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Oligomerization of isobutene with a beta-zeolite membrane: Effect of the acid properties of the catalytic membrane

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ABSTRACT

Isobutene oligomerization was performed using a ceramic membrane with a film of zeolite beta, where three different zeolite molar ratios SiO_2/Al_2O_3 were evaluated. The reaction was studied in a membrane reactor within the 373–423 K temperature range. Analyses of the reaction products suggest a complex pattern of isobutene dimerization and isomerization and the main reaction product was 2,2,4-trimethypentane (2,2,4 TMP) for all catalytic tests conducted.

1. Introduction

During 2003, MTBE was phased-out from the gasoline pool in many countries. Its water solubility made it suspect for the cause of significant pollution in lakes and underground water sources [1]. MTBE production has been a major consumer of isobutene from the C_4 hydrocarbon stock and as a result the phase-out has caused a major decline in isobutene downstream consumption [2]. Among the possibilities for process revamping, or the design and application of new technologies for replacing MTBE, one is the use of indirect alkylation [3], which may involve the synthesis of DIB (di-iso-butene or iso-octene) by dimerizing isobutene [4]. Isobutene dimerization could give an additional value to this compound, through the synthesis of isooctanes, valuable compounds that could substitute for the MTBE formerly used during gasoline reformulation. The dimerization of olefins can be carried out under relatively mild conditions in the presence of heterogeneous catalysts, such as the ion exchange resins used in the Bayer process [5] and solid phosphoric acid SPA [4]. However, the supported acid catalysts have been reported to provoke a negative environmental impact, corrosion, potential handling risks and waste disposal problems.

An important aspect in the use of heterogeneous catalysts and catalytic membranes is that that they are incorporated in processes that have a minimal impact on health and the environment. Such characteristics are known as green chemistry [6–8]. In addition, we were motivated in this work by the knowledge that one of the main problems associated with dimerization is the control of selectivity due to the significant exothermicity of the process and the presence of side reactions (trimers formation). In 2001, Piera et al. [9] reported the dimerization of isobutene employing a membrane reactor with an internal fixed bed acid resin, Amberlyt^{TM} 15 that allowed the preferential extraction of the dimer. As result of using the membrane reactor the selectivity for the dimer was improved. In this same sense, underlining the previous experience of our group, Torres et al. [10], showed that the oligomerization of olefins in a forced-flow catalytic membrane reactor (acid beta-zeolite) allowed control of the reaction time within the catalyst pore system and allowed for a 60% conversion rate and 60% dimers selectivity. However, if a comparison is made with the work reported by Fritsch et al. [11], who applied a forced-flow membrane (acid Nafion®) reactor in order to dimerize isobutene, the researchers attained only a 45% conversion and 80% selectivity. On the other hand, isobutene oligomerization through solid acids like these catalytic membranes, promotes the isooctane production and yields different product distributions as a function of the acidity force of the membrane. In view of the considerations above, the present work is a study of different acid beta-zeolite membranes for the dimerization of isobutene in order to attain high conversion and selectivity rates under the forced-flow catalytic membrane reactor configuration. The use of a catalytic membrane reactor is novel in that it is expected to favour selectivity to isooctane's and to increase conversion rates.

2. Experimental

2.1. Catalytic membrane preparation

Commercial tubular α-alumina supports (2-μm size pores, T1-70, Pall Exekia) with dimensions: 25 cm length, and 1.0/0.8 cm

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outer/inner diameters were used as porous supports. The beta-zeolite membranes were prepared by *in situ* crystallization onto the inner surface of the porous supports. The beta-zeolite precursor gel was prepared as follows: sodium hydroxide (>99% Mallinckrodt) was dissolved in distilled water and small pieces of aluminum foil (99.9%, Merck) were added and stirred with slight heating until complete dissolution. Then, a mixture of tetraethylammonium hydroxide (TEAOH 35%, Aldrich) and potassium hydroxide (Merck) was added to the solution. Subsequently, Aerosil 300 silica (Degussa)® was added to the mixture with continuous stirring at room temperature until homogeneity was attained. Finally the resulting gel was aged for 48 h at 298 K. Three SiO_2/Al_2O_3 molar ratios were used at the following gel molar compositions:

MZB 60	$3.20\ Na_2O{:}1.62\ K_2O{:}1Al_2O_3{:}60\ SiO_2{:}22.5\ (TEA)_2O{:}1080\ H_2O$.
MZB 90	$3.20\ Na_2O{:}1.62\ K_2O{:}1Al_2O_3{:}90\ SiO_2{:}22.5\ (TEA)_2O{:}1080\ H_2O$.
MZB 120	$3.20\ Na_2O{:}1.62\ K_2O{:}1Al_2O_3{:}120\ SiO_2{:}22.5(TEA)_2O{:}1080\ H_2O$.

After zeolite synthesis the membrane was brushed and washed with water followed by overnight drying at 393 K. The zeolite membrane was calcined for 3 h at 823 K, under air flow and cooled to room temperature. The ion exchange cycle was performed using 350 mL aqueous 0.5 M NH_4NO_3 at 353 K under constant stirring for 3 h and the volume of solution used had a liquid/solid ratio of 20 [10,12].

2.2. Characterization

2.2.1. Gas permeation

In order to verify that the film was free from macro and micro defects the membrane was mounted in a stainless steel module and affixed using graphite seals. The permeation cell was allowed to stabilize for 2 h at 298 K, closing off one of its ends (dead-end). Prior to calcining the membrane to eliminate the template, it was subjected to a dried nitrogen flow fed through a mass flow controller over the outer surface of the membrane to check whether there were macro-defects or fissures in the zeolite film. The pressure was increased up to 2 bar and the gas flow in the permeate side was continuously monitored with a soap bubble meter. No measurable flow was detected.

2.2.2. X-ray diffraction (XRD)

The membranes were analyzed by XRD with a Bruker D8 Discover instrument equipped with a Gadds Bruker system, with $CuK\alpha_{1,2}$ radiation, a beam size of 500 μm, a Göbel mirror monochromator and a HI-SATAR area detector, a laser beam and a light microscope. The configuration used was for high resolution and the detector was fixed at 30 cm for detecting 17.5 2θ degrees. In order to measure the amount of beta-zeolite that was grown on the ceramic membrane surface the grazing incident beam technique (GIBT) was used to obtain the diffraction patterns.

2.2.3. Scanning electron microscopy (SEM)

The topographical and cross-section morphology of the membrane were observed by means of a scanning electron microscope (SEM) Leica Zeiss LEO-LTD, Model 440. The samples were fractured and the inner surface, "top layer", and the side, "cross-section", of the membrane were analyzed. In order to complement the membranes characterization, the beta-zeolite powder was produced as explained above and was analyzed with the following two techniques:

2.2.3.1. Nitrogen adsorption–desorption measurements. The BET specific surface area and average pore diameter were determined by multipoint N_2 physisorption using a Micromeritics instrument (ASAP 2020), at liquid N_2 temperature (77 K). Prior to carrying out the analyses all the samples were degassed at 573 K and 10^{-4} Torr pressure during 300 min.

2.2.3.2. Acidity determination. Acidity was determined by means of NH_3-TPD at different temperatures with the aid of a Catalyst Analyzer BELCAT-B instrument. The samples were heated for 1 h at 673 K under an ultrapure He gas flow, cooled to 323 K and the gas flow was changed to NH_3 (NH_3/He 10%, Infra) for 40 min. After saturation, a He purge was performed for another 30 min at the same temperature. Finally, the samples were heated under He flow at 10 K min^{-1} heating rate to 973 K.

