Isobutane alkylation with butenes in gas phase

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A B S T R A C T

This article studies the isobutane alkylation with butenes using solid acid catalysts in order to analyze the reaction in the gas phase, at temperatures higher than those typically used in the liquid phase. Y zeolite and mordenite exchanged with lanthanum are used as catalysts. As the reaction temperature is increased, the cracking rate also increases; consequently, at short reaction times, a very low concentration of trimethylpentanes and other C8 products in the liquid fraction can be observed. After an induction period in which coke deposition occurs decreasing the cracking rate, these compounds appear in the product. The length of this induction period changes as a function of the reaction temperature. Based on these results, we tested a process in which the reaction temperature is increased during the run, carrying out the reaction in the gas phase at atmospheric pressure. Using this procedure, we found that the production of trimethylpentanes is largely increased. This is because as the catalyst deactivates due to coke deposition at a given temperature, consequently losing activity for hydrogen transfer, the increase in temperature accelerates the gasification of coke residues, thus cleaning the surface. For this reason, a higher amount of coke is found in catalysts used at higher temperatures, since under these conditions coke precursors are gasified thus avoiding pore mouth plugging, and making possible a more efficient use of the internal surface.

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1. Introduction

Alkylate gasoline is a valuable fraction to be added to the gasoline pool, since it has both a high motor and research octane number [1] and low volatility. The alkylation of isobutane with C4 olefins to produce trimethylpentane (TMP) is currently carried out in liquid phase using sulphuric or hydrofluoric acids as catalysts. Due to the inherent risks of these materials, and problems associated with their disposal, there has been considerable interest to replace these liquids by solid acid catalysts. Different materials have been used for this reaction such as zeolites [2–5], sulfated zirconia superacids [6,7], and heteropolyacids [8,9]. Y zeolite is one of the most studied catalysts [2,5,10–18]. X-zeolite [19–23], mordenite [3], EMT [14,16], and MCM-22 [3,4] were also tested. Several of these catalysts showed good activity and selectivity to TMP. However, in all cases deactivation is produced at short times and, therefore, commercial developments based on these solid catalysts have not been achieved. The most important problem is that these catalysts rapidly deactivate due to coke deposition. It seems that the activity needed to catalyze the alkylation reaction unavoidably catalyzes the olefin oligomerization and the multiple alkylation reaction, these two reactions being involved in coke formation. Therefore, it

is very important to work on the process design in order to favor the alkylation of isobutane with butenes and minimize the oligomerization and formation of high molecular weight compounds. Many alternatives have been explored following this idea. Subramaniam et al. [24–26] studied alkylation in supercritical conditions, in order to favor the removal of carbonaceous residues. In other cases, the continuous regeneration with hydrogen using a metal containing catalyst has been proposed [27,28]. A high isobutane/olefin ratio was used obtaining an extended catalyst-life, in the order of hours [5]. The reactor type is perhaps the most important factor in order to improve the catalyst-life. The CSTR is one of the best options, since this reactor operates with low olefins concentration [29].

The reaction temperature has a major impact on the deactivation rate, since this process involves many different reactions such as oligomerization, cracking, hydrogen transfer, aromatization, and physical processes such as adsorption–desorption and diffusion. The latter step is a critical one in the case of the products of this reaction (trimethylpentanes) mainly when using microporous catalysts. Each of these steps has different activation energy, and consequently a change in temperature modifies the relative rates of each of them. At low temperature, the adsorption and oligomerization processes prevail. At high temperature the aromatization of coke residues occurs. There is an optimum temperature at which the cracking–desorption of heavy molecules is favored, thus minimizing the deactivation [18,30–32]. Therefore, the adjustment of the relative rates of hydrogen transfer, oligomerization, cracking

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and diffusion, can be obtained by changing the acidity and the pore structure of the catalyst, or by changing these parameters together with the reaction temperature and the phase in which the reaction takes place.

The alkylation reaction is carried out in liquid phase when using solid acid catalysts, in order to facilitate the dissolution of coke precursors. However, in order to increase the diffusion of reactant and products, it would be more convenient to carry out the reaction in the gas phase [15]. It has been determined that the apparent kinetic constant is approximately equal to the inverse of the particle diameter for a typical zeolite catalyst. For example, the Thiele modulus is 1 for a zeolite crystal of 3 μm. Because of these facts, Wei and co-workers [15] concluded that the isobutane alkylation reaction is severely diffusion limited for all particle diameters at 100 °C.

The objective of this work is to study the alkylation reaction with isobutane with C4 olefins in the gas phase, using solid acid catalysts in a temperature range wider than that typically used for this reaction in the liquid phase. In order to compensate for the lower catalyst stability when this reaction is carried out in the gas phase, higher temperatures are selected to favor the desorption–cracking of heavier oligomers. Y zeolites and mordenites are used, both in the protonic form and after ion exchange with lanthanum.

