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Influence of the zeolite structure and acidity on the hydroisomerization of *n*-heptane

A. Patrigeon*, E. Benazzi, Ch. Travers, J.Y. Bernhard

Institut Français du Pétrole, 1 & 4 Avenue du Bois Préau, 92852 Rueil Malmaison Cedex, France

Abstract

Different acid solids loaded with 1 wt.% of Pt have been studied in *n*-heptane hydroisomerization in order to determine the influence of porosity and acidity (considered measured by the activity) on selectivities. The open solids like Y and β zeolites and a pillared clay present different activities towards *n*-C_7 conversion but similar selectivities. Consequently, acidity seems to be a less important parameter in *n*-C_7 isomerization than porosity. Very different results were obtained as a function of the solid structure and so *n*-heptane hydroconversion appears to be a simple and rapid method to obtain data concerning the porosity of unknown zeolite structures. The highest content of multibranched isomers was obtained on open solids but the value predicted by the thermodynamic was never reached due to the fact that cracking of multibranched isomers is initiated quickly. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: *n*-heptane conversion; Porosity; Acidity; Isomerization; Cracking

1. Introduction

Bifunctional metal/acid catalysts are used in industrial hydroisomerization of C_5–C_6 paraffins. On these catalysts, the paraffin transformation involves hydrogenation and dehydrogenation steps on the metallic sites, isomerization or cracking steps on the acid sites and diffusion steps of the olefinic intermediates from acid to metallic sites and inversely. So activity and selectivity depend on the characteristics of the acid and of the metallic sites. However, when the catalyst is well balanced (strong hydrogenating function), the acid function is the limitating one and the product distribution depends essentially on acidity and pore structure of the acid solid [1]. In the case of longer paraffins like *n*-heptane, the parasite reaction of cracking is more rapid and then prevents to obtain high yields of multibranched isomers.

In this work, the catalytic properties in *n*-C_7 conversion in presence of hydrogen of different solid acids loaded with platinum have been evaluated in order to study the influence of porosity and acidity on selectivities and to determine the more selective catalysts for multibranched isomers.

2. Experimental

First, open acid solids, where no sterical limitation was supposed to occur, were studied: a Y zeolite, two β zeolites with global atomic ratios equal to 13 and 94, respectively (called H-β(13) and H-β(94)) [2], a silica–alumina and a silicon-pillared beidellite synthesized in fluoride medium [3]. Then solids with a more restricted structure were studied: a ZSM-22 zeolite

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* Corresponding author.

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Table 1
Main characteristics of the studied solids

	Type	$(Si/Al)_G$	S_{BET} (m^2/g)	D^a	Windows	Channel dimensions (Å)
H-Y	FAU	16	824	3	12 MR[b]	7.4
H-β	BEA	13	678	3	12 MR	(7.6 × 6.4) + (5.5 × 5.5)
H-β	BEA	94	733	3	12 MR	(7.6 × 6.4) + (5.5 × 5.5)
Silica–alumina	–	0.5	305	–	–	Mesoporous
Pillared clay	–	2.3	535	–	–	$d_{001} = 36$
H-EU-1	EUO	16	402	1	10 MR	(4.1 × 5.7) + large side pockets
H-ZSM-22	TON	36	157	1	10 MR	4.1 × 5.5

[a] Dimensionality of the porous structure.
[b] Member ring of oxygen atoms.

and an EU-1 zeolite. The main characteristics of each solid acid are presented in Table 1.

The zeolite samples were loaded with 1 wt.% Pt by incipient wetness impregnation using $Pt(NH_3)_4Cl_2$ as precursor. That amount of Pt was chosen in order to have a strong hydrogenating function. Then, the solids were calcined under air flow at 420°C for 4 h. Reduction was performed under H_2 flow at 450°C in the catalytic reactor. The reaction was carried out at atmospheric pressure in a fixed-bed microreactor. The temperature was fixed between 190 and 320°C depending on the catalyst activity and then the *n*-heptane conversion was changed by varying the contact time (defined as the ratio of the weight of catalyst to the weight of *n*-heptane injected per hour) between 0.1 and 4 h. The molar ratio H_2/*n*-heptane was chosen equal to 2. The reaction products were analysed on-line using a GC with an FID detector and an HP-PONA (50 m × 0.2 mm) capillary column.

