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Room temperature olefins oligomerization over sulfated titania

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Oligomerization reaction was carried out at room temperature using sulfated titania as catalyst. Total isobutene conversion was obtained with high stability for a long period of time. In case of deactivation, total reactivation of the catalyst was reached.

Olefins oligomerization might be an attractive alternative to produce liquid hydrocarbons by using the C_3–C_4 paraffin/olefins fraction of the FCC units. Usually, olefins oligomerization is carried out in liquid phase, using liquid acids impregnated in solid supports as catalyst. Unfortunately, the disposal of this kind of catalyst produces important pollution and their substitution for solid acid catalysts is a matter of research in many laboratories.[1,2] The main challenges in catalysts designed for this reaction are focused to reach high selectivity to C_8–C_{12} olefins, avoiding the formation of heaviest olefinic products (C_{16}+) and maintaining at the same time the stability of the catalyst. Looking to tailored solid acid oligomerization catalysts, results obtained in the isobutene oligomerization over sulfated titania are presented in this communication.

The catalyst was prepared by the following methodology: concentrated sulfuric acid was added to a reflux glass system containing 200 ml of *tert*-butyl alcohol (Baker 99.9%) and 200 ml of double distilled water, to reach pH 3. Then, 84.5 ml of titanium tetra-butoxide were added drop wise under constant stirring under the same conditions until gelling. The gel was dried at 100 °C for 24 h and then calcined at 400 °C in flowing air for 3h. The XRD pattern of the calcined sample showed only the anatasa crystalline phase. The textural properties were characterized by using the BET technique, showing a surface area value of 126 $m^2\ g^{-1}$. acidity of the sample was performed by FTIR-pyridine adsorption on sulfated TiO_2 as has been recently reported.[3] The FTIR-pyridine absorption spectra at difference desorption temperatures is shown in Fig. 1, where the peaks assigned to Lewis sites (1445, 1490 and 1600 cm^{-1}) can be clearly observed. A Lewis/Brønsted sites ratio equal to 4 was calculated. The stability of the pyridine adsorbed was maintained at temperatures over 300 °C in vacuum conditions. Such behavior is considered as evidence of the stability of the acid sites in the catalyst. The band corresponding to Brønsted sites (1545 cm^{-1}) shows lower intensity in comparison to the Lewis sites bands (1445, 1490 and 1600 cm^{-1}). The displacement of the band at low energies (1275–1323 cm^{-1} corresponding to S=O bonds with coordinated water can be observed.[3] The sulfur content present in the sample was 0.68% wt.

The catalytic performance was evaluated for the isobutene oligomerization reaction using a fixed bed reactor under the following conditions and procedure: 2 g of the catalysts were activated at 400 °C in flowing nitrogen. After the activation treatment, the temperature was lowered to 30 °C and a mixture of isobutane/isobutene 80 : 20 w/w was fed into the reactor under a pressure of 100 psi, to ensure that the hydrocarbon mixture was in the liquid phase. Isobutane was used as solvent because it was the more abundant paraffin in the real feed (Table 1), however other paraffins such as normal butane could be employed instead. The initial WHSV value used for isobutene oligomerization was 2.5 h^{-1} For the second experiment, flux rate was increased to reach a WHSV value of 5 h^{-1} using N_2 as a diluent.

The analysis of products was made in all the cases by FID-gas chromatography (Varian Mod. CX3400), equipped with a PONA column of 50 m and coupled to a workstation. The conversion was calculated as a function of isobutene converted and the selectivity is reported as C_8–$C_{12}^{=}$ or $C_{16}^{=}$ % mol fractions, which contain a maximum of 1% of $C_{20}^{=}$. All the liquid products were olefins.

Isobutene conversion was 100% for WHSV of 2.5 h^{-1} and 80% for 5 h^{-1}, tests 1 and 2, respectively. Catalyst did not show an appreciable deactivation during at least 48 h on stream. For the test with WHSV of 2.5 h^{-1}, the conversion remains at 100% until 100 hours on stream without catalyst deactivation, showing that we have long time stability during the process. Gas product was only isobutane in test 1 and a mixture of isobutane with no reacted

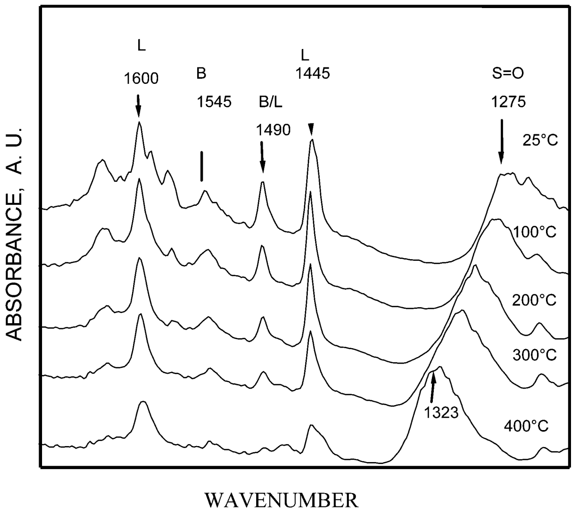

Fig. 1 FTIR-pyridine absorption spectra at difference desorption temperatures.

Table 1 Real feed composition

Component	Mol%
Propane	2.9
Propylene	1.7
i-Butane	29.2
n-Butane	7.0
1-Butene	15.1
Isobutylene	18.2
cis-2-Butene	10.4
trans-2-Butene	15.1
1,3-Butadiene	0.4

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isobutene in test 2 (Fig. 2). Selectivity pattern changes were insignificant in both experiments.