2. Experimental

2.1. Catalysts

- Na-Y zeolite provided by UOP in the sodium form (Y-54) Si/Al = 5.3.
  Crystallinity degree: 85%. Finally the catalyst was calcined at 530 °C, for 3 h.
- La-H-Y zeolites: Na-Y zeolite was exchanged with La(NO$_3$)$_3$, 0.58 M, following two different procedures:
  (1) exchange with La(NO$_3$)$_3$ in reflux, for 4 h, drying at 100 °C, calcining at 550 °C for 4 h, and then a second ion exchange step, using the same conditions as in the first one. The exchange level was 91%. This sample is labeled LCL-Y. Crystallinity degree: 93%,
  (2) exchange with La(NO$_3$)$_3$ in reflux, for 4 h, drying at 100 °C, calcining at 550 °C, and then a second ionic exchange step, using NH$_4$NO$_3$, for 4 h at reflux, drying and then calcining at 550 °C. Exchange level: first exchange: 68%, second exchange: 21%. In the second exchange, lanthanum was not detected in the final solution. This sample is labeled LCH-Y. Crystallinity degree: 97%.

Similar procedures were used to obtain mordenite exchanged with lanthanum and ammonium (samples LCL-MOR, LCH-MOR). H-Mordenite provided by PQ Corporation (CBV30A), Si/Al = 15, was used as starting material. The crystallinity degree was 89% and 90% for the LCL-MOR and LCH-MOR, respectively.

2.2. Activity test

The alkylation reaction of isobutane with a mixture of C4 linear olefins was carried out in the gas phase at temperatures between 80 °C and 150 °C, and at atmospheric pressure, in a fixed-bed reactor. Prior to reaction, the catalyst was pre-treated heating in air from room temperature up to 250 °C at 2 °C/min. After 2 h at this temperature, the reactor was cooled to reaction temperature and purged with helium for 30 min. After this, the gas mixture was stabilized at the desired flow rate bypassing the reactor. Finally, the isobutane/olefins mixture was sent to the reactor. The space velocity was WHSV = 1 h^{-1} referred to the olefins. The IC4 was premixed with the olefins, and stored in a stainless steel vessel. The

molar ratio used in this study was 15. The C4 olefins fraction contained 38% l-butene, 22% *trans*-2-butene, 14% *cis*-2-butene and 26% isobutene. In order to analyze the products coming out of the reactor, a 10-loop valve was used. Reactions in the liquid phase were also carried out, and selected results are presented for comparison purposes.

2.3. Coke characterization

The temperature-programmed oxidation (TPO) was carried out using a modified technique. CO$_2$ produced during coke burning was converted to CH4 in a methanation reactor containing a nickel/kieselguhr catalyst and operating at 400 °C. A H$_2$ stream was fed to this reactor, in order to quantitatively convert CO$_2$ into CH$_4$. This compound was then continuously monitored by an FID detector. Typically, 10 mg of coked catalyst were placed in a quartz cell, and heated at 12 °C/min, using 6% O$_2$/N$_2$ as carrier gas flowing at 40 cm^3/min. Additional details of the technique can be found elsewhere [33]. The calibration of the system was carried out with pulses of 1.26% CO$_2$/He.

2.4. Pyridine temperature-programmed desorption (TPD)

To evaluate the acidity of the samples, pyridine temperature-programmed desorption was carried out. The catalysts were pre-treated in situ in N$_2$ flow during 1 h at 250 °C. After cooling down to room temperature, nitrogen was bubbled in pyridine and flowed through the sample during 15 min. After this, pure nitrogen was flowed and the temperature was increased up to 150 °C, until no pyridine was detected. The TPD experiment was carried out heating at 12 °C/min, from 150 °C up to 700 °C. Pyridine was detected using a FID detector after methanation, as above explained.

3. Results and discussion

The acidity of the catalysts used in this work has been previously reported [18]. The main observations carried out by NH$_3$ TPD analyses are the following:

- Mordenite catalysts have a lower amount of acid sites than the catalysts based on Y zeolite.
- Mordenite has a fraction of its acid sites with stronger acidity as compared to LCH-Y and LCL-Y catalysts, as indicated by a high temperature NH$_3$ desorption peak.
- LCH-Y has a higher number of acid sites than the LCL-Y, although the NH$_3$ desorption occurs in the same temperature range.

