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Preparation of Pt-ZSM-5 zeolite membrane catalysts for the isomerization of linear alkane

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KEYWORDS Catalytic zeolite membrane; Pt catalyst; Pentane; Isomerization.	Abstract. A ZSM-5 supported membrane was synthesized by the secondary growth method. The Pt-ZSM5 membrane was prepared by the impregnation method. This membrane was characterized by a single gas permeation step at room temperature. The isomerization of <i>n</i> -pentane was selected as a probe reaction for evaluating the catalytic performance of the membrane. In particular, the effects of the space velocity and the time on stream were considered. After the catalytic tests, the membrane was characterized by Scanning Electron Microscopy (SEM), Energy-Dispersive X-ray spectroscopy (EDX), and X-Ray Diffraction (XRD). N ₂ permeance for the membrane, after calcination, was equal to 2.9×10^{-7} mol/m ² .s.Pa, indicating the coverage of the larger support pores by the zeolite crystals. This result was also confirmed by the SEM investigation. In addition, XRD analysis showed that the ZSM-5 was the desired zeolite type. During the catalytic tests, the reduction of the nC ₅ conversion and the increase of the iC ₅ selectivity with Weight Hourly Space Velocity (WHSV) were observed. The nC ₅ conversion decreased from 30 to over 70. On the other hand, its conversion on catalyst enhanced from 10% to approximately 38% with an increase in the reaction temperature from 250 to 450°C.
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1. Introduction

The isomerization of catalytic linear alkanes to branched alkanes is an important industrial reaction due to the increasing demand for iso alkanes, which are used as a substitute for octane boosters instead of aromatic and oxygenate compounds that are subjected to stringent environmental limitations [1–4]. Gasoline is composed of a large number of linearchain compounds with a low octane number. Nevertheless, these compounds may rise when gasoline is exposed to the isomerization reaction through which linear-chain molecules are transformed to branched molecules [5,6]. In isomerization reactions, a mixture of di-branched, mono-branched, and linear molecules is formed; therefore, the conversion of linear paraffins in the isomerization reaction is limited by the thermodynamic equilibrium [7,8]. The linear paraffins from the isomerization process effluent are separated and recycled at the entrance of the isomerization reactor. A Membrane Reactor (MR) consists of a combination of

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the distribution process or membrane separation with a chemical reactor in one system. Chemical processes are easier to implement due to the integration of distribution/separation and reaction, producing much lower processing costs than the costs of applying more conventional processes [9,10]. There are many scientific reports on the synthesis, characterization, and development of catalysts for pentane isomerization. Aboul-Gheita et al. evaluated the effect of Pt concentrations on the SZ catalyst performance [11]. The Ir/Pt-HZSM5 zeolite catalyst was prepared by the saturation of iridium on Pt-HZSM5 zeolite. The effect of Si/Al ratio on n-pentane isomerization using Ir/Pt-HZSM5 was studied by Setiabudi et al. The Ir/Pt-HZSM5 zeolite catalyst showed the highest activity for the isomerization of n-pentane at an Si/Al ratio of 23 [12,13]. The n-pentane isomerization on the Zn/HZSM-5 zeolite catalyst was carried out by Setiabudi et al. Their results indicated the iC5 conversion associated with the promotive effect of H_2 as a carrier gas [13]. To the best knowledge of the current author, there is no existing report on pentane isomerization using catalytic MRs.

Zeolites characterized by a regular structure and thermal and chemical stability have shown a major potential for combined systems of separation/reaction as an MR [14–18]. These advantages support zeolite membranes as a new technique for organic synthesis and particular separation in the chemical industry [19– The MFI-type zeolite (ZSM-5 and aluminum-22]. freesilicalite-1) with a pore size of 0.58 nm can separate nC_5 (minimum kinetic diameter = 4.3Å) from 2methyle pentane (minimum kinetic diameter = 5Å) selectively based on the difference in adsorption strength Thus, MFI membrane is employed as and size. a separator and, also, an MR for diverse reactions such as linear alkane (C5-C7) isomerization [13,23,24], providing better product selectivity. A study of alkane isomerization using the MFI membrane reactor was performed by Gora and Jansen [25]. They passed a feed (iso-hexane/n-hexane) on the outer side of a tubular membrane. The conversion of n-hexane to iso-hexane was achieved by the permeation of $n\,C_6$ through the membrane and in the catalyst phase.

In this study, a zeolite catalytic MR, for the first time, was used for the isomerization of nC_5 . The prepared membrane was characterized by Scanning Electron Microscopy (SEM), Energy-Dispersive X-ray spectroscopy (EDX), and X-Ray Diffraction (XRD) analyses. Moreover, the permeation property was also evaluated before and after the calcination step. Finally, the MR performance for nC_5 isomerization was studied as a function of space velocity and time on stream.

