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Studies on supported triflic acid in alkylation

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Abstract

A thermally stable solid acid catalyst has been prepared by treating amorphous silica gel with trifluoromethanesulphonic (triflic) acid (TFA) at 150°C in a closed glass vessel. A solvent such as 1,1,2-trichloro-2,2,1-trifluoro-ethane (Freon 113) can be conveniently used to dissolve TFA. The obtained material is an active catalyst in the alkylation of isobutane with *n*-butenes to yield high-octane gasoline components. In the reaction it behaves like a truly solid catalyst not leaching TFA in the solution for about 24 h. The catalyst characterisation has been performed by ^{1}H- and ^{19}F-NMR and IR spectroscopy. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The alkylation of isobutane with *n*-butenes to yield saturated-branched octanes is a reaction of great interest in the refining industry. The products have high octane number and are commonly used for gasoline blending. Current production is based on strong mineral acids, i.e. sulphuric and fluoridric acids, used in large amounts. For safety and environmental reasons it is desirable their substitution with non-corrosive solid catalysts. To this purpose, a number of solid acids has been investigated up to now, such as Y zeolite [1], sulphated zirconia [2], SbF_5 [3], ß zeolite [4]. All these catalysts deactivate rapidly unless they are used in conjunction with a peculiar reactor [3].

Different catalytic systems have been studied in which TFA is adsorbed on various solids, but they are all subject to leaching. To circumvent this problem, Haldor Tøpsoe A/S has developed a new fixed bed alkylation process [5] in which TFA adsorbed on SiO_2 is carried through the reactor by the feed stream. Subsequently, liquid TFA is recycled back to the top of the reactor.

Here we report a synthetic method through which the TFA is stabilised on SiO_2 surface obtaining an active solid-like catalyst.

2. Experimental

2.1. Materials

TFA (CF_3SOH) (98%), Fluka, was used as received. Silica gel (60 F_{254}) (SiO_2), Fluka (pore volume 0.75 ml/g, pore size 6 Å) was heated at 400°C for 24 h under air flow.

2.1.1. Synthesis of catalysts without solvent: catalyst A

SiO_2 was impregnated with TFA in a glass tube under dry nitrogen flow. The glass tube was sealed and heated in an oven at a temperature (150°C) slightly below the boiling point of TFA. The TFA/SiO_2 volume ratio was between 0.1 and 0.5.

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2.1.2. Synthesis of catalysts with solvent: catalyst B

Fifty millilitres of a solution consisting of 2 ml of TFA in 48 ml of anhydrous solvent, trifluoroacetic acid (catalyst B1) or Freon 113 (catalyst B2), was placed in a previously flame-heated flask under nitrogen, and 20 ml of pretreated SiO_2 was added to this solution.

This suspension was stirred for 30 min, then the solvent has been stripped off under vacuum for 3 h. After this period the solid, consisting of TFA/SiO_2, was placed in a glass vial which has been sealed and maintained at 150°C for 24 h.

2.2. Reaction apparatus

The catalysts were tested in a fixed bed reactor at the temperature of 25°C and pressure of 20 bar. In each run, 10 ml of catalyst was used. The reagents, pure isobutane and a mixture of isobutane/1-butene (10/1), were fed alternatively by two HPLC pumps: pure isobutane is fed for 20 s and then stopped while the feeding of the mixture of isobutane/1-butene began; after 10 s the feeding of the mixture stopped and the feeding of pure isobutane started again. Under the reaction conditions they were in the liquid phase. WHSV referred to 1-butene was $0.04\,h^{-1}$. Reaction samples were taken by cooling the effluent and analysed on a poly(dimethylsiloxane) capillary column and a Hewlett Packard 5890 gascromatograph.

2.3. Conversion and selectivity definition

Conversion and selectivity are defined as follows:

$$\text{Conversion} = \frac{\text{moles of butene reacted}}{\text{initial moles of butenes}}$$

$$\text{Selectivity} = \frac{\text{moles of saturated octanes}}{\text{moles of butene reacted}}$$

$$\text{Tmps selectivity} = \frac{\text{moles of trimethylpentanes}}{\text{moles of saturated octanes}}$$

2.4. Characterisation techniques

2.4.1. NMR spectroscopy

The samples were introduced in an NMR test tube and spectra were recorded on a Bruker AMX-300 spectrometer, operating at the ^{1}H-NMR frequency of 300.13 MHz and at the ^{19}F-NMR frequency of 282.23 MHz. The acquisition parameters for all spectra were set to 30° flip angle with a recycle delay of 4 s between scans.