In this work, we carried out pyridine TPD using a methanator-FID to increase the detection sensitivity, and also to better quantify the number of acid sites. Fig. 1 shows the TPD profiles obtained with LCL-Y and LCH-Y catalysts. The pyridine desorption occurs in the same temperature range for both of them, although in the case of the LCH-Y catalyst the pyridine needs a higher temperature to desorb completely from the catalyst surface. This would indicate that there is a small fraction of acid sites with higher strength on this catalyst as compared to those on the LCL-Y one. In addition, a major difference between these two catalysts is the amount of acid sites. The LCH-Y has 1.35 mmol/g and the LCL-Y has 0.95 mmol/g. This higher acid-site density is a very important parameter, related to the activity and stability of these materials.

3.1. Liquid yield and trimethylpentanes production

Fig. 2 shows the amount of liquids obtained per gram of olefin fed to the reactor (g of C5+ hydrocarbons/g of olefin fed) (Fig. 2A and C), and the TMP fraction in the liquid (Fig. 2B and D). Fig. 2A
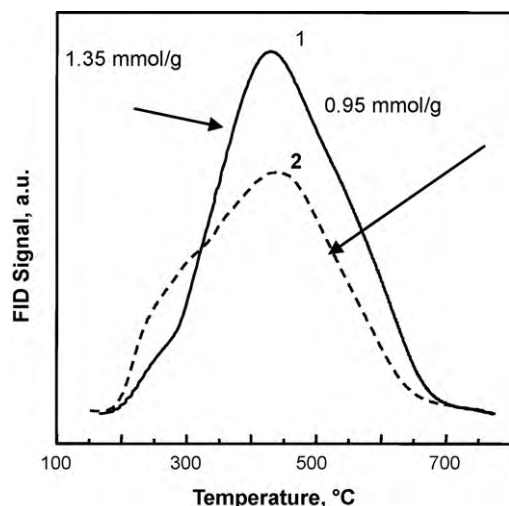
Fig. 1. Pyridine TPD profiles for LCH-Y (curve 1) and LCL-Y (curve 2) catalysts.

and B shows results obtained with the LCL-Y catalyst at 112 °C and 120 °C in the gas phase, and with the LCH-Y catalyst in the liquid phase at 80 °C. This latter result is used as reference in order to compare the catalytic performance when the reaction is carried out either in the gas or in the liquid phase. Fig. 2C and D corresponds to results obtained with the LCH-Y catalyst, in the gas phase, at different temperatures.

The highest value of liquid yield is obtained with the LCH-Y catalyst at 150 °C during the first 10 min of reaction (Fig. 2C). This liquid yield is even higher than that obtained with the same catalyst in liquid phase at 80 °C (Fig. 2A). This could be due to a faster desorption and diffusion out of the pores of the alkylation products. The evolution of TMPs with time follows the typical pattern found in fixed-bed reactors. There is an initial increase at the beginning of the reaction, and then a sudden drop, which is due to the catalyst

deactivation due to coke deposition. When the reaction is carried out in the liquid phase or in the gas phase, the sudden drop of TMPs occurs in both cases at the same time at which the dimethylhexenes (DMH=) start coming out in the products stream. These compounds are not formed at the beginning of the reaction. However, the coke deposition leads to a loss in the hydrogen transfer capacity, and because of this, olefinic oligomers appear among the products.

As shown in Fig. 2, it is possible to obtain a high liquid yield with zeolite LCH-Y in the gas phase. It is very interesting that the maximum in the TMP fraction in the liquid shifts to higher times on stream, as the reaction temperature is increased. This can be seen for the LCL-Y catalyst at 112 °C and 120 °C (curves 2 and 3, Fig. 2B), and for the LCH-Y catalyst at 80 °C, 120 °C, and 135 °C (curves 1–3, Fig. 2D). In other words, the induction period needed to obtain the main product increases as a function of the reaction temperature unless it is very high, such as 150 °C (curve 4, Fig. 2D). In this latter situation, the fast olefin oligomerization–aromatization prevails and the deactivation occurs faster, thus decreasing the induction time. However, at this temperature, even though the liquid yield is high at the beginning of the reaction, the main products are in the C5–C7 fraction, and consequently the selectivity to TMP is low.

In the case of the mordenite catalyst, it was found that the highest liquid yield was obtained working in gas phase at 90 °C (results not shown).