2.3. Catalytic activity test

The isobutene oligomerization reaction was carried out in a membrane reactor comprised of stainless steel cylinder jacket containing the ceramic membrane. A couple of graphite joints were used for fitting the ceramic membrane to the metallic cylinder. This configuration was divided in two chambers: the outer one was used for feeding the pure isobutene gas-phase (>99.999% purity) controlled with fine valves, and the inner chamber was used for collecting the product. The pressure was monitored by means of a Cole-Palmer transducer, Mod.07356, placed at the reactor inlet while the reaction zone was surrounded by a three heating zone-electrical furnace. The reaction temperature was monitored using a West 2054 controller and the products trapped in a condenser at the reactor outlet were analyzed for hydrocarbons with a FID-gas chromatography (Agilent 6890 equipped with a PONA column of 50 m) coupled to a workstation. In a typical experiment, the catalyst membrane was pre-treated at 773 K under flowing nitrogen (20 mL min^{-1}) for 1 h. After activation, the temperature was reduced to 373 K. The reaction conditions were as follows: the isobutene volumetric flow rate was adjusted to 41 $cm^3\ min^{-1}$ corresponding to WHSV = 53 h^{-1} in the 373–423 K temperature range. Separation of the fractions obtained did not represent an important problem in the process because of their very different boiling points. The conversion was calculated with respect to isobutene, according to the following expression:

$$X(100) = \frac{F_{in} - F_{out}}{F_{in}} X100$$

where X is the conversion, F_{in} is the number of isobutene moles injected per hour per gram of catalyst and F_{out} is the number of isobutene moles present in the product stream per hour per gram of catalyst.

The selectivity was expressed as C_8 fractions computed by taking the total number of moles of product formed using the expression:

$$S_i(100) = \frac{P_i}{P_t} X100$$

where S_i is the selectivity to each fraction, P_i is the number of moles formed of each fraction product per hour per gram of catalyst and P_t is the total number of moles of product formed per hour per gram of catalyst.

The following compounds: 2,3,4 trimethylpentane (2,3,4 TMP), 2,2,4 trimethylpentane (2,2,4 TMP), 2,5-dimethylhexane (2,5 DMH), 2,4-dimethylhexane (2,4 DMH), from Aldrich, and PIANO from AccuStandard ASTM-P-0035, lot B2040312, were used to name the reaction products.

3. Results and discussion

3.1. Characterization

The X-ray diffraction pattern of the top layer of the membrane showed the characteristic peaks of a typical beta-zeolite. The position of the reflections ($2\theta = 7.69$ and $2\theta = 22.37$, i.e. $d_{hkl} = 0.3972$ nm),

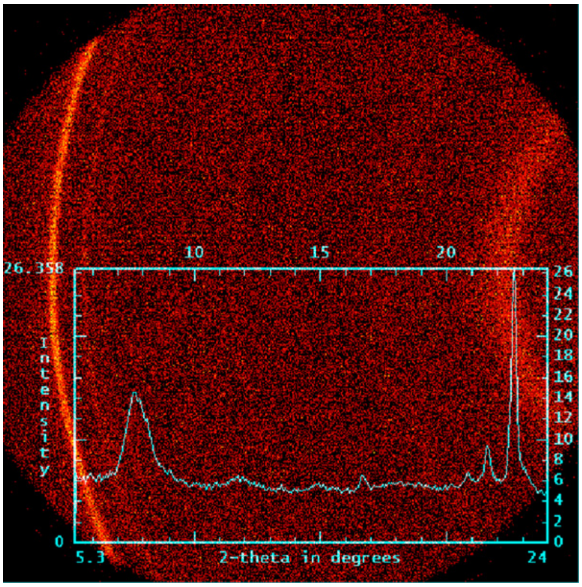

Fig. 1. X-ray diffraction pattern of the beta-zeolite film with a SiO_2/Al_2O_3 molar ratio of 120.

Table 1
Textural and acid properties of the zeolitic catalytic membranes.

