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Isobutane / 2-butene alkylation on MCM-22 catalyst. Influence of zeolite structure and acidity on activity and selectivity

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The catalytic behavior of the novel MCM-22 zeolite for the continuous alkylation of isobutane with 2-butene has been investigated at a temperature of 50°C, 2.5 MPa total pressure, and a variety of olefin space velocities. At high olefin conversions the MCM-22 zeolite showed a very high initial cracking activity attributable to strong Brønsted acid sites, as well as to the existence of strong diffusional restrictions of the TMP's (formed inside the zeolite) to exit through the channels. At short times on stream (TOS), TMP's account for ca. 40% of the C_8 fraction. The olefin conversion and the cracking activity rapidly decline with TOS, while the alkylate product became richer in dimethylhexenes, indicating a predominance of 2-butene dimerization and a loss of hydrogen transfer activity as the catalyst aged. Moreover, MCM-22 gives less TMP's than large-pore zeolites (USY, beta, mordenite), but more than the medium-pore ZSM-5 at similar 2-butene conversion. The latter catalyst was much more selective for olefin dimerization than for isobutane alkylation, presumably because formation of the bulkier TMP's was strongly impeded in its smaller pores.

Keywords: isobutane/2-butene alkylation; zeolites; MCM-22; USY; beta; mordenite; ZSM-5; influence of structure

1. Introduction

Increasing the contribution of alkylation gasoline to the actual gasoline pool is a very attractive option to meet the new specifications on gasoline composition stated by the CAA amendments starting in 1990. Alkylation gasoline is mainly formed by low reactive multibranched paraffins, and has a relatively low vapor pressure and high research (RON) and motor (MON) octane numbers, with the

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added bonus of a low sensitivity factor (difference between RON and MON). However, the expected increase in alkylation capacity is often conditioned by the need to replace sulfuric and hydrofluoric acids – the catalysts used in the actual commercial units – by more environmental friendly solid acid catalysts.

This has generated great research effort in the last decades, and as a consequence several solid acids have been proposed as alkylation catalysts [1]. Among them, solid superacids of the sulfated zirconia type [2–6] and zeolites [5,7–10] were seen to give a high initial alkylation activity, but they deactivated rapidly with TOS. Large-pore zeolites, specially those of the faujasitic type, either in the acid form or exchanged with di- and trivalent cations, have been viable candidates for the alkylation reaction [7–10]. Zeolite beta, a high-silica large-pore tridirectional zeolite with pore diameters smaller than those of faujasite [11], has also been shown active and selective for alkylation during the initial reaction stages [5].

Along with the desired alkylation reaction, oligomerization of the olefin feed is an important competing reaction which finally leads to the deposition of high-molecular weight unsaturated compounds which remain adsorbed on the catalyst acid sites causing the observed loss of activity. In the case of zeolites, and owing to the electrostatic fields existing inside the microcavities which favor adsorption of olefins in preference to paraffins [12], the formation of oligomers is specially favored. However, the extent of oligomerization would depend, in principle, not only on the zeolite composition (Si/Al ratio), but also on the size and geometry of the pore system. There is, therefore, still an incentive to search for new zeolite structures that, while maintaining a good initial alkylation activity, would also decrease polymerization and consequently improve the stability towards deactivation.

Recently [13], a new high-silica zeolite, MCM-22, has been synthesized and has found a wide application for numerous hydrocarbon transformation processes [14–16]. Its catalytic behavior seems to be intermediate between that of medium- and large-pore zeolites [17].

Following the increasing interest in this new zeolite, we have investigated its catalytic properties (activity, selectivity, and stability) for the alkylation of isobutane with 2-butene. Moreover, its catalytic performance is compared with other zeolites of different structures (USY, beta, mordenite, and ZSM-5) under the same experimental conditions.

2. Experimental

2.1. CATALYSTS PREPARATION AND CHARACTERIZATION

The MCM-22 sample was synthesized using hexamethyleneimine (HM) as template, following the procedure described in ref. [16]. The crystallization of the synthesis gel was performed in 60 ml teflon-lined stainless-steel autoclaves at 150°C and 60 rpm for seven days. After that, the solid was filtered, washed, dried at 80°C, and finally calcined in air at 580°C for 3 h to remove the organic material. The acid form of MCM-22 was obtained by successive exchange (2 M NH_4Cl solution at 80°C) and calcination (550°C for 3 h) steps.

The X-ray powder diffraction (Phillips PW 1830, Cu Kα radiation) pattern of the calcined MCM-22 sample showed only the peaks corresponding to a pure crystalline phase of MCM-22, according to the positions and intensities given in ref. [16].

The crystals of MCM-22 were seen to have a hexagonal platelet morphology, with an average diameter of 0.4 μm as determined by scanning electron microscopy (SEM).

The other zeolite catalysts used in this study were obtained from commercially available products. Thus, the USY (CBV 712), beta, and ZSM-5 (CBV 5020) samples were supplied by PQ Corporation, the two former in the acid form, and the latter, which was calcined at 550°C for 3 h to obtain the acid form, in the ammonium form. The mordenite was obtained, starting from a commercial Conteka sample in the ammonium form, by successive exchange–calcination steps.