2.4.2. IR

FT-IR spectra were carried out in transmission in the 4000–400 cm^{-1} region, resolution 1 cm^{-1}, with an FT-IR mod. 2000 Perkin Elmer spectrometer. Self-supported pellets (thickness 10 mg/cm^2) were placed in the pyrex cell with KBr optical windows, where thermal treatments and in situ reactions were performed.

As far as thermal stability evaluation is concerned, the samples were treated under vacuum at increasing temperature (from 21 till 400°C) for 1 h.

The acidity distribution was evaluated according to the following method: 13.3 mbar of pyridine were loaded at 21 or 200°C on the activated sample (300°C, 1 h, 10^{-3} mbar). After 1 h interaction, desorption (1 h, 2×10^{-3} mbar) at increasing temperature (21–300°C) was performed and the corresponding spectra monitored, as already described. The density of the acid sites was evaluated from the peak area of the IR signals at 1455 (Lewis type) and 1545 cm^{-1} (Brønsted type), taking the extinction coefficient from Take et al. [6]. The error in peak area determination was ca. 10%. The acid strength distribution was evaluated from the capacity of the acid sites to retain pyridine after desorption at a given temperature. In situ adsorption of TFA on SiO_2 pellet was performed at reduced pressure (vapour pressure of TFA at 25°C) and at 100°C.

3. Results and discussion

3.1. Catalyst synthesis and reactivity

TFA grafted on SiO_2 (catalyst A) catalysed the alkylation of isobutane with 1-butene at room temperature to yield a mixture of saturated octanes and other products (Table 1). After 1 h of time on stream (t.o.s.), butene conversion was complete with an almost total selectivity to saturated octanes. Trimethylpentanes content in the octane fraction was 68% with the balance being predominantly dimethylhexanes. No methylheptanes were detected. Small amounts of C_4–C_7 and C_{9+} hydrocarbons were also present. As

Table 1
i-Butane alkylation with catalyst A[a]

Time on stream (h)	Butene conversion (mol%)	Selectivity to saturated octanes (mol%)	TMPs[b] selectivity in C_8 fraction (mol%)
1	99	99	68
3	99	95	68
24	99	79	69

[a] Conditions: 25°C, 22 bar.
[b] Trimethylpentanes.

the t.o.s. increased, catalyst deactivation manifested itself with a decrease of selectivity. After 3 h the selectivity to saturated octanes was 95% and after 19 h the selectivity dropped to 79%. On the contrary 1-butene conversion remained total till 24 h. During this period trimethylpentanes content in the octane fraction was constant (68%).

The catalyst A behaved as a truly solid catalyst and no TFA was found in the effluent. The leaching of acid phase has been tested in two different ways. The first one regards the leaching in the effluent, which has been bubbled time to time in boiled distilled water. Such water solution has been titrated with NaOH 0.01 N (indicator Neutral Red), no acidity has been detected. The second one regards the catalyst: after reaction the catalyst has been treated with large amount of boiled distilled water to extract the supported acid phase. Such solution has been titrated, as described above, and the acid content is 98–99% of the original content.

Increasing the TFA/SiO_2 volume ratio in the synthesis from 0.1 to 0.4, active catalysts were obtained, having good stability to elution. Increasing such ratio, there were not significant changes neither in 1-butene conversion nor in alkylate composition. When the TFA/SiO_2 volume ratio in the synthesis was higher than 0.4 the catalytic system was not stable and TFA was found in the effluents within 15 min of t.o.s. Also when liquid triflic acid is simply adsorbed, without successive thermal treatment, on silica, the loss of the acid has been detected in the effluent after about 30 t.o.s. and it is complete within 1.5 h.

Through acid titration of different portion of fresh catalyst A, it was found that the acid distribution was not uniform. A new synthetic method (catalyst B) was developed in order to obtain a catalyst with a uniform acid distribution and, possibly, to improve its catalytic performances: TFA was dispersed on the SiO_2 support using solvents, either trifluoroacetic acid (catalyst B1) or Freon 113 (catalyst B2).