3. Results and discussion

3.1. Influence of porosity and acidity on cracking and isomerization selectivities

For each studied solid, the yields of monobranched isomers (MB), multibranched isomers (MuB) and cracked products (CP) versus the *n*-heptane conversion were plotted. Fig. 1 reports the yields obtained on H-β(13) zeolite. At low conversion, the monobranched isomers are predominant, they are clearly primary products of the reaction. When the *n*-C_7 conversion increases, the monobranched yield reaches a maximum (54 wt.%) and then decreases. The multibranched yield, which is very low at low conversion, also increases with the conversion, goes through a maximum (25 wt.%) and then decreases. The multibranched maximum yield is shifted towards the higher conversions compared to the monobranched

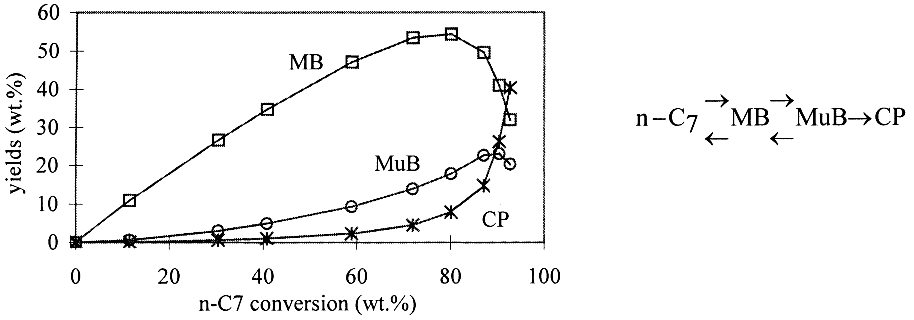

Fig. 1. Yields of MB, MuB and CP on Pt/H-β(13) in *n*-C_7 conversion at 210°C and corresponding apparent pathway of reaction.

Table 2
Catalytic performances in n-heptane conversion at the maximum yield of isomers

Catalysts	T (°C)	Conversion (wt.%)	iC$_7$ (wt.%)	CP (wt.%)	MB (wt.%)
H-Y/1% Pt	250	83	73	10	50.5
H-β(13)/1% Pt	210	83	73	10	53
H-β(94)/1% Pt	260	83	72	11	52
Silica–alumina/1% Pt	320	82	65	11	49
Pillared beidellite/1% Pt	260	87	76	11	53
ZSM-22/1% Pt	240	84	78	6	73
EU-1/1% Pt	220	79	58	21	47

maximum yield, which shows that the multibranched formation is consecutive to the formation of monobranched isomers. The cracked products appear at medium conversion (50 wt.%) and increase strongly at high conversion. They are clearly secondary products of the reaction.

These results show that the scheme of the reaction on Pt/H-β is a consecutive one, indicating that the hydrogenating function is probably not limitating. A similar reactional pathway has been obtained on H-β(94), H-Y, silica–alumina and pillared clay although they have been tested at different temperatures. Due to the fact that the hydrogenating function did not seem limitating, we have considered that the acid function was the limitating one and consequently that the activity of a solid was a good measure of its global acidity (number of acid sites and intrinsic acid strength).

Table 2 reports for these catalysts the maximum yield of isomers (iC$_7$) obtained by varying the contact time, the corresponding reaction temperature, n-C$_7$ conversion, yield of CP and MB.

Thanks to their working temperatures in n-C$_7$ conversion, we can order the open solids in function of their activity: H-β(13) $>$ H-Y $>$ H-β(94) $\sim$ pillared clay $>$ silica–alumina. However the H-Y, the two H-β zeolites samples and the pillared clay lead to the same maximum yield of isomers at the same n-heptane conversion. The cracking yield is low (10 wt.%) and the corresponding monobranched yield is high (about 50 wt.%). On the silica–alumina, the maximum yield of isomers is lower (only 65 wt.%) but the cracking yield is similar to those obtained with the other solids even though silica–alumina works at a higher temperature (320°C). In fact, contrary to what happens on the other solids, aromatics are produced on the silica–alumina (yield of 6 wt.% at 82 wt.% of n-C$_7$ conversion) because of the higher temperature of test. In conclusion, the studied open solids lead to different activities but same global isomerization and cracking selectivities are obtained. The higher acidity of zeolites compared to the silica–alumina one enables to convert the n-heptane at a lower temperature and to prevent the aromatic formation but does not lead to lower cracking. Acidity does not seem to be a key parameter for selectivities in n-C$_7$ conversion.