2. Experimental

2.1. Materials

The chemicals used for the membrane preparation include tetraethoxysilane (TEOS, ACROS) as a silica source, aluminumisopropoxide (AIP, Merck) as an aluminum source, tetrapropylammonium hydroxide ((TPAOH, 1 M aqueous solution, Merck) as an organic structure-directing agent (the template), and triethylenetetramine (Trien, Merck) as a chelating agent. All of the solutions were prepared by adding sodium hydroxide (Merck) and distilled water.

Membrane supports were made of porous α -Al₂O₃ asymmetric tubes (*IKTS*, *I.D.* = 7 mm, *O.D.* = 10 mm, L = 100 mm, dpore = 100 nm). The tubular support used for removing possible dust and oil materials inside the pores was cleaned with acetone by an ultrasonic cleaner for 1 hour. Afterward, the support was boiled in distilled water for 1 hour and, then, dried in a furnace at 120°C for 2 hours.

2.2. Membrane preparation

ZSM-5 zeolite membranes were synthesized by the secondary growth method. This method, separating the nucleation from crystal growth, allows optimizing each step independently. The method is carried out in two stages: seeding and growth. In this work, the membranes were seeded by means of the procedure used by Garofalo et al. [26]. After the seeding, the crystals were grown by transferring the synthesized solution into the inner support positioned in a Teflonlined autoclave. The zeolite layer on the outer surface of the support was formed without wrapping it with Teflon tape. Finally, the hydrothermal treatment was carried out by putting the autoclave in a preheated furnace. The operating conditions used for the growth are reported in Table 1.

After performing the hydrothermal synthesis, the synthesized membranes were washed several times with distilled water and, then, dried at 100°C for 8 hours to remove the water adsorbed in the pores of zeolite. After the synthesis, the prepared membrane was calcined up to 753 K to remove the template. Calcination was

Table 1. Operating conditions used for the hydrothermal treatment [35].

Molar composition	2.7 TPAOH: 46 SiO ₂ :5 Na ₂ O: Al ₂ O ₃ : 1.3 Trien: 2500 H_2O
Solution aging	12 hours
Temperature	$180^{\circ}\mathrm{C}$
Time	24 hours

performed using a furnace at heating and cooling rates of 1 K/min.

2.3. Pt-ZSM-5 catalytic membrane layer

For obtaining the HZSM-5 membrane, Na⁺ ions present in the zeolite layer were exchanged with ammonium in a 0.1 M NH₄Cl solution for 4 hours at 95°C. This procedure was repeated three times. Then, the cation-exchanged membrane was dried at 50°C and, then, heated up to 450°C for 3 hours [27]. Pt/zeolite catalyst layers were prepared by impregnation with an aqueous solution of hexachloroplatinic acid hydrate for 24 hours. The catalysts were dried after saturation and activated under H₂ atmosphere for 3 hours at 623 K.

2.4. Zeolite membranes characterization

Powder X-ray diffraction (XRD, D5000 Siemens, Germany) was performed on the material scratched off the membrane surface. The morphology of the zeolite membrane was observed by Scanning Electron Microscopy (SEMCamScan MV2300, Check Republic). The Energy Dispersive Spectroscopy (EDS) and element mapping were applied to analyze the dispersed elements of the membrane sample. Before performing MR experiments, C_5 isomer permeation properties including separation factor and permeance of the membrane were evaluated in a continuous flow system. The isomerization reaction of *n*-pentane was selected to evaluate the catalytic activity of the prepared zeolite membrane.

The total pressure on the permeate side was kept at 1 atm for binary permeation tests, and the used membrane pressure difference (Δp) was 0.1–1 bar. A nitrogen stream was applied to eliminate the permeating species by sweep. Both components can permeate the feed solution and, afterward, separation can be achieved due to differences in diffusion rates, sorption rates, and the molecule capability to block

