 3 also shows that the 2,2,4-TMP isomer is the most favored in the full range of temperatures studied on the superacid catalyst.

Moreover, the very low concentration of olefins in the alkylate product may indicate a very high hydrogen transfer activity on the SZ catalyst, even at olefin conversions below 100%. Indeed, it has been shown that when zeolites are used as alkylation catalysts, the olefinicity of the product sharply rises when butene is detected in the product stream (17, 18), that is, for olefin conversions below 100%. Hydrogen transfer reactions are thought to occur from

TABLE 4

Influence of Reaction Temperature on the Initial (TOS = 1 min) 2-Butene Conversion and Product Selectivity Obtained with the SO_4^{2-}/ZrO_2 Sample SZ-II[a]

Reaction temperature (K)	263	275	305	323
2-Butene conversion (wt%)	47.2	85.9	89.0	92.4
Product distribution (wt%):				
i-P	10.2	24.0	38.2	41.1
n-P	—	—	0.1	0.3
2,2-DMB	0.1	0.8	1.5	2.8
2,3-DMB	3.0	4.3	5.2	4.1
2-MP	1.4	3.5	4.8	5.0
3-MP	1.0	1.7	2.3	2.4
n-H	0.1	—	—	0.2
2,2-DMP	—	0.1	0.2	0.5
2,4-DMP	3.5	5.5	4.9	3.9
2,2,3-TMB	0.2	0.3	0.3	0.4
3,3-DMP	0.1	0.3	0.4	0.7
2-MH	0.4	1.0	1.1	1.5
2,3-DMP	1.5	1.8	2.0	1.9
3-MH	0.4	0.7	0.8	1.1
2,2,4-TMP	26.3	25.5	15.3	10.4
2,2-DMH	0.2	0.4	0.4	0.8
2,5-DMH	1.3	—	1.8	2.8
2,2,3-TMP	9.5	11.0	4.5	3.2
2,4-DMH	0.7	0.8	0.9	1.0
2,3,4-TMP	10.3	5.0	3.7	2.8
2,3,3-TMP	12.8	7.4	4.8	3.7
2,3-DMH	1.0	0.9	0.8	1.0
3,4-DMH	1.2	0.4	0.4	0.4
Octenes	1.3	1.3	1.0	1.7
C_{9+}	13.5	3.3	4.6	6.3

[a] Olefin WHSV = 2 h^{-1}; $i\text{-}C_4/2\text{-}C_4^{=}$ = 15 mol/mol.

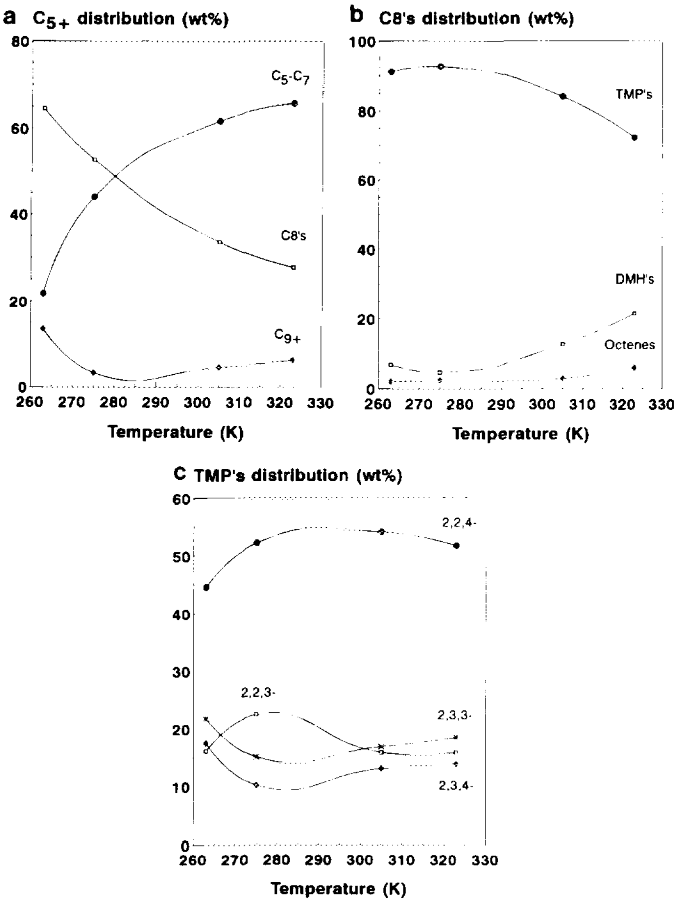

FIG. 3. Influence of reaction temperature on initial (TOS = 1 min) product distribution obtained on the SO_4^{2-}/ZrO_2 sample SZ-II (olefin WHSV = 2 h^{-1}; i/o ratio = 15).

isobutane molecules during the initial reaction stages (13), thus forming the *t*-butyl cations required to initiate the reaction chain while saturating the carbocations formed on the acid sites, facilitating their desorption:

$$i\text{-C}_8^+ + i\text{-C}_4 \xrightarrow{\text{H TRANSFER}} i\text{-C}_8 + t\text{-C}_4^+ . \qquad [8]$$

If the hydrogen transfer activity of the catalyst is low, desorption of the carbocations occurs by giving back a proton to the catalyst (Eq. [9]) with formation of the corresponding olefin:

$$i\text{-C}_{8+} \longrightarrow i\text{-C}_8 = +\text{H}^+\text{-cat.} \qquad [9]$$

The high initial hydrogen transfer activity observed for the SZ catalyst can be ascribed, in principle, to the high electrophilic character of the carbocations when adsorbed on the superacid sites.