Membrane	Surface area ($m^2\,g^{-1}$)	Pore volume ($cm^3\,g^{-1}$)	Mean pore (Å)	Acid capacity ($mol\,NH_3\,g^{-1}$)
MZB 120	237	0.172	29.07	1.82×10^{-3}
MZB 90	396	0.208	21.79	3.07×10^{-3}
MZB 60	455	0.244	21.46	4.60×10^{-3}

corresponds to the peaks with the greater intensity of the reference, commercial PQ beta-zeolite. The XRD pattern obtained under GIBT conditions showed considerable homogeneity in color and the same intensity on the sample, suggesting that the beta-zeolite film is homogeneous under the alumina support (Fig. 1).

The textural and acidic properties of the membranes reported in Table 1 show the relationship between acidity and the SiO_2/Al_2O_3 molar ratio of the gel precursor. The largest number of acid sites per mol $[NH_3]$/g obtained was MZB 60, with the surface area ($m^2\,g^{-1}$) of 455 $m^2\,g^{-1}$ while MZB 120 had a surface area of 237 $m^2\,g^{-1}$. These results show that by modifying the Al_2O_3/SiO_2 molar ratio it becomes possible to have three different acidity zeolite membranes.

Fig. 2(a) and (b) are micrographs of the top layer of the MZB 120 membrane and Fig. 3 shows a cross-section of the zeolite film. SEM analysis for the different membrane sections confirmed the absence of any macro-defects or fissures. This figure also shows that the zeolite film is constituted by grains forming a polycrystalline network and that the membrane thickness exceeded 4 µm.

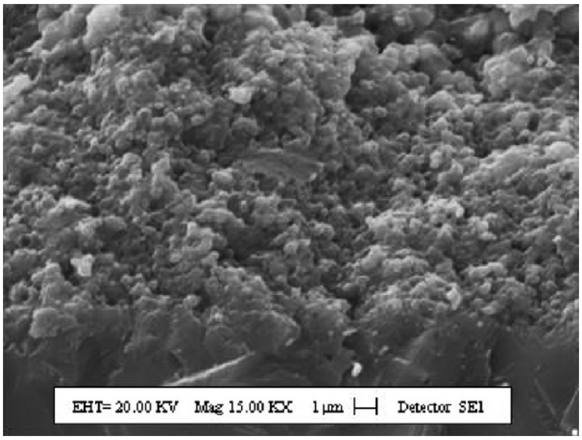

Fig. 3. Scanning electron microphotograph of the cross-section of the MZB120 sample.

During the permeation tests no measurable N_2 gas flow was detected on the side of the permeate. Therefore, since the pores of the zeolite film were blocked the only possibility for the gas to cross the membrane would be through defects or fissures indicating that the membrane did not present macro-defects or fissures, evidenced by the SEM analysis of the membrane's surface (Figs. 2 and 3).

3.2. *Catalytic activity*

The catalytic membranes were tested for isobutene oligomerization in the 373–423 K temperature range with WHSV = 53 h^{-1}. The effect of varying the WHSV has been studied elsewhere [4], though in this work it remained constant. Under this condition, the MZB 60 catalytic membrane displayed very low isobutene conversion at 373 K, while with the other two membranes, MZB 90 and MZB 120, the latter yielded the greatest conversion, as shown in Fig. 4. The most efficient oligomerization performance was recorded for the MZB 60 sample at 383 K, with a 66% conversion and 92% selectivity for the C_8 fractions, which were maintained along the temperature range studied without deactivation being detected. A comparison between the other membranes showed 84% for MZB 90 and 74% for MZB 120 of selectivity (Fig. 5). Results reported in Figs. 4 and 5 show that dimer's production has a relationship with membrane acidity. Hauge et al. [13], reported similar results relating the catalytic acidity to the catalyst performance for the dimerization of isobutene and proposed fast deactivation of the zeolite due to possible blocking of the inner pores by large oligomers. In contrast, for the membrane reactor, fouling of the

