

Isobutane/butene alkylation: regeneration of solid acid catalysts

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Abstract

The regeneration of Y-zeolite catalysts used during the isobutane alkylation reaction is studied. Coke is characterized by temperature-programmed techniques and measuring the H/C ratio. The coke deposited under supercritical conditions is very similar (TPO profile and amount) to the coke deposited in liquid phase. The regeneration was carried out in many ways. Air was used for heating with at a low rate, and holding the temperature at low values for long times. Platinum was incorporated in the zeolite to catalyze the coke combustion or to provide an additional route for coke gasification, such as hydrogenation. Ozone was used to remove most of the coke, followed by a second step with H₂ or He. Hydrogen peroxide was studied as an alternative low-temperature oxidation compound. It was found that the ozone treatment, followed by a hydrogen treatment, is an effective way to regenerate this microporous catalyst. The ozone not only eliminates a large fraction of the coke but also changes the characteristics of the small amount of coke left on the catalyst, making it easier to be burnt. The treatment with hydrogen peroxide at 90°C also removes a large fraction of coke, but without changing significantly the characteristics of the coke left after the treatment. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The alkylation of isobutane with C₄ olefins provides a high-quality gasoline, the alkylate, which is a component of the gasoline pool. This product has a high octane number, a low Reid vapor pressure, and a high H/C ratio. Industrially, this process is carried out in liquid phase using HF or SO₄H₂ acid as catalysts. The problems associated with the handling and disposal of these acids, and the environmental and potential hazards specially in the case of HF, have raised the interest in the development of an alternative process using solid acid catalysts.

Many different types of solids have been studied for the isobutane alkylation since the pioneer work

of Weitkamp [1]. Zeolites [2,3], heteropolyacids [4,5], sulfated zirconia [6,7] among other materials have been studied. Industrial laboratories have carried out important efforts in the search for new processes [8–11]. In spite of all these researches, the fast deactivation of the solid acid catalysts has not yet been solved. Activity and selectivity towards the trimethylpentanes (TMPs) are adequate in many of the solids investigated, but the stability is generally very poor.

Only few studies deal with either coke characterization [12,13] or the regeneration of solid acid catalysts in this reaction [14]. In a recent report, Weitkamp and Traa [15] emphasize that it is necessary to ‘investigate in detail the available, and perhaps, novel techniques for removing carbonaceous deposits’.

We have previously reported about the coke characterization and regeneration of zeolite catalyst [16,17].

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It has been found that those catalysts that show better stability are the catalysts that form more coke. This was associated with the deactivation mechanism that takes place on microporous materials such as mordenite and Y-zeolite, where both site coverage and pore plugging occur. The more effective use of the internal surface is: the better the stability, the higher is the amount of coke deposited.

The reason why it is necessary to increase the temperature up to very high values, e.g. 600°C [14], to regenerate the catalyst with air is that coke changes its structure from aliphatic to aromatic while temperature is increased during the regeneration. This severely complicates the regeneration, making it necessary to explore other possibilities in order to regenerate the catalyst. The regeneration with ozone has been shown to be effective for coke removal, but it requires long times of treatment [17].

In this work, we present additional data about coke characterization and study several different options for catalyst regeneration. The regeneration in air is compared with other procedures, such as combined treatments with ozone followed by helium or hydrogen, the incorporation of Pt to the catalyst in order to catalyze the coke combustion and hydrogenation, and the use of hydrogen peroxide for low-temperature regeneration. The coke formed during the isobutane alkylation under supercritical conditions is also analyzed by temperature-programmed oxidation (TPO).

