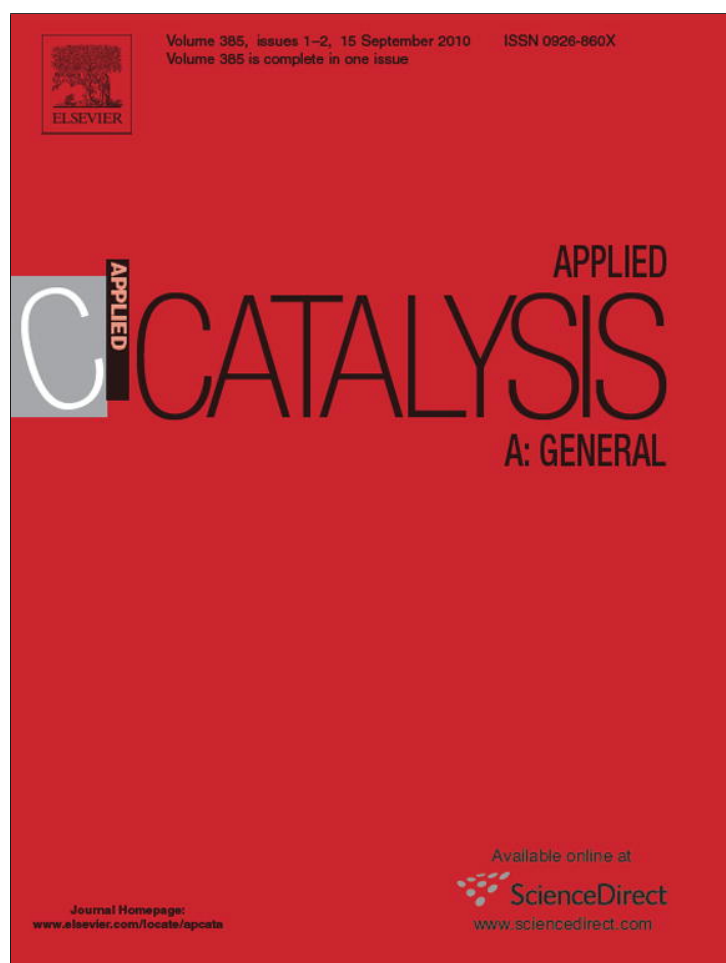


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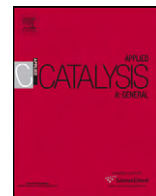


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Isobutane alkylation with solid catalysts based on beta zeolite

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ABSTRACT

The isobutane alkylation with butenes is a reaction in which the substitution of mineral acids, such as sulphuric and hydrofluoric acids, by solid acid catalysts is highly desirable. Solid catalysts with good activity and selectivity for this reaction have been previously reported. However, bad stability is a major drawback in most cases. In this work, catalysts based on beta zeolite, exchanged with lanthanum were studied. It was found that these catalysts have lower activity than the Y zeolite both, in the protonic form, or with lanthanum in replacement of protons. EDX analyses showed that lanthanum is practically fully removed from the zeolite structure during an exchange with ammonium nitrate, even though the catalyst was precalcined. The total acidity as measured by pyridine temperature-programmed desorption is similar in the beta and the Y zeolites. However, the former zeolite has stronger acid sites, and because of this, the deactivation process occurs faster. Pulses of 1-butene at different temperatures can be used as a technique to predict the catalytic behavior of acid catalysts in the alkylation reaction. Using this technique, it was possible to determine that the beta zeolite is deactivated during the alkylation reaction by pore mouth plugging. The addition of platinum to the beta zeolite is useful in order to regenerate the catalyst using hydrogen at 80 °C, although long times are needed to accomplish this regeneration.

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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. Faujasites exchanged with lanthanum have been studied since the pioneering work of Weitkamp [12]. There are several reports in which these catalysts are studied [10,18–20,22,24–28]. Mordenite exchanged with lanthanum has also been tested in this reaction [18]. There are several factors that have a strong influence on the catalytic activity of lanthanum-exchanged zeolites, as

discussed and reviewed by Lercher et al [19,21–23]. It has been proposed that the residual sodium left on the catalyst after ion exchange defines the activity [23]. It is much more difficult to fully remove it in the case of the Y zeolite as compared to the X zeolite, due to the lower concentration of sites that can accommodate multivalent cations. The residual sodium weakens the Brönsted acid sites. As the Si/Al ratio in the zeolite increases, the amount of isolated Al sites decreases. Consequently, it is more difficult to accommodate the trivalent lanthanum cation. Another effect of La³⁺ is that it can generate strong Brönsted acid sites by hydrolysis of water [27,29]. Another change generated by the lanthanum exchanged in the zeolites, is that it can cause a polarization of the zeolite framework and this increases the strength of the Brönsted acid sites [30].

Beta zeolite has also been matter of investigation [31–38]. It possesses relatively high density of Brönsted acid sites [37] and favorable pore structure [38]. In contrast to the common belief that a higher aluminum content zeolite leads to more stable performance for alkylation, Smirniotis et al. [31] observed different optimum Si/Al ratios of beta zeolites depending on feed conditions. The beta zeolite with Si/Al ratio equal to 15 was the best regarding the stability, as compared to other beta zeolites with Si/Al ratios of 6, 8.5 and 30. These results were obtained for a feed with isobutane/olefin ratio equal to 20.

In spite of the good catalytic behavior of the beta zeolite, and the beneficial effects of lanthanum on the ion exchange sites in

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the zeolite, there are no reports using beta zeolite exchanged with lanthanum.

The deactivation is produced by coke deposition. This carbonaceous deposit presents aliphatic structure [10] which becomes aromatic as the temperature increases during the regeneration [18]. This transformation is catalyzed by acid sites. Consequently, after a regeneration procedure in which a fraction of coke remains on the catalyst, a selective poisoning of the active sites is observed. For this reason, when the coke is eliminated with air, the temperature should be increased to values higher than 500 °C to eliminate the carbonaceous deposits and to restore the activity. Various procedures have been studied to eliminate the coke at low temperature, such as solvent extraction [18], regeneration with ozone and hydrogen peroxide [39,40], and incorporation of a metal to promote the oxidation of coke or possibly hydrogenate it at low temperature [40]. The regeneration with ozone enabled the complete elimination of coke, however, this procedure requires a long time to, in the order of hours. The regeneration with hydrogen made at temperatures similar to that of the reaction, allowed recovering the activity in similar times than the ozone treatment, when the catalyst contained Pt or Pd. In all these reports, the regeneration studies were carried out using catalysts completely deactivated. Other option that has been studied is carried out the alkylation reaction under supercritical conditions, with the idea of removing the coke during the reaction [41–47].

