The Influence of Textural and Compositional Characteristics of Nafion/Silica Composites on Isobutane/2-Butene Alkylation

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Nafion/silica composites of different surface areas and polymer contents were prepared using a sol–gel technique. Their catalytic behavior was measured for the liquid phase alkylation of isobutane with 2-butene. A maximum initial (TOS = 1 min) activity and selectivity to trimethylpentanes as well as slower decay were detected for the sample with the smallest surface area (10 m^2 g^{-1}) and a Nafion content of 20 wt%. Catalysts with the same polymer content but a larger surface area showed a considerably lower initial activity and selectivity; deactivation was faster. This can be explained by the fact that, in composites with a greater surface area—highly dispersed Nafion—the sulfonic groups of the polymer interact to a greater extent with the silanol groups of the silica, resulting in a decrease in the activity of the sulfonic groups. In the same way, when the Nafion content is varied in those composites with a large and similar BET area, the rates of deactivation are inversely proportional to the amount of resin in the sample. Moreover, a silica-supported Nafion catalyst, prepared by impregnation, has given results as good as those obtained with the more active Nafion/silica composite. The effect of the process variables (TOS, temperature, and isoparaffin/olefin molar ratio) on the activity and selectivity of these catalysts was studied as well. Comparison of these catalysts with other solid acid materials, such as an H-Beta zeolite and a sulfated zirconia, shows that the Nafion/silica samples behave more like H-Beta than like the sulfated zirconia catalyst. © 1999 Academic Press

Key Words: isobutane/2-butene alkylation; Nafion; Nafion/silica composites; H-beta; sulfated zirconia.

INTRODUCTION

Alkylation of isobutane with low-molecular-weight olefins is one of the most important refining process for the production of high-octane (RON and MON), low Red vapor pressure (RVP) gasoline (1). At present the demand for alkylate is growing due to environmental concerns about reducing aromatics and olefins in the gasoline pool. There are also very good reasons for replacing the liquid acid catalyst with solid acids that have fewer adverse effects on the environment. In this respect, strong solid acids including chlorinated alumina (2), Nafion-H (3–5), sulfated zirconia (6–8), heteropolyacids (9, 10), and large pore zeolites

(11–21) were evaluated as potential catalysts with variable success.

The alkylation of isobutane/olefins is thermodynamically favored at low temperatures. Conventional reaction temperatures on solid catalysts are in the range of 20 to 150°C. In this temperature range organic resins can also be used as catalysts, and Nafion has been claimed to be an active and selective catalyst for alkylation of isobutane/2-butene (3). Unfortunately, the very small surface area of Nafion (0.02 m^2 g^{-1}) strongly limits the number of available acid sites, especially in nonpolar media. Thus, Nafion does not seem to be potentially suited for use as a commercial catalyst. The accessibility of acid sites in Nafion has been recently increased by entrapping nano-sized particles of Nafion resin within a highly porous silica network using a sol–gel technique (22). The procedure involves the partial depolymerization of the resin, followed by acid hydrolysis and further condensation of a silicon alcoxide, usually tetramethylorthosilicate (TMOS) or tetraethylorthosilicate (TEOS), in a solution containing the partially depolymerized resin. Then a gel is formed and the nano-sized (<100 nm average diameter) Nafion resin particles are entrapped in the silica matrix. The result is a composite material in which the polymer surface area is much greater than that of the original resin, with a corresponding increase in the number of accessible acid sites. These composite catalysts were applied to various acid-catalyzed, reactions such as 1-butene isomerization (23), Friedel–Crafts alkylation of aromatics (24), α-methylstyrene dimerization (25, 26), and Fries rearrangement (27), yielding much higher reaction rates than those observed on the original ion-exchange resin.

There is no doubt that the textural properties of the resulting composite, i.e., surface area and pore size distribution, may have an important impact on the catalytic properties of the material, especially when large molecules react or are formed during the reaction. In this work, nano-sized Nafion dispersed in silica catalysts were prepared on the one hand by keeping the amount of resin constant while changing the surface area of the composite from 10 to 245 m^2 g^{-1} and, on the other hand, by maintaining a similar

BET surface area while changing the content of Nafion in the composite. The influence of these catalyst variables on the alkylation of isobutane with trans-2-butene was studied.

