Catalytic behavior of sulfated TiO$_2$ in light olefins oligomerization

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Abstract

Isobutene oligomerization was carried out at room temperature over sulfated-titania sol–gel catalysts prepared by three methods; (i) "in situ" sulfation using sulfuric acid, (ii) gelling with nitric acid and sulfation (a), and (iii) gelling with ammonium hydroxide and sulfation (b). XRD spectra identified anatase as the crystalline phase in all the sulfated samples. The specific surface areas were 126, 115 and 62 m^2/g, and FTIR-pyridine total acidity was 280, 105 and 160 mmol/g, showing L/B ratios of 3.65, 1.82 and 1.25, for the "in situ", sulfated (a) and sulfated (b) samples, respectively. For the isobutene oligomerization carried out in a continuous flow reactor, the "in situ" sample showed 100% of conversion even after 90 h in stream, with selectivity to C$_8$–C$_{12}$ olefins of 76%. In TiO$_2$ sulfated (a) the initial conversion was 100%, and it was maintaining during 40 h with selectivity to C$_8$–C$_{12}$ olefins of 88%. On the other hand, TiO$_2$ sulfated (b) sample showed a continuous and pronounced lost in activity. In this case the selectivity to C$_8$ olefins, it evolves with time and reaches values of 70%. It has been proposed that the catalytic behavior of the sulfated TiO$_2$ catalysts strongly depends on the relative Lewis/Brönsted sites abundance. At higher L/B ratio corresponds higher catalyst stability.
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1. Introduction

Fuel reformulation is without doubt a worldwide trend, according to US and European legislations, which are focused to the reduction of evaporative emissions and the complete fuel combustion. Oligomerization of light olefins produced in the FCC units [1] might be an attractive alternative to produce liquid hydrocarbons as components of gasoline, diesel and high value petrochemical products [2]. Usually, olefins oligomerization to obtain fuels is carried out in liquid phase, using phosphoric acid impregnated in a solid support or ionic exchange resins as catalysts, which present important disposal problems or strong deactivation, respectively [3,4].

The main challenges in the design of catalysts for this reaction are focused to reach high conversion and high selectivity to C$_8$–C$_{12}$ olefins, avoiding the formation of heaviest olefinic products (C$_{16}$$^+$), which are out of the boiling range of gasoline. At the same time, high stability of the catalyst in function of time is required.

Solid acid catalysts as zeolites [5–8] and sulfated zirconia [9] has been reported as active catalysts for light olefins oligomerization. Looking to tailored solid acid oligomerization catalysts, in the present work sulfated TiO$_2$ were obtained by the sol–gel method, characterized by XRD, FTIR-pyridine absorption and evaluated in the isobutene oligomerization at room temperature.

2. Experimental

2.1. "In situ" sulfation

Two-hundred milliliters of bidistilled water and 200 ml of ter-butanol were mixed in a glass flask under reflux and

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stirring, then sulfuric acid (Baker 99%) was added to this solution until adjust at pH 3. Then, 84.5 ml of titanium *n*-butoxide (Aldrich 98%) were slowly added, maintaining the solution under reflux for 24 h. After gelling the sample was dried at 70 °C for 24 h and annealing at 400 °C in air for 12 h.

2.2. Acid gelling medium and sulfation (a)

In a glass flask under reflux were put 200 ml of *tert*-butanol and 200 ml of water. Afterwards, the solution was adjusted with nitric acid (Baker 99%) to pH 3. Then, 84.5 ml of titanium *n*-butoxide (Aldrich 98%) were added by dropping and maintained under stirring. After gelling the sample was dried at 70 °C (TiO$_2$-reference a). Sulfation was done by adding 5 ml of an ammonium sulfate 1N solution per gram of material to dried sample, with continuous stirring. The sample was maintained with the ammonium sulfate solution for 4 h at these conditions. Finally, water excess was evaporated and the sample was annealing at 600 °C in air for 4 h.

2.3. Basic gelling medium and sulfation (b)

The sample was prepared in the same way that described above, but using ammonium hydroxide Baker 99% (NH$_3$ 35% vol in water) to adjust pH at 9 (TiO$_2$-reference b). The sulfation procedure was made in the same fashion as for the acid sulfation.

3. Characterization

3.1. X-ray diffraction

The catalyst samples were characterized by X-ray diffraction (XRD), by using Cu Kα radiation, in Siemens D-500 equipment. The signals intensity was measured by step scanning in the 2θ range between 10 and 110° with a step of 0.02° and a measuring time of 2 s per point. Diffraction peaks were obtained with a pseudo Voight function to model the peak profiles [10,11].