When catalyst B1 was used (Table 2), it was found that 1-butene conversion was complete and the selectivity to saturated octanes was comparable to that obtained with catalyst A. On the other hand, the trimethylpentanes content in octane fraction was slightly lower (60% instead of 68%) and the catalyst life was one third (8 h). After this time, the leaching of triflic acid was observed. A possible explanation of this phenomenon could be the dehydrating effect of trifluoroacetic acid, which can remove a part of silanol groups, and therefore prevent the interaction of TFA with SiO_2. Actually, when the catalyst was prepared with a SiO_2 pretreated at 800°C, temperature at which vicinal silanol groups are completely removed [7],

Table 2
i-Butane alkylation with catalyst B1[a]

Time on stream (h)	Butene conversion (mol%)	Selectivity to saturated octanes (mol%)	TMPs[b] selectivity in C_8 fraction (mol%)
1	99	89	66
3	98	95	60
6	98	95	60

[a] Conditions: 25°C, 22 bar.
[b] Trimethylpentanes.

Table 3
i-Butane alkylation with catalyst B2[a]

Time on stream (h)	Butene conversion (mol%)	Selectivity to saturated octanes (mol%)	TMPs[b] selectivity in C_8 fraction (mol%)
1	98	88	86
2	96	95	86
5	98	98	84
25	97	80	83

[a] Conditions: 25°C, 22 bar.
[b] Trimethylpentanes.

free TFA was found in the effluents, after only 10 min of t.o.s.

Using Freon 113 as solvent in the catalyst preparation, the resulting material was characterised by a uniform distribution of acidity. As far as its catalytic performances is concerned (Table 3), 1-butene conversion (98%) and selectivity to saturated octanes (95%) were the same as those obtained with the catalyst A, but the trimethylpentanes content in the octane fraction was much higher (86 vs. 68%). In this case there was not a significant difference in catalyst life with respect to that of catalyst A.

3.2. Physico-chemical characterisation

3.2.1. ^{1}H- and ^{19}F-NMR analysis

To characterise the molecular interactions between TFA and the support, the ^{1}H- and ^{19}F-NMR spectra of some significant samples have been recorded. The main spectral parameters are the chemical shift (δ) and the signal half-height linewidth ($\Delta\omega_{1/2}$). For ^{1}H-NMR spectra, the chemical shift values depend on the electronic depletion of the acid hydrogen nucleus; consequently a higher value of chemical shift may be considered as a measure of increased acid strength, while the linewidth $\Delta\omega_{1/2}$ is related to the strength of the interaction between TFA and SiO_2 surface. For ^{19}F-NMR spectra, the chemical shifts are not much influenced by the acid strength because the fluorine nuclei on the trifluoromethyl group are not directly involved in the acid–base equilibrium. The linewidth $\Delta\omega_{1/2}$ is still influenced by the interaction with the SiO_2 surface.

The ^{1}H-NMR spectra of pure TFA and catalyst A ($TFA/SiO_2 = 1/10$ volume ratio) are shown in Fig. 1. The chemical shift of the single peak ($\delta = 12$ ppm) observed in the two spectra is substantially unchanged, which suggests that the acid strength of TFA is maintained after deposition on SiO_2. On the other hand, a significant difference is evident for the $\Delta\omega_{1/2}$ of the acid, which is very large in catalyst A ($\Delta\omega_{1/2} = 600$ Hz) compared with that of pure acid ($\Delta\omega_{1/2} = 2$ Hz), due to strong interaction between TFA and SiO_2. The same effect is observed on the corresponding ^{19}F-NMR spectra.

The ^{1}H-NMR spectra of the sample prepared treating TFA with SiO_2 with prevalently isolated silanols groups (SiO_2 pretreated at 800°C) is shown. The chemical shift of the single peak ($\delta = 12$ ppm) is still substantially unchanged, while the linewidth ($\Delta\omega_{1/2} = 449$ Hz) is intermediate as regards the two spectra seen before possibly signifying that there is still an interaction between TFA and SiO_2 although not as strong as in the catalyst A.