EXPERIMENTAL

Catalyst Preparation

Six different Nafion resin/silica composites, NS-1 to NS-6, were prepared using tetraethylorthosilicate as a source of silica and a Nafion resin solution (22). The surface area and pore diameter were tailored by controlling the pH during preparation. The Nafion resin loading in the composite material was changed by increasing the amount of the Nafion resin solution used in the preparation procedure. Nafion NR 50, the commercial proton form of Nafion resin, was obtained from Fluka and used in the form of a 5 wt% solution, which is prepared under pressure, in a mixed alcohol water system (28). The equivalent weight of the polymer is typically 1100 and its acid capacity 0.89 meq H^+/g. For comparison, a SiO_2-supported Nafion catalyst (IN-1) was prepared by impregnation using the 5 wt% solution mentioned above. In this case, pure SiO_2 was prepared by the same procedure as used for the NS-1 sample.

Textural properties of the catalysts were obtained from the adsorption–desorption isotherms of N_2 at 77 K using the BET method and an ASAP 2400 (Micromeritics) apparatus. Thermogravimetric analysis (TG-DTA) was performed in a NEST instrument using 20 mg of sample and kaolin that had been calcined at 1100°C as a reference material. The temperature was increased from 25 to 800°C at a rate of 10°C min^{-1} in a controlled atmosphere of dry air. Elemental analysis was carried out in a FISONS EA 1108 CHSN-O apparatus. The latter two techniques enabled us to verify the amount of Nafion resin within the composites. Microstructural analysis was carried out using scanning electronic microscopy (SEM) and energy-dispersive X-ray analysis (EDX) in a JEOL JSM 6300 LINK ISIS instrument, which showed that the Nafion resin and the silica are intimately mixed at a microscopic level. The acid capacity was obtained by simple acid/base titrations, after previous ion exchange of 1 g of the catalyst with a large excess of sodium chloride (100/1 Na$^+$ to H$^+$). The resultant sample was filtered and thoroughly washed with deionized water. The exchanged solution was titrated again with NaOH. The physicochemical properties of the NS and IN catalysts and of Nafion NR 50 are reported in Table 1 and Fig. 1.

Reaction System and Experimental Procedure

Liquid phase alkylation experiments were carried out in an automated stainless steel fixed bed continuous reactor, by feeding 2 ml per minute of a calibrated mixture of isobu-

TABLE 1

Physicochemical Properties of Nafion/silica Composites (NS 1-6), a Silica-Supported Nafion Catalyst Prepared by Impregnation (IN-1) and Nafion NR 50

Sample	Surface area ($m^2 g^{-1}$)	Pore diameter (nm)	Pore volume ($cm^3 g^{-1}$)	Nafion resin wt (%)[a]	Acidity (meq $H^+ g^{-1}$)[b]
NS-1	10	10.3	0.03	20	0.21
NS-2	125	11.1	0.35	20	0.22
NS-3	158	9.8	0.37	20	0.23
NS-4	245	5.2	0.32	20	0.20
NS-5	175	7.9	0.35	53	0.47
NS-6	190	9.7	0.47	13	0.13
IN-1[c]	25.4	20.9	0.13	16	0.16
Nafion NR 50[d]	0.02	—	—	100	0.89

[a] Determined from the thermogravimetric results.
[b] The number of acid sites was determined by titration.
[c] Surface area data of the pure silica.
[d] Commercial Nafion.

tane (>99% purity) and *trans*-2-butene (>99% purity) with isobutane/2-butene molar ratios of 15 and 30, at 2.5 MPa nitrogen pressure. Samples were analyzed "on-line" in a GC equipped with a multiloop sampling system, a 100-m capillary column (fused silica, Supelco) and a FID detector. A more detailed description of the reaction system and the experimental procedure can be found elsewhere (13). Process variables, i.e., olefin WHSV from 1 to 8 h^{-1}, reaction temperature from 305 to 353 K, and isobutane/2-butene molar ratio from 15 to 30, were modified to obtain different initial conversions. All catalysts were "fresh." They were pelletized, crushed, and sieved, and particles from 0.59 to 0.84 mm in size were selected. The catalyst test of pure Nafion resin was conducted by physically mixing particles from 0.59 to 0.84 mm in size with inert silica (50/50 wt%).
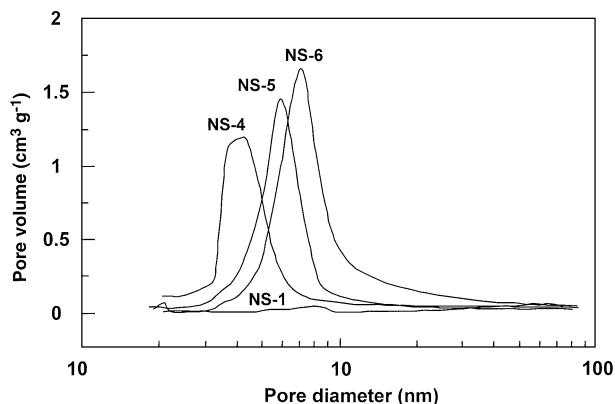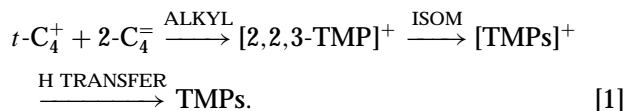