The physicochemical characteristics of all the above zeolite catalysts are given in table 1. The Na_2O content is below 0.05 wt% in all samples.

The acidity of the final catalysts was measured by IR spectroscopy (Nicolet 710, FTIR spectrometer) combined with adsorption of pyridine and desorption at different temperatures. A more detailed description of the experimental procedure is given elsewhere [18]. The amount of pyridine retained on both Brønsted and Lewis sites at different temperatures for all the zeolite samples is shown in table 2.

2.2. CATALYTIC EXPERIMENTS

The alkylation reactions of isobutane (>99% purity) with trans-2-butene (>99% purity) were performed in an automated continuous fixed-bed stainless

Table 1
Physicochemical characteristics of the zeolite catalysts

Zeolite	Crystallinity (%)	Si/Al ratio		Na_2O[b] (wt%)
		bulk	framework[a]	
USY	85	5.8	13.6	0.05
beta	70	13.0	–	0.02
mordenite	90	14.0	–	0.04
ZSM-5	100	26.5	–	0.02
MCM-22	90	15.0	–	0.03

[a] Calculated using the equation given by Fichtner-Schmittler [20].
[b] From chemical analysis.

Table 2
Acidity of the different zeolite samples as measured by IR–pyridine at increasing desorption temperatures

Zeolite	Acidity (μmol Py / g catalyst)[a]					
	Brønsted			Lewis		
	250°C	350°C	400°C	250°C	350°C	400°C
USY	80	32	13	29	18	14
beta	84	48	30	83	69	72
mordenite	71	41	22	45	37	24
ZSM-5	48	35	19	4	4	3
MCM-22	99	73	50	35	31	31

[a] Calculated using the extinction coefficients given in ref. [21].

steel reactor at 50°C reaction temperature and 2.5 MPa total pressure, for which both reactants and products are maintained in the liquid phase. An isobutane/2-butene molar ratio of 15 was used in all the experiments. A detailed description of the experimental procedure, as well as a scheme of the reaction system used, is given in ref. [10]. By using this reaction system we are able to determine the instantaneous conversion and product distribution on a given catalyst from very short times on stream ($\leqslant 1$ min), and hence practically in the absence of deactivation. This system is adequate to compare the catalytic behavior of several catalysts having different decay characteristics as is the case here.

Zeolite particles of 0.59–0.84 mm, for which the process is not controlled by internal diffusion, were diluted with inert silica (50% by weight) before being introduced into the reactor. Different initial olefin conversions were obtained by varying the 2-butene space velocity, WHSV, between 1 and 4 h^{-1}.

Reactants and products were analyzed immediately at the exit of the reactor in a GC (Varian 3600) using a 100 m capillary column (Fused silica, Supelco), and an FID detector.

3. Results and discussion

3.1. ALKYLATION ON ZEOLITE MCM-22

3.1.1. Initial activity and selectivity

The 2-butene conversion obtained at 1 min TOS on the MCM-22 sample at different olefin WHSV is presented in fig. 1. At low WHSV the olefin conversion is very high, but a strong decrease of the activity of the zeolite is observed on increasing WHSV. The change of alkylate composition as a function of the initial 2-butene conversion is given in figs. 2a–2c. A very high cracking activity is obtained

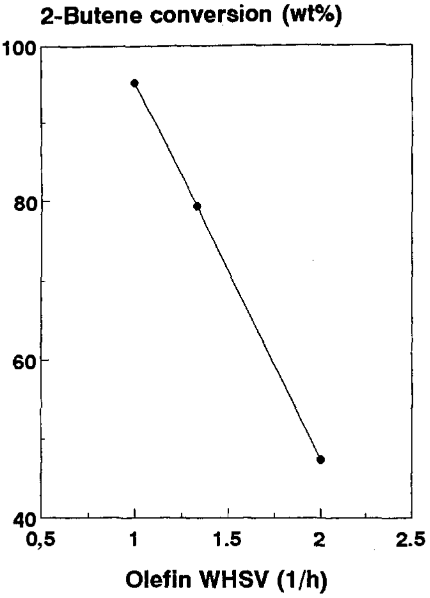


Fig. 1. Initial 2-butene conversion obtained on the MCM-22 catalyst at different olefin WHSV.

on MCM-22 at high conversion levels, as stated by the concentration of lighter C_5–C_7 compounds (about 63 wt%) in the C_{5+} alkylate product (fig. 2a). At lower conversions, the amount of cracked products strongly decreases, while that of C_8's and heavier C_{9+} increases (fig. 2a). The increase of C_{9+} with decreasing conversion is much more pronounced than that of C_8's, which suggest that most of the C_5–C_7 products are formed by cracking of the C_{9+}.