2. Experimental

2.1. Catalysts

Y-zeolite (UOP, Y-54) with a Si/Al ratio of 5.3 was used. The sodium form of the zeolite was exchanged with $(\text{NO}_3)_3\text{La}$ 0.58 M, in reflux, for 4 h, drying at 100°C, calcining at 550°C, and then a second ionic exchange with NO_3NH_4 , for 4 h at reflux, drying and then calcining at 550°C. The exchange level was 68% in the first exchange, and 21% in the second. Lanthanum was not detected in the final solution after the second exchange. The crystallinity degree of these samples was checked by XRD to be 97%. This catalyst is labeled LCH-Y. This catalyst has a good activity and selectivity towards TMPs production [15]. Similarly, a catalyst was prepared carrying out

the first exchange with NO_3NH_4 and the second exchange with $(\text{NO}_3)_3\text{La}$ (HCL-Y), and another catalyst using $(\text{NO}_3)_3\text{La}$ in both steps (LCL-Y).

Platinum was deposited in LCH-Y catalyst by wet impregnation with $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$, and then calcined at 500°C. The catalyst contains 0.5% Pt (Pt/LCH-Y).

2.2. Activity test

The alkylation reaction of isobutane with a mixture of C4 linear olefins was carried out in liquid phase at temperatures between 25 and 80°C, and at 30 kg/cm², in a fixed-bed reactor. The space velocity was $\text{WHSV} = 1 \text{ h}^{-1}$ referred to the olefins. The molar ratio of isobutane/olefins in the feed was 15. Y-zeolite catalysts, used in isobutane alkylation under supercritical conditions using carbon dioxide as diluent [18], were also analyzed. Experimental details can be found elsewhere [18].

2.3. Coke characterization

Coke was characterized by TPO. These experiments were carried out using a modified unit. The CO_2 produced during the coke burning is converted to CH_4 in a methanator reactor. A H_2 stream is fed to this reactor, which is loaded with a Ni catalyst, in order to quantitatively convert CO_2 into CH_4 . This compound is then continuously monitored by a flame ionization detector (FID). With this configuration, the sensitivity and resolution of the classical TPO technique is greatly improved. Typically, 10 mg of coked catalyst is loaded into a quartz cell, heating at 12°C/min, using 5% O_2/N_2 as carrier gas. Additional details of the technique can be found elsewhere [19]. The H/C ratio has been measured for a selected sample, by analyzing the CO_2 production and O_2 consumption as the temperature is linearly increased, as described elsewhere [20].

2.4. Regeneration

Regeneration experiments were carried out according to the following procedures:

- *In air.* Heating at different rates, up to different final values.
- *In ozone.* The ozone was generated by flowing air between two electrodes at high electrical potential.

The stream coming out of this equipment contains 1% O₃ approximately.

- *In hydrogen.* Regeneration in H₂ was carried out with the Pt/LCH-Y catalyst.
- *Combined treatments.* Using ozone in a first step, and then a second step with either H₂ or He.
- *With hydrogen peroxide.* Coke was extracted in a soxhlet apparatus using methylene chloride and a mixture of benzene plus methanol [16]. Also, deactivated catalysts were treated in hydrogen peroxide at different temperatures and for different times.

3. Results and discussion

3.1. Coke characterization

The H/C ratio has been measured in an LCH-Y catalyst, coked at 50°C. Results are shown in Fig. 1 together with the TPO profile. The amount of coke on this catalyst is 14%. While the TPO profile shows the release of hydrocarbonaceous deposits starting below 100°C, the CO₂ and O₂ concentrations start changing at 300 and 250°C, respectively. This is in agreement with previously reported results [16], where we have shown that the first peak in the TPO is due to the desorption of hydrocarbons from the coked catalyst. This peak can be completely removed by heating under an inert gas. Therefore, the gasification of these hydrocarbons does not consume O₂ and consequently does