FIG. 1. Pore distribution of several Nafion/silica nanocomposites prepared with different surface areas and Nafion contents (see details in Table 1).
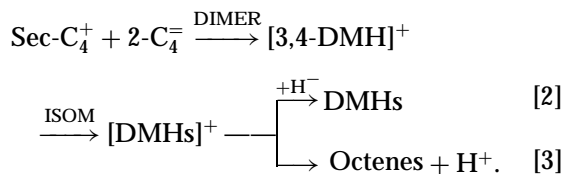
RESULTS AND DISCUSSION

Influence of the Textural Properties of the Catalyst on Activity and Selectivity

Liquid phase alkylation of isobutane with 2-butene on acid catalysts yields trimethylpentanes (TMPs) as the primary products of alkylation by means of the following reaction:

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

$$\xrightarrow{\text{H TRANSFER}} \text{TMPs}. \qquad [1]$$

The real primary 2,2,3-TMP product isomerizes rapidly on the acid sites to give 2,2,4-TMP, which, thermodynamically, is the most favored isomer. A consecutive alkylation step can occur before the C_8 carbocations are desorbed, giving carbocations with 12 or 16 carbon atoms which can either desorb, remain adsorbed on the catalyst, or crack to give different products ranging from C_3 to C_{9+}. The yield of 2,2,4-TMP can be increased by a parallel self-alkylation process involving two isobutane molecules. Dimerization of the olefin leads to dimethylhexanes (DMHs) or octenes ($C_8^=$) depending on the hydrogen transfer activity of the catalyst, as described in Eqs. [2] and [3] (1):

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

$$\xrightarrow{\text{ISOM}} [\text{DMHs}]^+ \longrightarrow \begin{cases} \xrightarrow{+H^-} \text{DMHs} & [2] \\ \longrightarrow \text{Octenes} + H^+. & [3] \end{cases}$$

The results shown in Fig. 2 and Table 2 clearly indicate that, on a Nafion/silica composite (catalyst NS-1), the above reactions take place and that C_5, C_6, C_7, and especially C_8
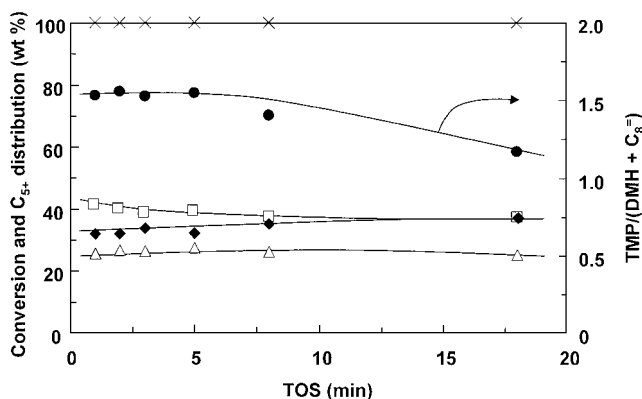
FIG. 2. Variation of the 2-butene conversion and distribution of C_{5+} products in wt% with time on stream in the isobutane/2-butene alkylation on NS-1 catalyst. Experimental conditions: $T = 353$ K; olefin WHSV = 2 h^{-1}; isobutane/2-butene (I/O) molar ratio = 15. 2-Butene conversion (×). Selectivity (in wt%): C_5–C_7 (△), C_8 (□), C_9 (◆), and TMP/(DMH + $C_8^=$) ratio (●).
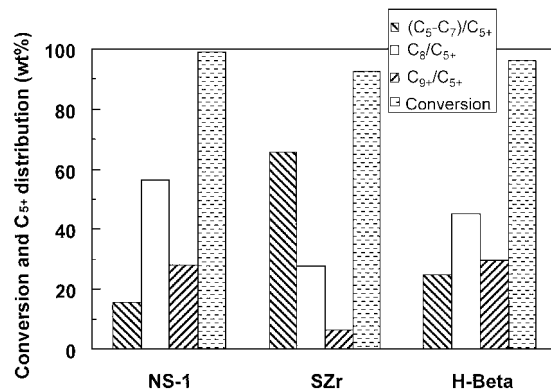
FIG. 3. Conversion of 2-butene and distribution of C_{5+} products in wt% of NS-1, sulfated zirconia (SZr), and H-Beta catalysts (7). Experimental conditions: TOS = 1 min; $T = 323$ K; olefin WHSV = 1 h^{-1} (NS-1, H-Beta) and 2 h^{-1} (SZr); isobutane/2-butene (I/O) molar ratio = 15.