3. *Olefin space velocity.* Figure 4 shows the influence of olefin WHSV on 2-butene conversion and product distribution obtained at 1 min TOS, 275 K reaction temperature, and isoparaffin/olefin (i/o) ratio of 15. Under these conditions a strong decrease of the olefin conversion when increasing olefin space velocity (WHSV) can be observed. A significant change in the product distribution also occurs: the amount of cracked products decreases, while that of C_8 and heavier C_9^+ hydrocarbons increases when increasing olefin WHSV. With regard to the C_8 fraction, TMPs are the predominant compounds, but their concentration slightly decreases at higher WHSV in favor of DMHs and octenes. These results show that at high space velocities, dimerization of the butene is slightly favored against alkylation, but even in the less favorable conditions used in this work, the latter is still the main reaction taking place on the superacid catalyst. Among the TMPs, 2,2,4-TMP is the more abundant isomer, its formation being favored at lower olefin space velocities.

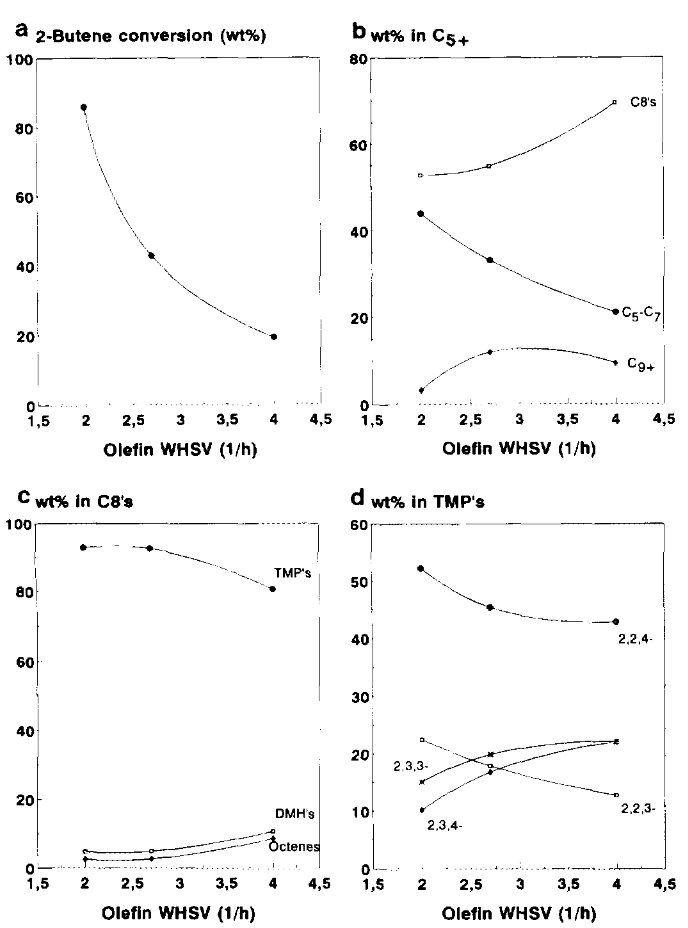

FIG. 4. Influence of olefin WHSV on initial (TOS = 1 min) olefin conversion and product distribution obtained on sample SZ-II (T = 275 K; i/o ratio = 15).

