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Isobutane alkylation catalyzed by supported perfluoroalkanedisulphonic acids

P. Ingallina*, A. de Angelis, W.O. Parker, Jr., and M.G. Clerici
EniTecnologie, via F. Maritano 26, I-20097 San Donato Milanese, Italy

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Silica supported perfluoroalkanedisulphonic acids (PFAS-SiO_2) catalyze the alkylation of isobutane with *n*-butene to yield mainly high-octane trimethylpentanes. PFAS-SiO_2 activity is highly dependent on the PFAS employed, on the preparation method and on the reaction conditions adopted. ^1H and ^{29}Si MAS NMR spectroscopy were used to evidence the changes in surface silanols caused by impregnating silica with perfluoroethanedisulphonic acid. A possible active species is hypothesized on the basis of the data acquired through NMR spectroscopy.

KEY WORDS: solid acids; alkylation of hydrocarbons, perfluoroalkanedisulphonic acids

1. Introduction

In the refining industry the alkylation of isobutane with butenes is a reaction of great interest because the products (mainly trimethylpentanes) are high-octane components for gasoline blending. In industrial processes strong mineral acids are used as catalysts, such as sulphuric and fluoridric acid, in nearly stoichiometric amount. The processes are very efficient but have some critical aspects. The process based on H_2SO_4 produces large quantities of spent acid to be regenerated (8000 tons/day worldwide [1]), while HF may form, in case of accidental leakage, toxic and corrosive fogs.

In both academic and industrial research centers solid acid catalysts, such as Y zeolite [2], sulphated zirconia [3,4], SbF_5 [5], β zeolite [6], MCM-22 [7], supported trifluoromethanesulphonic acid [8,9,10] and Nafion supported on silica [11] have been studied as possible alternatives to HF and H_2SO_4. Some of these catalysts [5,8,12] have been developed up to the pilot plant scale but no commercial unit has ever been started up.

We have shown in previous works [9,10] that supported trifluoromethanesulphonic acid (TFA) is able to alkylate isobutane with high selectivity to trimethylpentanes yielding a maximum productivity of $18.6\,g_{\text{octane}}/g_{\text{catalyst}}$. TFA is stable to elution when the catalyst activity is high. Only at the end of the reaction, when the activity declines, is a partial loss of the active phase observed. Two different hypotheses were suggested to justify the stability to elution of supported triflic acid on silica [13]. According to the first proposal, the stability might be attributed to the formation of a solid compound (hydroxonium triflate) between TFA and water present on the silica surface. According to the second one, a true chemical bonding between silanols and the sulphonic acid group of TFA is formed.

On these bases, we have investigated a new catalytic system, constituted by perfluoroalkanedisulphonic acids (PFAS), supported on silica. PFAS are solid at room temperature and their melting point is higher than that of hydroxonium triflate (34 °C). Also, the acid strength of PFAS is such that a chemical bonding between PFAS and silanols is expected to be at least as strong as that of TFA and silanols.

Here we report on the catalysts produced using different PFAS (perfluoromethanedisulphonic, perfluoethane disulphonic and perfluoropropanedisulphonic acid) supported on silica.

2. Experimental

2.1. Materials

SO_3, $SOCl_2$ and trifluoromethanesulphonic (triflic) anhydride were used as received. SiO_2 (60 F_{254}), Fluka, was heated at 400 °C for 24 h under airflow. The purity (97%) of PFES was determined by the ^1H NMR (400 MHz) spectra of its solution in dimethylsulfoxide-d_6, on a Varian VXR-400 spectrometer.

2.1.1. Catalyst preparation

(1) 12 meq (3.58 g) of perfluoroethanedisulphonic acid (PFES) dihydrate was dissolved in 100 ml of thionyl chloride under dry nitrogen atmosphere in a glove box. Ten grams of silica was added and the suspension was stirred overnight at room temperature. The solvent was then distilled off under vacuum, and the catalyst stored under dry nitrogen.

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* To whom correspondence should be addressed.
E-mail: pingallina@enitecnologie.eni.it

(2) 12 meq (3.58 g) of PFES dihydrate was dissolved in 100 ml of SO_3 (a), or $SOCl_2 + 20\%$ trifluoromethanesulphonic anhydride (b), or $SOCl_2 + 5\% SO_3$ (c) under dry nitrogen atmosphere in a glove box. Ten grams of silica was added and the suspension was stirred overnight at room temperature. The solvent was then distilled off under vacuum, and the catalyst stored under dry nitrogen.