As far as the nature of the species formed during the synthesis of the catalyst, it has been hypothesised that water molecules produced by the silica surface during the heating treatment with TFA, yield a monohydrated TFA. This is a very strong acid, as confirmed by ^{1}H-NMR spectra of samples obtained by dosing water molecules to TFA. In fact, it was found that the chemical shift of hydrated TFA corresponds to that of pure acid ($\delta = 12$ ppm) up to a water-to-acid molar ratio of 1, while it decreases as the molar ratio is higher than 1 (e.g.: $TFA{\cdot}2H_2O$: $\delta = 10$ ppm). According to this hypothesis, the formation of solid monohydrated TFA ($TFA{\cdot}2H_2O$) (m.p. 34°C) [8], is consistent with the solid-like behaviour of the catalyst.

In the synthesis of catalyst B2 the removal of Freon 113 from the impregnated SiO_2/TFA was monitored by ^{19}F-NMR (Fig. 2) at 100°C. The spectra show the

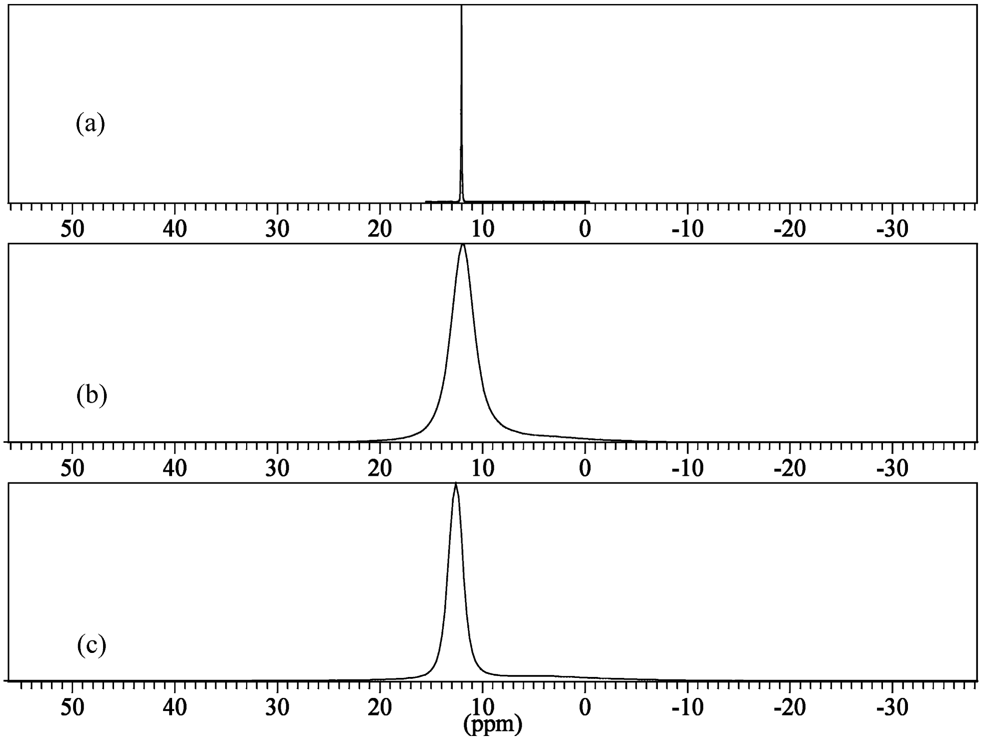


Fig. 1. ^{1}H-NMR spectra of liquid TFA (a); catalyst A (b); sample prepared treating TFA with a SiO_2 with isolated silanol groups (c).

total disappearance of Freon 113 which is totally removed after treatment at 100°C for 180 min (Fig. 2c). Besides, the catalyst obtained (catalyst B2) shows a very low ^{1}H chemical shift, very close to that of catalyst A, confirming that the impregnation of SiO_2 with a TFA solution in Freon 113 allows obtaining a strong acid catalyst.