In this work, the beta zeolite is studied as a catalyst for the alkylation of isobutane with C4 olefins. Both, the protonic form of the zeolite, and after partial and total exchange with La, are used. The selected beta zeolite, has a Si/Al ratio equal to 15 since as above mentioned, its stability is good. The catalyst containing Pt is also analyzed with the purpose of regenerating it at low temperature in hydrogen. This material is used in reaction-regeneration cycles. A transient adsorption technique is used to assess the interaction between the catalyst and the butene. Results obtained with the beta zeolite are compared with those obtained with the Y zeolite working under the same experimental conditions.

2. Experimental

2.1. Catalyst preparation

A beta zeolite (from UOP, Si/Al=15) in protonic form was employed (B-H). This zeolite was exchanged with a 0.58 M La(NO₃)₃ aqueous solution, during 6 h in reflux. Then it was filtered and dried at 100 °C, and finally calcined at 550 °C. This material was used for a second ionic exchange with NH₄NO₃ 0.5 M during 6 h in reflux, drying and calcining at 550 °C. This catalyst is labelled B-LCH. A similar procedure was followed to prepare another catalyst, B-LCL, using La(NO₃)₃ also in the second ion exchange. The B-H catalyst was used to prepare the Pt-B-H catalyst by dry impregnation in order to achieve 0.5 wt% Pt. The results are compared with those obtained with the Y zeolite (Y-54 from UOP, Si/Al=5.3), prepared following the same procedure as in the case of the B-LCH. The Y zeolite prepared in this way is labelled as Y-LCH. The Y zeolite was also ion exchanged in two steps with NH₄NO₃ (Y-H). Additional details of the preparation of the Y zeolite can be found elsewhere [18].

2.2. Catalytic tests

The alkylation reaction was carried out in a fixed bed reactor, at 30 atm and 80 °C, with a molar ratio isobutane/C4 olefins = 15, and an olefin spatial velocity WHSV = 1 g olefin/(g catalyst h). The catalyst was pretreated in situ at 250 °C in helium, or in hydrogen at 500 °C for the catalyst containing Pt. The reaction was carried out during 40 min; then the catalyst was purged with helium at

the same temperature for 30 min. Due to the rapid deactivation of the materials and complexity of the mixture to be analyzed, the reaction products were collected at different times in a heated multiloop valve and analyzed by gas chromatography.

The catalysts were regenerated with air or hydrogen in different conditions, taking samples before the regeneration in order to determinate the coke content.

2.3. Coke characterization

The coke was characterized by temperature-programmed oxidation (TPO), or by hydrogenation. The experiments were carried out using a modified technique [48] in which the gases coming out of the sample cell passed through a methanation reactor. A H₂ stream was fed to this reactor, which was loaded with a Ni catalyst, and where CO and CO₂ were converted to CH₄. This compound was continuously measured using a FID detector. Under these conditions (400 °C, 6% O₂, 40 ml/min), a 100% conversion of CO_x was reached and in this way the sensitivity of the technique was greatly improved.

The analysis cell was loaded with approximately 10 mg of catalyst and the analyses were performed employing a heating rate of 12 °C/min starting from 20 °C. Equipment calibrations were performed using pulses of CO₂ diluted in He.

2.4. Catalyst characterization

2.4.1. X-ray diffraction (XRD)

The analyses were carried out with a Shimadzu XD-D1 instrument with a monochromator, CuK_α radiation and a scanning rate of 0.5°/min. The crystallinity degree was determined by measuring the intensity that corresponds to the crystalline substance, and the intensity that corresponds to the halo due to the amorphous substance. The ratio of these two intensities is then used to calculate the concentration of the crystalline phase.

2.4.2. Surface area and pore volume

Nitrogen adsorption was employed to determine BET surface area, and pore volumes were estimated by means of t-plots. The determinations were carried out on a fresh catalyst, pre-treated under vacuum at 250 °C during 3 h, using a Micromeritics Accusorb 2100 sorptometer.

2.4.3. Temperature-programmed reduction TPR

The experiments were carried out with fresh samples of Pt-B-H catalysts, in an Okhura TP-2002S system. The TPR runs were conducted using a heating rate of 10 °C/min in a flow of 5% H₂/Ar (45 ml/min) up to 600 °C.

2.4.4. CO chemisorption

Dynamic CO chemisorption measurements were carried out by sending 250 μl pulses of 5% CO/He on 0.2 g samples of fresh Pt-B-H catalyst. The He used as carrier and to purge the catalyst was purified through a MnO trap before contacting the sample. The system described in Section 2.3 was employed to quantitatively transform CO into CH₄, and was then detected by FID.

In order to determine the CO adsorption capacity, consecutive pulses were sent until the amount of CO leaving the sample was the same as that by-passing the sample. The adsorption capacity (CO/Pt) was calculated using the sum of the differences between the size of the pulses when by-passing the cell and the pulses that go through the cell.

2.4.5. Temperature-programmed desorption (TPD)

2.4.5.1. Pyridine TPD. These experiments were carried out to evaluate the acidity of the samples. The catalysts were pretreated in

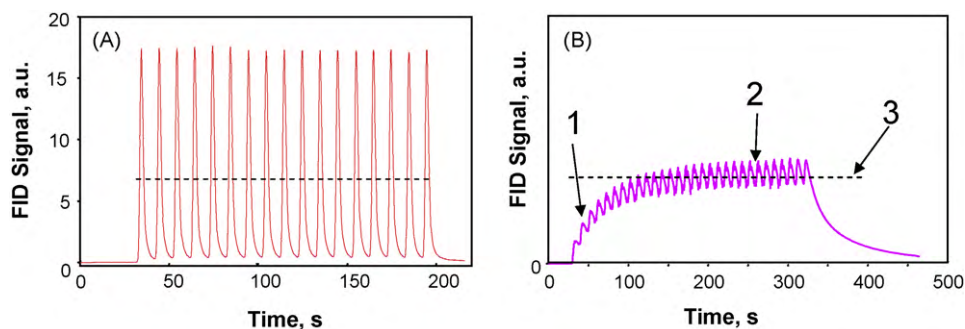


Fig. 1. 1-Butene pulses experiments. (A) Blank experiment and (B) example of a result. Labels 1, 2, 3: see text.

situ in N_2 flow at $350^\circ C$ during 1 h. 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 $150^\circ C$, until no pyridine was detected. The TPD experiment was carried out heating at $12^\circ C/min$. Pyridine was detected using a FID detector after methanation, using a setup similar to that described in Section 2.3.

