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n-Hexane Hydroisomerization Over Composite Catalysts Based on BEA Zeolite and Mesoporous Materials

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Abstract Composite catalysts based on HBEA zeolite and Pt loaded mesoporous materials—Al/SBA-15, Al/MCM-41 and PCH—where studied in *n*-hexane hydroisomerization. Textural characterization showed that the Pt particles are mainly at the external surface. A synergistic effect was achieved for Pt-PCH + HBEA composite, where an increase in di-branched products was observed.

Keywords *n*-Hexane hydroisomerization · Composite catalysts · BEA · Mesoporous materials

1 Introduction

The current specifications for gasoline fuels impose strong restrictions on aromatic compounds content [1]. In this context, the hydroisomerization of linear paraffins (C_5–C_6) plays an important role since the isomers obtained (highly branched) allow the maintenance of adequate octane number. This reaction is generally carried out over bifunctional catalysts, containing small metal particles such as Pt or Pd dispersed on an acid support. The most common catalysts are Pt/highly chlorinated alumina, Pt/HMOR zeolite [2] and Pt/sulphated zirconia [3]. According to the bifunctional mechanism, *n*-alkenes resulting from the dehydrogenation of *n*-alkanes on metallic sites can undergo skeletal isomerization on acid sites, the resulting products being subsequently hydrogenated on other metallic sites. The properties of the light alkane hydroisomerisation catalysts is then determined by the balance between hydrogenating and acid functions [4]. The introduction of the metal precursors directly on one-dimensional pore structures, like MOR zeolite, can cause a partial blockage of the pores. In fact, due to metal particles growing near the pore opening during the reduction step, the access of reactants and reaction intermediates to the interior of the porous structure become considerably limited [5].

As it was observed, for instance, by Parton et al. [6] there is a synergistic behaviour when two zeolites with a different pore structure, namely Pt/ZSM-12 and Pt/deep bed steamed Y (Pt/DB-Y) were used, since a greater isomerisation yield of *n*-decane was found, when compared with the individual zeolite. Le Van Mao [7] tested hybrid catalysts, comprising two components: microporous (ZSM-5) and several mesoporous materials in aromatization of *n*-butane. According to this author the beneficial effect of the hybrid system, when compared with ZSM-5 zeolite alone, is attributed to the formation of a micropore–mesopore continuum within the hybrid catalysts system which decreases the resistance to the outward diffusion of products, mainly for bulkier product molecules. Kinger et al. [8] also found higher activity and selectivity for composite catalysts made of HMCM-22 or BEA with MCM-41 or SiO_2 in *n*-heptane hydroisomerization. The results were explained by the faster adsorption and desorption rates of reactive molecules in the composite.

MCM-41 and SBA-15 are ordered honeycomb mesostructured members of M41S family, being SBA-15 a more stable structure due to the higher thickness of its walls.

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Since the surface of these materials is only weakly acidic, the introduction of tetrahedrally coordinated aluminium (Td-Al) in their structure is a way to create some Brönsted acid sites and ion-exchange properties [9].

Porous clays heterostructures (PCHs) are relatively new clay based materials which present high specific surface areas (700–1,000 m^2 g^{-1}). The porosity of these materials is within the large micropores to the small mesopores [10]. Galarneau et al. [11] demonstrated the possibility of using a gallery templated approach for preparing PCHs materials. These authors used surfactants and long chain amines to direct the polymerization of a silica source within the clay galleries. After removing the organic molecules from the structure (e.g. by a thermal treatment), a porous structure of silica walls within the clay sheets is obained. Although PCHs were studied mainly as adsorbents [12, 13], there are also some publications reporting their behaviour as catalysts [14, 15] and their high hydrothermal stability, in relation to other mesoporous materials such as MCM-41, was also shown [16].

The purpose of this work is to study the performance of composite catalysts based on a microporous and a mesoporous component in the catalytic reaction of *n*-hexane hydroisomerization. The microporous component is the BEA zeolite and the mesoporous materials are Pt loaded Al/SBA-15, Al/MCM-41 and PCH. The results are compared with those obtained by the isolated constituents containing the same amounts of metal.