Selectivities of 82 to 87% for $C_8^=$–$C_{12}^=$ and 18 to 13% for the $C_{16}^=$ olefin fractions were obtained respectively (Fig. 3). The shape selectivity pattern to the desired C_8–C_{12} products is an important result since the formation of long chain olefin products ($C_{16}^=$) is minimized to acceptable values.

Wetness, as well as sulfur compounds, are factors which modify the rate of deactivation in most of the commercial catalysts, when they are present in the feed of the industrial processes. In test 3, with a WHSV of 2.5 and at room temperature, an isobutane/isobutene mixture was fed in the presence of water (15% vol.). Catalyst deactivation was not observed, and selectivity to $C_8^=$–$C_{12}^=$ was slightly increased (Fig. 2 and 3). Chellappa *et al.*,[4] report that selectivity and stability were improved by water addition in the oligomerization of butenes over sulfated zirconia. The effect of water is to inhibit long chain products formation and cracking side reactions. Water would modify the surface acidity, in our case mainly by coordination with the Lewis or Brønsted acid sites, optimizing the B/L ratio or by altering the redox properties of the sulfated species.[5] Also it is necessary to take account of a second role of water, since it has been reported that acid sites could be regenerated with N_2/water addition to the reactant system, according to the opinion of some authors.[6,7] Looking for an exhaustive resistance to deactivation, test 4 was carried out using a mixture of “real” FCC C_3–C_4 fraction (Table 1), which contained mercaptanic sulfur compounds in concentrations of 150 to 200 ppm. In similar way to the other test, only isobutene reacted under these conditions. After 24 h in stream with this “real” feed, an important decay in activity was observed (Fig. 4).

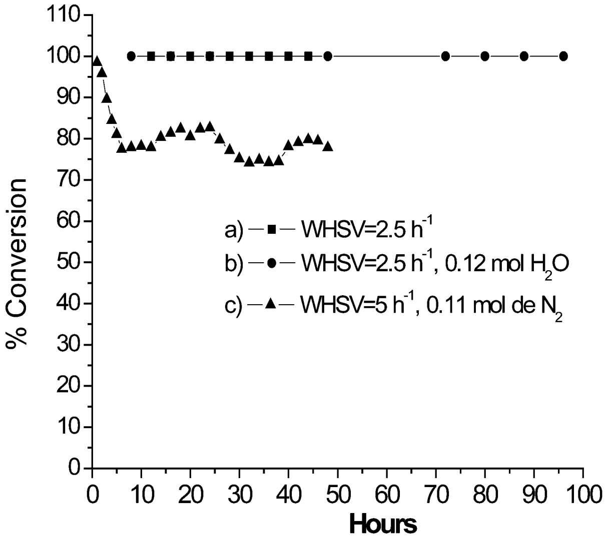

Fig. 2 Conversion *vs.* time on stream.

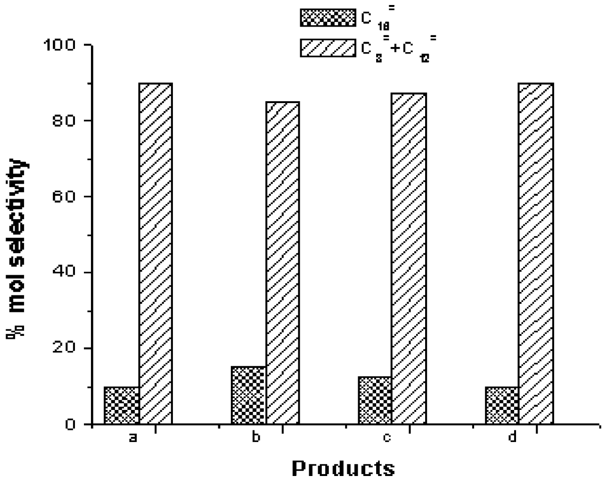

Fig. 3 Selectivity pattern a) WHSV = 2.5 h^{-1}; b) WHSV = 2.5 h^{-1}, 0.12 mol H_2O; c) WHSV = 5 h^{-1}, 0.11 mol N_2 and d) After reactivation.

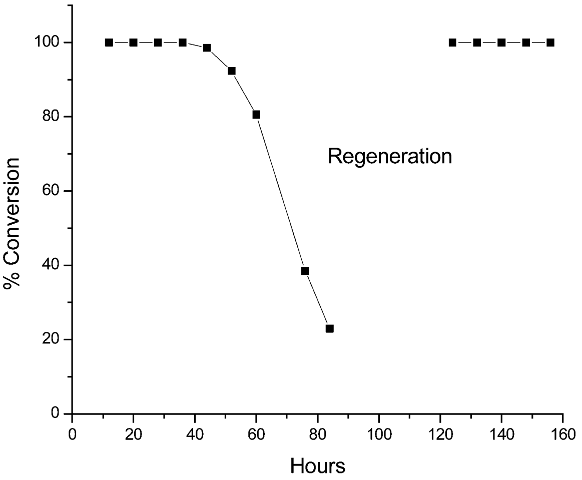

Fig. 4 Catalytic performance after reactivation

To proceed to the catalyst regeneration: the hydrocarbon feed was stopped and the reactor temperature increased to 400 °C; then an air flow (60 ml min^{-1}) was admitted in the reactor and after 2 h when the temperature had diminished to 28 °C the reaction was initiated under the conditions previously described. Activity and selectivity were recovered to initial values after regeneration (Fig. 3 and 4). We conclude that sulfated titania can be used as a highly active and selective catalyst for the isobutene oligomerization. The sulfated titania shows a very stable performance as catalyst for the oligomerization reaction; however, it is susceptible to deactivation from the effect of feed contaminants, which can be totally removed by a simple *in situ* regeneration step, easily applicable to an industrial process. Moreover, to our knowledge, it is the first time that the use of sulfated TiO_2 has been reported for olefin oligomerization at room temperature, in a liquid phase heterogeneous process.

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