On the other hand, not all the C_8's initially formed on the zeolite come from the direct alkylation of isobutane with 2-butene: a significant amount of C_8's is produced from dimerization of the olefin. Indeed, trimethylpentanes (TMP's) would be the primary alkylation products from isobutane and 2-butene, while dimerization of the 2-butene would give dimethylhexanes (DMH) and dimethylhexenes (DMH=). The distribution of the C_8's at different conversions shown in fig. 2b indicates that under low conversion conditions (high WHSV) octenes, mainly dimethylhexenes, are the majoritary products of the C_8 fraction obtained on the MCM-22 zeolite even at 1 min TOS. Under these conditions the zeolite surface is presumably covered by carbenium ions formed from the olefin (reaction (1)), and as a consequence of the preferential adsorption of olefins versus paraffins on Al-rich zeolites [12], especially at the relatively low temperatures used in the alkylation reaction, the actual isoparaffin/olefin ratio inside the zeolite pores would be much lower than in the external liquid phase. This determines that the probability of the sec-butyl carbenium ion to react with a molecule of 2-butene to form a dimethylhexyl cation (reaction (2)) would be much higher than the abstraction of a H^- from isobutane to form the tert-butyl cation (reaction (3)) needed to initiate

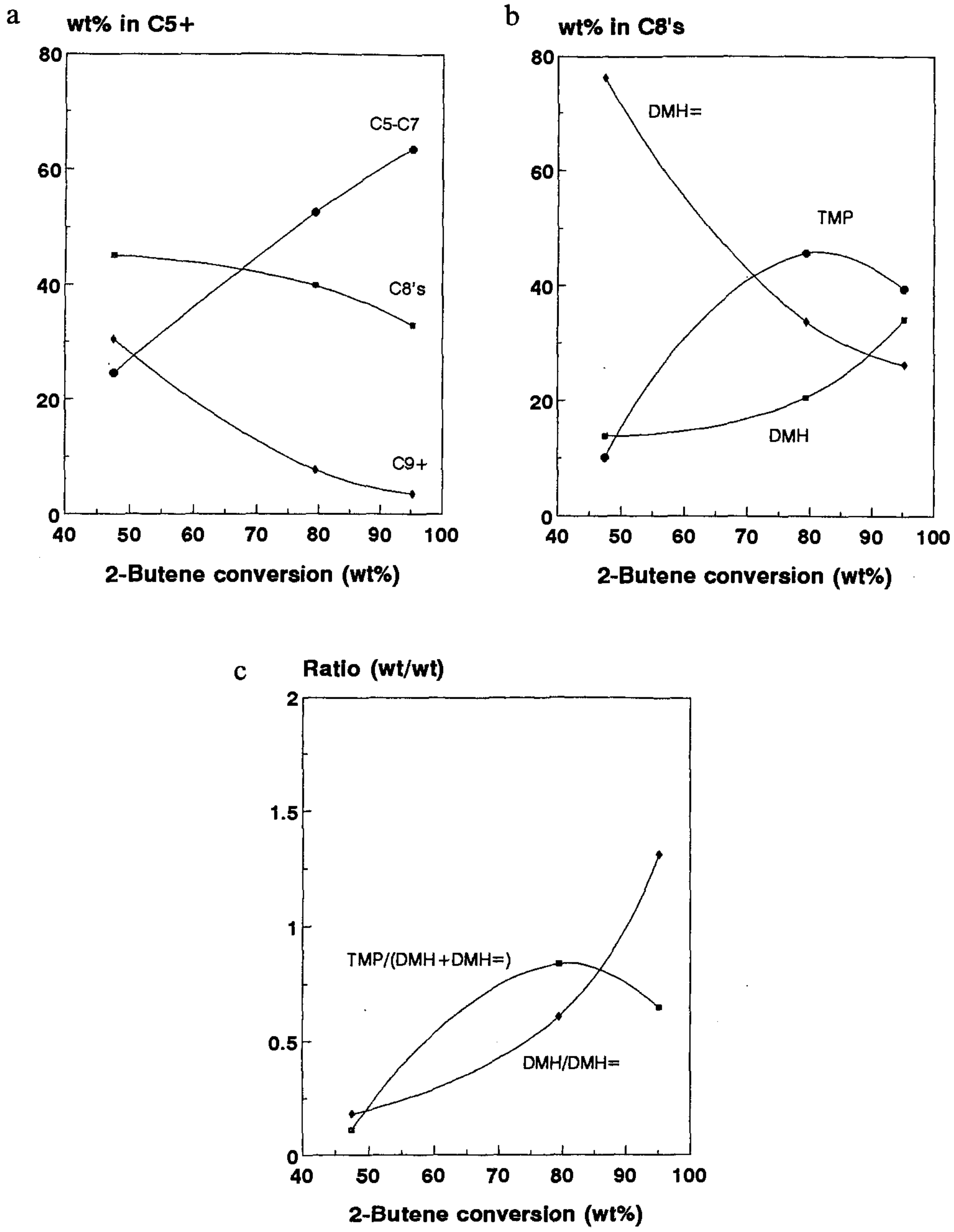
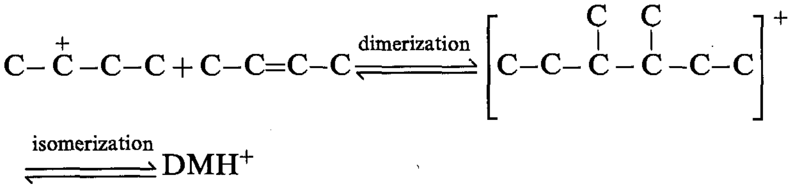