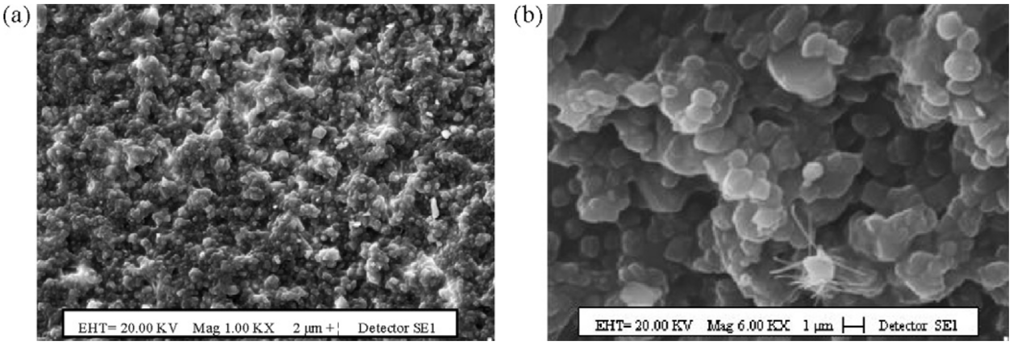

Fig. 2. Scanning electron microphotographs of the top layer of the MZB120 sample: (a) 1000KX and (b) 15000KX.

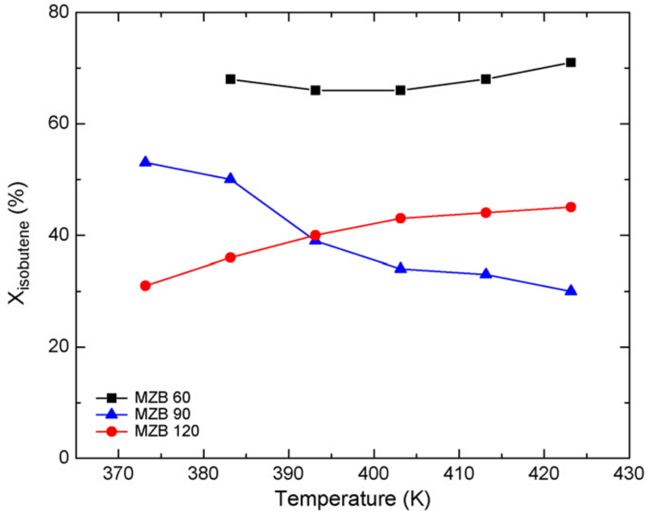

Fig. 4. Isobutene conversion as a function of temperature: (a) MZB60, (b) MZB90, and (c) ZB120.

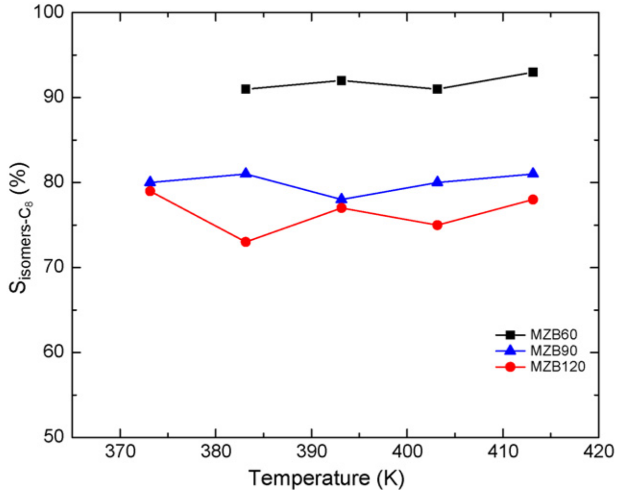

Fig. 5. Isobutene selectivity to C_8 compounds as a function of temperature: (a) MZB60, (b) MZB90, and (c) MZB120.

