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Oligomerization of isobutene on sulfated titania: Effect of reaction conditions on selectivity

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Abstract

On sulfated titania prepared by gelling titanium alkoxide with sulfuric acid, isobutene oligomerization was carried out under different operating conditions. Under severe conditions [temperature 140 °C, pressure 600 psi and weight hourly space velocity (WHSV) of 2.5 h^{-1}], the catalyst reached 100% isobutene conversion and selectivity for $C_{12}^{=}$ and $C_{18}^{=}$ olefins of 54 and 39%, respectively. Meanwhile, under soft conditions (28 °C, 100 psi and 10 h^{-1}), conversion decreased from an initial value of 55–25% after 30 h on stream, while the selectivity for $C_{8}^{=}$ increased from 42 to 60%. After 90 h on stream, catalyst activity was recovered by introducing nitrogen into the feed and the conversion then reached 90%. These results show that by varying the operating conditions over a sulfated titania catalyst, isobutene oligomerization can be controlled to the desired $C_{8}^{=}$ or $C_{12}^{=}$ olefin yield.

Keywords: Sulfated titania; Isobutene oligomerization; Gasoline production; Acid catalysts; Olefin dimerization; Olefin oligomerization

1. Introduction

Fuel reformulation is now carried out on a worldwide basis due to US and European legislation, which is focused on reducing evaporative emissions and on complete fuel combustion. In this context, an interesting route for the production of high-octane ecologically friendly gasoline is the dimerization of light olefins. This process is particularly attractive, since the olefin C_4 fraction of the FCC process can be used as a feed, with isobutene, 1-butene and 2-butenes, the main components of this fraction. When the olefin source is isobutene, highly substituted $C_{8}^{=}$ olefins are obtained [1–4].

The oligomerization process using phosphoric acid on a silica support as catalyst has been used for several years to produce gasoline [5]. The reaction is carried out at temperatures over 200 °C, and products range from the dimer ($C_{8}^{=}$) to higher polymeric olefins ($C_{16}^{=}$).

The trimer products of isobutene oligomerization are also of interest, due to the industrial use of triisobutylene as a source of neoacid compounds in the production of dodecylbenzene or for gas-oil additives [6,7]. The scientific interest in and commercial importance of butene oligomerization have led to the search for new solid catalytic materials that can avoid the formation of higher molecular weight olefins due to their controlled acidity. Among the catalysts reported for this reaction, other than phosphoric acid over silica, are Ziegler–Natta-based catalysts [8], zeolites [9,10], sulfonic resins [11], benzyl sulfonic acid on silica [12], mica montmorillonite [13], titanium oxide [14] and zirconium oxide [15,16]. In addition, modification of the above-mentioned oxides with sulfates, tungstates or phosphates has been widely recommended by several

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authors to modify the acidic properties and stabilize the support [14,16,17].

Olefin oligomerization is a reaction for which the activity and selectivity strongly depend on the operating conditions. With this in mind, in the present work, we report the effect of operating conditions, such as temperature, pressure and weight hourly space velocity (WHSV) on the activity, selectivity and stability of a sulfated titania prepared by gelling titanium alkoxide in a sulfuric acid medium.

2. Experimental

The sample, termed ''in situ'' sulfated titania, was synthesized according to the following procedure: 200 ml of bidistilled water and 200 ml of *tert*-butanol were mixed in a glass flask under reflux and stirring, then sulfuric acid (Baker 99%) was added to adjust the solution to pH 3. Then, 84.5 ml of titanium *n*-butoxide was slowly added to the flask, maintaining the solution under reflux for 24 h. After gelling, the sample was dried at 70 °C for 24 h and annealed at 400 °C in air for 3 h.

3. Characterization

3.1. X-ray diffraction

The titania synthesized was characterized by X-ray diffraction (XRD) using Cu Kα radiation on a Siemens D-500 instrument. The XRD spectrum for sulfated titania is shown in Fig. 1, from which it can be observed that sulfation stabilizes the anatase phase. Only, the anatase phase was present in the sample and the crystallite size obtained was 11.7 nm.

3.2. Specific surface area

The BET-specific surface area of the sample was calculated from a nitrogen adsorption isotherm using Micromeritics ASAP-2000 apparatus. The value obtained was 126 m^2/g.