dimethylhexanes, octenes, and trimethylpentanes are obtained. A comparison of these results with those obtained with the original Nafion resin NR-50 shows that the former gives a much higher activity, owing to the greater number of acid sites accessible to the reactants.

When the catalytic properties of NS-1 were compared with those of H-Beta zeolite and SO_4^{2-}/ZrO_2 at a similar level of conversion (Fig. 3), the order of selectivity to TMPs measured at 1 min TOS is NS-1 > H-Beta > SO_4^{2-}/ZrO_2. Like other solid acid catalysts, the Nafion/silica composite decays rapidly during the alkylation of isobutane with 2-butene (Fig. 4a) due to acid site poisoning by deposition of heavy molecules formed mainly by oligomerization of the olefin. The deactivation brings about a decrease in the density of the acid sites which, in turn, makes it more difficult for the catalyst to transfer hydrogen, thus causing the ratio TMP/(DMH + $C_8^=$), i.e., alkylation/oligomerization ratio, to shift toward lower values (Fig. 4b). With respect to the distribution of TMP, 2,2,4-TMP is the most important isomer (Table 2) because, in addition to thermodynamic reasons, it increases in amount due to the tendency of Nafion-H to catalyze the self-alkylation of isobutane (3).

Taking into account that products larger than the reactants are formed during the alkylation of isobutane with 2-butene and also that the reaction is carried out in the liquid phase, diffusion effects can have important effects on catalyst activity and selectivity. Thus, changes in the catalytic behavior of these catalysts will probably occur when the characteristics of the Nafion/silica composite change. Thereafter, as the BET surface area of the composite increases the maximum activity is obtained on the sample with the smallest surface area (NS-1 sample, Table 2). This sample also gives the largest (TMP/DMH + $C_8^=$) ratio (Fig. 4b) and the lowest deactivation (Fig. 4a). The reproducibility of the results is excellent: a second catalyst sample

Initial (TOS = 1 min) 2-Butene Conversion and Product Distribution Obtained on the Different Nafion/Silica Composites and Nafion NR 50[a]

Catalyst:	NS-1	NS-2	NS-3	NS-4	NS-5	NS-6	NR 50
Nafion resin (wt%):	20	20	20	20	53	13	100
Surface area (m^2 g^{-1}):	10	125	158	245	175	190	0.02
2-Butene conversion (wt%)	100	98.8	88.7	95.0	95.0	90.1	41.1
	(98.3)[b]	(85.0)[b]	(58.3)[b]		(78.4)[b]		
Distribution of C$_{5+}$ (wt%)							
C$_5$–C$_7$	25.6	22.5	12.8	25.5	25.8	19.3	14.7
C$_8$	42.3	41.4	49.7	54.1	40.4	62.0	43.3
C$_{9+}$	32.1	36.1	37.4	20.4	33.8	18.7	42.0
Distribution of C$_8$ (wt%)							
TMP	60.5	57.7	44.5	51.1	59.3	43.7	42.0
DMH	33.5	32.8	29.4	31.2	31.1	27.1	25.5
C$_8^=$	6.0	9.5	26.1	17.7	9.6	29.2	32.5
TMP/(DMH + C$_8^=$) ratio	1.53	1.36	0.80	1.04	1.46	0.78	0.72
Distribution of TMPs (wt%)							
2,2,4-	41.1	41.0	37.1	39.5	41.8	36.1	34.5
2,2,3-	13.9	13.2	14.0	13.2	13.9	14.7	14.5
2,3,4-	27.4	29.4	32.1	31.6	27.1	33.2	33.0
2,3,3-	17.6	16.4	16.7	15.7	17.2	16.0	16.0