3.2. Specific surface areas

BET specific surface areas of the samples were measured using an ASAP-2000 Micromeritics apparatus. The areas were calculated from the nitrogen adsorption isotherm using the BET method. Pore size diameter distribution was obtained from the desorption isotherm, using the BJH method.

3.3. FTIR-pyridine adsorption

Total acidity and Lewis/Brönsted sites ratio [12–14] were determined by FTIR-pyridine adsorption, in a Nicolet 170 SX spectrometer by means of a Fourier transform infrared (FTIR). The annealed material was pressed into thin self-supported wafers. Then, they were placed in a glass Pyrex

cell with CaF$_2$ windows coupled to a vacuum line, in order to be evacuated (1×10^{-6} torr) in situ at 400 °C for 30 min. The adsorption was carried out on the cell at 25 °C by breaking a capillary tube, which contains the pyridine. The pyridine excess was desorbed with vacuum from room temperature to 400 °C in 100 °C steps. The quantities of adsorbed pyridine were obtained from the integrated absorbance of the respective bands.

4. Catalytic activity evaluation

The catalytic behavior was evaluated for the isobutene oligomerization reaction using a fixed bed reactor, with dimensions of 1.7 cm of diameter and 5.7 cm of length, respectively. The operation conditions and evaluation procedure were as follows: 2 g of the catalysts were activated at 400 °C in flowing nitrogen. After the activation treatment, temperature was lowered to 28 °C and a mixture of isobutane/isobutene 80:20 w/w was feed into the reactor under a pressure of 100 psi, assuring that the hydrocarbon mixture were in liquid phase [15,16]. Initial WHSV value used for isobutene oligomerization was 5 h^{-1}.

The analysis of products was made in all the cases by FID-gas chromatography (Varian model CX3400) equipped with a PONA column of 50 m and coupled to a workstation. The conversion was calculated in function of isobutene converted and the selectivity is reported as C$_8^=$, C$_{12}^=$ and C$_{16}^=$ %mol fractions. Low concentrations of C$_{20}^=$ ($\leq$1%) were found in all the cases.

5. Results and discussion

5.1. X-ray diffraction

The XRD spectrums for selected samples are shown in Fig. 1, where it can be seen that sulfation stabilizes the anatase phase. In all sulfated (a) and (b) samples, anatase
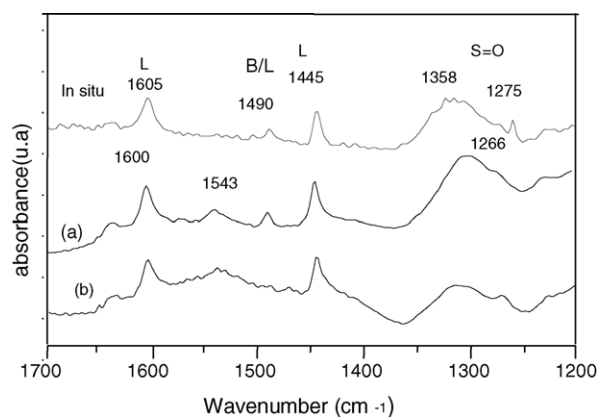

Fig. 1. XRD pattern for TiO$_2$-reference (a), TiO$_2$-sulfated (a) and TiO$_2$ sulfated "in situ".

Table 1
Crystallite sizes for TiO_2 and TiO_2-sulfated samples

Catalyst	Anatase, d (nm)	Rutile, d (nm)	Anatase/rutile, ratio (w/w)
In situ	11.7		–
TiO_2 reference (a)	48	59	3.35
TiO_2 reference (b)	49	63	4.26
TiO_2-sulfated (a)	34		–
TiO_2-sulfated (b)	35		–

and rutile phases coexist and the crystallite size for anatase was 48–49 nm and for rutile 59–63 nm (Table 1). For in situ prepared sample the crystallite size obtained for the anatase phase was the smaller one (11.7 nm) in TiO_2-sulfated (a) and (b) samples crystallite size of 34–35 nm are reported.

From the results reported in Table 1, it can be seen that the sulfation by "in situ" method or with ammonium sulfate the anatase phase was stabilized. In reference TiO_2 (a) and (b) preparations, a mixture of anatase-rutile phases was obtained. In these results the crystalline phase effect in activity is discarded, since the three sulfated samples only the anatase phase was obtained.