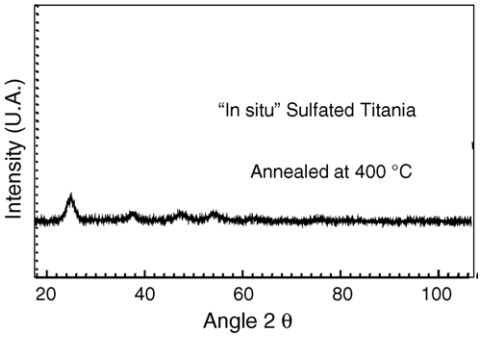

Fig. 1. XRD pattern for ''in situ'' sulfated titania.

Table 1
Brönsted and Lewis acid sites present in the ''in situ'' sulfated titania

Catalyst	Adsorption temperature	Brönsted sites	Lewis sites	Total acidity
''In situ'' sulfated titania	Room	97	410	507
	100	100	314	414
	200	77	281	358
	300	63	235	298
	400	27	155	182

3.3. Fourier-transform infrared (FTIR)-pyridine adsorption

Total acidity and the ratio of Lewis/Brönsted sites were determined by Fourier-transform infrared-pyridine adsorption in a Nicolet 170 SX spectrometer. The annealed material was pressed into thin self-supporting wafers. They were then placed in a glass Pyrex cell with CaF_2 windows coupled to a vacuum line and evacuated (1×10^{-6} Torr) in situ at 400 °C for 30 min. Adsorption was carried out on the cell at 25 °C by breaking a capillary tube containing the pyridine. Excess pyridine was desorbed under vacuum from room temperature to 400 °C in steps of 100 °C. The values obtained from the FTIR spectra are shown in Table 1.

3.4. Catalytic evaluation

The catalytic behavior was evaluated for isobutene oligomerization using a fixed bed reactor, with dimensions of 1.7 cm in diameter and 57 cm in length. The evaluation procedure was as follows. A 1 g portion of the catalyst was activated at 400 °C in flowing air. After the activation treatment, the temperature was lowered to 140 °C in flowing nitrogen and then a mixture of high-purity isobutane/isobutene (80:20, w/w) was admitted into the reactor. The pressure of the reactor was adjusted to maintain the hydrocarbon mixture in the liquid phase. Isobutane was only used as a diluent in the feed, because it is the more abundant paraffin in the fluid catalytic cracking (FCC) olefin fraction (the ratio iC_4/nC_4 contained in the paraffin fraction of the feed is 4:1); however, other paraffins, such as *n*-butane could be used instead. The composition of a typical FCC olefin fraction used as a feed in industrial processes is shown in Table 2. Traces of butadiene are also present in this fraction and lead to fast deactivation of the catalyst [18].

The WHSV, temperature and pressure settings were varied to study the effect of these parameters on the catalyst behavior.

Table 2
Current FCC feed composition

Component	mol%
$C_3^=$	1.7
C_4	36.2
$C_4^=$	61.6
Others	<0.4

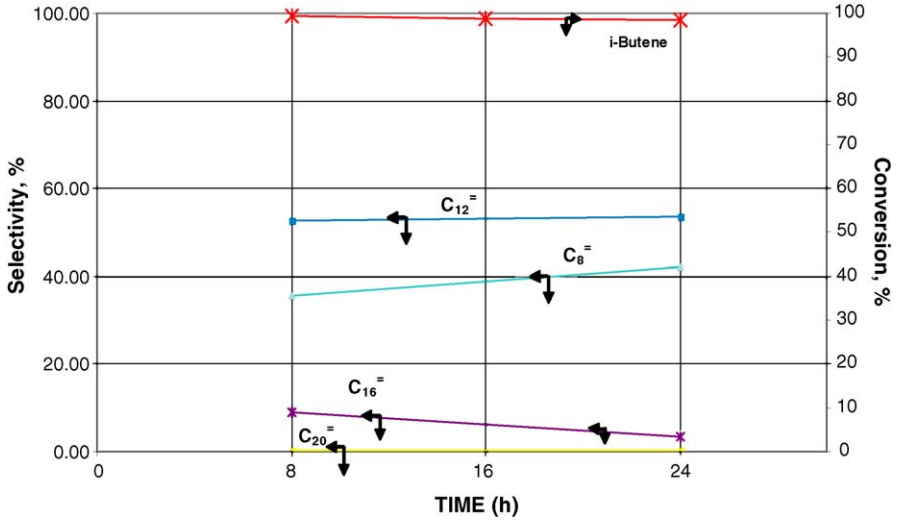

Fig. 2. Oligomerization of isobutene (140 °C, 600 psi, WHSV = 2.5 h^{-1}).