(3) 12 meq (4.18 g) of perfluoropropanedisulphonic acid (PFPS) dihydrate (a) or 12 meq (2.98 g) of perfluoromethanedisulphonic acid (PFMS) dihydrate (b) was dissolved in 100 ml of thionyl chloride under dry nitrogen atmosphere in a glove box. Ten grams of silica was added and the suspension was stirred overnight at room temperature. The solvent was then distilled off under vacuum, and the catalyst stored under dry nitrogen.

2.2. Reaction apparatus

The catalysts were tested in a fixed-bed reactor (diameter 0.76 cm, length 26 cm) at a temperature of 25 °C and pressure of 20 bars. In each run, 10 ml (*ca.* 11 g) of catalyst was used. The reaction mixture isobutane/1-butene (10 : 1 ratio) was fed by an HPLC pump (mode 1).

In alternated feeding mode, the reagents, pure isobutane and a mixture of isobutane/1-butene (10 : 1 ratio), were fed alternately by two HPLC pumps: pure isobutane was fed for 20 s and then stopped while the feeding of the mixture of isobutane/1-butene was started; after 10 s the feeding of the mixture stopped and the feeding of pure isobutane started again (mode 2).

Under the reaction conditions the feed was in the liquid phase. WHSV referred to 1-butene was $2.8\,h^{-1}$. Reaction samples were collected and analyzed on a poly(dimethylsiloxane) capillary column (spb-1, Supelchem) and a Hewlett-Packard 5890 gas chromatograph.

2.3. Conversion and selectivity definition

Conversion and selectivity are defined in the following way:

Conversion: moles of butene reacted/initial moles of butenes
Selectivity: moles of saturated octanes/moles of butene reacted
TMP's selectivity: moles of trimethylpentanes/moles of saturated octanes

2.4. NMR spectroscopy

Solid state spectra were obtained using powdered samples (*ca.* 200 mg), contained in 7 mm zirconia rotors undergoing magic angle spinning (MAS) at 5 kHz, and a Bruker ASX-300 spectrometer. All sample manipulations were carried out under nitrogen atmosphere in a glove box. ^1H spectra were collected using a 70° rf pulse (4 μs), 5 s relaxation delay and 88 scans. These conditions gave quantitative spectra since the longest longitudinal relaxation was 3.5 s. ^{29}Si spectra (59.59 MHz) were obtained using high power ^1H decoupling, a 70° rf pulse (5 μs), 5 s relaxation delay and 10 000 scans. These conditions did not give quantitative spectra (see section 3.2). Chemical shifts were referenced externally to tetrakis (trimethylsilyl) silane (at −9.8 and −135.2 ppm) for ^{29}Si and to water (at 4.8 ppm) for ^1H.

3. Results and discussion

3.1. Catalyst synthesis and reactivity

PFAS are highly hygroscopic materials. It was not possible to remove the last two moles of water per mole of acid with any common physical method. Bulk dihydrate PFAS were not active in isobutane alkylation, catalyzing only butene oligomerization. A possible explanation for the poor catalytic properties of PFAS dihydrate is attributed to its low surface area and fast deactivation phenomena.

The surface area of the catalysts was increased by dispersing PFAS on a support with high surface area (amorphous silica). Strongly dehydrating solvents were used in operation, allowing us to increase the acidity of the sulphonic groups. Such solutions were used to impregnate the support. The solvent was slowly removed under vacuum.

3.1.1. Effect of solvent

Thionyl chloride, sulphuric anhydride, a mixture of thionyl chloride and sulphuric anhydride and a mixture of thionyl chloride and trifluoromethanesulphonic anhydride were investigated as solvents. All these compounds are able to react with water, possibly dehydrating PFAS and increasing their acid strength. The effect of different solvents on catalytic properties of the materials was investigated with $PFES\text{-}SiO_2$ (table1).