2.4.5.2. Butene TPD. In order to determine the level of interaction between the catalyst and the butene, which is one of the reactants in the alkylation reaction, butene TPD experiments were carried out. The samples were pretreated as described in the pyridine TPD experiments, and then contacted with a flow of pure olefin during 15 min at room temperature. After this, the FID signal was stabilized in N_2 flow and then the sample was heated at $12^\circ C/min$.

2.4.6. Microscopy analysis

Scanning electron microscopy (SEM) of B-H, B-LCH and B-LCL samples at 25 KV were carried out using an electron microscope (JEOLJSM 35C). The atomic elemental analyses were obtained using an energy-dispersive X-ray analysis (EDX) system attached to the SEM instrument. In order to ensure that the data collected was representative of the whole sample, scans were made at more than one location. The reproducibility verified indicates homogeneous zeolite particles.

2.5. Dynamic analysis of 1-butene – catalyst interaction

The dynamic adsorption-desorption of the olefin on the surface of the different catalysts was studied by carrying out experiments in which consecutive pulses of 1-butene diluted in N_2 were sent to the sample cell at different temperatures.

Samples were pretreated as above described, and then the temperature was stabilized at the desired value. In most of the experiments, the first set of pulses was sent at $60^\circ C$. Once this temperature was stabilized, pulses of 2% of 1-butene in N_2 were sent to the sample every 10 s, using N_2 as carrier. Typically, 20 pulses were sent. Then, after the signal was stabilized, the temperature was increased $10^\circ C$ up to $70^\circ C$, and a new series of pulses was sent. The procedure was repeated increasing the temperature up to $100^\circ C$. Then, new series of pulses were carried out but decreasing the temperature at 90, 80, 70 and $60^\circ C$. This experimental design provides information regarding the strength of the interaction and if it is reversible or not. In addition, the comparison of the results obtained at each temperature while increasing the temperature with those obtained when decreasing the temperature, provides information regarding the deactivation that the 1-butene left on the surface produces on the adsorption capacity.

Fig. 1A shows the signal obtained in the blank experiment, carried out with an empty cell. The dotted line is the average value. Fig. 1B shows an example of the signal obtained with a zeolite cat-

alyst. It can be observed that in this case the pulses coming out of the cell level out after approximately 200 s (20 pulses) with an average amount of butene coming out of the cell equal to the injected amount (label 3). Label 1 indicates a transient zone in which the average value is clearly lower than the input amount. Therefore, this type of signal indicates that certain amount of butenes are being irreversibly adsorbed on the catalyst. The small and constant amplitude observed in the zone with label 2 indicates that one or both of the two following processes are taking place: (a) diffusion in and out of the micropore system; (b) adsorption and desorption in a pseudo-steady state. In both cases, all the butene that was injected comes out of the cell. If the butene is irreversibly adsorbed, due to the decrease in the number of adsorption sites the oscillation amplitude should increase as the number of pulses increases. If the mean value of the signal is lower than that corresponding to the blank, then the butene is being irreversibly adsorbed on the catalyst.

The responses obtained for each material are compared with that observed when the pulses were performed with an empty cell, i.e. a blank experiment.

This experimental design has the objective of developing a simple, fast analytical tool to screen catalysts for the isobutane alkylation reaction, using very small amounts of catalyst and reactants.

3. Results and discussion

3.1. Catalyst characterization

The XRD results shown in Fig. 2 indicate that the crystalline structure of beta zeolite is not modified by the different treatments followed during the preparation. The crystallinity degree of the samples is 98%, taking 100% for the original H-B zeolite. The exchange of protons with lanthanum up to different degrees (samples b and c) does not modify the crystallographic structure, as seen

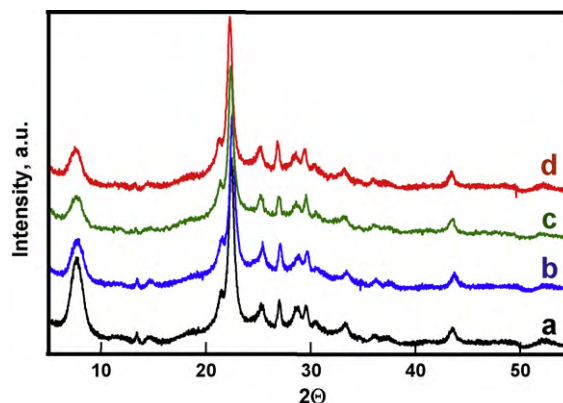


Fig. 2. XRD spectra: (a) B-H, (b) B-LCH, (c) B-LCL and (d) Pt(0,5)-B-H.

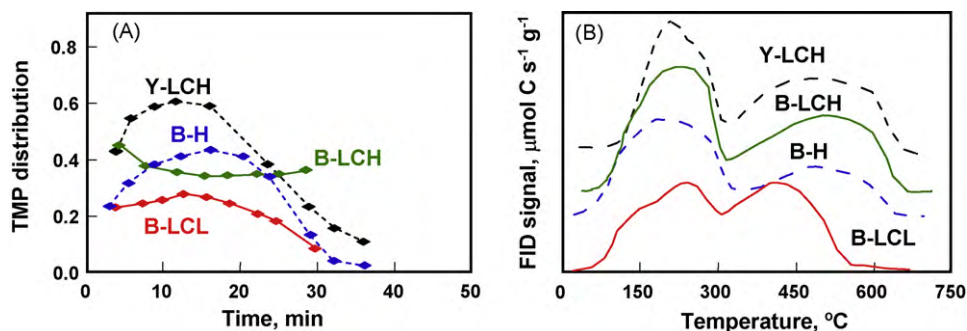


Fig. 3. (A) Content of TMPs in C5+ fraction for different catalysts. Reaction at 80 °C. (B) TPO profiles of catalysts shown in (A).

in Fig. 2. Only a minor decrease in the intensity of the diffraction peak at 8° is observed. After platinum addition, the support also maintains its structure and crystallinity.