Analysis of the products in all cases was by flame-ionization detector (FID) gas chromatography (Varian model CX3400) equipped with a PONA column of 50 m and coupled to a workstation. 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 $C_{20}^=$ (<1%) were found in all cases.

The WHSV value was calculated as a function of the isobutane/isobutene mixture fed (g h^{-1}) and the weight of catalyst used (g). The effect of addition of diluents in the feed was also studied.

4. Results and discussion

The catalytic behavior of the sulfated titania catalyst for isobutene oligomerization under operating conditions of 140 °C, 600 psi and 2.5 h^{-1} is shown in Fig. 2. It can be noted that conversion of 100% was maintained for 16 h, with average selectivity of 54% for $C_{12}^=$, 39.5% for $C_8^=$ and 6.3% for $C_{16}^=$ fractions. When the WHSV was increased from 2.5 to 5 h^{-1}, keeping the temperature and pressure constant, the activity was maintained and selectivity for the $C_8^=$ fraction was slightly improved (Fig. 3). This behavior is probably a result of the lower contact time between isobutene and the active sites of the catalyst, thus diminishing the formation of $C_{12}^=$ and higher olefins.

To investigate milder operating conditions that those mentioned above, the pressure of the reactant system was decreased to 400 psi and the temperature to 28 °C, keeping the WHSV at 5 h^{-1}. In this test, the conversion of isobutene was also 100%, with a slight increase in the selectivity for $C_8^=$ and $C_{16}^=$, which reached average values of 66.7 and 13.1%, respectively. In contrast, the $C_{12}^=$ fraction was diminished to 19.6% (Fig. 4). This temperature effect could be explained by the non-reversibility of the reaction.

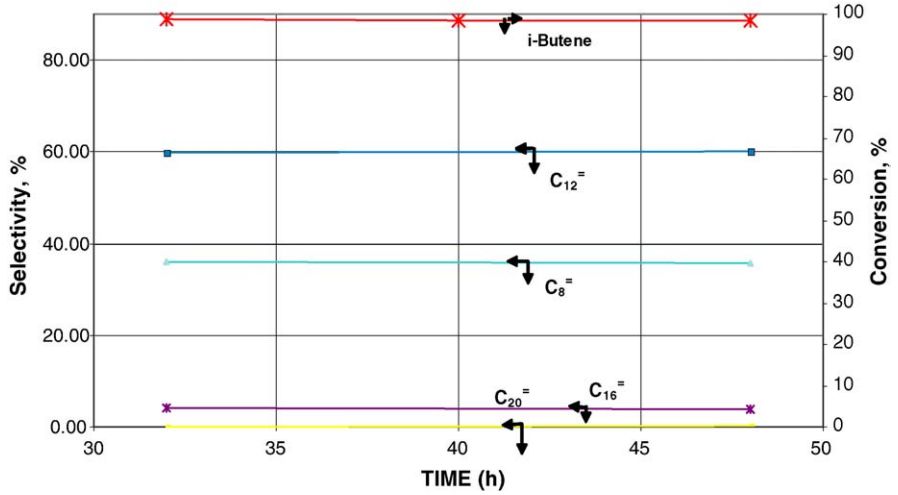

Fig. 3. Oligomerization of isobutene (140 °C, 600 psi, WHSV = 5 h^{-1}).

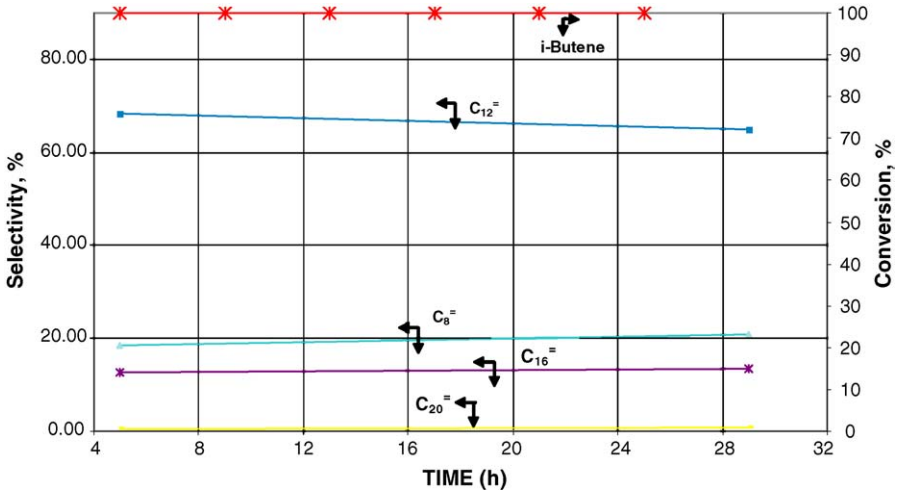

Fig. 4. Oligomerization of isobuteno (28 °C, 400 psi, WHSV = 5 h^{-1}).