Thionyl chloride was an adequate solvent yielding an active and selective catalyst. Butene conversion was 98% and saturated octane products were 69%. The trimethylpentane content in the octane fraction was 75%. Adding to $SOCl_2$ a minor amount of sulphuric or triflic

Table 1
Isobutane alkylation with $PFES/SiO_2$. Influence of the solvent[a]

Dehydrating solvent	Conversion[b] (%)	Selectivity[b] (%)	TMP's selectivity[b] (%)
$SOCl_2$	98	69	73
$SOCl_2 + SO_3$	95	8	15
$SOCl_2 + (CF_3SO_2)_2O$	88	43	75
SO_3	75	18	66

[a] Feeding according to mode 1.
[b] Samples taken at 2 h t.o.s.

Table 2
Isobutane alkylation. Effect of the acid chain length of PFAS[a,b]

Catalyst	C_4^{2+} conversion (%)	C_8 selectivity (%)	TMP's selectivity (%)
PFMS-SiO_2	71	58	61
PFES-SiO_2	98	69	73
PFPS-SiO_2	97	80	69

[a] Feeding according to mode 1.
[b] Samples taken at 2 h t.o.s.

Table 3
Isobutane alkylation on PFES/SiO_2. Effect of reaction temperature[a,b]

Temperature (°C)	TMP's selectivity (%)	C_5–C_7 selectivity[c] (%)	C_8 selectivity[c] (%)	C_9^+ selectivity[c] (%)
25	69	21	69	10
−25	94	4	94	2

[a] Feeding according to mode 1.
[b] Butene conversion is always total.
[c] Samples taken at 2 h t.o.s.

anhydride produced more active but less selective catalysts. While on PFES-SiO_2 prepared by this route the conversion of butene was complete, the selectivity to saturated octanes was considerably decreased to 8% (SO_3) and 43% (triflic anhydride), respectively. At the same time, a high cracking activity, causing the production of a significant fraction of low molecular weight hydrocarbons, was observed. Both conversion and selectivity were reduced when pure sulphuric anhydride was used as solvent. Butene conversion became only 75% as against the 98% obtained by the use of $SOCl_2$. The selectivity to saturated octanes was 18%, while the quantity of by-products due to cracking activity was high.

These data show that the best compromise between activity and selectivity is shown by the catalyst prepared in thionyl chloride. A tentative explanation of the effectiveness of this solvent is based on its unique dehydrating properties. The more powerful dehydrating agents, i.e., the sulphuric and triflic anhydrides, possibly yield an exceedingly acidic catalyst, affected by high cracking activity. Also, when $SOCl_2$ reacts with water, the acids produced are HCl and SO_2, which are quickly removed from the reaction equilibrium. It may be pertinent to mention here that in the alkylation catalyzed by H_2SO_4 the optimum acid composition contains 0.5–1% water [14].

3.1.2. *Effect of chain length of PFAS*

The effect of the chain length of the perfluoroalkyl group was studied by supporting perfluoromethanedisulphonic acid (PFMS), perfluoroethanedisulphonic acid (PFES) and perfluoropropanedisulphonic acid (PFPS) on silica, with the aid of $SOCl_2$ as the solvent. The results are shown in table 2.

PFMS-SiO_2 was the least active catalyst, based on butene conversion (71%). A possible explanation of this behavior is provided by an increased resistance to dehydration of PFMS. On the contrary, PFES-SiO_2 and PFPS-SiO_2 yielded almost quantitative butene conversion. The content of trimethylpentanes in the saturated octane fraction was close to 70%, the balance being predominantly dimethylhexanes. No methylheptanes were detected. The cracking activity was not negligible for all three catalysts, as shown by the C_8 selectivity decreasing from 58% (PFMS-SiO_2), to 69% (PFES-SiO_2) and 80% (PFPS-SiO_2). On this basis, however, the chain length appears to have an effect on this side reaction: increasing the number of carbon atoms in the PFAS reduced the cracking activity.

3.1.3. *Effect of temperature*

In an attempt to minimize the cracking activity of the catalysts, the reaction was carried out below 0 °C. The catalytic performances of PFES-SiO_2, prepared from thionyl chloride, at 25 and −25 °C are compared in table 3. At the lower temperature, the selectivity to saturated octanes increases up to a value of 94%, while the conversion of butene remains complete. At the same time, the selectivity to trimethylpentanes is 94%, being generally higher than 85% for all catalyst life considered (table 4).