The Si/Al ratio obtained by EDX with the B-LCH and with the B-LCL catalyst was practically the same as that corresponding to the B-H zeolite, i.e. 15. On the other hand, the La/Al ratio obtained with this technique was practically 0 for the B-LCH catalyst, and 0.35 for the B-LCL catalyst. It is very interesting to observe that in the case of the B-LCH catalyst, within the precision of the EDX technique, most of the lanthanum was removed from the catalyst after the two ion exchange steps, first with lanthanum nitrate, and second with ammonium nitrate. According to this result, during the second ion exchange most of the lanthanum that was introduced in the catalyst during the first ion exchange with lanthanum nitrate was removed. In the case of the B-LCL catalyst, the La/Al ratio corresponds to a complete exchange of the protons, since in this case the stoichiometric value is La/Al = 0.33. This value indicates that a very high percentage of protons have been exchanged by lanthanum.

3.2. Catalytic activity

3.2.1. Influence of catalyst composition

Fig. 3 shows activity results and TPO profiles of different catalysts. Fig. 3A shows the distribution of trimethylpentane (TMP) in the C5+ fraction (including iso-pentane). It can be observed that Y-LCH zeolite presents the best yield in TMP. The beta zeolite in protonic and LCH forms presents a similar behavior, while when it is completely exchanged with La, (B-LCL), it has a lower activity. In all cases, except with the B-LCH catalyst, a pronounced drop in the activity is observed, within 20–30 min times on stream. As mentioned above, the B-LCH catalyst has a negligible amount of lanthanum, and consequently its composition is quite similar to that of the B-H catalyst. Nevertheless, the very small amount of lanthanum that might have been left on this catalyst is enough to lead to a slightly different catalytic behavior, as can be seen in Fig. 3A. Similar concentration of TMP is obtained with B-LCH as compared to the B-H, even though a better stability is displayed. When the TMP concentration goes down, an increase in the dimethylhexenes concentration is produced (not shown). These compounds are formed by dimerization of the butenes and indicate that the catalyst is deactivated for the hydrogen transfer reaction, and therefore mainly dimerization products are obtained. The hydrogen transfer capacity is essential in the alkylation reaction. Therefore, regarding catalytic activity the Y zeolite is better than the beta zeolite, at least in the conditions used in these tests. Another important conclusion from these results is that in the case of the beta zeolite, the exchange of protons by lanthanum does not lead to a better catalytic activity, as found in the case of Y zeolite [18,23], X zeolite [21–23] and even with mordenite zeolites [18].

In a previous work [18] we reported a correlation between the activity for TMP production and the quantity of coke left on

Table 1

Coke content on the catalysts after the alkylation reaction at 80 °C.

Sample	Coke content (wt%)
B-H	11.9
B-LCL	7.4
B-LCH	10.9
Y-LCH	15.2

the catalyst during the reaction. The more active catalysts contain a higher amount of hydrocarbon deposits. This relationship was observed even for a given catalyst when comparing the catalytic performance under different reaction conditions (e.g. changing the temperature). Table 1 shows the amount of hydrocarbon residues left on the catalysts during the reaction. Comparing with the activity results shown in Fig. 3A, it can be seen that the better the TMP yield, the higher the amount of coke. The Y-LCH zeolite, which produced the highest quantity of TMP, is the catalyst in which the major quantity of coke was deposited (15.2 wt%). Furthermore, beta zeolite fully exchanged with lanthanum (B-LCL), which produces the lower amount of TMPs, presents the lowest amount of coke (7.4 wt%). Therefore, it seems that in all the catalysts active for isobutane alkylation with butenes, the sites involved in this reaction are also involved in the successive alkylation reactions leading to compounds such as C12, C16, etc. These compounds of large size cannot diffuse outside the pores and remain on the catalyst as carbonaceous deposits. For this reason, the catalysts that produce more TMPs, produced a higher amount of coke. If the catalyst deactivates too fast due to pore mouth blocking, as in the case of a mordenite catalyst, the internal surface of the catalyst is not fully used and consequently a lower amount of coke is deposited [18]. The TPO profiles also give information regarding the acidity of the samples. It can be noticed that the profiles that correspond to the B-H and B-LCH catalysts finish at 650 °C approximately, while in the case of the profile that corresponds to B-LCL finishes at 550 °C. It has been demonstrated that the second peak in the TPO profile results from the reorganization of the hydrocarbon deposits left on the catalyst during the reaction. This reorganization changes the aliphatic structure to an aromatic structure, and occurs on the acid sites during the heating carried out in order to burn or strip off these deposits. The stronger the acid sites, the deeper the aromatization of the carbonaceous residues, and therefore, higher temperature is needed to fully removed them from the catalysts. The TPO profiles shown in Fig. 3, suggest that the acidity of the B-LCL catalyst is weaker than in the case of the B-H and B-LCH catalysts.

3.2.2. Influence of reaction temperature

Fig. 4 shows the activity results of the B-LCH catalyst at 50, 80, and 90 °C, and the corresponding TPO profiles obtained with the deactivated catalysts after these reactions. It can be seen that when the reaction is carried out at 80 and 90 °C there are no differences

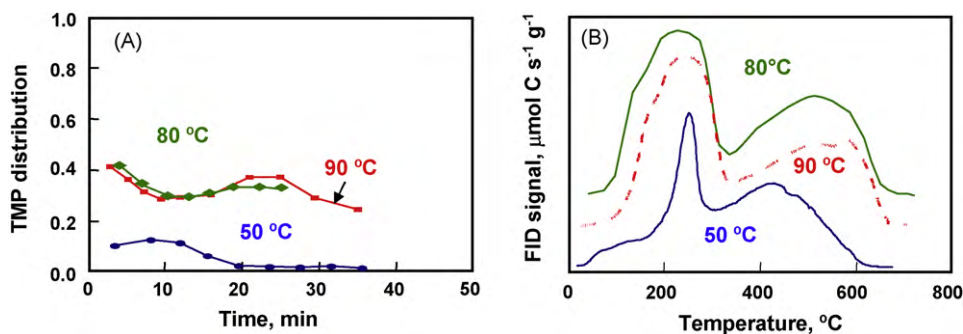


Fig. 4. (A) TMP fraction in C5+ for B-LCH catalyst at different temperatures; (B) TPO profiles of the catalyst after reaction.