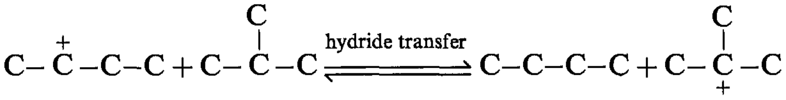
Fig. 2. Distribution of compounds in the C_{5+} alkylate (a), C_8 fraction (b), and product ratios (c) obtained on the MCM-22 sample as a function of the initial (1 min TOS) 2-butene conversion.

the alkylation reaction to form the desired TMP's (reaction (4)). This could also explain why C_{9+}, which are presumably formed by oligomerization of the olefin, are the main alkylate products at low olefin conversions (fig. 2a).

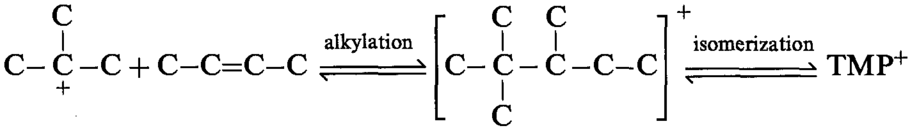
$$C{-}C{=}C{-}C + H^+{-}ZeO^- \rightleftharpoons C{-}\overset{+}{C}{-}C{-}C + ZeO^- \qquad (1)$$



$$C{-}\overset{+}{C}{-}C{-}C + C{-}C{=}C{-}C \xrightleftharpoons{\text{dimerization}} \left[C{-}C{-}\overset{\overset{C}{|}}{C}{-}\overset{\overset{C}{|}}{C}{-}C{-}C\right]^+ \xrightleftharpoons{\text{isomerization}} DMH^+ \qquad (2)$$



$$C{-}\overset{+}{C}{-}C{-}C + C{-}\overset{\overset{C}{|}}{C}{-}C \xrightleftharpoons{\text{hydride transfer}} C{-}C{-}C{-}C + C{-}\underset{+}{\overset{\overset{C}{|}}{C}}{-}C \qquad (3)$$



$$C{-}\underset{+}{\overset{\overset{C}{|}}{C}}{-}C + C{-}C{=}C{-}C \xrightleftharpoons{\text{alkylation}} \left[C{-}\underset{\underset{C}{|}}{\overset{\overset{C}{|}}{C}}{-}\overset{\overset{C}{|}}{C}{-}C{-}C\right]^+ \xrightleftharpoons{\text{isomerization}} TMP^+ \qquad (4)$$

By contrast, at very high conversion levels the true alkylation (reaction (4)) is much more favored, although an appreciable amount of dimers (DMH's and dimethylhexenes) is still formed (fig. 2b) on the MCM-22 sample. The increase of the alkylation/dimerization ratio and of the hydride transfer rate when increasing conversion can be clearly observed from the results presented in fig. 2c.

3.1.2. Catalyst deactivation

Along with the behavior in the absence of deactivation discussed above, the decay characteristics of the MCM-22 catalyst during the alkylation process could also be discussed by taking samples of products at different TOS. Thus, the 2-butene conversion and the change in product distribution (at olefin WHSV = 1 h^{-1}) as the catalyst ages are given in figs. 3a–3c. It can be seen in fig. 3a that the olefin conversion drops rapidly after a few minutes TOS and then stabilizes after 10–15 min. The evolution of the different alkylate products during this period of time can be followed in figs. 3b–3c. It is observed there that the cracking activity of MCM-22 strongly decreases just from the first stages of the reaction, approaching zero at TOS higher than 15 min under the reaction conditions used in this study. By contrast, the amount of C_8's continuously increases with TOS, being the majoritary fraction of the alkylate ($\sim$ 80 wt%) at higher TOS. On the other hand, the formation of heavier products (C_{9+}) rapidly rises during the initial stages, goes through a maximum, and then slightly decreases in favor of C_8's.

Fig. 3c also shows that the concentration of the alkylated trimethylpentanes (TMP) in the C_8 fraction continuously decreases with TOS, but the rate of decrease is lower during the first minutes. A similar behavior is found for dimethylhexanes, but the amount of dimethylhexenes sharply rises as the catalyst ages.