3.2. Product distribution

Fig. 3 shows the results of product distribution in the C5+ fraction during the alkylation reaction in liquid and gas phase at 80 °C, and in the gas phase at 150 °C, obtained with the LCH-Y catalyst. This figure shows the components produced by cracking. Other compounds like trimethylpentanes (TMP) and dimethylhexanes are not shown in this figure. It can be seen that at 80 °C in the gas phase, the compounds shown in Fig. 3 appear in the product stream after an induction period. While 2,3-dimethylpentane (23DMP) and 2,4-dimethylpentane (24DMP) are obtained from the beginning of
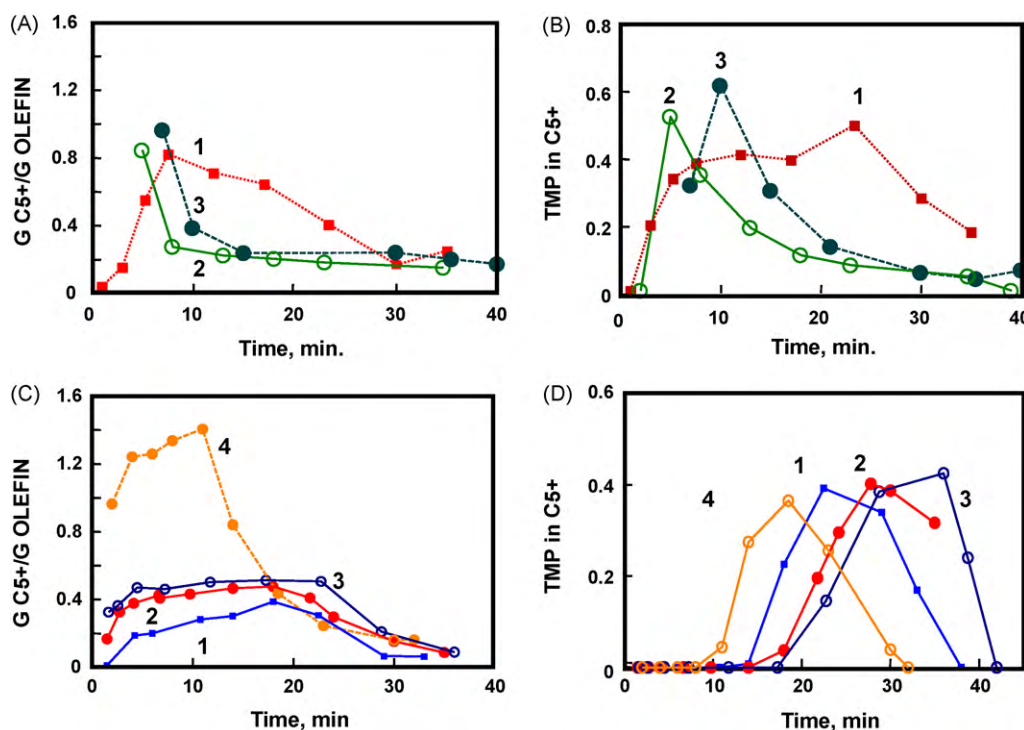

Fig. 2. Liquid yield and TMP distribution in C5+ fraction; (A) and (B): (1) LCH-Y, liquid 80 °C, (2) LCL-Y, gas 112 °C, (3) LCL-Y, gas 120 °C; (C) and (D): LCH-Y, gas phase: (1) 80 °C, (2) 120 °C, (3) 135 °C, (4) 150 °C.
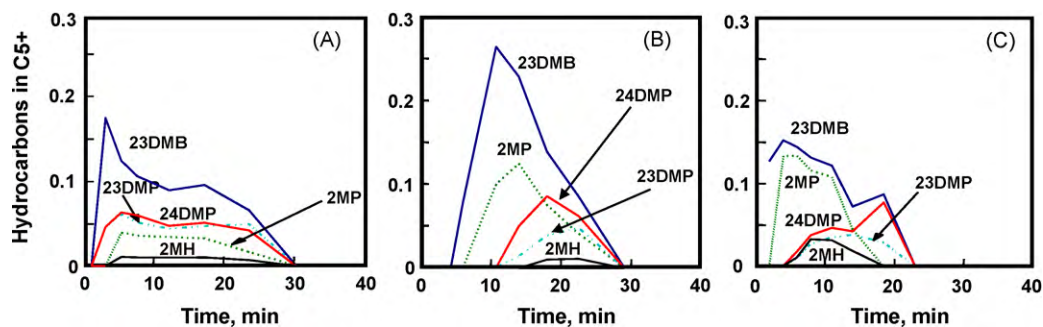
Fig. 3. Products distribution in the C5+ fraction obtained with LCH-Y catalyst; (A) at 80 °C, liquid phase; (B) at 80 °C gas phase; (C) at 150 °C gas phase.

the reaction in the liquid phase at 80 °C, in the gas phase these compounds are observed after 10 min. The main products obtained in the liquid phase are dibranched paraffins, while in the gas phase the 2-methylpentane (2MP) is one of the most important products. The C7 compounds are formed by the cracking of C12 hydrocarbons, which leads to the formation of C5 + C7 or two C6 hydrocarbons. It is interesting to observe that at 150 °C, these products are obtained after a shorter induction period as compared to 80 °C (compare Fig. 3B and C). The higher temperature favors the formation of these products from the beginning of the reaction, suggesting that lower amounts of coke deposits would be forming on the catalyst when the reaction is carried out at high temperatures such as 150 °C. The stability is only slightly better in the case of the reaction carried out at 80 °C in the liquid phase as compared to the same temperature in the gas phase (compare Fig. 3A and B). The 2,3-dimethylbutane (23DMB) is a high octane component, with a RON = 104.3, and is one of the major components in the C5+ fraction both when the reaction is carried out in the liquid and in the gas phase.