or inhibit the other from penetrating the pores. The experimental setup used for performing the separation tests and the catalytic reactions is shown in Figure 1. The catalytic zeolite membrane was placed in a membrane module and sealed by O-rings. This reactor was placed inside an electrical oven to control the reaction temperature. The gas feed was controlled by a mass flow controller. The injection of pentane into the MR was carried out by means of a syringe pump. The outlet flow of the pump was evaporated in the gaseous form by using thermal wires that are wrapped around the steel tubes connected to the membrane modulus. Hydrogen gas was applied as a reactant in the processes under research. Nitrogen gas was used as a sweep stream on the permeate side of the membrane module. A nitrogen stream was applied to eliminate the permeating compounds by the sweep side in the membrane separation tests. The flow rate of gases was controlled by mass flow controllers. Gas was injected into the zeolite catalyst membrane cell, and the permeate and retentate pressures were controlled by back pressure regulators. Moreover, the differential pressure on the zeolite membrane was controlled by differential pressure gauges. Both of the retentate and permeate were evaluated online using gas chromatograph of Teif Gostar Company with a capillary column and a flame ionization detector (Serial No.: p2085307, Cat. No. TR-110222, ID: 0.25, l: 25 m, TRB-1, Tecknokroma). The experiments were performed in H_2 at 250°C and at a constant H_2/HC molar ratio 4.8.

The selectivity (or separation factor) of the membrane is defined through the following equation:

$$\alpha = (yi/yj)/(xi/xj), \tag{1}$$

where yi, yj and xi, xj are the molar fractions of components i and j on the permeate (y) and the feed (x) sides, respectively.



Figure 1. Scheme of the setup used for membranes characterization.

The total conversion of the *n*-pentane $(X_{n-pentane})$ is calculated as follows:

$$X_{n-pentane} = \frac{\sum A_i - A_{n-pentane}}{\sum A_i} \times 100,$$
(2)

Further, the selectivity (S) is described for the reaction product, or the asset of products, through Eq. (3):

$$S_i = \frac{\sum A_i}{\sum A_i - A_{n-pentane}} \times 100, \tag{3}$$

where A_i is the corrected chromatographic area for a particular compound, which is used to express the conversion and selectivity as molar percentages [28].

3. Results and discussion

Before calcination, the membrane was gas tight, indicating that the synthesized membrane was defect-free. After calcination, the single gas permeation test was performed at room temperature by using nitrogen as gas. The N₂ permeance was equal to 2.9×10^{-7} mol/m² s Pa and about 30×10^{-6} mol/m² s Pa for the bare support and the membrane, respectively. The lower membrane permeance with respect to the bare support indicates that, at least, the larger support pores are covered with the zeolitic layer.

Then, $nC_5/2MB$ mixture (70/30) was separated using the synthesized Pt-ZSM-5 membrane. As shown in Figure 2, the selectivity decreased as the feed pressure increased. This phenomenon results from the growing number of transports through the non-zeolite pores with the feed pressure. This result confirms the presence of defects in the zeolite layer. The same results were found by a BZSM-5 zeolite membrane [29].

The isomerization of *n*-pentane was considered as a probe reaction to evaluate the catalytic activity of the prepared catalytic zeolite membrane. The catalytic test was performed at 250° C in accordance with the



Figure 2. $nC_5/2MB$ selectivity versus feed pressure (70/30 mixture, T = 493 K).



Figure 3. Effect of Weight Hourly Space Velocity (WHSV) on the pentane isomerization (conversion and selectivity); (sample: Pt-ZSM-5 membrane; molar ratio $H_2/HC = 4.82$; $T = 250^{\circ}C$).

results obtained in the same process in previous works. Figure 3 shows the experimental results in terms of conversion and selectivity in the case of the isomerization of n-pentane as a function of the space velocity.

The experimental data, indicating an increase in the space velocity, were used to determine the decrease rate of the conversion and the increase rate of the selectivity. One way to account for this result is the fact that an increase in the space velocity causes a reduction in the contact between reagents and catalytic sites and, thus, the pentane conversion decreases. At the same time, an increase in the space velocity suppressed the side reaction of 2MB as the selectivity increased. In general, the nC_5 conversion reduced through the rising WHSV, and the reaction products shifted far away from the thermodynamic equilibrium and obtained a particular value regardless of nC₅ flow rate, while the selectivity of isomerization increased through the increasing WHSV. Given that the WHSV has a critical impact on reaction kinetics, high WHSV causes a reaction-rate-limited conversion and low WHSV leads to an equilibrium-limited conversion [30]. Figure 4 shows the conversion of n-pentane and selectivity as a function of the time on stream.

It is possible to observe the nC_5 conversion getting slower easily over time on stream, while the selectivity remains constant, probably because of coke deposition on acidic sites. In fact, different papers have reported that strong Lewis acidic sites in the absence of hydrogen become active sites for the formation of dehydrogenated carbonaceous species, turning into a precursor of coke on the surface of the catalyst [31,32]. The performances of both powdered Pt-ZSM-5 catalysts that were reduced at temperatures of 250 and 450°C are presented in Figure 5. The catalysts that were reduced at 450°C were more active in pentane iso-



Figure 4. nC₅ conversion and 2MB selectivity versus time on stream (sample: Pt-ZSM-5 membrane; molar ratio of H₂:HC = 1.6; WHSV = 0.026 h⁻¹; $T = 250^{\circ}$ C).