[a] Experimental conditions: $T = 353$ K, Olefin WHSV = 2 h^{-1}, iC_4/2-$C_4^=$ molar ratio of 15 except.[b]
[b] Values in brackets were obtained at WHSV = 3.8 h^{-1}; the other experimental conditions were constant.
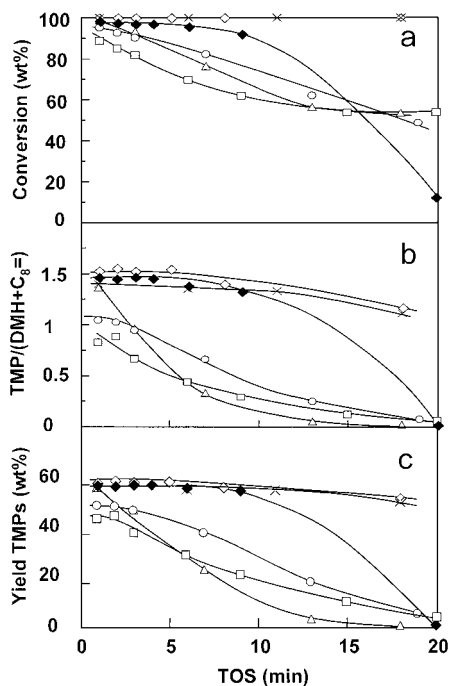

FIG. 4. Variation of the conversion of 2-butene in wt% (a), TMP/(DMH + C$_8^=$) ratio (b), and (c) yield of TMPs with time on stream, obtained in the isobutane/2-butene alkylation, on 20 wt% resin Nafion/silica nanocomposites with varying surface area. NS-1 ($\diamond$, $\blacklozenge$), NS-1* ($\times$), NS-2 ($\triangle$), NS-3 ($\square$), NS-4 ($\bigcirc$). Experimental conditions as in Fig. 1 except for NS-1 ($\blacklozenge$), WSHV = 3.8 h^{-1}. The NS-1* sample is a different batch of synthesis of the same catalyst than NS-1.

(NS-1*) gives practically the same values (Fig. 4). These results are surprising. We had expected that the greater dispersion of resin, as detected by SEM on those samples with larger surface area, would result in higher catalytic activity, since all pores in all the samples are in the region of the mesopore. The opposite occurred (Fig. 5) and can be explained by the fact that composites with a larger surface area have a greater number of silanol groups resulting in more interaction between the active phase and the silica support. In this way, a charge transfer may occur from the protons of the sulfonic groups to the silanol groups of the silica, decreasing the acid strength of the resin. This was confirmed by Pálinkó et al. (29) using physical characterization techniques. They showed that the interaction between –SO$_2$OH groups of Nafion and the silanols of the silica leads to a decrease in acidity, "due to the levelling effect of the hydrating environment." Thus, the greater the number of silanol groups, together with the dispersion of the organic polymer, the weaker the global acidity of the active phase. Consequently, the catalytic conversion will be lower, and the activity for oligomerization will be higher with respect to alkylation. A similar type of interaction explains the intrinsically lower acidity and activity of heteropolyacids (HPA), highly dispersed on a silica support, with respect to concentrations above the monolayer (10). In our case, if there are 60-nm spherical particles of Nafion in the composite, then its surface area becomes 50 m^2 g^{-1}. It is evident that increasing the surface area of the silica cannot increase the area of the Nafion above that value. On the contrary, the
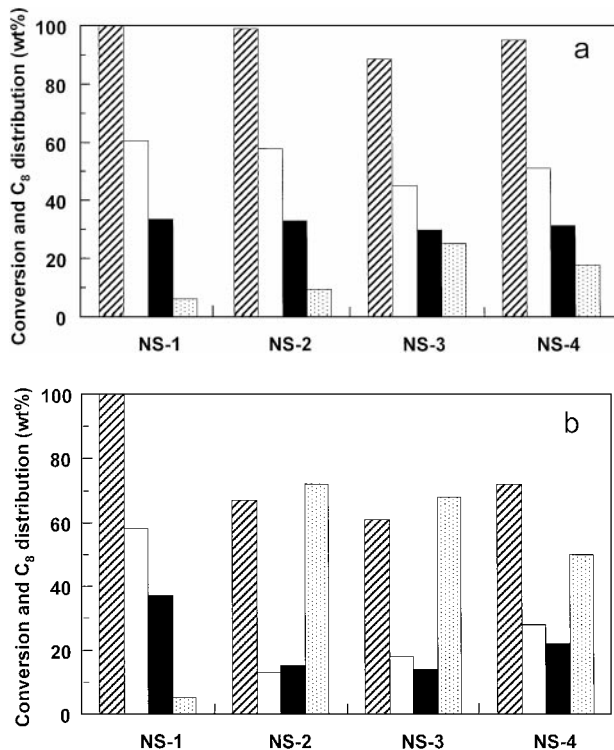
FIG. 5. Influence of the surface area of the catalyst on the 2-butene conversion and C$_8$ distribution at 1 min TOS (a) and 10 min TOS (b). Catalysts with a Nafion resin content of 20 wt%. Same experimental conditions as in Fig. 1. 2-Butene conversion (▨). Selectivity (in wt%): TMP (□), DMH (■), C$_8^=$ (▨).