3.2.2. FT-IR analysis

The FT-IR analysis was performed only on catalyst A. The spectrum of catalyst A has been compared with the spectrum of SiO_2. The grafting of TFA on SiO_2 gives rise to a new IR signal at 1417 cm^{-1} and two changes in the OH region. In particular it has been observed a decrease of the intensity of the 3734 cm^{-1} signal, due to internal vicinal SiOH groups, and the formation of a broad absorption at 3495 cm^{-1}, due to H bonds between reactant and SiO_2 silanols (Fig. 3). The main characteristic IR signals of TFA in gas phase are: 1195 (stretching of CF_3 group, very strong), 1400 (stretching of SO_2 group, strong) and 3397 cm^{-1} (stretching of OH group, broad). Among them, only the $SO_2{}^{2-}$ vibration at 1417 cm^{-1} revealed to be well detectable in catalyst A and therefore used for its identification.

The thermal stability of the catalyst was evaluated during evacuations in dynamic vacuum at increasing temperatures. The intensity of the IR signal at 1417 cm^{-1} decreases after evacuation at 100, 200, 300°C to 98, 80, 70% of the intensity of the signal at 21°C, respectively (not shown). These results together with the observation that thermal treatments in vacuum have a more dramatic effect on the stability of adsorbent–adsorbate than thermal treatment at standard pressure, suggest that the thermal stability of the catalyst is quite good.

The acid distribution of the catalyst after activation at 300°C (temperature at which the stability of the system has been confirmed) was determined by pyridine adsorption/desorption and shows the presence of both Brønsted (250 μmol/g) and Lewis (112 μmol/g) acid sites (Fig. 4). Their density is comparable at 21

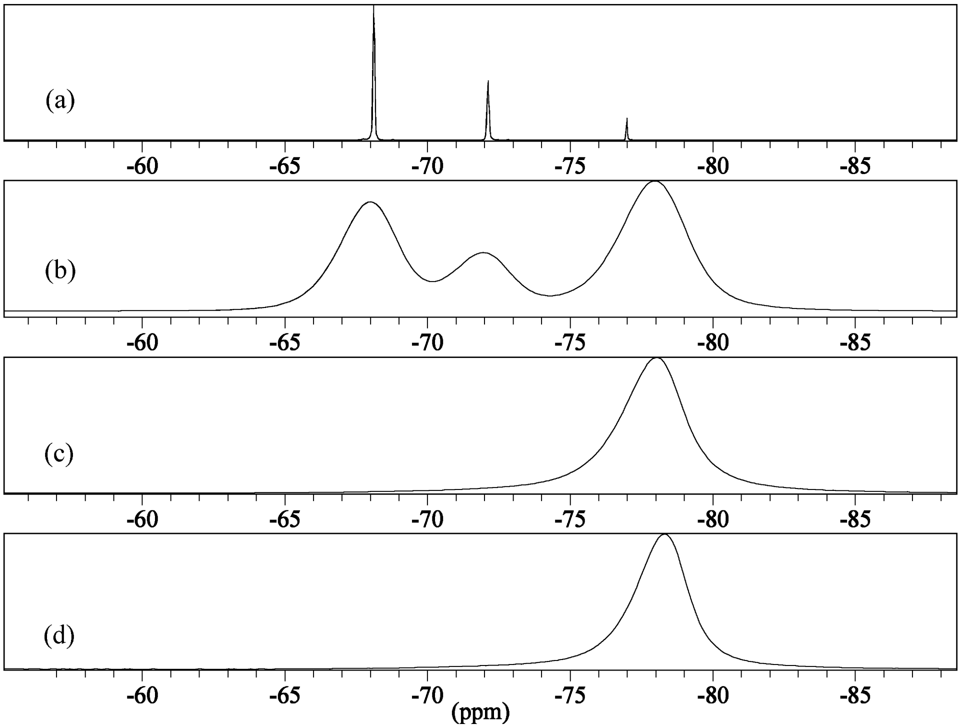


Fig. 2. ^{19}F-NMR spectra of the solution of TFA (signal at −77 ppm) in Freon 113 (signals at −68 and −72 ppm) (a); of the SiO_2 impregnated with the preceding solution after 45 minutes at 100°C (b); of the same sample after 180 minutes at 100°C (c); and of catalyst A (d).