For the studied solids with a more restricted structure, a different reactional pathway has been obtained. Figs. 2 and 3 report the yields of MB, MuB and CP versus the n-heptane conversion for H-ZSM-22 and H-EU-1, respectively.

The H-ZSM-22 zeolite is very selective in MB isomers: at 84 wt.% of n-C$_7$ conversion, 93 wt.% of the formed isomers are monobranched. Certainly because of the restricted structure, the multibranched formation is very limited and consequently cracking is very low (6 wt.% at 84 wt.% of n-C$_7$ conversion) as monobranched isomers are more difficult to crack [4].

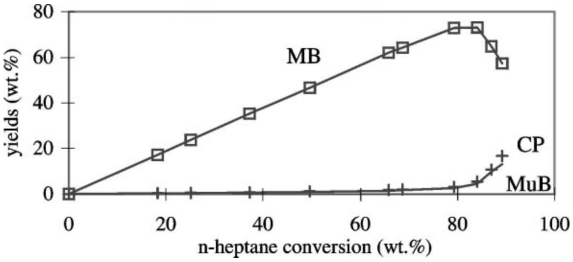

Fig. 2. Yields of MB, MuB and CP in n-C$_7$ conversion on Pt/H-ZSM-22 at 240°C.

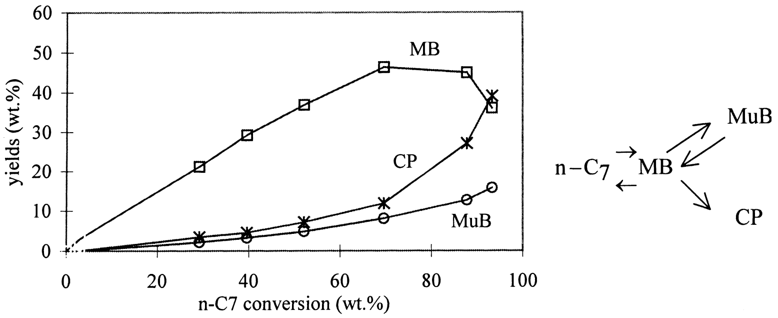

Fig. 3. Yields of MB, MuB and CP in *n*-C_7 conversion on Pt/H-EU-1 at 220°C and corresponding apparent pathway of reaction.

The H-EU-1 zeolite gives much more cracking than H-ZSM-22 and open solids (21 wt.% at 79 wt.% of *n*-C_7 conversion). Both MB and MuB are formed but CP appear from low conversions. Consequently, CP formation does not appear consecutive to multibranched formation like in the case of H-β(13) (Fig. 1) but parallel (Fig. 3). However, the fact that among the cracked products, only *iso*-butane and propane are detected and no *n*-butane means that there are MuBs which crack and not MBs. In fact, the MuBs crack very quickly in the EU-1 zeolite compared to the H-β zeolite. This behaviour could be related to the large and deep side pockets of the EU-1 zeolite which are circumscribed by 12-membered oxygen rings (cross section of 6.8 Å × 5.8 Å, depth of 8 Å [5]). They allow the MuB formation contrary to the more restricted ZSM-22 zeolite. Nevertheless, in order to reach the gas phase, the MuBs need to diffuse through the 10 MR windows and this diffusion is probably slower than in the case of open solids like H-Y, H-β or pillared clay. Consequently, the isomerized paraffins spend a longer time in the channels which favours further rearrangements and then cracking. We can also speculate that a dimerization-cracking mechanism occurs in the side pockets because molecules with five and six carbon atoms are detected but no methane neither ethane.

Among the studied solids, we can distinguish three behaviours in *n*-C_7 hydroisomerization and these differences are strongly related to the solids porous structure. The open solids lead to same cracking and global isomerization selectivities whatever the acidity and the resulting working temperature. The solid with the more restricted structure (H-ZSM-22) is very selective into MBs and leads to very little cracking. As for the H-EU-1 zeolite, although its porosity is less restricted than the ZSM-22 one, because of the presence of large side pockets, it produces more cracking. Selectivities is clearly more governed by porosity than by acidity.

Then, we have studied the MB distribution on the one hand and the MuB distribution on the other hand for the different porous solids.