FIG. 6. Influence of the Nafion resin content (wt%) of the catalyst on the 2-butene conversion and C$_8$ distribution at 1 min TOS (a) and 10 min TOS (b). Catalysts with a similar area, 158–190 m^2 g^{-1} (Table 1). Same experimental conditions as in Fig. 1. 2-Butene conversion (▨). Selectivity (in wt%): TMP (□), DMH (■), C$_8^=$ (▨).

former will contribute to the decrease in acid strength as a result of the above-mentioned interaction between the sulfonic groups of the Nafion resin and the silanols of silica.

If this is true, then one would expect that, as with HPA, low contents of resin mean lower activity which increases with resin content. This is indeed the case in Fig. 6: catalysts with a similar surface area show higher activity as the Nafion content increases. However, there is not a linear correlation between the Nafion content and the rate of the reaction. A fourfold increase in polymer produces a one- to threefold increase in the reaction rate. At present we do not have an explanation for this, but one hypothesis is that the dispersion of polymer, and therefore its coverage by silica, is not the same for all the particles and/or the size of the Nafion particles is not identical in the different composites.

The negative effect of the interaction between the sulfonic groups of the Nafion and the silanols of the silica on the acid strength of the catalyst may be more important in reactions catalyzed by strong acid sites, but may be irrelevant in less demanding reactions.

Considering the negative effect of the interactions between Nafion and silanol groups, it may be useful to investigate the catalytic behavior of the Nafion/silica catalyst prepared by impregnating the depolymerized resin on a
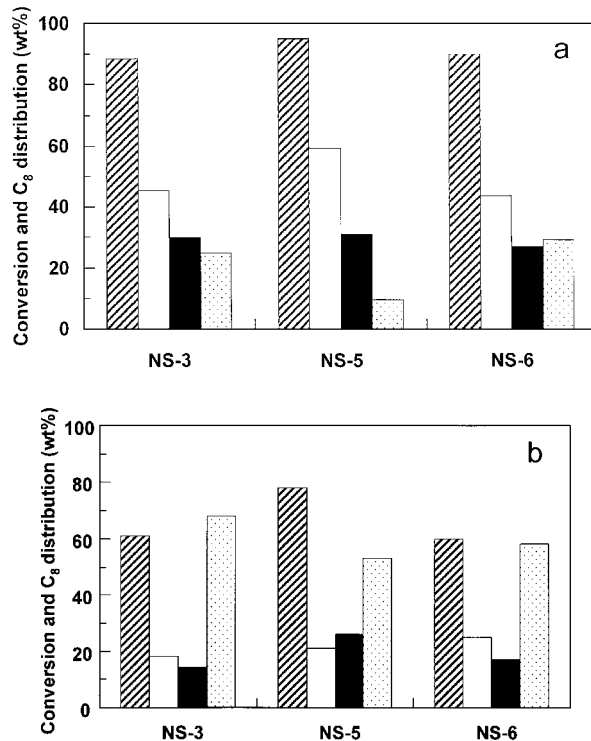
preformed silica with the same textural properties as those of sample NS-1. This was done by filling the pores with the exact amount of Nafion. The total Nafion content of the final sample (IN-1) was 16 %wt, which corresponds to that of the NS-1 sample. Figure 7 shows the catalytic behavior of
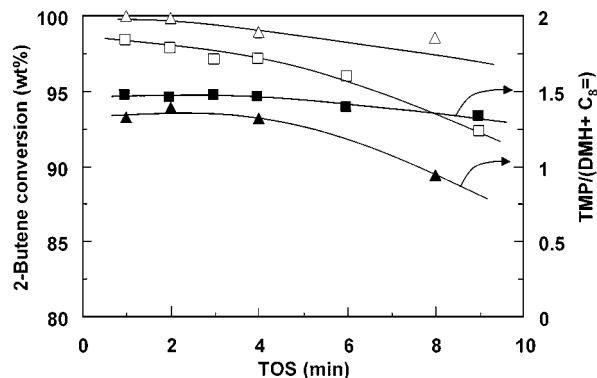