3.1.4. *Catalyst lifetime and productivity*

A lifetime test was performed at −25 °C, using PFES-SiO_2. Table 4 shows that the yield of saturated octanes reaches a maximum (94%) after 2 h on stream, then the catalyst undergoes deactivation, with a decrease in conversion and selectivity. After 6 h, the yields of saturated C_8 are as low as 34%. The trimethylpentane fraction, however, is constantly higher than 85% for all the catalyst life.

The productivity, defined as grams of saturated octanes per gram of active phase, reached values of 1.7

Table 4
Isobutane alkylation on PFES-SiO_2. Catalyst life[a]

Time on stream (h)	Saturated octane yield (%)	TMP's selectivity (%)
1	65	87
2	94	94
3	85	87
4	68	90
5	39	90
6	34	86

[a] Feeding according to mode 1.

Table 5
Isobutane alkylation. Effect of feeding mode

Catalyst	Feeding	Catalyst life (h)	Productivity g_{C_8}/g_{cat}
PFES-SiO$_2$	mode 1	7	1.7
PFPS-SiO$_2$	mode 1	9	3.6
PFES-SiO$_2$	mode 2	25	12
PFPS-SiO$_2$	mode 2	126	87

and 3.6 for PFES-SiO$_2$ and PFPS-SiO$_2$, respectively, under the above conditions. In order to improve it, the reaction mixture (isobutane/1-butene: 10:1) and pure isobutane were alternately fed in the reactor. The aim was to stop the growth of heavy deactivating by-products on the catalyst surface and to facilitate their removal by the isobutane treatment. Table 5 shows that the productivity was greatly increased in the alternate feeding mode: 7 times more for PFES-SiO$_2$ and 24 times more for PFPS-SiO$_2$. The maximum productivity, observed on PFPS-SiO$_2$, was 87 $g_{octanes}/g_{catalyst}$, a value that is greater than the one obtained with our previous supported catalyst (18.6 $g_{octanes}/g_{catalyst}$ for CF$_3$SO$_3$H-SiO$_2$ [8]). Moreover, it is comparable to the best productivity reported in the literature for a supported catalyst (102.4 $g_{octanes}/g_{catalyst}$ in the case of BF$_3$-Al$_2$O$_3$ [15]).

3.2. Characterization

The interaction between the PFES and silica was investigated by NMR spectroscopy. Spectra of SiO$_2$ and PFES-SiO$_2$ were made under the same experimental conditions to allow a quantitative comparison.

^{29}Si MAS spectra are plotted with the same vertical scale in figure 1. The spectrum of silica shows a broad composite signal centered near −110 ppm. Spectra collected with longer recycle times (*e.g.*, 60 s) indicated a very lengthy longitudinal relaxation time for the ^{29}Si nuclei. The only efficient source of relaxation is via the silanol protons, since molecular oxygen was excluded during the sample preparation. Thus, the signals in spectra of figure 1 arise from nuclei that are incompletely relaxed (*i.e.*, the recycle time was not long enough to allow complete relaxation between scans). Silicon nuclei bearing one hydroxyl (silanol) give a signal near −100 ppm, which is an apparent shoulder to the main signal. Geminal silanols (−90 ppm) do not survive preparation treatment (heating at 400 °C). After impregnation the signal area decreases (figure 1) and this is attributed to the loss of silanol protons which reduces the relaxation rate of all Si nuclei even further.

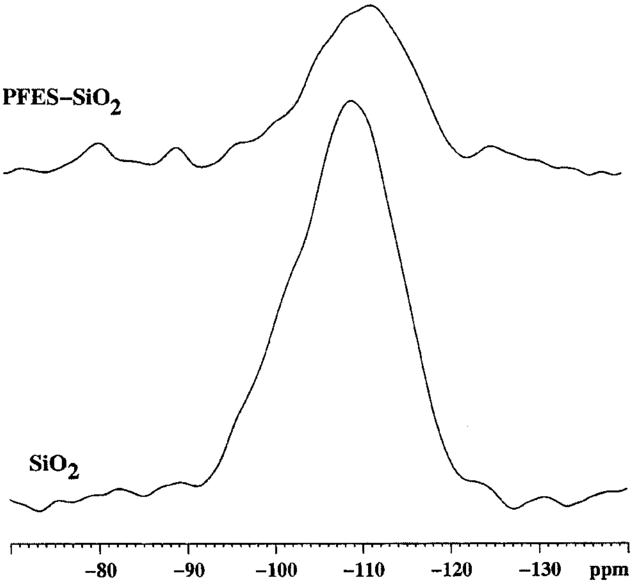

Figure 1. ^{29}Si MAS NMR spectra of SiO$_2$ and PFES-SiO$_2$ plotted with the same vertical scale.