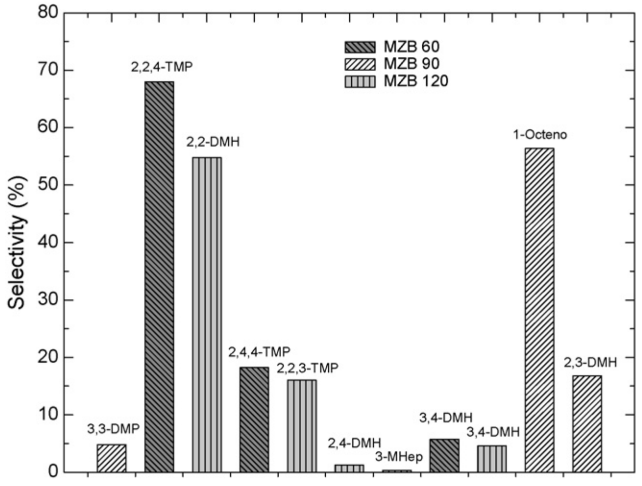

Fig. 6. Product distributions (selectivity to C_8) obtained after reaction of isobutene at 393 K from membranes MZB60, MZB90 and MZB120.

pores was not detected because the monomers were forced to diffuse through the pores. Fritsch et al. [11], reported very similar results employing a polymeric membrane.

All catalytic tests showed that the acid-zeolite membrane produced the oligomerization of isobutene and skeletal isomerization of reaction products. Distribution of the compounds however, depended on acidity properties of the membrane and the reaction conditions. The main products were: 2,2,4 trimethylpentane (2,2,4 TMP), 2,2-dimethylhexane (2,2 DMH), 2,2,3 trimethylpentane (2,2,3 TMP) and 3,4-dimethylhexane (3,4 DMH) (Fig. 6). When we compared the product distribution obtained from the three membranes, the most important compound for different tests was (2,2,4 TMP). At 423 K, there were also identified pentanes iC_5 and nC_5 and hexanes 2-MP, 3-MP. These results suggest that different reaction types take place; oligomerization, isomerization, disproportion, cracking and hydrogen transfer, in series and parallel, although there was no evidence of precursor coke species. It is important to note that the MZB 90 membrane attained a 24% deactivation in contrast with 17% for MZB 120 at 423 K. All catalytic tests were run continuously for 96 h.

4. Conclusions

The synthesis of beta-zeolite membranes with different acidities was carried out. In the oligomerization of isobutene the catalytic membrane exhibited high activity towards isobutene dimers. This can be attributed to the surface acidity of the membrane and the control of short residence time within the zeolite membrane active pores thus eliminating the large butane oligomers C_{16}. The catalytic membrane reactor showed better performance for this reaction in comparison with other reactor types and configurations.

References

[1] F.E. Ahmed, Toxicol. Lett. 123 (2001) 89.
[2] M. Honkela, A. Kolah, J. Aittamaa, Chem. Eng. Process. 45 (2006) 329.
[3] A.K. Kolah, Q. Zhiwen, S.M. Mahajani, Chem. Innovation 31 (2001) 15.
[4] M.J. Tsai, R. Kolodziej, D. Ching, Hydrocarbon Process. 81 (2002) 81.
[5] K. Weissermel, H.-J. Arpe, Industrielle Organische Chemie, VCH, Weinheim, 1990.
[6] J.H. Clark, Green Chem. 1 (1999) 1.
[7] K. Wilson, J.H. Clark, Pure Appl. Chem. 72 (2000) 1319.
[8] J.H. Clark, Acc. Chem. Res. 35 (2002) 791.
[9] E. Piera, C. Téllez, J. Coronas, M. Menéndez, J. Santamaría, Catal. Today 67 (2001) 127.
[10] M. Torres, L. López, J.M. Domínguez, A. Mantilla, G. Ferrat, M. Gutiérrez, M. Maubert, Chem. Eng. J. 92 (2003) 1.
[11] D. Fritsch, I. Randjelovic, F. Keil, Catal. Today 98 (2004) 295.
[12] M. Torres, M. Gutiérrez, L. López, V. Mugica, R. Gómez, J.A. Montoya, Mater. Lett. 62 (2008) 1071.
[13] K. Hauge, E. Bergene, D. Chen, G.R. Fredriksen, A. Holmen, Catal. Today 100 (2005) 463.