2 Experimental

2.1 Materials

The experimental procedures concerning the synthesis of Al/SBA-15 and Al/MCM-41 are described elsewhere [17, 18]. The PCH used in this work was prepared from a natural Portuguese clay, from the Porto Santo Island, previously charactererised in detail [19]. A 0.5 M aqueous solution of cetyl trimethyl ammonium bromide, CTAB (Aldrich) was added to a clay suspension (1 g of clay in 100 cm^3 of water) and the mixture kept overnigth under stirring at 50 °C. The resulting material was separated by centrifugation, washed with water until pH ~ 7. To the air-dried sample decylamine (Aldrich, 95%) and tetraethoxysilane (Aldrich, 98%), in a molar ratio 20:150, respectively, were added under stirring. The resulting solid was dried and afterwards calcined at 650 °C for 5 h [12].

HBEA zeolite with Si/Al = 12.5 was supplied by PQ Corporation. The mesoporous materials and HBEA zeolite were loaded with 1 (wt %) Pt, using the incipient wetness impregnation technique, with $H_2PtCl_6 \cdot xH_2O$ solutions. The composite catalysts were prepared by mixing in a ceramic mortar, for 5 min, adequate quantities of zeolite and mesoporous material to obtain 1 (wt %) Pt in the composite. After metal loading all samples were dried and calcined at 300 °C for 3 h under air flow of 12 L h^{-1} g^{-1} with a heating rate of 1 °C min^{-1}. After these treatments the samples were named Pt-HBEA, Pt-M and Pt-M + HBEA, where M = Al/SBA-15, Al/MCM-41 or PCH.

2.2 Methods

Textural properties were studied by N_2 adsorption at −196 °C using an automatic Micromeritics (ASAP 2010) apparatus. Prior to data acquisition the samples were outgassed for 2 h at 300 °C.

The catalytic tests were performed in a continuous flow reactor at 250 °C under a total pressure of 1 atm. The samples were previously reduced in situ under H_2 flow (6 L h^{-1} g^{-1}) at 500 °C for 3 h. The reaction feed consisted of a mixture of H_2 and *n*-hexane (H_2/n–C_6 = 9) and the space velocity was changed from 6.6 to 53.4 h^{-1}. To evaluate the catalysts deactivation a return point was determined at the initial space velocity. The reaction products were analysed by gas chromatography (HP 6890) equipped with a FID detector and a CP-SQUALANE capillary column. The results are reported as conversion (molar percent of reactant converted) and product selectivity (moles of product divided by moles of *n*-hexane reacted, in percentage).

3 Results and Discussion

To evaluate the effect of metal deposition in the samples texture the adsorption isotherms of nitrogen at −196 °C (not shown) were determined before and after Pt deposition. Regarding PCH, the configuration of the initial part of both isotherms denotes the presence of a microporous structure, with a wide porous distribution, which does not seem to be affected by the metal deposition. The slope observed for higher relative pressures indicates the presence of a mesoporous structure or an external surface, which suffers some changes in consequence of the Pt introduction procedure. HBEA zeolite presents a type I isotherm typical of microporous materials. Al-SBA-15 and Al-MCM-41 show type IV isotherms characteristic of regular mesoporous materials.

The adsorption isotherms were analysed through the application of BET equation ($0.05 < p/p^0 < 0.15$) to obtain the specific surface area, S_{BET}. It must be noted that due to the microporous nature of BEA zeolite structure S_{BET} value should be considered as an apparent surface area. The α_S method was used to estimate the microporous volume

(V_{micro}) and the external surface area (S_{ext}). The total porous volume (V_{total}) was estimated considering the amount of N_2 adsorbed at $p/p^0 = 0.95$ and the mesoporous volume (V_{meso}) calculated by the difference $V_{total}-V_{micro}$, except for MCM-41 where it was determined from α_S representations. The results obtained are presented in Table 1. The analysis of the results shows that only for HBEA sample a decrease in V_{micro} is observed upon Pt introduction. This fact can be justified by the occurrence of some loss of cristallinity during the calcination treatments, due to framework defects typical of BEA zeolite [20].