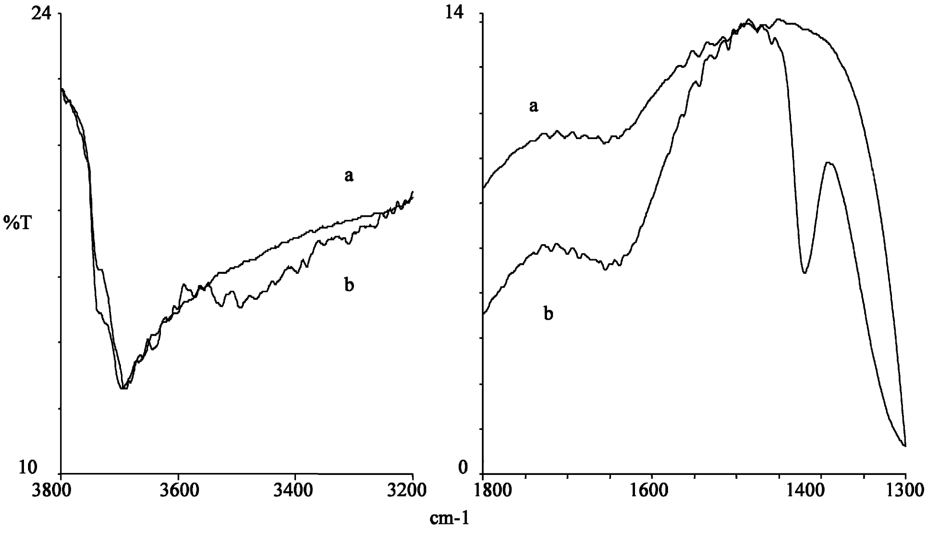


Fig. 3. IR spectra of SiO_2 (a) and catalyst A (b).

Fig. 4. Difference spectra of catalyst A after adsorption/desorption of pyridine at 21 (a), 100 (b) and 200°C (c).

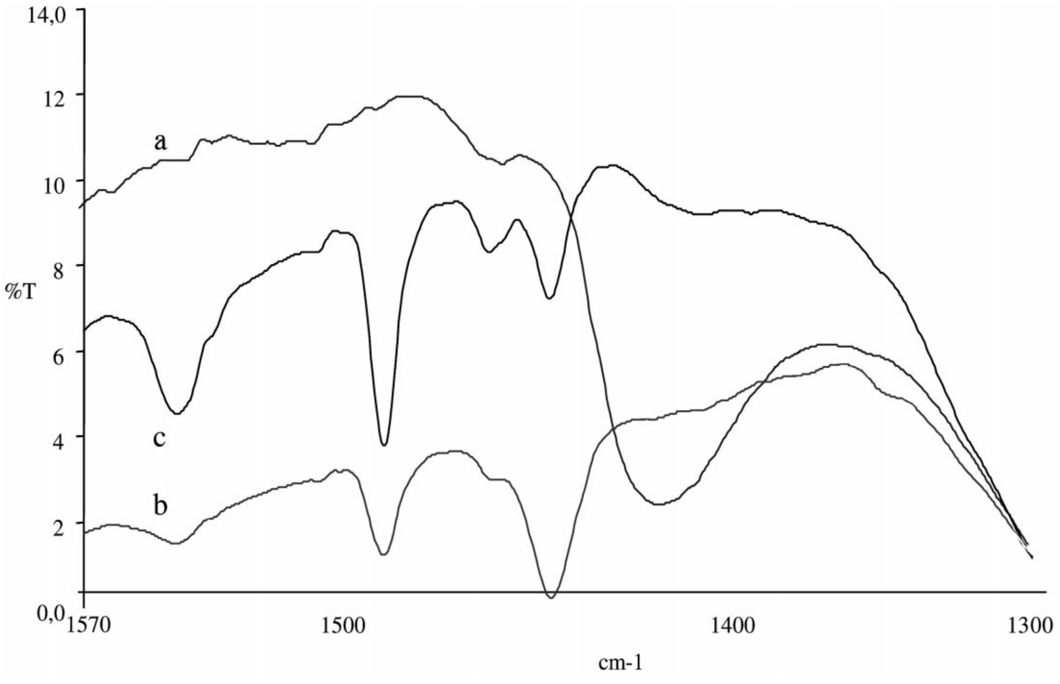
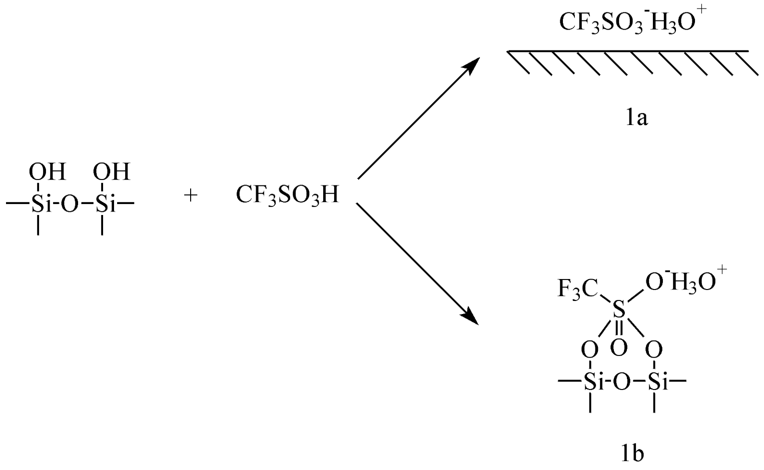