3.2. *Influence of porosity on monobranched isomers distribution*

In order to study the MB distribution, we have plotted the 2-MC_6/3-MC_6 ratio versus the *n*-C_7 conversion (Fig. 4). For open solids like H-Y, the two H-β and the pillared clay, this ratio is equal to 1 (which is a value very close to the thermodynamic one, see Fig. 4) and does not vary with the conversion. That means that 2-MC_6 and 3-MC_6 reach the thermodynamic equilibrium from low conversions. It is generally admitted that the carbenium ion undergoes rearrangements via protonated cyclopropane (PCP) to give a branched carbenium or a smaller carbenium and an olefin by cracking [6]. Because more PCP intermediates can convert *n*-C_7 into 3-MC_6 than into 2-MC_6, 3-MC_6 is expected to be mainly produced on solids where no sterical constraints are supposed to occur. Nevertheless, our results have shown that it is not the case as the 2-MC_6 and the 3-MC_6 are produced is same quantities on the open studied solids. This phenomenon could be explained by quick methyl shifts occurring from 3-MC_6 to 2-MC_6 to reach the equilibrium values [7].

On H-ZSM-22, 2-MC_6/3-MC_6 ratio is higher than 2 at low conversion and decreases until reach-

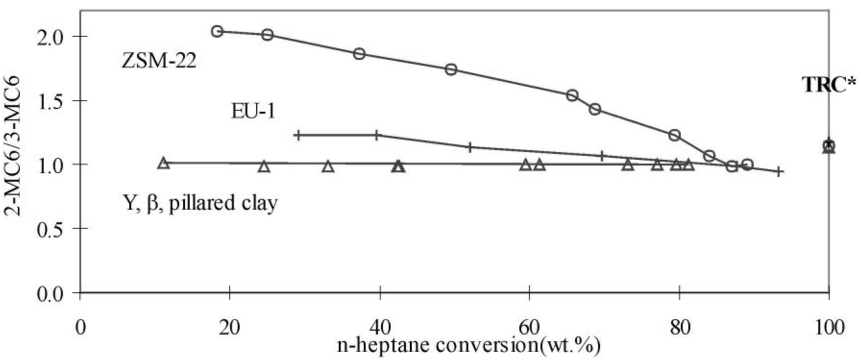

Fig. 4. Variation of the $2\text{-MC}_6/3\text{-MC}_6$ ratio in $n\text{-C}_7$ conversion.

ing the value 1 when the conversion increases. The H-ZSM-22 zeolite strongly favours the formation of 2-MC_6 in comparison with the formation of 3-MC_6. For the H-EU-1 zeolite, the $2\text{-MC}_6/3\text{-MC}_6$ ratio is higher than 1.2 at low conversion and decreases when the conversion increases. Like for the H-ZSM-22, the methylhexanes seem to reach the equilibrium only at high conversion. The reasons why the ZSM-22 and other 10 MR tubular molecular sieves like ZSM-23 and SAPO-11 strongly favour the terminal methyl branching are still under debate. A first theory postulates that only the linear paraffin can diffuse into the pores and that the methyl branching occurs at the pore mouth [8]. This interpretation is based on results obtained on paraffins longer than *n*-heptane. Others explain these results by transition state shape selectivity [9]. The transition state required for internal methyl branching would be larger than the transition state required for terminal methyl branching, so the latter would be strongly favoured. Moreover, the jump of methyl is very impeded on H-ZSM-22 as the monobranched equilibrium is only reached at very high conversion. The H-EU-1 zeolite shows selectivities between the open solids ones and the H-ZSM-22 ones, reflecting by this way its intermediate porosity. Similar behaviour of the EU-1 zeolite has already been mentioned in *n*-decane test [10].

Like for isomerization and cracking yields, the solid structure seems to have a strong influence on the methylhexane distribution at low conversion. The $2\text{-MC}_6/3\text{-MC}_6$ ratio at low conversion increases when the solid structure is more and more restricted.

3.3. Influence of porosity on multibranched isomers distribution

In order to study the MuB distribution, we have defined the *R* ratio as the $(2,3\text{-DMC}_5 + 2,4\text{-DMC}_5)/(2,2\text{-DMC}_5 + 3,3\text{-DMC}_5 + 2,2,3\text{-TMC}_4)$ ratio that is to say the less bulky MuBs to the bulkiest MuBs ratio. Fig. 5 reports the *R* ratio against the $n\text{-C}_7$ conversion for the different studied solids.