Alcántara et al. [6] reported that the reaction reversibility of butene oligomerization over amberlyst resin becomes important above 100 °C; in our case, the splitting of $C_{12}^{=}$ and $C_{16}^{=}$ did not occur because a lower temperature was used.

The effect of WHSV of 10 h^{-1} on activity and selectivity is reported in Fig. 5. It can be observed that under these conditions the conversion of isobutene decreases to 67%, showing further deactivation after 8 h on stream with a value of 52.5%. The selectivity was also affected: initial values of 38% for $C_8^{=}$, 54% for $C_{12}^{=}$ and 7% for $C_{16}^{=}$ were obtained, which decreased with the loss of activity to 46, 48 and 5%, respectively. At high WHSV, the contact time for reactants and catalyst improves the complete adsorption–desorption equilibrium for isobutene molecules over the active sites of the catalyst. This behavior is consistent with the findings reported in other works, in which high selectivity for the dimer was reported [19,20].

The effect of the pressure during oligomerization can be observed in Fig. 6, for which the pressure was reduced to 100 psi and the temperature and WHSV were kept at the same values as for the previous test. The initial conversion rate was 55% and showed a pronounced decrease of almost 57% with respect to the initial value after 32 h on stream (Fig. 6). As a positive effect of the loss in activity, the selectivity for dimerization was improved from 42 to 59% for the $C_8^{=}$ fraction.

This deactivation of the catalyst can be attributed to the presence of a gas–liquid mixed phase in the reactants, which blocked active sites on the catalyst by the deposition of high molecular weight olefins [21].

An important factor in the oligomer adsorption–desorption equilibrium is the presence of an inert diluent in the feed [22]. The above hypothesis was corroborated when $N_{2(g)}$ was added as a diluent in the feed under the same

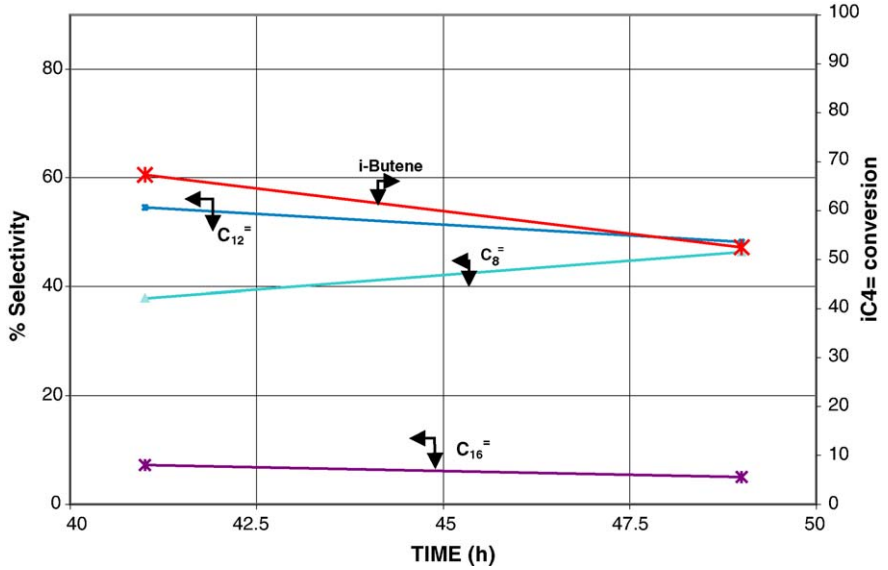

Fig. 5. Oligomerization of isobutene (28 °C, 400 psi, WHSV = 10 h^{-1}).