not produce CO₂. Fig. 1B shows that O₂ is consumed between 200 and 350°C with no CO₂ production, which clearly indicates that initially it reacts with the hydrogen of the hydrocarbons with high H/C ratio present in the coke. It has been previously proposed that the second peak in the TPO of isobutane alkylation catalysts comes from the reorganization of the hydrocarbons left on the catalyst during the reaction, changing from an aliphatic to an aromatic structure due to the increment in temperature and the acidity of the catalyst that catalyzes this reorganization [16]. This change is also related to a change in the H/C ratio. The global H/C ratio is 0.97, but at high temperatures the O₂ consumption is almost the same as the CO₂ production indicating that at this temperature the H/C ratio is very low. Fig. 1 also shows that the difference between O₂ consumption and CO₂ production gradually decreases as temperature is increased, what indicates that the H/C ratio of coke left after thermal treatment in an oxygen-containing carrier gas decreased as a function of temperature. Fig. 1B shows that the O₂ consumption is higher than the CO₂ production until the temperature is 550°C approximately, where they become very similar. This indicates that the coke left on the catalyst after an oxidation up to 550–600°C is highly dehydrogenated. For this reason, the regeneration of this acid catalyst is severely complicated, very high temperatures being necessary for long times in order to fully remove the coke [14,16].

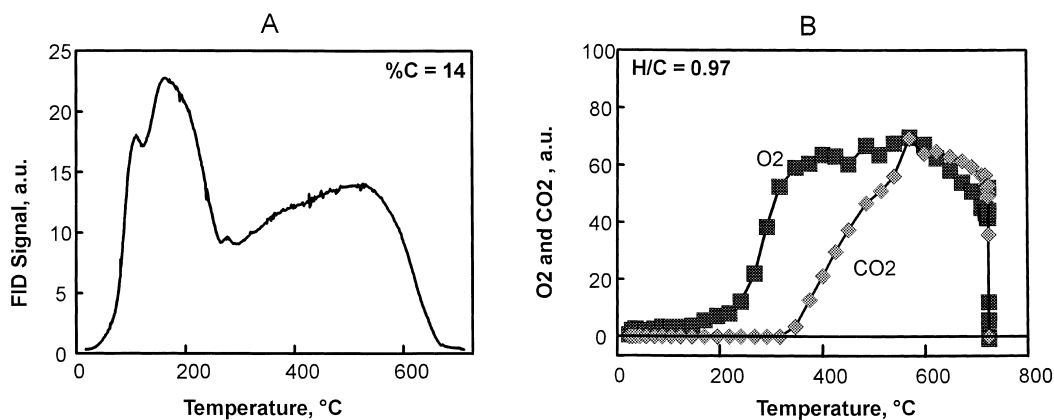


Fig. 1. (A) TPO profiles of LCH-Y coked catalyst; (B) O₂ consumption and CO₂ production as a function of the temperature during coke burning. LCH-Y coked catalyst.

3.2. Coke deposition under supercritical conditions

In order to decrease the amount of coke deposited during the reaction, the alkylation of isobutane under supercritical conditions was studied by Clark and Subramaniam [18], since the solubility of coke precursors should increase under these conditions. The TPO profiles of samples coked at 50°C both in liquid phase and under supercritical conditions (2250 psig with CO₂ as diluent) are presented in Fig. 2. The activity data for these experiments were previously reported [18]. It has been found that the catalyst retains selectivity towards TMPs, but with a very low conversion. The TPO profiles shown in Fig. 2 indicate that the coke deposited under supercritical conditions is very similar to the coke deposited in liquid phase, both in amount and nature, as measured by TPO. Only a minor difference in the profile is observed: the better resolution of the first peak in the case of the coke deposited under supercritical conditions, what could be related to a smaller amount of coke in the outer surface of the zeolite. According to our previous results, it seems likely that the extraction that could take place during the reaction under supercritical conditions is being effective only in the outer surface of the catalyst. The coke molecules formed inside the pores cannot come out through the small pore mouth. Then, only a small fraction of the surface is taking part in the reaction under this conditions, and the activity is