Regarding the mesoporosity, the effect of the metal deposition is observed only in PCH and Al/SBA-15 materials. The increase of V_{meso} and S_{ext} observed for Pt-PCH is, most probably, due to a different aggregation of the crystals as a result of the Pt deposition method (incipient wetness impregnation followed by thermal treatments—calcination and reduction). In the case of Pt–Al/SBA-15 the decrease of the mesoporous volume can be related to the pore dimensions of this structure which are significantly higher than those of the other mesoporous solids (PCH and MCM-41). In fact, the porous size distributions for Al/MCM-41, PCH and Al/SBA-15 are centered at 32, 30 and 70 Å, respectively [12, 18]. So, in the case of Pt–Al/SBA-15 it is most likely that some Pt particles are located inside the pores. For all samples a more or less important increase of S_{ext}, was observed after Pt deposition, suggesting that the metal particles are preferentially located at the external surface. This is in agreement with the results reported in Ref. [21], where, using transmission electronic microscopy (TEM) images, it was observed that incipient wetness impregnation led to poor metal dispersions, with Pt particles located preferentially at the external surface of the material.

The total conversion as a function of the contact time (1/WHSV) is presented in Fig. 1 for Pt-HBEA, Pt-M and Pt-M + HBEA. The catalyst Pt-HBEA zeolite shows always a higher conversion when compared to the mesoporous and the composite catalysts, reaching a maximum conversion around 50 (mol%). The mesoporous and composite catalysts present a maximum conversion around 10%, except Pt–Al/MCM-41 with a maximum conversion not better than 4%. The catalyst deactivation, %ΔConv., calculated as the difference between the initial conversion and the conversion obtained at the return point, both determined at the lowest space velocity, divided by the initial conversion is presented in Table 2. Pt-HBEA and the composite catalysts present deactivation values close to 10% and the catalysts based on mesoporous materials.

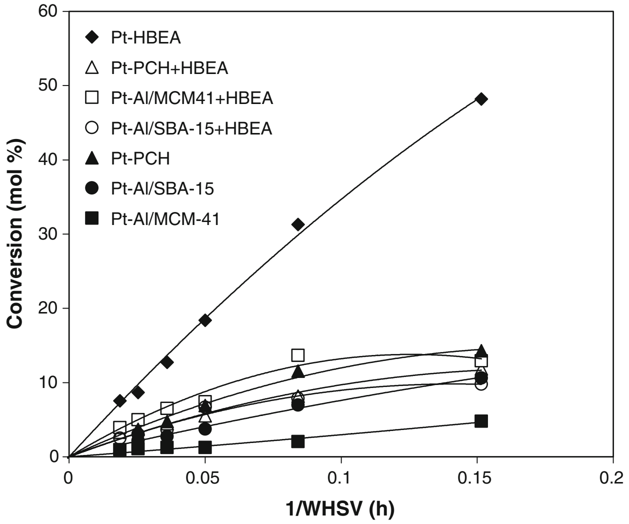

Fig. 1 Total conversion as a function of contact time for *n*-hexane hydroisomerization at 250 °C

(Pt–Al/SBA-15 and Pt-PCH) show a much higher deactivation. This behaviour can be explained considering that Pt particles are located mainly at the external surface of the crystals. Consequently, inside the porous structure isomerisation and cracking reactions are occurring only at the acid sites, without further hydrogenation of the reaction intermediates. Since the pore dimensions of all the essayed materials allow the formation of high molecular weight

Table 1 Specific surface area (S_{BET}), microporous volume (V_{micro}), mesoporous volume (V_{meso}), total volume (V_{total}), and external surface area (S_{ext})

Sample	S_{BET} ($m^2\ g^{-1}$)	V_{micro} ($cm^3\ g^{-1}$)	V_{meso} ($cm^3\ g^{-1}$)	V_{total} ($cm^3\ g^{-1}$)	S_{ext} ($m^2\ g^{-1}$)
HBEA	616	0.17	0.46	0.63	240
Pt-HBEA	569	0.13	0.47	0.60	280
PCH	612	0.23	0.16	0.39	88
Pt-PCH	610	0.22	0.20	0.42	156
Al/MCM-41	882	–	0.67	0.72	35
Pt–Al/MCM-41	896	–	0.68	0.74	39
Al/SBA-15[a]	695	ND	1.10	ND	ND
Pt–Al/SBA-15[a]	683	ND	0.82	ND	ND

[a] From Ref. [18]

Table 2 Deactivation percentage (%ΔConv.) and selectivities to the reaction products obtained during hydroisomerization of *n*-hexane at T = 250 °C at identical conversion (≈10%)