This decay behavior, which follows the general trends already observed for other zeolites [9,10], can be explained by recalling that the cracking of C_{9+} to give

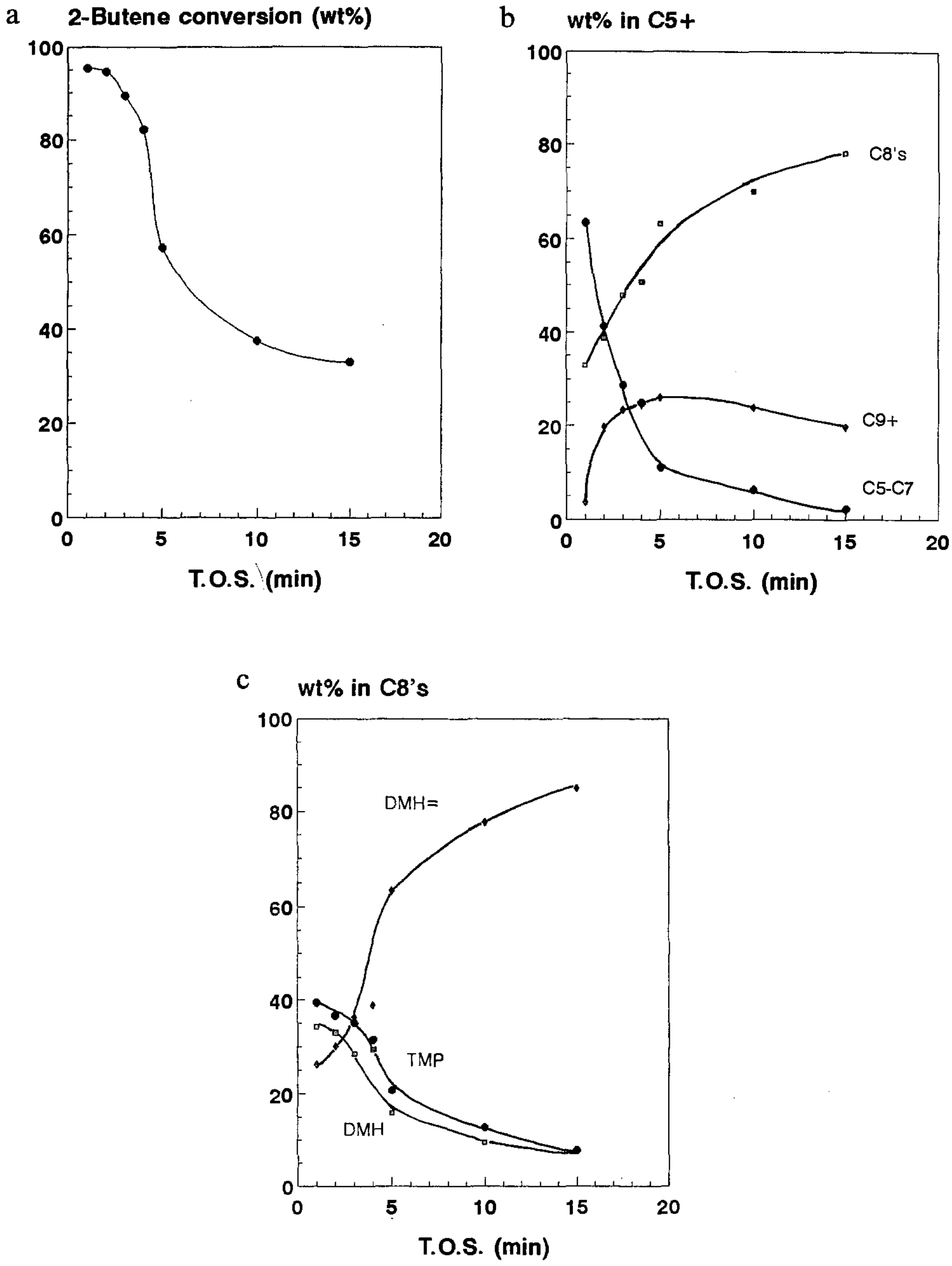


Fig. 3. 2-butene conversion (a), C_{5+} alkylate product distribution (b), and C_8's composition (c) evolution with time on stream (TOS) for the MCM-22 catalyst.

lighter products occurs on the strongest Brønsted acid sites of the zeolite. These sites deactivate faster than those of weak and medium strength. Then, the acid sites responsible for alkylation start to be poisoned, causing a rapid decrease in TMP's, while those of lower acid strength still remain active for olefin dimerization (reaction (2)). At the later stages of the reaction, where dimerization of the 2-butene prevails over the true alkylation, the hydrogen transfer activity of the MCM-22 zeolite is lost and desorption of the dimethylhexyl cations occurs according to the reaction

$$[\mathrm{DMH}]^{+}\text{–}\mathrm{ZeO}^{-} \rightarrow \mathrm{DMH{=}} + \mathrm{H}^{+}\text{–}\mathrm{ZeO}^{-} \tag{5}$$

forming the dimethylhexenes observed at longer reaction times (fig. 3c).

3.2. INFLUENCE OF ZEOLITE STRUCTURE AND ACIDITY

It can be seen in table 2 that the concentration of total Brønsted acid sites (250°C desorption temperature) is very similar in all the zeolites, except for the ZSM-5 sample, which is lower. This would indicate, in the other cases, a similar framework composition, as could also be deduced from the Si/Al ratios shown in table 1.