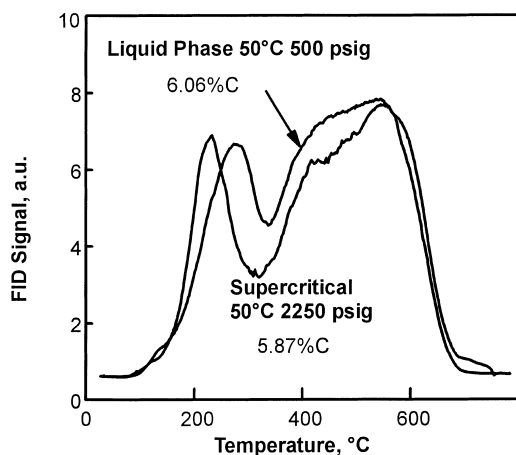


Fig. 2. TPO profiles of H-Y zeolite coked in liquid phase at 50°C, 500 psig, and under supercritical conditions, 50°C, 2250 psig, using CO₂ as diluent.

therefore very low. It could be interesting to test these reaction conditions with a mesoporous material.

3.3. Regeneration with air

In our previous work [16], we have used many different regeneration procedures with air, changing the heating rate, the final temperature and the time at this final temperature. Final temperatures in the range 285–500°C, only led to partial coke removal, and therefore to an incomplete activity recovery. As previously mentioned, the reason why it is not possible to fully remove the coke, which initially has a high H/C ratio, is the reorganization of its structure. Fig. 3 shows an additional evidence. An LCL-Y zeolite, coked at 80°C, was regenerated in air heating both at 12 and 3.7°C/min. The changes in the relative rates of coke gasification and aromatization are reflected in changes in the relative sizes of the first and second peak of the TPO profile. The first peak corresponds to hydrocarbons that desorbed upon heating, and the second peak to the coke that changes its initial aliphatic structure to an aromatic one. This result demonstrates how sensitive the coke structure is to the thermal treatment.

Fig. 4 shows the results of an experiment carried out using even a lower heating rate, and a low final temperature in order to determine if at such a low temperature as 180°C, it is possible to gasify the coke without changing the structure. The TPO profile of the

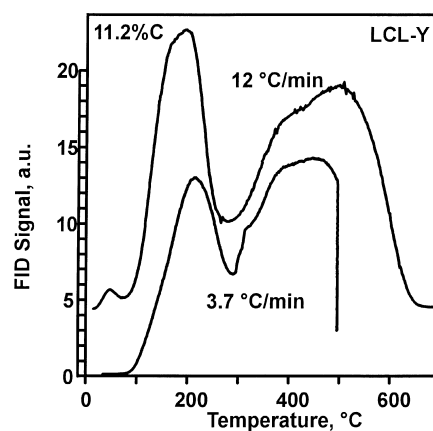


Fig. 3. TPO profiles of an LCL-Y zeolite after reaction at 80°C. Heating rates: 12 and 3.7°C/min.

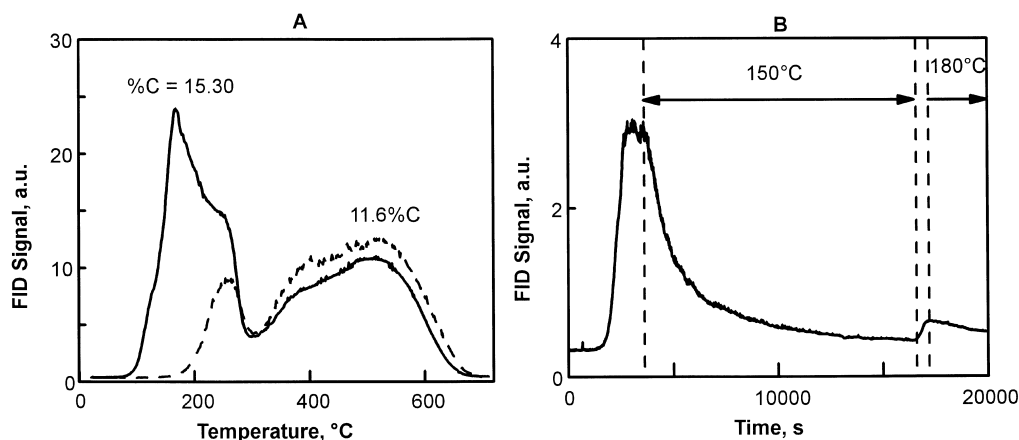


Fig. 4. TPO profiles for partial coke burning experiments at low heating rate, and low final temperature. LCH-Y catalyst coked at 150°C in gas phase. (A) TPO before (full line) and after (dashed line) coke burning; (B) FID signal during coke burning, temperature program: from 20 to 150°C, at 3°C/min, holding the final temperature for 3 h, and then heating up to 180°C at 3°C/min. Final time: 45 min.