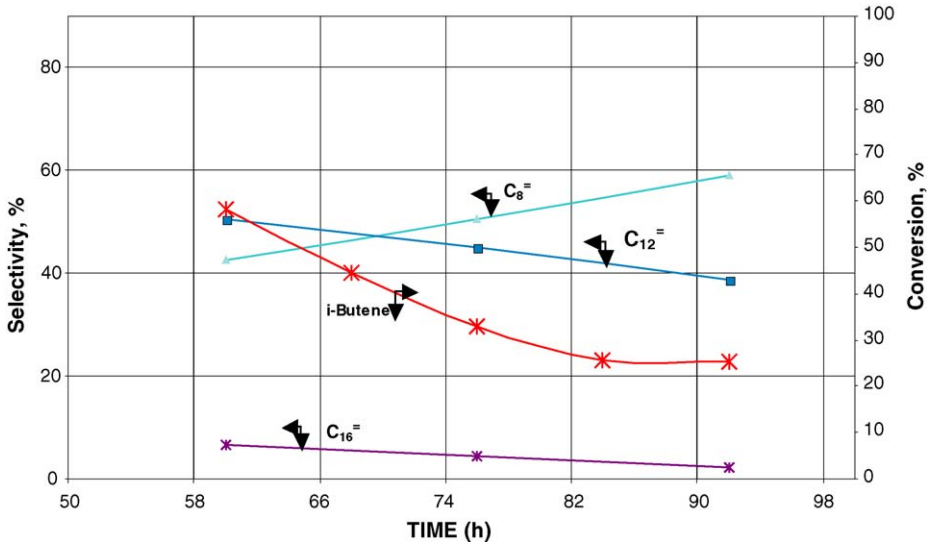

Fig. 6. Oligomerization of isobutene (28 °C, 100 psi, WHSV = 10 h^{-1}).

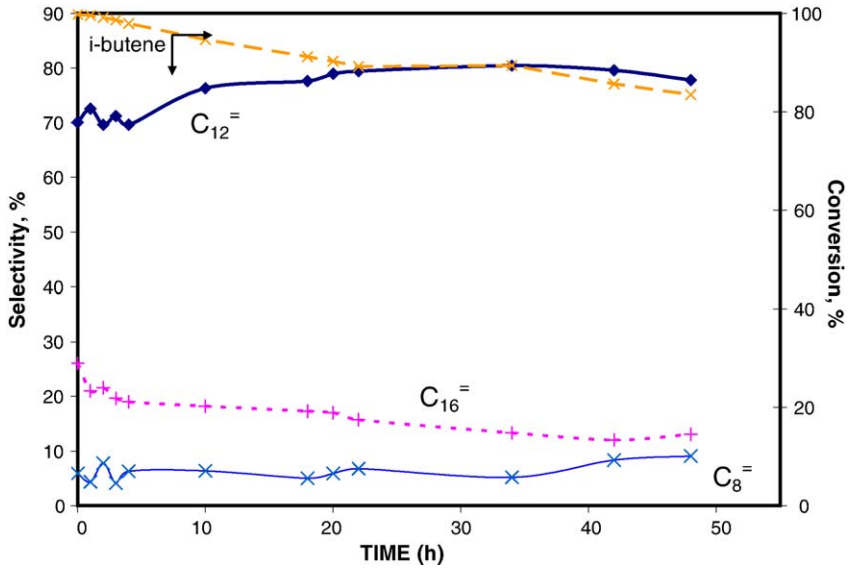

Fig. 7. Oligomerization of isobutene (28 °C, 100 psi, WHSV = 10 h^{-1}, with N_2 a 2 ml s^{-1}).

reaction conditions as the previous experiment. In Fig. 7, it can be observed that the deactivation rate was not as pronounced as that in the experiment in Fig. 6, because the presence of $N_{2(g)}$ diminished the contact time for reactants on the catalyst surface, improving the catalyst stability. Furthermore, the rate of adsorption–desorption of heavy components on the catalyst surface, as well as the inhibition or ''washing'' of blocked active sites of the catalyst, depend on the diluent/hydrocarbon ratio in the feed [22].

5. Conclusions

In situ sulfated titania was an active catalyst, even under mild operating conditions. High selectivity for dimerization was found when the re-adsorption of $C_8^=$ produced in the dimerization reaction was blocked. This re-adsorption step can be minimized by modifying the contact time between isobutene and the active sites of the catalyst.

The addition of an ''inert'' diluent to the olefin feed had a positive effect on the stability of the catalyst due to the effect of ''washing'' of adsorbed high molecular weight olefins deposited on the active sites.

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