Figure 5. Effect of reduction temperature of catalytic activity of Pt-ZSM-5 zeolite powder at 250°C.

merization than those reduced at 250° C. The pentane conversion on the Pt-ZSM-5 catalyst increased from 10% to about 38% due to an increase in the reaction temperature from 250° C to 450° C. In addition, the reaction selectivity for catalysts reduced at 450° C was more than that reduced at 250° C. Therefore, it is expected that the reduction of the catalytic layer at 450° C may increase the conversion and selectivity of pentane isomerization.

After performing the catalytic experiments, the zeolite layers grown on the alumina supports were analyzed by XRD, SEM, and EDX. The XRD patterns of α -Al₂O₃ tubular support (Figure 6(b)) and ZSM5 powder (Figure 6(c)) were compared with those recorded for powder scratched on the surface of the membrane. The characteristic peaks of ZSM5 zeolite and alumina can be observed in the composite membrane spectrum (Figure 6(a)). In Figure 6(a), the peaks at 7–9° and 22.5–24.5° correspond to the MFI-type zeolite, indicating the presence of the desired zeolite.



Figure 6. X-Ray Diffraction (XRD) spectra: (a) Powder scratched from membrane (b) α -Al₂O₃ support, and (c) ZSM5 powder [34].

Extra peaks correspond to the alumina support and $R-TiO_2$ (rutile phase) intermediate layer [20].

SEM micrographs of the membrane are shown in Figure 7. A mostly uniform and compact zeolite layer was present on the alumina support (see Figure 7(a)). In addition, the thickness of the zeolite layer on the support was about 50 mm, as shown in Figure 7(b). For comparison purposes, the image of bare support is also reported (Figure 7(c) and (d)).

EDX analyses were also carried out on the membrane cross-section of the ZSM5 layer. The presence of Si, Al, and Pt was detected (see Figure 8).

The elemental chemical mapping revealed that Si and Al were the major elements present along



Figure 7. Scanning Electron Microscopy (SEM) micrographs: (a) Cross-section, (b) top-view of the Pt-ZSM5 membrane, (c) cross-section, and (d) top-view of the bare support.



Figure 8. Energy Dispersive Spectroscopy (EDS) elemental analysis on the Pt-ZSM-5 membrane.

the thickness of the membrane. In addition, oxygen was also present outside the zeolite layer as a major component of the support (see Figure 9).

The results presented in this work demonstrate the possibility to perform the *n*-pentane isomerization by using zeolite membrane loaded with Pt. Usually, a zeolite catalytic membrane offers a good dispersion of catalytically active and nano-sized particles in a thin zeolite layer by improving the contact between the reactants and the catalytic site and reducing the by-pass problem [33]. However, to improve the performance of a process using catalytic zeolite membrane, it is very important to reduce the concentration of defects in the zeolite layer. In fact, it is well known that zeolite membrane functions very well in a process where liquid species are involved, while the limits are set when gas species are involved because of their small sizes;



Figure 9. Energy Dispersive Spectroscopy (EDS) elemental mapping images of Pt-ZSM-5 membrane.

therefore, the necessity to have membrane defect-free should be considered [36].

4. Conclusion

ZSM5 supported membranes were synthesized by the secondary growth method. Pt-loaded zeolite membranes were prepared by the impregnation method. Scanning Electron Microscopy (SEM) analysis showed the formation of an almost uniform and compact layer on the alumina support. This result was also confirmed by the N_2 permeance of the membrane, measured after the calcination step. In addition, Energy Dispersive Spectroscopy (EDS) analysis confirmed the presence of Pt, Si, Al, and O in the zeolite layer. The catalytic tests showed the possibility to perform the nC_5 isomerization by using the Pt-ZSM5 membrane. Moreover, it was also observed that the nC_5 conversion decreased and the iC₅ selectivity increased with Weight Hourly Space Velocity (WHSV) due to the reduced contact time. It was also found that the nC_5 conversion decreased with time on stream, probably owing to the coke formation.

Nomenclature

EDS Energy Dispersive Spectroscopy MR Membrane Reactor

SEM	Scanning Electron Microscope
WHSV	Weight Hourly Space Velocity
XRD	X-Ray Diffraction

List of symbols

A	[-]	the chromatographic area
	-	_

- S [dimensionless] selectivity
- X [dimensionless] the total conversion
- x_i [dimensionless] molar fractions of components i in the feed
- y_i [dimensionless] molar fractions of components *i* in permeate
- α [dimensionless] the separation factor

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