coke left on the catalyst after this treatment indicates that it has changed the structure, with an increase in the amount of coke with an aromatic structure (the second peak has increased its size as compared to the standard analysis). This agrees with results obtained by Flego et al. [12], who studied the modifications of coke structure as a function of evacuation temperature, for catalysts coked during isobutene alkylation. They found that as temperature is increased, the aromatic character of coke increases and the amount of oligomers decreases. On the other hand, Guisnet and Magnoux [21] studied the modifications of pyrene deposited on a zeolite, as a coke model molecule. They found that upon heating in oxygen beyond 250°C, highly polyaromatic compounds are formed. These compounds are insoluble in methylene chloride. According to these authors this change does not occur when heating in nitrogen. However, this conclusion was obtained with a 'coke' (pyrene) quite different from the real alkylation coke. The same author reported that the coke formed from propene or from isobutene on a zeolite is transformed from oligomers to aromatics when heated under vacuum [22]. Therefore, there are strong evidences that coke changes its structure while heated, becoming more dehydrogenated and increasing the aromatic character, what leads to a more difficult to be burnt coke.

According to all the experiments we carried out in order to regenerate the catalyst with air, it seems

that the reorganization of the coke leading to a highly dehydrogenated/aromatized coke is unavoidable, independent of the temperature program used for the regeneration.

3.4. Regeneration with ozone

An HCL-Y zeolite was coked at 80°C, unloaded from the reactor, and regenerated at 125°C for 4 h in ozone. Fig. 5A shows the TPO profile of the deactivated catalyst after the ozone treatment, which contains 1.74% C. It has been shown that the ozone treatment not only reduces the amount of coke on a catalyst but also changes the structure of the coke left after the treatment, which becomes easier to be burnt [17,23]. A similar result is shown in Fig. 5A. The coke, which originally needs temperatures higher than 600°C to be fully removed in air, is now transformed into a partially oxidized coke that displays the maximum in the TPO profile at around 330°C, and a shoulder between 400 and 550°C. In our previous study [17], we showed that with a long treatment in ozone, it is possible to recover the initial catalyst activity, because all the coke could be removed with the ozone. Since the coke after the ozone treatment needs lower temperatures to be burnt with air, we studied the combination of ozone treatment, followed by hydrogen or helium stripping. Fig. 5 shows the results. Fig. 5A shows the signals obtained during the treatments in

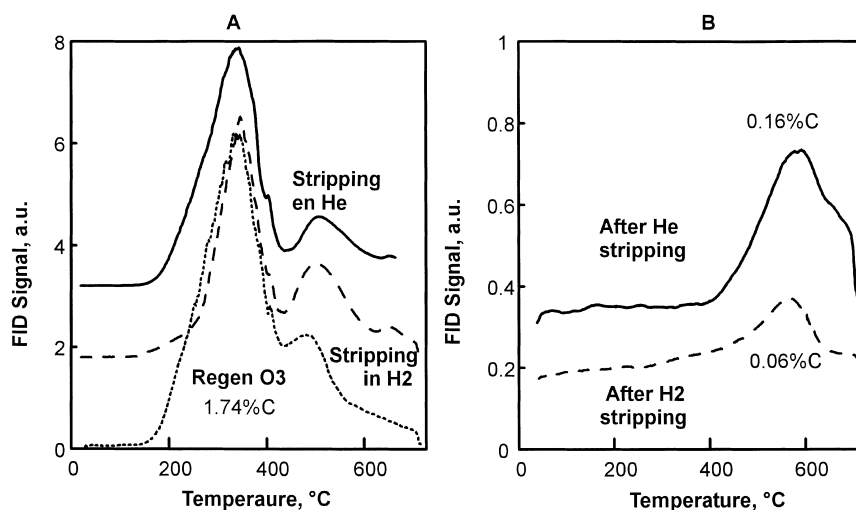


Fig. 5. (A) TPO profiles of the catalyst regenerated with ozone for 4 h at 125°C. Stripping in He and in H₂ of the HCL-Y zeolite, after regeneration in O₃ for 4 h; (B) TPO profiles of the catalyst after the stripping in He and in H₂ (catalyst regenerated in O₃).