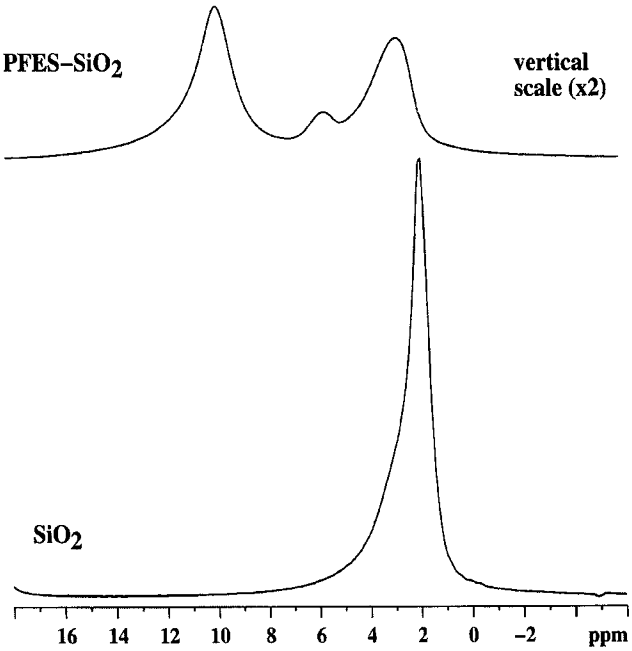

Figure 2. ^{1}H MAS NMR spectra of SiO$_2$ and PFES-SiO$_2$.

^{1}H MAS NMR gives more detailed information on the surface silanols. As seen in figure 2, a composite signal near 2 ppm arises from the silanol protons. No water molecules are present due to the drying treatment and exclusion of humidity during manipulations. After impregnation with PFES (10% by weight) the total ^{1}H signal area decreases to half its original value. This loss of signal area is not due to insufficient relaxation, as for ^{29}Si, but rather to a real loss of protons during de-hydroxylation reactions driven by SOCl$_2$. The PFES-SiO$_2$ sample gives 3 signals at 9.6, 5.5 and 2.7 ppm. The last signal is attributed to isolated silanols. The small signal at 5.5 ppm is attributed to weakly acidic (or H-bonded) protons.

The signal at 9.6 ppm is due to strongly acidic protons. Its signal area corresponds to 0.2 equivalents of the silanol protons originally present on the silica. The amount of silanol groups on the dehydrated silica surface is calculated to be *ca.* 1.6×10^{21} OH/g, from the surface area (350 m^2/g) and the Kiselev–Zhuravlev constant (4.6 OH/nm^2) [16,17]. Thus, there are *ca.* 3.2×10^{20} strongly acidic protons per gram of PFES-SiO_2. Given that 1.2 meq/g of PFES (or 7.2×10^{20} H^+/g) was impregnated on the silica, there is (on average) only one strongly acidic proton per PFES molecule. This is consistent with an interaction between PFES and SiO_2 in which one acid group is involved and the other is free.

4. Conclusions

PFAS can be supported on silica, obtaining catalysts active in the alkylation of isobutane with *n*-butenes. Saturated octanes are the major fraction in the mixture products. Trimethylpentanes are the main constituent of this fraction. The best results were obtained using thionyl chloride as the solvent for supporting PFAS.

All three PFAS-SiO_2 studied here are active. PFES-SiO_2 and PFPS-SiO_2 gave complete butene conversion with good (69–80%) selectivity of saturated octane. This selectivity was greatly increased (above 90%) by lowering the reaction temperature from 25 °C to −25 °C. Both catalyst lifetime and productivity were increased (7 times for PFES and 35 times for PFPS) by operating in the alternated feeding mode.

^1H MAS NMR studies of PFES-SiO_2 found only one strongly acidic proton per PFES molecule. This result is consistent with the hypothesis of an interaction between PFAS and silica in which one acid group is involved and the other is free.

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