The 2-butene conversion, alkylate yield, and a detailed distribution of the alkylate produced on the different zeolites including the MCM-22 at 1 min TOS, and hence, under minimal deactivation conditions, are compared in table 3. Despite the fact that all the zeolites studied give initial olefin conversions above 90%, the alkylate yield clearly depends on the type of zeolite used. Higher alkylate yields are obtained on large-pore zeolites, and in particular, the mordenite catalyst gives the highest alkylate yield. By contrast, the medium-pore ZSM-5 catalyst yields very little alkylate product. It appears then, that independently of the olefin conversion achieved, zeolites with larger pore dimensions are needed to obtain appreciable alkylate yields. In this sense, zeolite MCM-22 gives alkylate yields intermediate between medium (10MR) and large (12MR) pore zeolites.

Table 3 also shows differences in the distribution of C_{5+} products. Among the 12MR zeolites, mordenite is the most selective to C_8's owing to a very low cracking activity at these high conversions. This could be due to the very high hydrogen transfer activity of mordenite, which decreases the average life time of the carbocations facilitating their desorption from the zeolite acid sites before they undergo secondary reactions, such as cracking and destructive alkylation. Moreover, TMP's are the predominant compounds in the C_8 fraction for all the three large-pore samples: USY (74.1 wt%), beta (76.9 wt%), and mordenite (76.9 wt%), indicating a high initial alkylation activity.

On the other hand, zeolite ZSM-5 is even more selective to C_8's than mordenite, but in this case TMP's amount to only ca. 20 wt% of the fraction. These results suggest that, at the relatively low temperatures used for alkylation, the formation of the bulkier TMP's is strongly impeded inside the cavities of the medium-pore zeolite, and practically only dimerization of the 2-butene (reaction (2)) to form DMH's occurs even from the initial reaction stages. Indeed, no TMP's were

Table 3
Initial alkylation activity and selectivity (TOS = 1 min) obtained at 50°C, $i\mathrm{C}_4/2\text{-}\mathrm{C}_4^=$ molar ratio of 15, and olefin WHSV = $1\ \mathrm{h}^{-1}$ on different zeolites

	Zeolite				
	USY	beta	mord	ZSM-5	MCM-22
$2\text{-}\mathrm{C}_4^=$ conv. (wt%)	100.0	97.4	93.7	99.8	95.2
alkylate yield ($\mathrm{g\ C}_{5+}/\mathrm{g}\ 2\text{-}\mathrm{C}_4^=$ charged)	0.48	0.47	0.67	0.03	0.12
distribution of C_{5+} (wt%)					
C_5–C_7	32.8	29.9	7.9	6.2	63.4
C_8	40.9	50.6	70.2	83.5	33.0
C_{9+}	26.3	19.5	21.9	10.3	3.6
distribution of C_8's (wt%)					
2,2,4-TMP	27.9	40.3	44.0	5.7	1.5
2,2-DMH	0.0	0.0	0.4	0.0	0.0
2,5-DMH	1.7	4.3	3.8	4.1	8.2
2,2,3-TMP	6.6	5.9	8.1	6.1	2.7
2,4-DMH	2.4	1.6	1.3	20.4	2.5
2,3,4-TMP	19.6	20.2	12.1	7.4	13.0
2,3,3-TMP	20.0	10.5	12.7	1.7	19.7
2,3-DMH	11.0	12.8	11.0	43.0	12.4
3,4-DMH	10.5	2.4	1.3	3.4	10.0
dimethylhexenes	0.3	2.0	5.3	8.2	30.0
distribution of TMP's (wt%)					
2,2,4-	37.7	52.4	57.2	27.3	4.1
2,2,3-	8.9	7.7	10.5	29.2	7.3
2,3,4-	26.5	26.3	15.7	35.4	35.2
2,3,3-	26.9	13.6	16.6	8.1	53.4

observed during the alkylation of isobutane with 1-butene on pentasil-type (ZSM-5 and ZSM-11) zeolites at higher reaction temperatures [19]. The amount of TMP's obtained on the MCM-22 sample (ca. 37 wt% of C_8's) is in between that of medium- and large-pore zeolites. This could be an indication of the presence of higher void spaces in MCM-22 with respect to ZSM-5, although some steric restrictions for the diffusion of TMP's are also evident in the former zeolite. Moreover, the much higher initial concentration of C_8 olefins in MCM-22 would also suggest a very low hydrogen transfer activity.

Finally, the distribution of TMP's presented in table 3 shows that 2,2,4-TMP is the predominant isomer when large-pore zeolites are used as alkylation catalysts, its concentration increasing in the order: USY<beta<mordenite. The primary product when isobutane is alkylated with 2-butene is 2,2,3-TMP, which is the minoritary isomer on the large-pore zeolites. This indicates a rapid rearrangement of the trimethylpentyl carbenium ions on the zeolite acid sites giving a mixture of TMP isomers after desorption, with predominance of the thermodynamically favored 2,2,4-TMP. The distribution of TMP's obtained on the MCM-22 catalyst

shows, by contrast, a very low concentration of 2,2,4-TMP. The higher proportion of the less voluminous 2,3,4- and 2,3,3-isomers in MCM-22 would indicate some steric restrictions for the formation of the bulkier TMP isomers inside the channels of MCM-22 and/or larger restrictions of these to diffuse through the channels, when formed inside. Consequently they would be more extensively cracked than the other two sterically impeded isomers. The fact that this kind of shape selectivity is not observed in the case of the medium-pore MFI zeolite suggests that, on ZSM-5, the alkylation reaction takes place mainly at the external surface of this zeolite, while the less sterically demanding dimerization of the olefin may occur in the intracrystalline volume of the zeolite.