Sample	%ΔConv.	Selectivity (molar%)					
		C_1–C_5	2,3-DMB	2,2-DMB	2-MP	3-MP	Others
Pt-HBEA	8	1.5	7.3	2.3	52.8	32.2	4.0
Pt–Al/SBA-15	52.4	2.7	5.3	1.5	53.0	32.9	4.7
Pt-PCH	22.6	3.8	7.2	1.9	50.9	31.9	4.4
Pt–Al/SBA-15 + HBEA	10.4	0.5	4.1	0.8	53.5	35.2	6.0
Pt–Al/MCM-41 + HBEA	10.8	1.2	4.1	1.1	54.7	35.1	3.9
Pt-PCH + HBEA	11.0	0.9	9.7	1.1	49.1	35.0	4.2

compounds, which are coke precursors, the reactions taking place inside the porous structure led to a rapid deactivation, due to pore blockage. The fact that the deactivation is more pronounced on Pt–Al/SBA-15 allows us to conclude that Pt particles located inside the pores (as it was suggested by the adsorption data) are not enough to hydrogenate the reaction intermediates. On the other hand, the fact that Pt–Al/SBA-15 has a monodimensional structure favours its faster deactivation than that observed for Pt-PCH that admits bidimensional circulation. This type of results is, to our knowledge noticed for the first time in PCHs. In fact, although the mesoporous structures of PCHs is less uniform that that of MCM-41 and SBA-15 type materials, their structure allows an easier circulation of the molecules, rendering less relevant the deactivation by channel blockage.

Additionally the effect of surface acidity of the various materials in deactivation should not be disregarded, since the alumination of SBA-15 and MCM-41 generates acid sites on the surface of these solids that can also contribute to a faster deactivation.

The reaction products for all samples are the isomerization products, mono-branched methylpentanes (2-MP and 3-MP) and di-branched dimethylbutanes (2,3-DMB and 2,2-DMB) and light products with one to five carbon atoms (C_1–C_5). Small amounts of methylciclopentane (MCP) and benzene are also detected.

Table 2 shows the selectivity to the reaction products obtained during *n*-hexane hydroisomerization at 250 °C at identical conversion (≈10%). The results obtained for Pt–Al/MCM-41 are not presented since they are not comparable due to its low conversion (maximum 4%). As can be observed, the main reaction products are the mono-branched isomers 2-MP and 3-MP, which attain selectivities close to 90% for the composite samples Pt–Al/SBA-15 + HBEA and Pt–Al/MCM-41 + HBEA, and slightly lower for the other samples.

As the major purpose of the hydroisomerization reaction is to increase the production of di-branched isomers, due to their high octane number, the selectivities to 2,2-DMB and 2,3-DMB are presented in Fig. 2 at identical conversion (a) and the yields obtained in the conversion range from 2 to 20% for Pt-BEA and for composites Pt-M + HBEA (b).