The results obtained with the LCH-MOR catalyst at 80 °C in the liquid phase and at 90 °C in the gas phase show more important differences than in the case of the Y zeolite (not shown). At 80 °C in the liquid phase only 23DMP and 23DMB are observed, while in the gas phase several other compounds are obtained, including 2MP, 24DMP, and 2MH. Another important observation is that these products are obtained during longer times on oil at 90 °C in the gas phase as compared to the liquid phase at 80 °C. This indicates that at lower temperature the deactivation occurs faster. Therefore, with the mordenite it can also be concluded that an increase in temperature, accelerates the coke precursors desorption and diffusion out of the pores.

With the LCL-Y catalyst at 112 °C and at 120 °C in the gas phase, mono and di-branched isoparaffins were obtained only during the

Table 1
TMP/DMH lowest ratio obtained during the alkylation in gas phase at each reaction temperature. LCH-Y catalyst.

Temperature (°C)	TMP/DMH
80	9
90	10.8
120	5.8
135	3.7
150	1.9

first 10 min of reaction (not shown), while with LCL-MOR at 110 °C these products were not obtained during all the run.

It has to be kept in mind that the isobutane/olefin ratio inside the pores is different in the case of the reaction in the liquid phase compared to the reaction in the gas phase, even though the global isobutane/olefin ratio is the same. This ratio should be lower in the case of reaction in the gas phase, due to a preferential adsorption of the olefin. This phenomenon leads to a higher formation of C12, C16 and heavier hydrocarbons that then are cracked producing C5, C6, and C7 compounds [15]. Therefore, the temperature has to be chosen in order to compensate the higher olefin adsorption by increasing the cracking and desorption rates.

Table 1 shows the TMP/DMH ratio obtained with the LCH-Y catalyst during the reactions in gas phase at each temperature. The values shown in this table are the lowest values observed during each run. The TMP/DMH values obtained in the gas phase are similar to the results obtained for the reaction in the liquid phase, previously reported by other authors. For example, TMP/DMH obtained with beta zeolite was approximately 8 at low temperature (50–75 °C) and short times on oil, and below 1 at higher temperatures [34]. Higher values were found with LaX and LaY zeolites, in the order of 19 and 13 respectively, at short times on oil [23].
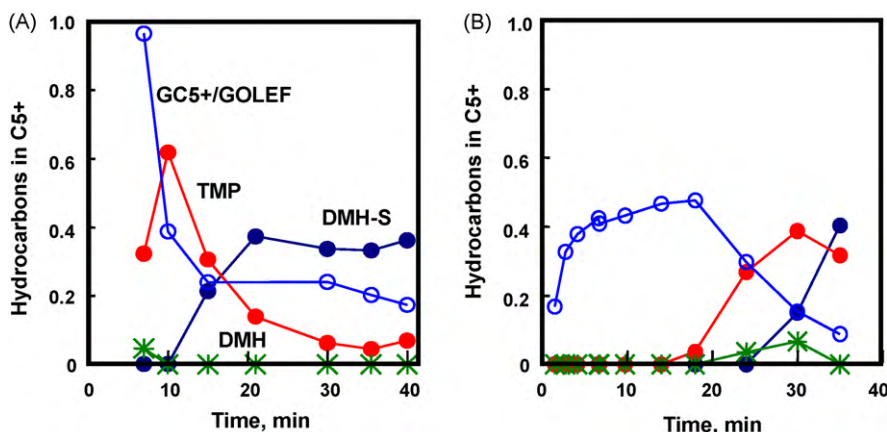

Fig. 4. Liquid yield and products distribution in the C5+ fraction, reaction in gas phase at 120 °C. (A) LCL-Y catalyst; (B) LCH-Y catalyst.
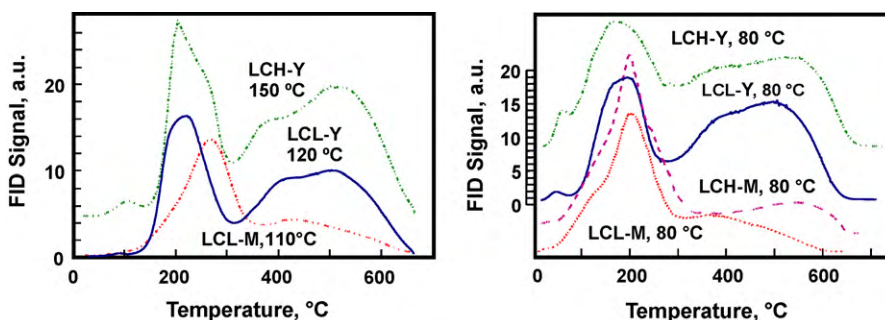
Fig. 5. TPO profiles of catalysts used in alkylation reaction; (A) gas phase; (B) liquid phase.