5.2. Specific surface areas

The specific surface areas of the samples are summarized in Table 2. It can be seen that the lowest specific surface areas correspond to the reference samples they have values of 23–27 m^2/g. In contrast, for sulfated samples the specific surface areas are comprised between 64 and 126 m^2/g, corresponding to the sample prepared "in situ" the highest value. These results show that sulfation of TiO_2 has a positive effect increasing the specific surface areas. On the other hand, the mean pore size diameters reported in Table 2 correspond to mesoporos range 123–153 Å. It must be noted that the "in situ" prepared sample the pore size diameter was of 48 Å.

5.3. FTIR-pyridine adsorption

The pyridine thermodesorption FTIR spectra of the TiO_2-sulfated samples are presented in Fig. 2. For TiO_2 sulfated (a), we can distinguish a band around the 1445 cm^{-1}, which is assigned to the adsorption of pyridine coordinated in sites Lewis. The band located at highest energy (1490 cm^{-1}) is associated to the presence of Lewis and Brönsted acids sites,

Table 2
Specific surface area and mean pore size diameter of the samples

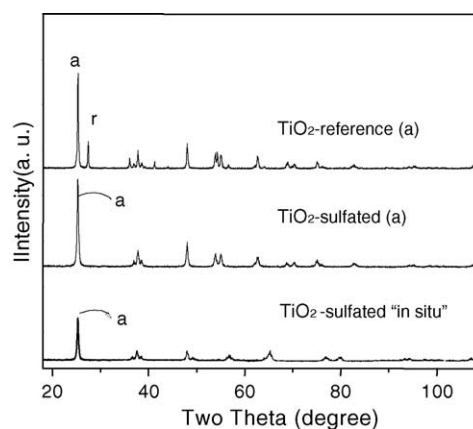| Catalyst	Surface area, BET (m^2/g)	Pore diameter (Å)
TiO_2-sulfated in situ	126	48
TiO_2 reference (a)	23	123
TiO_2 reference (b)	27	110
TiO_2-sulfated (a)	115	120
TiO_2-sulfated (b)	62	153

Fig. 2. FTIR-pyridine adsorption spectrum of TiO_2 sulfated samples: sulfated in situ, acid (a) and basic gelling medium sulfated (b).

due to the vibration of the pyridinic ring. The band showing at 1543 cm^{-1} indicates the presence of Brönsted acids sites in the solids, since pyridinium ions are formed by the transfer of protons from the acidic hydroxyl groups from the material to the organic base. The 1600 cm^{-1} band, which is identified as strong Lewis sites, follows a similar behavior of the 1445 cm^{-1} band. The band at 1575 cm^{-1} identified weak Lewis acid sites, and it disappears at 200 °C under vacuum.

Similar behavior can be observed for the TiO_2-sulfated (b) catalyst, with difference that the intensity of the pyridine absorption bands is smaller than those observed in the TiO_2-sulfated (a) catalyst. The wide band observed in the region of lower energies of the spectra presents a particular behavior during the thermal treatments. During this process it is shifted towards high wave numbers (1272–1331 cm^{-1}). These bands are related to the vibrations of S=O bonds (sulfate anchored on the surface of the solid).

For the "in situ" sulfated sample it must be noted that the absorption band corresponding to Brönsted sites (1543 cm^{-1}) is the smallest in the three samples. The bands correspondent to Lewis acid sites (1445 cm^{-1}) is clearly identified. Also, we can observed the displacement of the band at low energies corresponding to the S=O bonds by effect of water coordinated to adsorbed pyridine as occurring on the impregnated samples.

The only difference between the three catalysts is the preparation method. The behavior suggests that the sulfate ions have been bonded in different forms in each catalyst. The literature indicates that the presence de sulfates species with covalent S=O bonds on the oxide surface is necessary to obtained super acidity, but the exact nature of the catalytically active sites is not clear. Thus, it is suggested that the super acid centers are Lewis sites associated to the metal cation, whose acid strength is strongly enhanced by the electron induction effect of S=O in the sulfuric complex. Other suggestion is that the Lewis and Brönsted sites generated from adsorbed water molecules are responsible of the catalytic activity (Fig. 3).
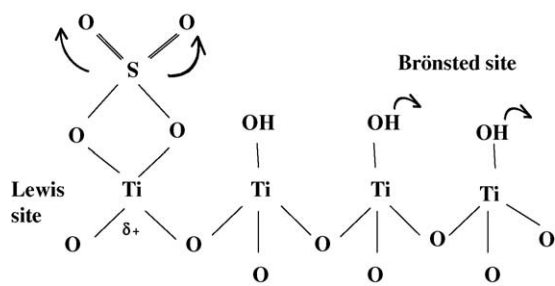
Fig. 3. Brönsted and Lewis acid sites present in the sulfated TiO_2.