Table 2

Coke content as a function of the temperature on B-LCH catalysts.

Temperature	Coke content (wt%)
50 °C	5.9
80 °C	10.9
90 °C	10.5

in the TMP production. However, a decrease in reaction temperature to 50 °C leads to a dramatic loss in the capacity of production of TMPs. Table 2 shows the amounts of coke found on these catalysts as determined by TPO analyses (Fig. 4 B). The amounts of coke deposited on the catalyst at 80 or 90 °C are very similar. In agreement with this, the activity at both temperatures is practically the same. In the reaction carried out at low temperature in which a low TMP production was observed, the amount of coke left on the catalysts is almost half the amount left at 80 or 90 °C. This is due to a very rapid deactivation at low temperature, because the process of adsorption-polymerization of olefins is faster than the desorption-cracking of the oligomers formed, as previously suggested when analyzing the behavior of other zeolites [18]. The reaction temperature strongly affects all the steps of the alkylation reaction. The diffusion of reactants into the pores and of products out of the pores is favored by high temperatures. The activation energy for cracking is higher than for hydride transfer. Consequently, an increase in the reaction temperature would lead to an increase in the amount of light products [32,33]. Another disadvantage when increasing the reaction temperature is that the TMP/DMH ratio decreases. If the temperature is too low, adsorption and oligomerization will prevail, and due to the low diffusivity at this temperature, a fast deactivation will occur. This can be observed in the experiment carried out at 50 °C. The catalyst lost the activity in half the time needed to fully deactivate the catalyst at 80 °C. Nivarthi et al. [33] found an optimum for zeolite H-BEA at 348 K, obtaining the highest octane selectivity and the highest TMP/DMH ratio. At lower temperatures, oligomerization dominated, and at higher temperatures cracking reactions dominated.

3.3. Acidity measurements

Fig. 5 shows the 1-butene TPD results. Each catalyst has a well defined profile. The Y-LCH zeolite displays a small peak at low temperature (90 °C), and a main peak at 200 °C. The amount of butene that corresponds to this profile is 2.29 mmol/g. At approximately 320 °C all the butene has been stripped off the catalyst. Samples B-H and B-LCH display a more complex profile, being very similar between them. A main desorption peak at 175 °C is present in both profiles, and a high temperature peak with a maximum at 290 °C is well resolved in the case of the B-LCH and is evident in the case of the B-H catalyst. The amounts of butene desorbed from these two catalysts are 1.5 and 1.78 mmol/g for B-LCH and B-H respec-

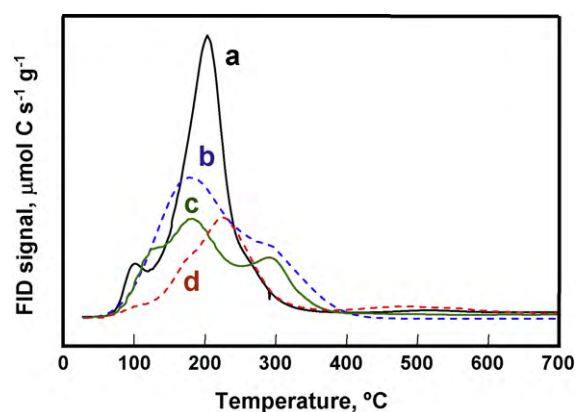


Fig. 5. 1-butene TPD. (a) Y-LCH, (b) B-H, (c) B-LCH and (d) B-LCL.

tively. The less active catalyst B-LCL shows the lowest adsorption capacity (1.19 mmol/g), with a main desorption peak at 220 °C and a shoulder at 175 °C. It is important to observe that B-H and B-LCH need more than 400 °C to remove the preadsorbed butene. Table 3 summarizes the amounts of pyridine and butene adsorbed on these catalysts.

The beta zeolite with a Si/Al equal to 15 has a theoretical concentration of Al sites of 1.05 mmol/g. Therefore, in all the catalysts used in this study, the amount of butene detected during desorption, corresponds to more than one butene molecule per acid site. This indicates that during the adsorption experiments, the butene oligomerizes leading to the deposition of butene in positions adjacent to the acid sites.

Fig. 6 shows the pyridine TPD profiles. The Y-LCH and B-H catalysts present a similar content of adsorbed pyridine, equivalent to 1.40 and 1.10 mmol/g respectively. However, in the case of the Y-LCH catalyst the desorption peak is centered at 440 °C, while the B-H and B-LCH catalysts display a peak at high temperature, approximately at 610 °C. This higher amount of strong acid sites found in the beta zeolite has a major impact in the catalytic activity. As shown above, these catalysts are fully deactivated at a lower amount of coke. Both 1-butene and pyridine TPD experiments indicate that the strength of the interaction between the butene and the zeolite is too high in the case of B-H and B-LCH. Even though the difference with Y-LCH is not very large, it is enough to lead to a catalyst with lower capacity to produce TMPs and to maintain the

Table 3

Acidity measurements by butene and pyridine TPD.

Sample	mmol pyridine/g	mmol butene/g
B-H	1.10	1.78
B-LCL	0.51	1.19
B-LCH	1.00	1.50
Y-LCH	1.40	2.29

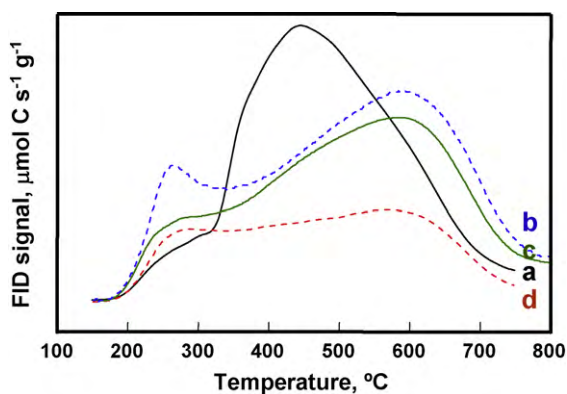


Fig. 6. Pyridine TPD: (a) Y-LCH, (b) B-H, (c) B-LCH and (d) B-LCL.

activity as a function of time on stream. The total amount of pyridine adsorbed corresponds to 1.00 mmol/g in the case of the B-LCH, and 0.51 mmol/g in the case of B-LCL. The B-H and B-LCH catalysts display similar capacity of pyridine adsorption, which is close to the theoretical value. The B-LCL has a much lower concentration of acid sites as compared to the B-H and B-LCH catalysts.