FIG. 7. Variation of the 2-butene conversion in wt% and TMP/ (DMH + C$_8^=$) ratio with the time on stream obtained in the isobutane/2-butene alkylation on both Nafion/silica composite (NS-1) and on a SiO$_2$-supported Nafion resin (IN-1) catalyst. Experimental conditions: $T = 353$ K; olefin WHSV $= 4$ h^{-1}; isobutane/2-butene (I/O) molar ratio $= 15$. NS-1 (□, ■), IN-1 (△, ▲).

both supported and composite Nafion catalysts. The IN-1 is slightly more active and decays more slowly than NS-1. The selectivity of these two catalysts is similar. After the reaction was monitored the Nafion content of the sample was determined by analyzing the S content of IN-1 catalyst, but no leaching of the polymer was detected.

Influence of Process Variables on Activity, Selectivity, and Catalyst Decay

The influence of TOS on the evolution of activity and selectivity for the different catalyst preparations is shown in Figs. 4, 5, and 6. On samples with the same Nafion content but with a different BET surface area, the catalyst with the smallest surface area (NS-1) deactivates more slowly (Figs. 4a and 5). Moreover, deactivation of the catalyst is accompanied by a decrease in selectivity to TMPs and an a higher number of octenes (Figs. 4b and 5). It is assumed (1) that alkylation requires stronger acid sites than does oligomerization. Thus, the results obtained suggest that the strongest acid sites, responsible for alkylation, are the first ones to be poisoned. Meanwhile, the catalyst with the lowest surface area (NS-1), postulated to have the highest number of strong acid sites and, as a result, the highest activity for isobutane/2-butene alkylation, deactivates more slowly for such a reaction. The samples with a similarly large BET surface area but different Nafion contents (NS-3, NS-5, NS-6) show deactivation rates which are inversely proportional to the content of resin (see Fig. 6). This again indicates that the number of the strongest acid sites increases with the Nafion content, as discussed above.

The most active catalyst (NS-1) was evaluated at different reaction temperatures at various WHSV and a isobutane/2-butene molar ratio of 15. The results obtained at 1 min TOS are shown in Table 3. As the reaction temperature increases, conversion also increases, whereas the ratio of alkylation/oligomerization increases only at a temperature of 323 K and decreases slightly at 353 K. The distribution of the different isomers in the fraction of TMPs is hardly affected by reaction temperature. The behavior of NS-1 with respect reaction temperature is more similar to H-Beta zeolite than to sulfated zirconia (7). Indeed, when the reaction temperature is decreased the sulfated zirconia is very selective to alkylation, while in the case of NS-1 and H-Beta zeolite, the selectivity shifts toward oligomerization. Taking these results into account, we propose that the reaction mechanism and the active sites involved in the alkylation of isobutane and 2-butene are the same on the zeolite and on the Nafion catalyst. Moreover, as a result of the interaction between the resin and the silica support, the acidity of the former is not much higher than that of the H-Beta zeolite. In the case of sulfated zirconia, it has been claimed that the acid strength of the Brønsted acid sites is low and that one electron acceptor type sites are responsible for the initiation of the chain reaction (30).