5.4. Catalytic activity

For TiO_2 sulfated "in situ", a total isobutene conversion was observed (Fig. 4). Average selectivity to $C_8^=$, $C_{12}^=$, $C_{16}^=$ and $C_{20}^=$, was 9, 67, 22 and 2%, respectively, maintaining this pattern almost constant during the time of reaction (Fig. 4). Not deactivation occurs in this period of time.

TiO_2 sulfated (a) sample showed high activity at the first 40 h of reaction, with a total conversion of isobutene, but a decreasing began at that point, losing almost 60% of activity at 75 h on stream (Fig. 5). Selectivity showed a sim-
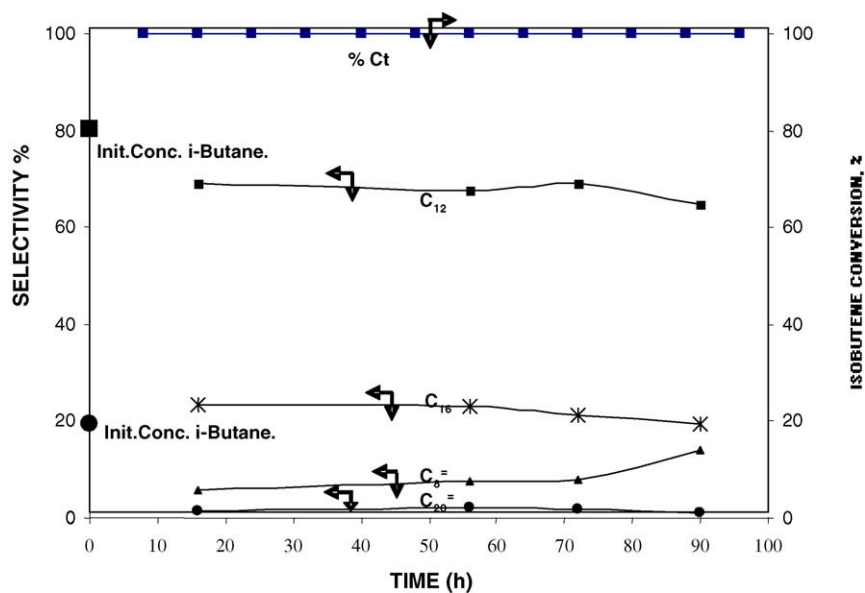
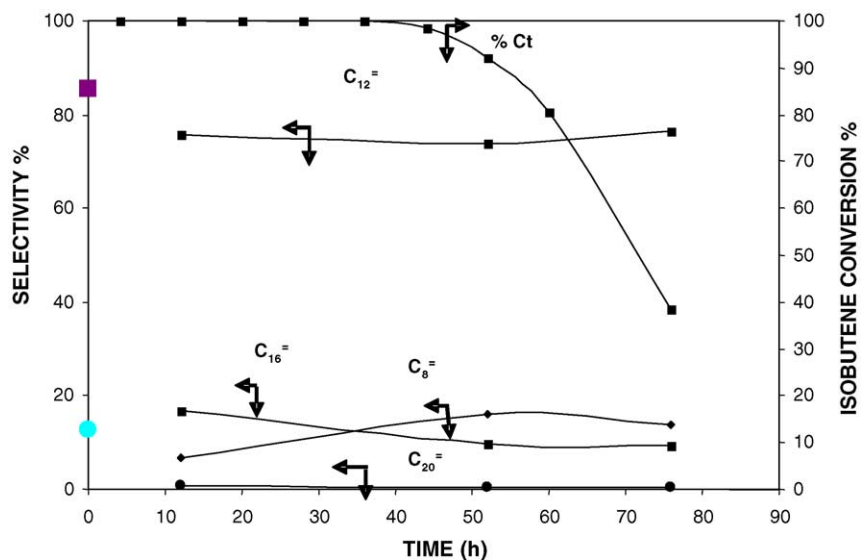