It is known that zeolites suffer a rapid deactivation during the alkylation reaction [7–10]. It has been reported [10] that the rate of deactivation depends, in the case of the large-pore Y zeolite, on the total concentration and strength distribution of the Brønsted acid sites, which would affect the rate of hydrogen transfer. However, deactivation is also expected to be influenced by the particular structure of a given zeolite catalyst. Indeed, the results presented in fig. 4 do show that the medium-pore ZSM-5 deactivates faster than the large-pore zeolites, probably due to blockage of pore mouths by olefin oligomers. Among the large-pore zeolites, the higher deactivation rate occurs for mordenite, as it could be expected owing to the structure formed by unidirectional 12MR channels. It is worth noting from fig. 4 the very low deactivation rate of zeolite beta, under the reaction conditions used, as compared to USY and mordenite. On the other hand, zeolite MCM-22 deactivates slightly faster than mordenite, but slower than ZSM-5.

As discussed earlier, the 2-butene conversion includes, besides the desired alkylation with isobutane, other parallel and consecutive reactions, such as cracking

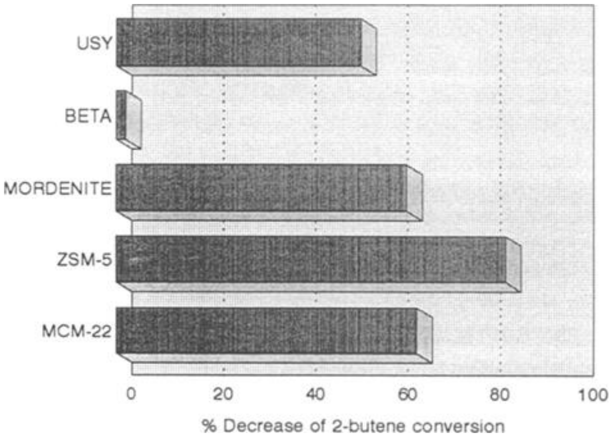


Fig. 4. Relative decrease of the initial 2-butene conversion after 15 min TOS for different zeolite structures: $T = 50°C$, i/o ratio = 15, and olefin WHSV = $1\ h^{-1}$.

and olefin dimerization/oligomerization. As seen for the MCM-22 (fig. 3b), the cracking activity of all the zeolites studied approaches zero after few minutes TOS. In order to differentiate between true alkylation and olefin dimerization, the concentration of TMP's and DMH's plus dimethylhexenes (DMH=) in the C_{5+} product have been plotted as a function of TOS in figs. 5a–5b. The loss of alkylation activity occurs at shorter TOS for ZSM-5, while the concentration of dimers on this zeolite approaches 100% after 10 min TOS. For the large-pore zeolites, the relative decrease of alkylation activity is higher for USY and mordenite. Furthermore, results from fig. 5a show that zeolite MCM-22 keeps its alkylation activity during a longer period of time in comparison to the other zeolites. If one looks at the acidity results in table 2, it can be seen that, despite the similar amount of total Brønsted acid sites (250°C desorption temperature) present on the zeolites studied here, zeolite MCM-22 has the highest concentration of the strongest acid sites, that is, those retaining pyridine at 400°C. Taking into account that these sites are the active sites for alkylation [10], and, therefore, for formation of TMP's (reaction (4)), one would expect the decline in alkylation activity as the zeolite deactivates to be dependent on the concentration of strong Brønsted acid sites in the "fresh" catalyst. Indeed, a linear correlation is found between the relative decrease of concentration of TMP's in the C_{5+} product after 15 min TOS for the different zeolites and the amount of Brønsted acid sites retaining pyridine at 400°C desorption temperature (fig. 6).