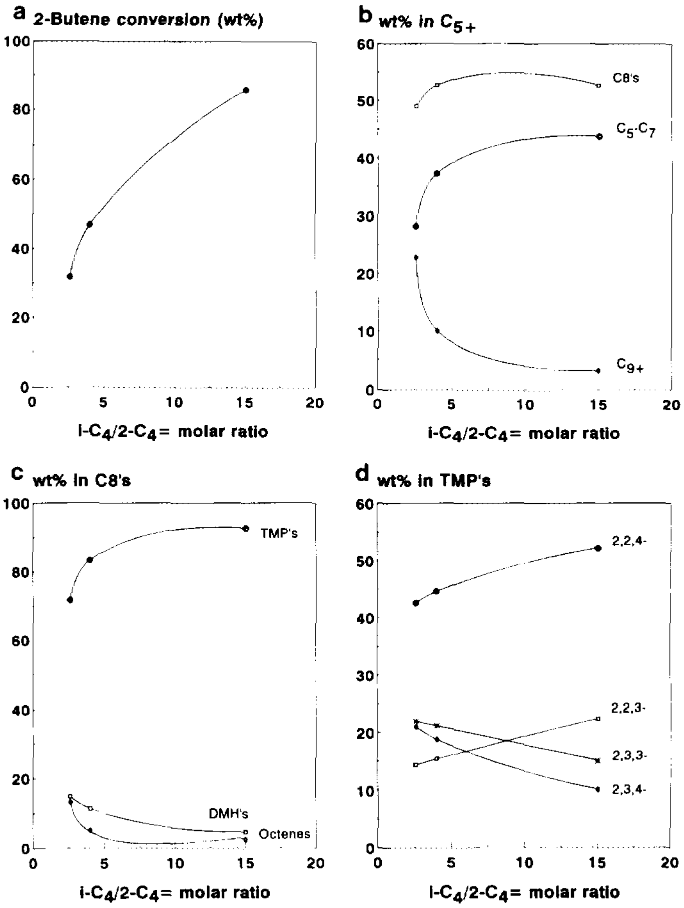

FIG. 5. Influence of isoparaffin/olefin (i/o) molar ratio on initial (TOS = 1 min) 2-butene conversion and product distribution obtained on sample SZ-II (T = 275 K; olefin WHSV = 2 h^{-1}).

4. *Isoparaffin/olefin ratio.* This parameter is crucial to control the yield and quality of the alkylate in commercial processes (13). In this work, it was varied between 2.6

and 15 (mol/mol) while keeping constant the other process variables, i.e., reaction temperature (275 K) and olefin WHSV (2 h^{-1}). The effect of the i/o ratio on the initial 2-butene conversion and product selectivity is depicted in Fig. 5. It can be seen there that the initial olefin conversion sharply increases when increasing the i/o ratio. Moreover, a strong decrease in the amount of heavier C_{9+} hydrocarbons is also observed when increasing the i/o ratio, as a consequence of the decrease in olefin polymerization reactions. This occurs because the higher the i/o ratio, the lower the probability of the olefin to undergo secondary reactions, such as oligomerization. Furthermore, Fig. 5 shows that DMHs and octenes, which are mainly formed by dimerization of 2-butene (Eqs. [2] and [3]), are also favored at low i/o ratios. Then, the quality of the alkylate is expected to increase when increasing the i/o ratio, as occurs in the commercial units using liquid acid catalysts. This can also be deduced from the distribution of TMPs (Fig. 5), in which a continuous increase of the most valuable 2,2,4-TMP is observed as the i/o ratio is increased.

CONCLUSIONS

Superacid catalysts of the SO_4^{2-}/ZrO_2 type give a very high initial activity for the alkylation of isobutane with 2-butene. However, at low olefin space velocities and relatively high reaction temperatures (above ca. 280 K), cracking of large C_{12}^+ or C_{16}^+ carbocations on the superacid sites is the main process taking place during the initial stages of the reaction. At lower temperatures, cracking reactions are strongly suppressed and alkylation of isobutane with 2-butene to give a mixture of TMPs becomes the predominant process occurring on the superacid catalyst. In contrast to what is observed when zeolites are used as alkylation catalysts, dimerization of the olefin feed to produce DMHs and octenes occurs to a much lower extent on the sulfated zirconia catalyst. This, in turn, results in a much higher TMP/DMH ratio, and consequently, a higher alkylate octane can be expected when using superacid catalysts. The TMP/DMH ratio sharply decreases when increasing reaction temperature above 300 K, probably because cracking of the more branched TMPs occurs to a higher extent than cracking of DMHs. Increasing olefin WHSV and decreasing the isoparaffin/olefin (i/o) ratio in the feed results in a sharp decrease of the initial olefin conversion, together with a decrease of the TMP/DMH ratio, with the consequent deterioration of the alkylate product. Moreover, at low i/o ratios polymerization of the olefin leading to heavier C_9^+ compounds is strongly favored. In regard to the TMPs distribution, the most valuable 2,2,4-TMP is the favored isomer initially formed on the superacid catalyst in the full range of reaction conditions studied.

On the other hand, superacid SO_4^{2-}/ZrO_2 catalysts were seen to deactivate very quickly with time on stream. The amount of cracked C_5–C_7 products strongly decreases from the beginning of the reaction, while TMPs are still formed during the first minutes TOS, and then sharply decrease at longer TOS. At the later stages of the reaction, when the hydrogen transfer activity of the catalyst is very low, octenes become the predominant compounds in the C_{5+} product. These results suggest that, under the reaction conditions used in this work, cracking occurs mainly on the superacid sites of the catalyst, and that these are the first sites to be poisoned. Then, deactivation of the alkylation sites follows, and finally only the sites of weak acidity show some activity for dimerization of the olefin in the later stages of the reaction.

In conclusion, it appears that solid superacids of the SO_4^{2-}/ZrO_2 type are initially active alkylation catalysts at very low reaction temperatures, where cracking reactions are strongly diminished. This, together with the fast catalyst decay, may represent a drawback of these systems to be commercially used. Then, if an optimum solid superacid alkylation catalyst is wanted, it should be prepared with a more adequate acid strength distribution in order to selectively produce C_8 alkylated products at the temperatures used in commercial operations while avoiding secondary cracking and polymerization reactions.

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