TABLE 3

Influence of Reaction Temperature on the Initial (TOS = 1 min) 2-Butene Conversion and Product Distribution Obtained on a Nafion/Silica Composite NS-1[a]

Reaction temperature (K):	305	323		353	
Olefin WHSV (h^{-1}):	2	1	2	2	8.3
2-Butene conversion (wt%)	49.1	98.9	66.4	100	63.2
Distribution of C$_{5+}$ (wt%)					
C$_5$–C$_7$	2.1	15.5	15.5	25.6	22.6
C$_8$	88.8	56.5	52.1	42.3	42.7
C$_{9+}$	9.1	28.0	32.4	32.1	34.7
Distribution of C$_8$ (wt %)					
TMP	41.4	71.6	62.4	60.5	50.7
DMH	11.1	24.6	23.4	33.5	27.0
C$_8^=$	47.5	3.8	14.2	6.0	22.3
TMP/(DMH + C$_8^=$) ratio	0.71	2.52	1.66	1.53	1.03
Distribution of TMPs (wt%)					
2,2,4-	40.4	42.8	42.4	41.1	40.2
2,2,3-	8.0	8.4	7.5	13.9	13.4
2,3,4-	32.5	31.2	31.9	27.4	29.1
2,3,3-	19.1	17.6	18.1	17.6	17.3

[a] Other experimental conditions: iC$_4$/2-C$_4^=$ molar ratio of 15.

The isoparaffin/olefin ratio is a very important variable in the alkylation process. Indeed, the larger this ratio, the greater the tendency of alkylation toward oligomerization, and the slower catalyst deactivation occurs. However, the high cost of separating products from the excess isobutane limits the isobutane/2-butene ratio that can be used. In this work, the isobutane/2-butene molar ratio (I/O) was increased from 15 to 30, and the results obtained are given in Fig. 8. This figure shows that the alkylation/oligomerization ratio ranges between ~1.5 and ~2.0, and the alkylation activity of the catalyst remains steady for longer reaction times. A similar effect was observed on H-Beta zeolite (15).
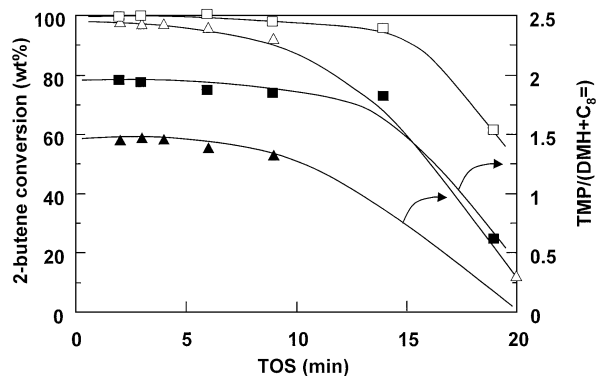

FIG. 8. Variation of the 2-butene conversion in wt% and TMP/(DMH + C$_8^=$) ratio with time on stream obtained in the isobutane/2-butene alkylation on NS-1 catalyst with an isobutane/2-butene (I/O) molar ratio of 15 and 30. Experimental conditions: $T = 353$ K; olefin WHSV = 4 h^{-1}. $I/O = 15$ (△, ▲), $I/O = 30$ (□, ■).

CONCLUSIONS

Nafion dispersed on silica is an active catalyst for the alkylation of 2-butene by isobutane. When the surface area of the Nafion dispersed on silica is varied, at a constant Nafion content, we observe higher activity and alkylation selectivity as well as slower deactivation of the catalyst on the Nafion/silica sample with the lowest BET surface area. This can be explained by the fact that in the region with the largest surface area and the greatest dispersion of Nafion, more intense interaction occurs between the sulfonic groups of the polymer and the silanol groups of the silica, resulting in a decrease in the acidity of the sulfonic groups. Thus, depolymerized Nafion supported by impregnation on a preformed silica gives results as good as those obtained on the Nafion/silica composite. On the other hand, when increasing the amount of resin on silica, with a BET area similar to that of the composite, the activity increases within the range of compositions studied here. When the catalytical behavior of these catalysts for isobutane/2-butene alkylation is compared with that of solid catalysts, such as zeolite H-Beta and sulfated zirconia, the Nafion/silica composites behave more similar like H-beta than like the sulfated zirconia catalyst.

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