Fig. 5. Influence of water addition on acid site nature: TFA addition at 100°C (a), pyridine adsorption at 21°C (b), plus water addition at 100°C (c).



Scheme 1.

and 100°C and decreases sharply after evacuation at 200°C (36 and 4 μmol/g, respectively).

In order to study the TFA–SiO_2 interaction, SiO_2 pellets were contacted with TFA vapour, at reduced pressure. In this case the intensity of the IR signal at 1417 cm^{-1} does not change even after evacuation at 400°C, meaning that the material so obtained is more stable and different from catalyst A. This is also proved by pyridine adsorption experiment, which showed only the IR signal at 1447 cm^{-1}, showing that, differently from catalyst A, only Lewis acid sites have been formed. After addition of H_2O vapour at 100°C one IR signal at 1545 cm^{-1}, due to Brønsted sites, appears. On the other hand, the signal due to Lewis sites is splitted into two bands at 1463 and 1447 cm^{-1} (Fig. 5c). This may be due to the simultaneous interaction of one pyridine molecule with one Brønsted and one Lewis acid site [9]. These results suggest that the Brønsted acid sites presence in catalyst A may be related to small amounts of water. These data also support the hypothesis of monohydrated TFA formation during the catalyst synthesis.

4. Conclusions

The catalysts produced by the grafting of TFA on SiO_2, according to the methods described, are stable to leaching and able to catalyse the alkylation of isobutane with *n*-butenes. Branched saturated octanes are the most important fraction in the product mixture. When the preparation of the catalyst was performed dissolving TFA in Freon 113, the catalyst had a uniform distribution of the acid sites and turned out to be more selective toward trimethylpentanes than the catalyst obtained in solventless conditions. Catalytic experiments demonstrated that SiO_2 support must have vicinal silanol groups in order to produce a catalyst stable to leaching.

As to its structure, qualitative information are provided by ^{1}H-NMR and IR spectra. The former shows that the linewidths of the stable catalysts A and B2 are larger than those of anhydrous TFA and of the material obtained from SiO_2 dehydrated at 800°C (only isolated silanols). The IR spectra show that Brønsted acid sites are present in the active and stable catalysts. These sites are also generated by adding small amount of water to TFA/SiO_2 produced by vacuum dehydrated silica. Both kind of spectroscopic evidences suggest that small amounts of water or partially dehydrated silica are necessary to generate stable and active catalysts.

In conclusion, catalytic and characterisation data suggest that, during the synthesis, there may be the formation of solid TFA·H_2O on SiO_2 surface. To our knowledge this compound was never reported as active catalyst and was never employed in *i*-butane alkylation. As to its formation and interaction with SiO_2 surface, two hypotheses are possible. In one case, TFA reacts with silanol groups to yield TFA·H_2O highly dispersed on SiO_2 surface (Scheme 1a). In the other case, TFA react with vicinal silanol groups to yield a real chemical bond with silicon. The water coming from this esterification is coordinated to the TFA giving grafted TFA·H_2O (Scheme 1b).

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