3.4. 1-Butene pulses

The interaction between the reactants and the catalyst was analyzed using a dynamic adsorption technique. Pulses of 1-butene were consecutively sent to the catalyst sample at different temperatures, both while going from low temperature (e.g. 60 °C) up to high temperature (100 °C), and then when the temperature was decreased, in steps of 10 °C. Fig. 7 shows results obtained with the Y-H and Y-LCH catalysts. The Y-H catalyst is very unstable during the reaction being fully deactivated in 10 min [18], as compared to the 30 min time on stream that the Y-LCH displays before being deactivated. The experiments shown in Fig. 7A indicate that the Y-H catalyst significantly changes its adsorption capacity, comparing

the pulses sent when increasing the temperature (curve labelled *inc.*, fresh catalyst) with those obtained when decreasing the temperature (curve labelled *dec.*), i.e. after butene adsorption at several temperatures. It means that the butene was irreversible adsorbed on this catalyst, thus changing the availability of acid sites. The small amplitude of the curve obtained with the deactivated catalyst (Fig. 7A, labelled *dec.*) and the fast stabilization means that the interaction with 1-butene is reversible and that there is no pore mouth plugging. If pore mouth plugging occurs, the amplitude must be the same as in the blank experiment, since neither diffusion in and out of the pores, nor adsorption-desorption can take place and, therefore, the signal should not be modulated. At 80 °C with Y-H, pulses sent when increasing the temperature and when decreasing the temperature are equal (Fig. 7B). This indicates that the adsorption sites are fully covered with 1-butene during the first and second set of pulses (at 60 and 70 °C respectively). Otherwise, these two series of pulses (curves in Fig. 7B) should be different. The amount of coke at the end of this series of pulses is only 0.8 wt%. Therefore, no pore mouth plugging occurs, and on the other hand, this small amount of coke is enough to decrease the adsorption capacity of the Y-H zeolite to a large extent.

The Y-LCH catalyst, which is much more stable during the alkylation reaction, displays a different behavior as compared to that of the Y-H zeolite (Fig. 7C and D). At 60 °C, the first series of pulses and the last one (after all the pulses at increasing and decreasing temperatures have been sent) are almost equal, with small amplitude. This indicates that the catalyst suffers small changes in its adsorption capacity, and that there is no pore mouth plugging. At 80 °C the adsorption-oligomerization processes occur faster than at 60 °C. Fig. 7D shows the results obtained at 80 °C with the Y-LCH catalyst. A higher signal with the deactivated catalyst is observed (curve *dec.*), as compared to the signal obtained when increasing the temperature (curve *inc.*). This indicates that a fraction of the butene fed during the consecutive pulses sent along this experiment, is deposited on the catalyst leading to an adsorption capacity loss. However, the difference between these two signals is not very large. The amount of coke deposits left on the Y-LCH catalyst after the 10

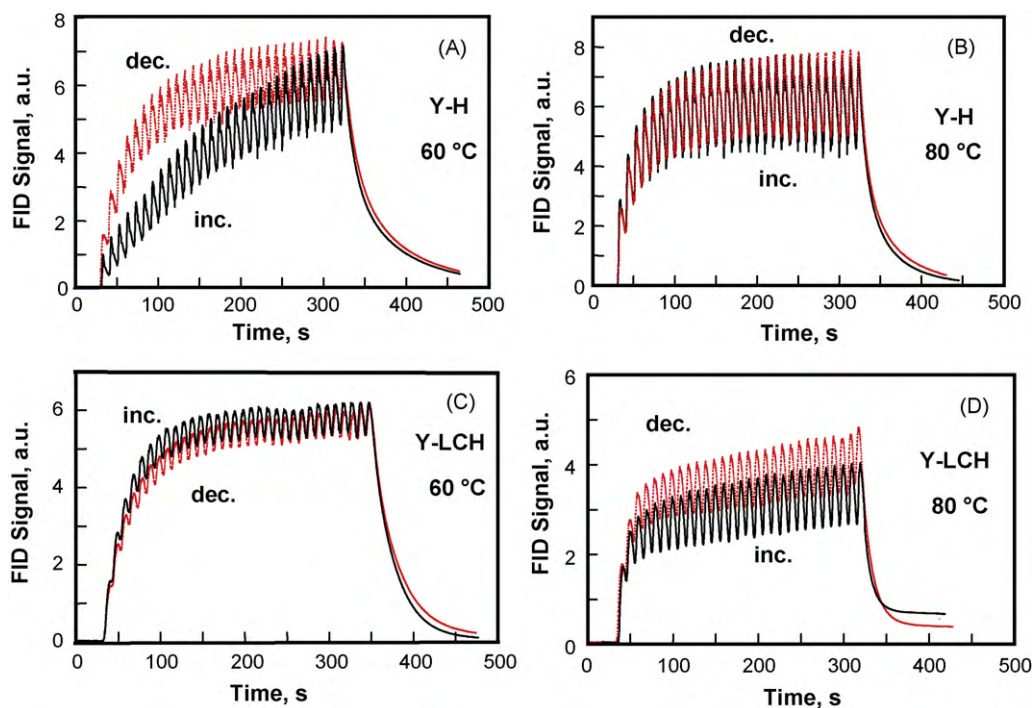


Fig. 7. Pulses of 1-butene. (A) Y-H, at 60 °C, (B) Y-H, at 80 °C; (C) Y-LCH at 60 °C; and (D) Y-LCH at 80 °C. Labels: *inc.*: pulses sent at the indicated temperature when increasing the temperature, *dec.*: pulses sent when decreasing the temperature.