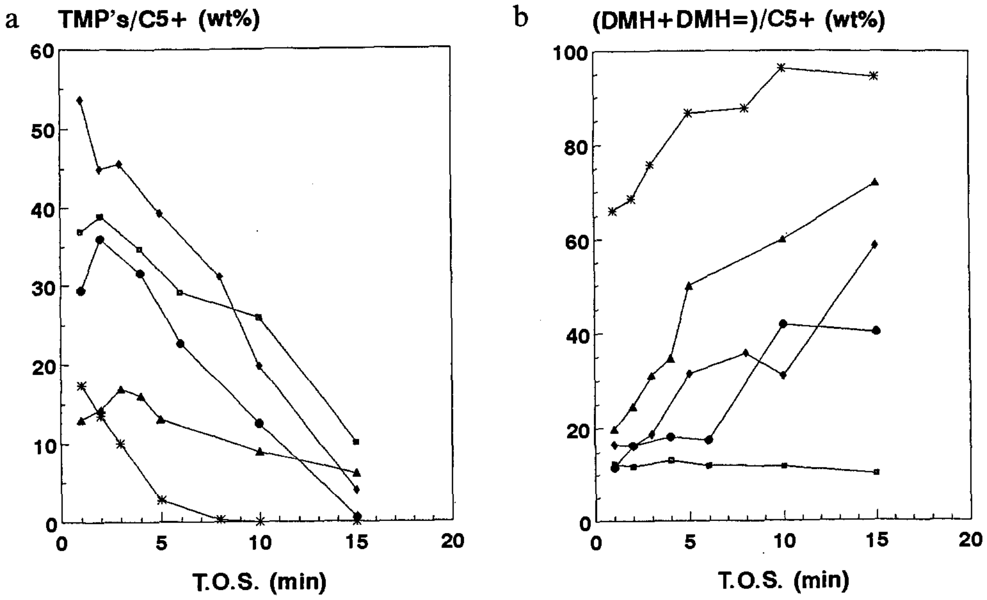


Fig. 5. Concentration of alkylated TMP's (a) and dimerized DMH + DMH= (b) products as a function of TOS for different zeolite structures: (◆) mordenite, (■) beta, (●) USY, (*) ZSM-5, and (▲) MCM-22.

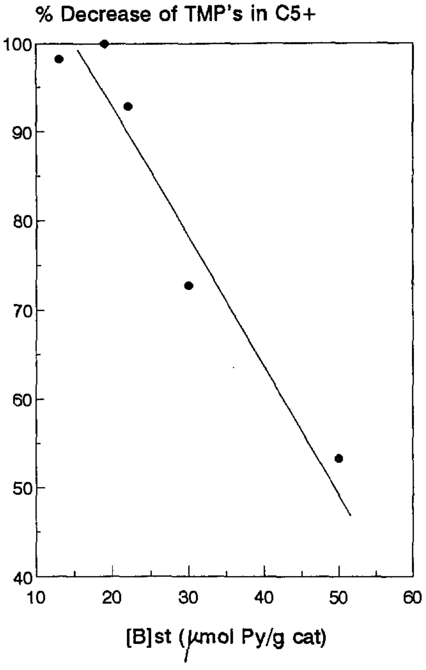


Fig. 6. Correlation between the relative decrease of TMP's after 15 min TOS and the concentration of strong Brønsted acid sites (400°C pyridine desorption temperature) in the "fresh" zeolite.

4. Conclusions

Zeolite MCM-22 has been shown to be an active catalyst for the alkylation of isobutane with 2-butene at relatively low reaction temperatures. It gives very high olefin conversions at low spaces velocities (WHSV). This zeolite has very strong Brønsted acid sites, which results in a very high cracking activity, specially at conversion levels above 80%. Decreasing initial 2-butene conversion by increasing WHSV results in a decrease of cracked C_5–C_7 products, and an increase of C_8's and heavier C_{9+} compounds. At high conversions the initial concentration of the desired TMP's accounts for ca. 40 wt% of the C_8 fraction, decreasing when increasing olefin WHSV in favor of dimethylhexenes, which are formed by dimerization of the 2-butene.

The olefin conversion obtained on MCM-22 starts to decrease rapidly after a few minutes TOS under the reaction conditions used here, and then stabilizes at ca. 30% after 15 min TOS. This decrease is accompanied by a strong decline of the cracking activity and an increase of C_8's and C_{9+}. However, the C_8 fraction becomes richer in dimethylhexenes in detriment of TMP's as the catalyst ages, indicating a change in the reaction pathway from alkylation, to olefin dimerization together with a loss of hydrogen transfer activity.

When compared to other zeolites (USY, beta, mordenite, ZSM-5), MCM-22 gives a similar initial 2-butene conversion (TOS = 1 min) under the same experimental conditions (olefin WHSV = 1 h^{-1}). However, the initial concentration of TMP's in the C_8 fraction is lower on MCM-22 than on the large-pore zeolites, but higher than on the medium-pore ZSM-5.

This is explained on the basis of steric factors, which limit the formation of the bulkier TMP's inside the pores of 10MR zeolites. According to this, one should expect the presence of larger void spaces in MCM-22 than on ZSM-5. Furthermore, the pore dimensions of MCM-22 seem to impose some steric restrictions for the diffusion of the bulkier 2,2,4- and 2,2,3-TMP isomers.

The relative decrease of 2-butene conversion with reaction time (TOS) for MCM-22 is slightly higher than for the large-pore USY and mordenite zeolites, but lower than for ZSM-5. Zeolite beta was seen to lose only a small fraction of its initial activity, in terms of olefin conversion, during the reaction period studied. However, the relative decrease of activity for the true alkylation, that is, for formation of TMP's, as the catalyst aged was seen to depend on the concentration of strong Brønsted acid sites in the "fresh" zeolite. In this respect, the concentration of TMP's in the C_{5+} product is seen to decrease at a much lower rate on the MCM-22 than on comparable catalysts.

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