Fig. 4A and B shows results obtained with LCL-Y and LCH-Y catalysts, in the gas phase at 120 °C. Fig. 1 shows the pyridine TPD profiles for both catalysts. These profiles clearly indicate that the acid strength distribution is very similar for both catalysts, even though in the case of the LCL-Y catalyst the profile is slightly shifted towards lower temperatures. Therefore, the acidity is weaker in this case. On the other hand, the total number of acid sites is significantly lower in the case of this catalyst, as indicated in Fig. 1. These differences in acidity have a major impact on the catalytic behavior. The main differences are: (i) the catalyst with lower acidity has higher initial liquid yield; (ii) it deactivates faster due to a lower cracking rate of coke precursors, and consequently a faster hydrogen-transfer activity loss is observed (compare the dimethylhexenes concentration curves for both catalysts); (iii) lower induction time needed to obtain TMP; (iv) even though the LCH-Y catalyst has a more stable liquid yield from the beginning, its selectivity towards TMP is lower at short times on oil (note that the TMP appears in the products at 17 min, while the liquid yield was above 40% at 5 min on oil).

3.3. Coke characterization

Fig. 5A and B shows the TPO profiles obtained with catalysts coked in the gas and in the liquid phase respectively. The first peak of these profiles corresponds to hydrocarbons that are released from the coked catalyst during the heating, and can be stripped off even under an inert flow [18]. This is the reason why this peak becomes narrower as the reaction temperature increases, since at higher reaction temperatures desorption and cracking of coke residues occur faster and, therefore, the fraction of hydrocarbons that are being released from the catalyst during the reaction increases. It can also be seen that the TPO profiles obtained with catalysts coked in the gas phase are very similar to those that correspond to catalysts coked in the liquid phase.

The effect of temperature on the TPO profiles is clearly observed in Fig. 6. This figure shows the TPO profiles obtained with LCH-Y catalysts coked at 80 °C, 120 °C, and 135 °C in the gas phase. It is very interesting to observe that the second part of these TPO profiles is exactly the same, which indicates that this part of the profiles is not formed during the reaction but during the thermal analysis while increasing the temperature, as previously suggested [18]. It has been demonstrated that the second peak corresponds to the transformation of the aliphatic deposits obtained during the alkylation reaction at low temperature, into aromatic structures. This change in structure occurs during the temperature-programmed analysis [18]. Because this change in structure occurs as the temperature is raised, very high temperatures are needed to fully remove the coke deposits. This second peak in the TPO profile is related to coke that is located mainly inside the pore structure. Because of this, the mordenite catalyst displays a TPO profile with a very small second peak, since pore mouth plugging occurs and consequently
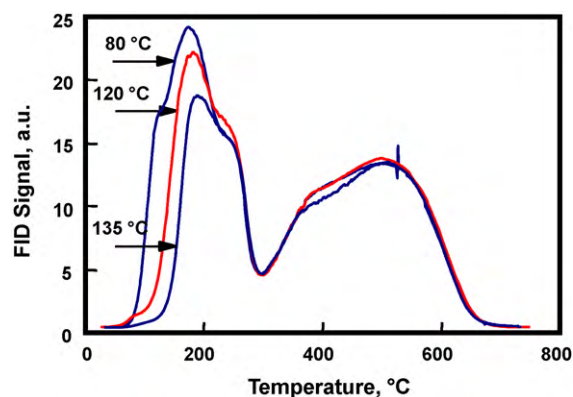

Fig. 6. TPO profiles obtained with LCH-Y catalysts coked at different temperatures in gas phase.

a small amount of coke is deposited inside the pores. On the other hand, the second peak in the case of the Y zeolite is very important in size, because this catalyst is active until all the surface is covered with coke. The difference between these profiles is in the first peak, which indicates that during the reaction at higher temperature, higher amount of residues are gasified, and the hydrocarbon deposits left on the catalyst need temperatures higher than those used during the reaction in order to be eliminated.

Table 2 shows the amount of coke deposited on several catalysts, used under different experimental conditions.

The amount of coke deposited on the catalysts during the alkylation reaction in the gas phase is, as a general trend, higher than that when the catalyst is used in the liquid phase. It can be concluded that due to the higher temperature used during the reaction in the gas phase, the cracking of the intermediate compounds that form coke, and their desorption and diffusion are greatly increased

Table 2
Coke deposited during gas and liquid phase alkylation.