Fig. 4. Catalytic behavior of TiO_2 sulfated "in situ".
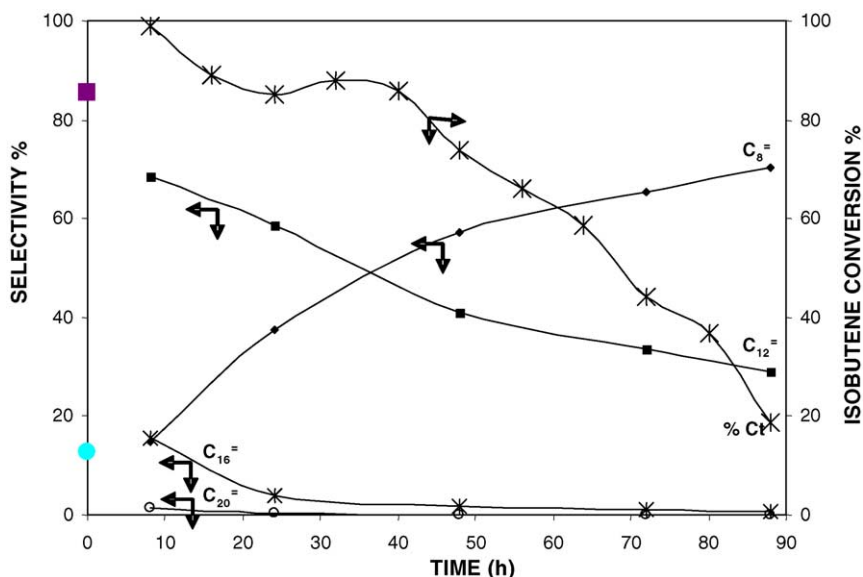

Fig. 5. Catalytic behavior of TiO_2 sulfated (a).

Fig. 6. Catalytic behavior of TiO$_2$ sulfated (b).

ilar pattern to the "in situ" sample, with average values of 13, 75, 11.5 and 0.5% for C$_8^=$, C$_{12}^=$, C$_{16}^=$ and C$_{20}^=$, respectively. Not noticeable changes were observed in function of time on stream, even when deactivation happened (Fig. 5).

For TiO$_2$ sulfated (b) the behavior was quite different: in this sample initial conversion of isobutene was 100%, suffering a pronounced lost of activity (Fig. 6). Selectivity to lighter olefins was better than the other samples, and it was improved in function of lost in activity of the catalyst, reaching values of 70, 29, 1 and 0% for C$_8^=$, C$_{12}^=$, C$_{16}^=$ and C$_{20}^=$, respectively, at the finish of the evaluation (Fig. 6). This effect was observed in oligomerization reaction carried out with other solid acid catalyst, in which selectivity was higher at lower conversion levels [16–18].

As is used above, the catalysts behavior not is depending of the TiO$_2$ crystalline phase. Oligomerization is a reaction, which is carried out in acid sites, the FTIR-pyridine absorption results showed that n the TiO$_2$ sulfated samples, Bronsted and Lewis sites exists. The difference is that the relative abundance of the first for each catalyst.

In comparing, the stability of the catalysts, it can be seen that the order showed is "in situ" > TiO$_2$ (a) > TiO$_2$ (b), which is the same order reported for the L/B acid sites ratio. These results suggest that both L and B acid sites are necessary for the oligomerization.

In reference to the catalyst TiO$_2$ sulfated (b), which shows strong deactivation, it must be noted to that such catalyst correspond to the biggest acid sites concentration. In Fig. 7, the reaction pathway of the oligomerization is shown. After the dimmer formation, the addition of one butene molecule will depend mainly of Bronsted acidity to stabilize the formation of the carbocation. The oligomerization to heavy olefins will be favored on catalyst showing a low L/B acids sites ratio. When deactivation is pronounced, the selectivity to dimers
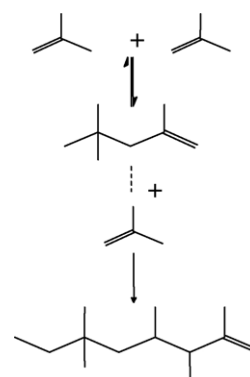

Fig. 7. Reaction pathways for the oligomerization reaction.

was increased because of the covering of active sites acid with high molecular weight olefins.

6. Conclusions

The main conclusion of the present work is the following: (i) sulfation of TiO$_2$ stabilize anatase as the principal TiO$_2$ crystalline phase; (ii) it is shown that sulfation has a positive effect in the specific surface area, being the sulfated samples those who showed the high BET specific surface area; (iii) on depending of the sulfation method, the relative abundance of L/B acid sites was modified; (iv) it was found that catalyst stability depends on this L/B ratio, being more stable at higher L/B ratio.

Acknowledgment

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