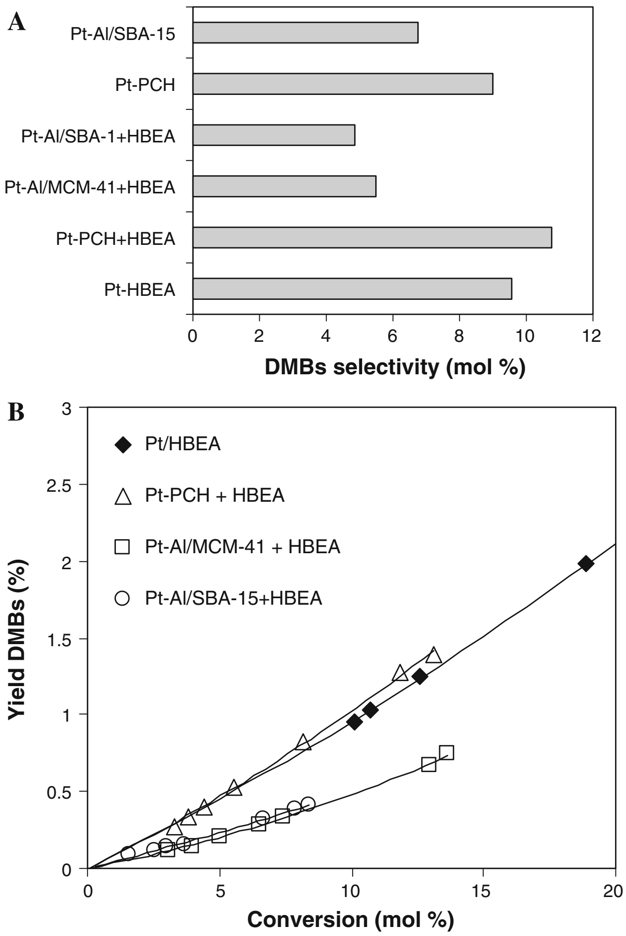

Fig. 2 Selectivity to di-branched isomers (2,2-DMB and 2,3-DMB) at identical conversion (≈10%) (**a**) and yields at the conversion range from 2 to 20% (**b**)

The highest selectivity and yields into di-branched products is observed for Pt-HBEA and, slightly above, for Pt-PCH + HBEA. On the other hand the lowest values are observed for the composites Pt–Al/SBA-15 + HBEA and

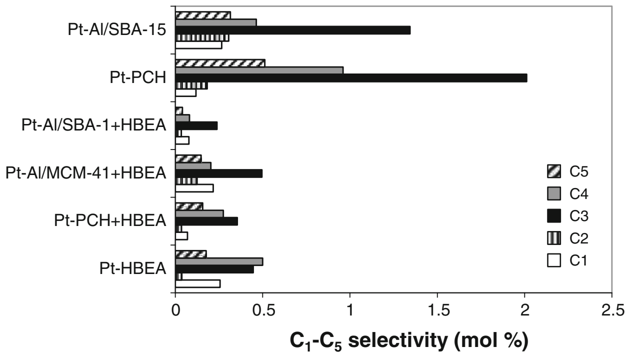

Fig. 3 Selectivity to light products (C_1–C_5) for *n*-hexane hydroisomerization at identical conversion ($\approx$10%)

Pt–Al/MCM-41 + HBEA. So, the desired synergistic effect between the microporous and the mesoporous components of the composite catalysts was only achieved with Pt-PCH + HBEA sample. It must be noted that Pt-PCH sample presents a DMBs selectivity higher than that obtained with the composites Pt–Al/SBA-15 + HBEA and Pt–Al/MCM-41 + HBEA and also with the mesoporous catalyst Pt–Al/SBA-15. This behaviour can only be explained on the basis of the structural characteristics of PCH, which facilitate the molecular circulation inside the porous structure and reduces the deactivation process. Nevertheless, since the catalytic behaviour of PCH is not well explored yet, other factors may contribute to the performance of this material.

The light products distribution (C_1–C_5) at identical conversion ($\approx$10%) is presented in Fig. 3. For all samples the more relevant products are the fragments with three carbon atoms (C_3) resulting from dimethylbutene cracking at the acid sites. The presence of C_4, more relevant for Pt-HBEA, and C_5 products in such amounts that are not proportional to C_1 and C_2 fragments, indicates the occurrence of dimerization reactions followed by cracking [22]. The significant amount of C_1 product shows the occurrence of hydrogenolyis reactions, indicating the presence of large metal particles and low metal dispersion.

4 Conclusions

In this work, the behaviour of composite catalysts based on the zeolite HBEA and several mesoporous materials (Al/SBA-15, Al/MCM-41 and PCH) were studied in the hydroisomerization of *n*-hexane. The textural properties, characterised by N_2 adsorption at low temperature, show an increase of the external surface area, which indicates the presence of high dimensions metal particles mainly at the outer surface of the crystals. In the *n*-hexane hydroisomerization the mesoporous and the composite catalysts present lower conversion when compared with Pt-HBEA zeolite. Regarding di-branched isomers, only Pt-PCH + HBEA sample showed an increased selectivity, when compared to the zeolite based catalysts. Only on this sample a positive effect between the two components of the composite was observed, which resulted in an improved catalytic behaviour. The distinct behaviour observed on this composite can only be explained taking into consideration the bidimensional structure of PCH material, which facilitates the molecular diffusion, when compared to the monodimensional structures SBA-15 and MCM-41.

Although the method used for Pt introduction led to a heterogeneous distribution of the metal, the experiments performed with the two components physically separated clearly show the existence of interaction between the zeolite and the mesoporous material, behaving as bifunctional catalysts.

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