For the open solids like the H-Y zeolite, the H-β zeolites and the pillared clay, this ratio is close to 0.8, which corresponds to the thermodynamic value on the whole range of conversion. Like for the MBs, the MuBs are formed via PCP intermediates and then probably quick methyl shifts occur to reach the thermodynamic equilibrium values. On ZSM-22 zeolite, *R* ratio is very high at low conversion because $2,4\text{-DMC}_5$ and $2,3\text{-DMC}_5$ are the only formed MuB. The other dibranched isomers appear only at high conversion and in very small amounts.

However, no $2,2,3\text{-TMC}_4$ is detected on ZSM-22 whatever the $n\text{-C}_7$ conversion. Like for the first branching, different explanations are proposed to explain the second branching on ZSM-22. The theory of the pore mouth and key-lock catalysis postulates that the second branching occurs at the external surface of the solid, the dibranched molecule being adsorbed between two adjacent pores [11]. Another theory is that, like for the first branching, the less bulky PCP intermediates during the second branching are strongly favoured explaining the low selectivi-

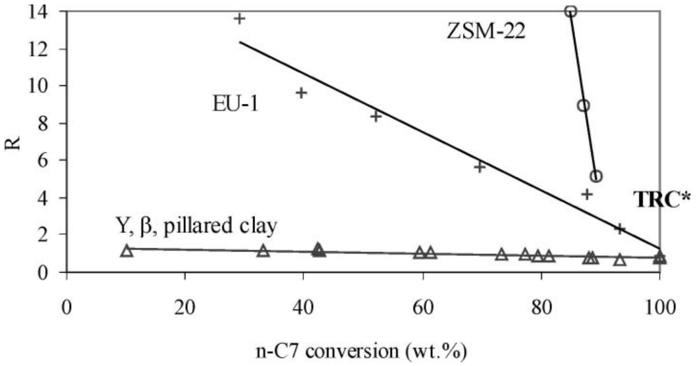

Fig. 5. Variation of the *R* ratio in n-C_7 conversion.

ties in dibranched isomers with proximate methyl groups [9]. For the H-EU-1 zeolite, the *R* value is comprised between the values obtained on open solids and the ZSM-22 values. All the MuBs are formed at low conversion except the tribranched one, but the 2,3-DMC_5 and the 2,4-DMC_5 are strongly predominant.

As a conclusion, the studied open solids have shown different activities towards n-C_7 conversion reflected by the working temperatures but same selectivities: maximum isomerization yield of 73 wt.% at 83 wt.% of n-C_7 conversion with a corresponding monobranched yield of 52 wt.%. Consequently, acidity is a less important parameter in n-C_7 isomerization than porosity. In fact the more restricted the structure, the higher the 2-MC_6/3-MC_6 ratio and the higher the $(2,3\text{-DMC}_5+2,4\text{-DMC}_5)/(2,2\text{-DMC}_5+3,3\text{-DMC}_5+2,2,3\text{-TMC}_4)$ ratio at low conversion. Consequently, the *n*-heptane hydroconversion appears to be an interesting and simple test like *n*-decane conversion [12] to obtain data concerning the porosity and the geometry of unknown zeolite structures as it has already been mentioned elsewhere [13]. To illustrate this, we have studied an NU-88 zeolite [14], whose structure is unknown, in *n*-heptane conversion at 210°C. At 36 wt.% of n-C_7 conversion, a 2-MC_6/3-MC_6 ratio of 1.3 and an *R* ratio of 7.8 were obtained. These values are close to the values obtained on the EU-1 zeolite, so we can make the hypothesis that the NU-88 zeolite does not have exclusively 12 MR windows or 10 MR windows. May be it has 10 MR channels with large side pockets like the EU-1 zeolite or it has multidimensional 10 MR channels. Other zeolites are under study to improve the *n*-heptane test as a way to estimate the void structure of unknown solids.