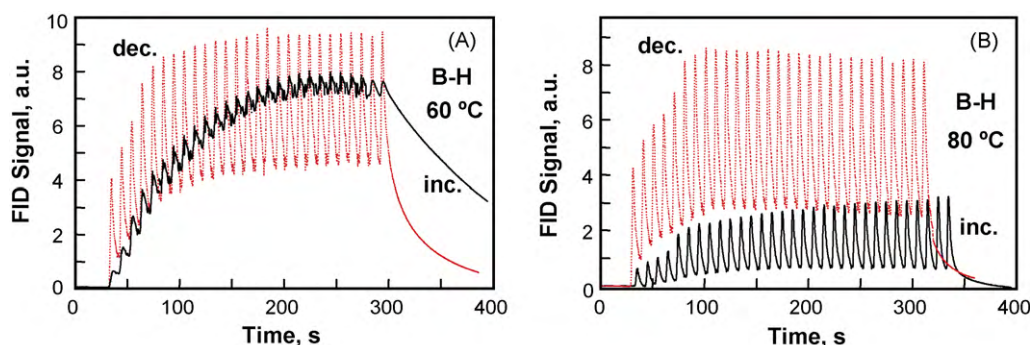


Fig. 8. Pulses of 1-butene. (A) B-H, at 60 °C and (B) B-H, at 80 °C. Labels: *inc.*: pulses sent at the indicated temperature when increasing the temperature, *dec.*: pulses sent when decreasing the temperature.

series of pulses is 5.37 wt%, considerably higher than in the case of the Y-H. Nevertheless, the effect of these carbonaceous deposits is much less toxic in the case of the Y-LCH catalyst than in the case of the Y-H catalyst.

Very different results are obtained with the beta zeolite, both in the protonic form (B-H) and with the zeolite exchanged with lanthanum (B-LCH). The pulses sent when increasing the temperature as compared to the pulses sent when decreasing the temperature are quite different, either in the amplitude of the oscillation (Fig. 8A), in the number of pulses required to reach a pseudo-steady state (Fig. 8A), or in the average value of 1-butene not adsorbed on the catalyst (Fig. 8B). A very important conclusion that can be obtained from these experiments is that the beta zeolite is much more sensitive to the presence of 1-butene than the Y zeolite. Because of this, the TMP production is higher in the latter. The large increase in amplitude observed in the case of the pulses sent when increasing the temperature, as compared to that when decreasing the temperature (Fig. 8A and B) indicate that there is a major change in the interaction between the catalyst and the 1-butene, and could be an indication that pore blocking occurs. Therefore, this deactivation mechanism is much faster in the B-H zeolite than in the case of the Y zeolite. In the case of the B-LCH catalyst, the increase in amplitude observed in the pulses sent while decreasing the temperature, is not as high as in the case of the B-H catalyst (not shown). This indicates, in agreement with acidity measurements, that even though the amount of lanthanum detected by EDX is quite small, it is enough to modify the acidity, and consequently the interaction with 1-butene.

A deactivated B-H catalyst was studied using this technique. The deactivated catalyst, and the catalyst after being treated in air at 100 °C, 200 °C, 300 °C, and 400 °C were analyzed by sending series of 1-butene pulses at 80 °C after each regeneration step. Results are shown in Fig. 9. The deactivated catalyst (curve a) displays a signal that is very similar to the blank, which indicates that there are no adsorption processes taking place, nor diffusion of the 1-butene in and out of the pore system of the zeolite. After a treatment at 100 °C (curve b), a small change is observed, indicating that a very small amount of coke is eliminated and no pore opening occurs. However, after regenerations at 200, 300 and 400 °C, there is a significant change in the amount of 1-butene that comes out of the cell. Firstly, the amplitude of the signal decreases and stabilizes in few pulses in a constant average value, lower than the amount of 1-butene injected to the sample. This indicates that there is a net adsorption of the olefin and therefore it means that the regeneration treatment recovers a fraction of the adsorption sites. The higher the temperature of the regeneration treatment, the higher the surface that is recovered and is active for 1-butene adsorption, as indicated by a decrease in the average value of the amount of 1-butene that is not adsorbed. In addition, the amplitude of the signal after regeneration at 200, 300 and 400 °C has little change as

the regeneration temperature increases, and is significantly smaller than the amplitude observed with the deactivated catalyst. This indicates that after the treatment at 200 °C the pores are unblocked, and the 1-butene can diffuse in and out of the pore system of the B-H zeolite. These results agree with those shown in Fig. 8B, in which a wide oscillation is found at the end of the experiment (curve *dec.*), with a mean value equal to the amount of 1-butene injected to the cell. The fresh catalyst has a much smaller amplitude and average value (curve *inc.*). Note that curves a and d in Fig. 9 are very similar to the curves shown in Fig. 8B, which indicates that the experimental design described in section 2.5 is very useful to quickly predict the activity and stability of the catalysts used in the alkylation reaction, and also to determine if pore mouth plugging occurred during the reaction.

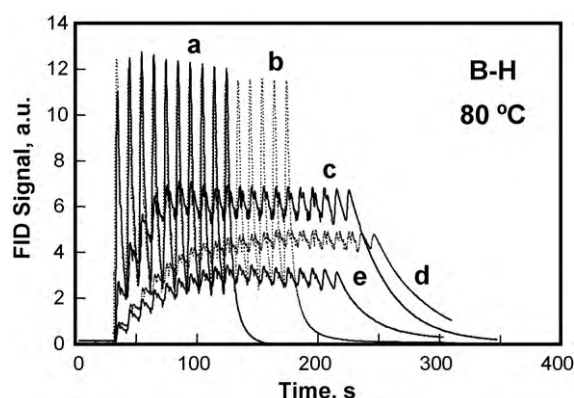


Fig. 9. Pulses of 1-butene at 80 °C. (a) Deactivated B-H catalyst; deactivated catalyst treated in air at: (b) 100 °C; (c) 200 °C; (d) 300 °C and (e) 400 °C.

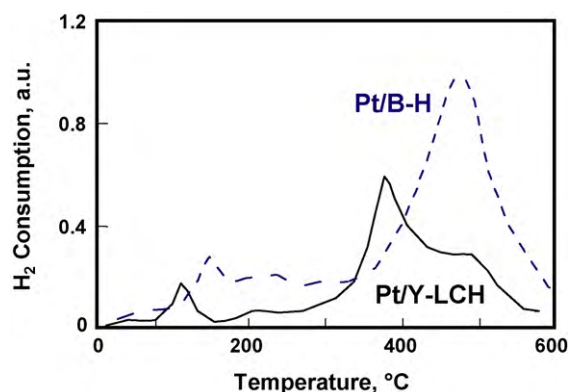


Fig. 10. TPR profiles of Pt-B-H and Pt-Y-LCH catalysts.