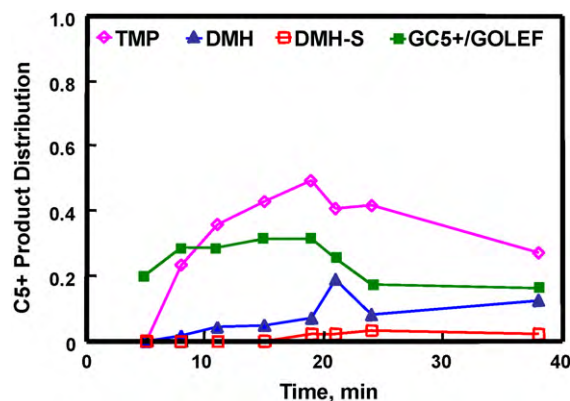| Catalyst	Gas phase		Liquid phase	
	Temperature (°C)	%C	Temperature (°C)	%C
LCL-MOR	110	6.85	80	5.64
LCH-MOR	80	8.42	80	5.62
	90	7.20		
	100	7.35		
	110	8.17		
LCL-Y	112	13.62	50	9.5
	120	13.00	80	11.2
LCH-Y	80	15.28	30	4.8
	90	14.01	50	14.7
	120	13.84	80	13.1
	135	15.01		
	150	14.5		
	110–170	16.50		

Fig. 7. Products distribution in the C5+ fraction. Experiment increasing the temperature from 110 °C to 170 °C. LCH-Y catalyst.

Fig. 9. TMP/DMH ratio during the temperature-programmed reaction experiment. Labels indicate the reactor temperature that corresponds to each sample taken for analysis.

compared to the rates of these steps in the liquid phase. For this reason, the pore mouth plugging does not occur at early stages during the reaction and a higher amount of coke can be deposited on the catalysts.

3.4. Process design

Activity results and the coke analysis above described can be summarized as follows:

- At short time on oil, the catalyst is very active and consequently a low selectivity is obtained.
- As the catalyst deactivates, the selectivity towards liquid formation and TMPs production, first increases and at higher coke content both parameters drop.
- At high temperature, a higher fraction of the coke deposits are stripped off the catalyst.
- The TPO profiles of catalysts coked at higher temperature in the gas phase indicate that the temperature needed to remove the coke deposits is not affected.

These facts suggest that the process can be designed with a different and simple strategy, such as starting the reaction at low temperature, and increasing it as a function of time. With this procedure, it should be possible to decrease the induction period needed to obtain the TMP observed at higher temperatures. Fig. 7 shows the result of one experiment in which the reactor temperature was increased from 110 °C up to 170 °C during the reaction with the LCH-Y catalyst. It can be seen that as the temperature is increased from 110 °C up to 170 °C, the TMPs are obtained with
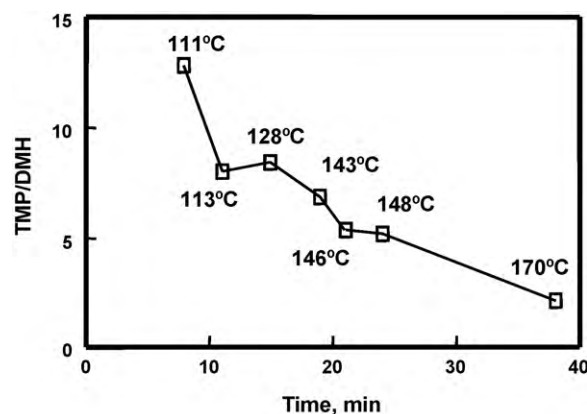
very good selectivity, and with a very low fraction of DMH=. This result shows that the loss of hydrogen-transfer activity due to coke deposition can be compensated by increasing the temperature, thus favoring the formation of TMPs, maintaining the formation of oligomerization products at a low level.

Fig. 8 shows results obtained in the gas phase at constant temperature (Fig. 8A) and at increasing temperature (Fig. 8B). At 135 °C at the beginning of the reaction, the LCH-Y catalyst does not produce C8 compounds, which appear in the products at 20 min time on stream. At 40 min the amount of C8 hydrocarbons drastically decreases. In the experiment in which the reaction temperature was increased during the reaction, the concentration of C8 hydrocarbons in the C5+ fraction is higher, being present in the product at 5 min on oil. It is interesting to note that up to 170 °C the C8 compounds are the main products. Table 2 shows the amount of coke deposited during this run. It can be seen that it is slightly higher than the amount of coke deposited at lower temperatures.

Even though this reaction strategy could be optimized, regarding the initial temperature and the heating rate, these results show that the hydrogen transfer capacity loss that occurs during the alkylation reaction due to hydrocarbons deposition can be compensated, at least partially, by a temperature increase maintaining the production of trimethylpentanes.