3.4. Limitating factors for a high multibranched yield

The results have shown that the highest content of MuBs was obtained on open solids. On the very restricted structure solid (H-ZSM-22), the multibranched formation was impeded and on H-EU-1, the MuMs cracked quickly because of the large side pockets. In the case of open solids, they all lead to the same maximum multibranched yield (25 wt.% at 88 wt.% of *n*-heptane conversion). We have wondered if that content corresponded to the thermodynamic one or not, that is to say that we have wondered if the *n*-heptane and its isomers reached the equilibrium concentrations during the n-C_7 conversion. That is why we have studied the $n\text{-C}_7/(n\text{-C}_7+\text{MB})$ and $\text{MB}/(n\text{-C}_7+\text{MB})$ ratios versus the contact time during the n-C_7 conversion on Pt/H-β(13) (Fig. 6). Then we have made the same study for the $\text{MB}/(\text{MB}+\text{MuB})$ and $\text{MuB}/(\text{MB}+\text{MuB})$ ratios (Fig. 7). Thermodynamic values from the Thermodynamic Research Center have been reported arbitrarily at a contact time of 3 h.

When the contact time is increased, n-C_7 fraction decreases and the monobranched fraction increases until reaching the thermodynamic equilibrium values from a contact time of 1 h (Fig. 6). Then the relative fractions remain constant. As for the multibranched fraction compared to the monobranched one (Fig. 7),

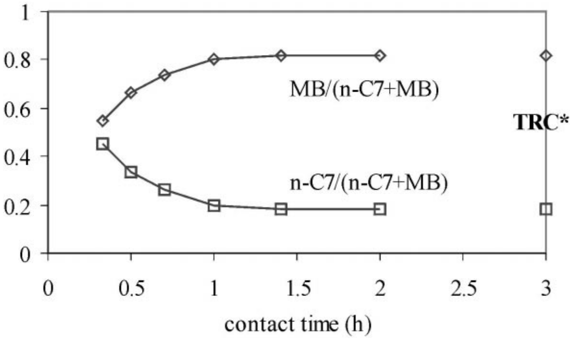

Fig. 6. Evolution of n-C$_7$/(n-C$_7$ + MB) and MB/(n-C$_7$ + MB) ratios in n-C$_7$ conversion on Pt/H-β(13) at 210°C.

it still increases at contact times higher than 2 h. That means that at 88 wt.% of n-C$_7$ conversion, which corresponds to the maximum multibranched yield and to a contact time of 1 h, n-heptane and the MBs are in equilibrium but the MBs and the MuBs are not. Only a MuB yield of 25 wt.% is obtained whereas the thermodynamic forecasts 43 wt.% at 210°C. In fact, they undergo cracking before reaching that value. To limit the cracking on bifunctional catalysts, the previous results on open solids have shown that temperature has no real influence. Whereas low temperatures favour the MuB compared to the others, H-β(94) and the pillared clay produce as many MuMs as H-β(13) which works 50°C lower. The effect of a higher H$_2$ pressure remains to be studied in order to evaluate its influence on the multibranched formation and cracking.

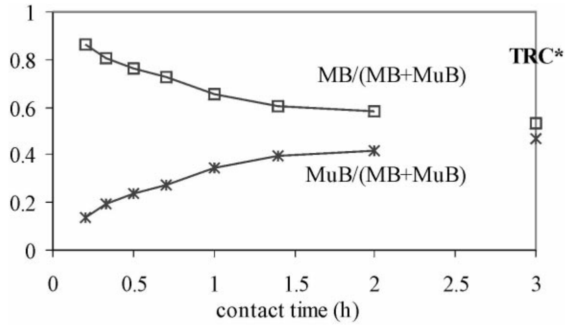

Fig. 7. Evolution of MB/(MB + MuB) and MuB/(MB + MuB) ratios in n-C$_7$ conversion on Pt/H-β(13) at 210°C.

4. Conclusion

The study of different acid solids in n-heptane hydroconversion has shown the major role of porosity on selectivities. On the contrary, the acidity does not appear like a key parameter as all the studied open solids have lead to same selectivities although working at different temperatures. Moreover, the n-heptane hydroconversion has revealed to be an efficient and simple test to obtain data concerning the porosity of unknown structures because the 2-MC$_6$/3-MC$_6$ ratio and the $(2,3\text{-DMC}_5 + 2,4\text{-DMC}_5)/(2,2\text{-DMC}_5 + 3,3\text{-DMC}_5 + 2,2,3\text{-TMC}_4)$ ratio at low conversion increase when the structure is more and more restricted. To favour the MuB, an open structure solid is essential to enable their formation without too much cracking. However, the thermodynamically multibranched content is never reached because of cracking.

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