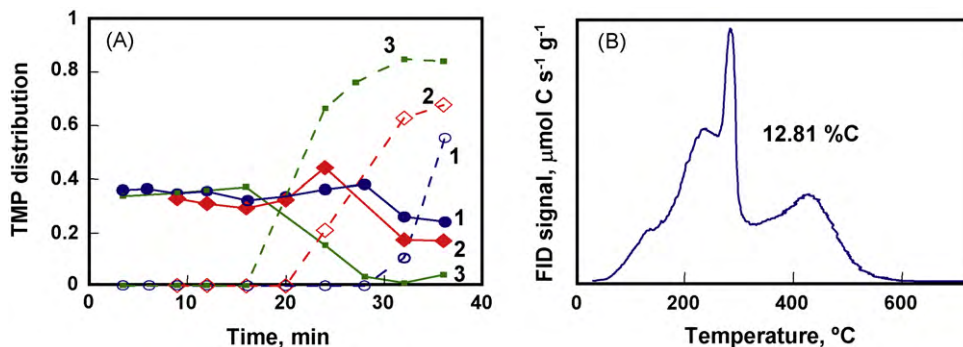


Fig. 11. (A) TMP and DMH = production in three successive cycles of reaction-regeneration. Regeneration in hydrogen at 80 °C, 12 h in the first regeneration, 8 h in the second one; (B) TPO at the end of the three cycles of reaction.

3.5. Regeneration of Pt-B-H

Fig. 10 shows the TPR profiles of the beta zeolite containing 0.5 wt% of Pt. For comparison, the profile of the Y zeolite partially exchanged with lanthanum (Y-LCH) and containing 0.5 wt% Pt, is included. In both cases, a small peak at low temperature that corresponds to the reduction of platinum oxide and a high temperature peak are observed. The dispersion of the Pt-B-H catalyst is 41%, as determined by CO pulse chemisorption.

The reduction of Pt supported on beta zeolite takes place at higher temperature as compared to the case in which it is supported on the Y-LCH catalyst. It is interesting to note that Pt reduces mainly at high temperature with a single peak at approximately 470 °C when deposited on beta zeolite. In the case of Pt supported on Y-LCH zeolite, the high temperature reduction occurs in two zones. The first one corresponds to the peak at 370 °C, while the higher temperature peak comes out at the same temperature as in the case of the beta zeolite, i.e. 470 °C approximately. These profiles indicate that in order to fully reduce the platinum, the catalysts must be treated at high temperature, e.g. 500 °C.

The Pt/B-H was used in consecutive reaction-regeneration cycles. Both the reaction and the regeneration were carried out at 80 °C. The regeneration was carried out in pure hydrogen at 8 kg/cm² pressure. The first one was performed over 12 h and the second one during 8 h. Before treatment with hydrogen, the reactor was opened, and a sample of catalyst was taken to analyze the content of coke. Fig. 11 shows the results of activity of the three cycles, and a TPO analysis after three cycles of reaction-regeneration. Fig. 11A shows the distribution of TMP and dimethylhexenes (DMH) (dotted line). In the first cycle (curve labelled '1') it is observed that the behavior is almost equal to that of the zeolite without Pt, with a content of TMP in the C5+ fraction of approximately 40%, and maintaining stability during 30 min. After this time on stream, a fast increase in the amount of dimethylhexenes occurs. It can be observed that in the three reaction cycles the same TMP concentration in the C5+ fraction is obtained. These results indicate that the activity is fully recovered, although the catalyst life is shortened, as indicated by the time at which the concentration of dimethylhexenes starts increasing. This behavior is repeated in the third reaction cycle.

This means that regeneration in hydrogen at 80 °C removes coke from a relatively large fraction of active sites, which maintain the same activity as the fresh catalyst. However, not all the sites are regenerated, as indicated by the decrease in the catalyst life. The TPO profile of the sample taken from the reactor at the end of the experiment is shown in Fig. 11B. It shows as the main difference with respect to the catalyst without metal, the sharp peak that appears at 250 °C, which corresponds to the burning of coke catalyzed by the Pt.

4. Conclusions

The beta zeolite showed good activity for the production of trimethylpentane, both in the protonic form or partially exchanged with lanthanum. However, the activity was slightly lower than that of the Y zeolite. The correlation between activity and coke content found in several catalysts previously reported is also found when comparing the beta zeolite in its different forms. The higher the activity for trimethylpentane production, the higher the amount of coke deposited on the catalyst. This suggests that the catalysts that are active for the isobutane alkylation reaction will unavoidably form coke and consequently this will deactivate the acid sites.

The B-H and B-LCH catalysts have stronger acid sites than the Y-LCH catalyst as determined by pyridine TPD. This leads to a faster deactivation of these catalysts, and in the case of the B-H, a faster pore mouth plugging. This was determined by dynamic adsorption analyses, using high frequency 1-butene pulses. According to these results, pore mouth opening takes place when heating the coked catalyst up to 200 °C.

The incorporation of platinum in the zeolite beta does not produce changes in the activity or stability of the catalyst, but makes it possible to regenerate the catalyst with hydrogen at low temperature (80 °C). Although this procedure requires a relatively long time, this could be reduced by optimizing the following variables: content and dispersion of the metal, hydrogen pressure, regeneration temperature, and mainly the level of deactivation at which the catalyst is regenerated. This low temperature regeneration does not require removing all the coke, as with the regeneration in air at high temperature which produces a selective deactivation for the reaction of TMP production. Therefore, processes based on low temperature regenerations appear as an option for implementing the alkylation of isobutane using solid catalysts.

The dynamic adsorption of 1-butene is very useful to assess the behavior of a solid catalyst in the alkylation reaction. In a simple experiment, it is possible to determine whether the acidity is at the right level in order to reversibly interact with 1-butene, without accumulation of a large fraction of coke deposits leading to a selective deactivation and adsorption capacity loss. This technique is also very useful to analyze the deactivated catalyst, and to determine if the deactivation was due to pore mouth plugging. The catalyst regeneration can be followed by sending pulses to the catalyst in different stages of the regeneration process, thus determining the conditions needed to open the pore mouths, and to recover the acid sites.

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