Fig. 9 shows the TMP/DMH ratio during the experiment in which the reaction was increased during the experiment. The overall behavior agrees with the experiments above described, i.e., with a decrease in the TMP/DMH ratio as a function of time, which in the case of the experiment shown in Fig. 9 also corresponds to an increase in temperature. A very important conclusion
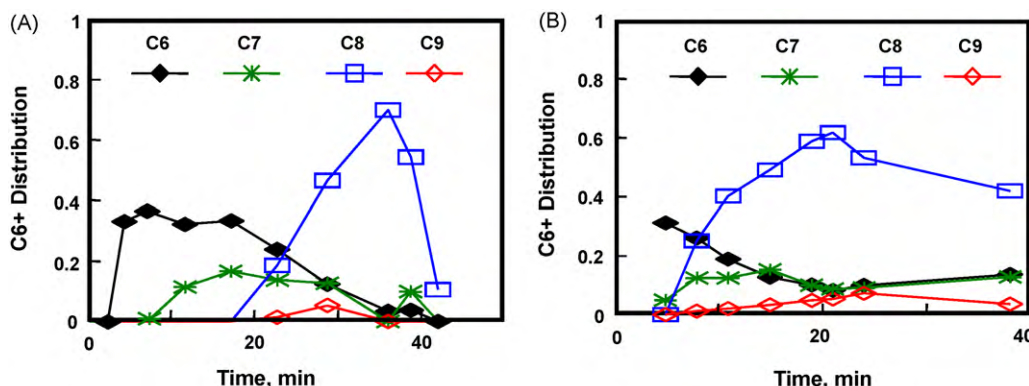

Fig. 8. C6+ Distribution with LCH-Y catalyst, gas phase. (A) At 135 °C, constant temperature; (B) temperature-programmed reaction from 110 °C up to 170 °C.

that can be drawn comparing the results of Table 1 and Fig. 9 is that the TMP/DMH ratio is higher in the experiment carried out by increasing the temperature, and therefore it means that the catalyst behavior is greatly improved. Trimethylpentanes (TMP) are the primary products from isobutane/butene alkylation, while dimethylhexanes (DMH) are mainly formed by dimerization of butene. Therefore, the initial TMP/DMH ratio can be taken as a measure of the intrinsic alkylation/dimerization activity ratio of the zeolite, and as the hydrogen transfer capacity decreases due to coke deposition, this ratio decreases with time on oil. The results shown by Lercher and co-workers [23,34] followed this pattern, with a pronounced decrease in the TMP/DMH as a function of time.

The TPO profile of the catalyst at the end of this experiment follows the same trend as those shown in Fig. 6 (not shown). The first peak is smaller than that shown for the catalyst coked at 135 °C, and the final temperature of the profile is the same, which indicates that the coke deposits have a similar burning behavior and the temperature needed to burn it off does not depend upon the reaction temperature. However, it has been established that at higher reaction temperature, the coke transforms its structure from aliphatic to aromatic. This change in coke structure could have an effect if a different regeneration strategy is followed, such as solvent extraction or hydrogenation.

These results show that the increase in the temperature during the reaction improves the overall catalytic behavior during the isobutane alkylation with butenes, and that it is possible to consider the gas phase as an alternative to carry out this process. This avoids the use of the extremely high pressures required in the case of carrying out the reaction in the liquid phase, especially at high temperatures, and on the other hand, it facilitates the diffusion of bulky molecules out of the pores, thus decreasing the rate of secondary reactions such as multiple alkylation and coke deposition.

4. Conclusions

The isobutane alkylation with C4 olefins can be carried out in the gas phase using solid acid catalysts, at higher temperatures than those used in the liquid phase. At 80 °C, the stability is better when the reaction is carried out in the liquid phase, which is assigned to both a lower olefin concentration on the catalytic surface and to a better extraction effect of the liquid phase. As the temperature is increased, the relative rates of olefin adsorption and desorption, diffusion, cracking and hydrogen transfer reactions change. Higher temperatures favor the cracking of oligomers and multiple alkylation products, and their diffusion out of the pores. High reaction temperatures lead to a very low production of C8 products at short reaction time, and as coke is deposited, the TMP production increases. In this way, the stability of the catalysts is improved. Taking into account that coke deposition decreases the cracking activity and the hydrogen transfer capacity, and on the other hand, that the increase in temperature has the opposite effect, a process in which the temperature is increased during the reaction was designed. In this way, it was possible to largely improve the liquid yield and the concentration of TMPs in the liquid, carrying out

the alkylation reaction in the gas phase at atmospheric pressure. Higher temperatures during the reaction also make it possible to slow down the pore mouth plugging, mainly due to a faster cracking rate of the hydrocarbons deposits. As a consequence, a better utilization of the internal surface takes place and a higher amount of coke can be observed when the reaction is carried out at higher temperature.

Acknowledgements

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