He and in H₂ (proportional to the amount of hydrocarbons release during the treatment) and Fig. 5B, the TPO profile of the coke left on the catalyst after these treatments. Both the H₂ and He stripping follow similar pattern. The stripping profiles display a main peak located between 200 and 400°C, and a smaller second peak between 400 and 600°C. The main difference is in the amount of coke removed during these two treatments. When using H₂, only 0.06% C was left on the catalyst, and when using He, 0.16% C. However, this small amount of coke needs high temperatures to be burnt in air, due to the coke restructuring that took place during the stripping carried out up to more than 600°C. It seems that in order to eliminate the second peak that appears in the stripping profiles, longer times in ozone are needed in such a way to eliminate the second peak (shoulder) in the TPO of the catalyst regenerated with ozone (Fig. 5A). If such peak is eliminated, a complete coke gasification could be achieved by combining the ozone treatment, followed by either air or hydrogen treatment up to 400°C, with a total time needed for this operation shorter than the one required in order to fully remove the coke with ozone only.

After a reaction–regeneration experiment, with four reaction cycles and three regeneration cycles in ozone (10, 12, 16 h, respectively), the catalyst was unloaded and separated in fractions. Fraction No. 1 corresponds to the top of the bed (inlet), and No. 5 to

the bottom (outlet). Fig. 6 shows the TPO profiles of these samples. It is possible to observe that the coke has a different structure at the top than at the bottom of the reactor. This is because during the first and second regeneration in ozone not all the coke was removed. This partially oxidized coke gasifies during the pretreatment in helium before the reaction, and readsorbs downstream the bed, and changes its structure becoming more condensed. This result shows the

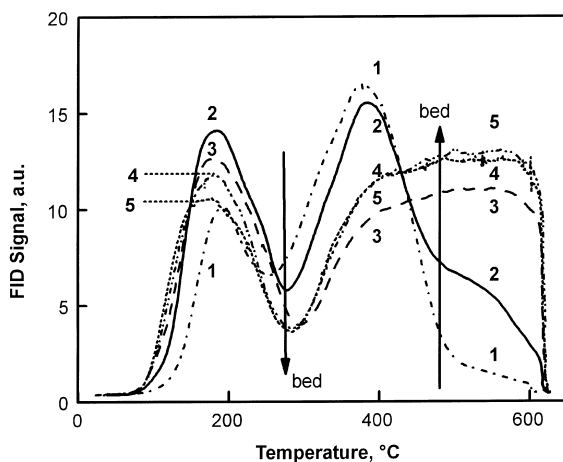


Fig. 6. TPO profiles of samples taken along the bed after four reaction–regeneration cycles. Regenerations with ozone at 125°C.

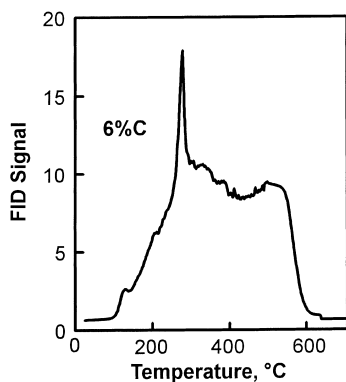


Fig. 7. TPO profile. Pt/LCH-Y catalyst, after reaction at 80°C, 25 atm.

importance of the complete coke elimination during regeneration. If coke is only partially removed, the fraction left on the catalyst, even being a very small amount, gradually becomes more difficult to be burnt.

3.5. Regeneration of Pt/LCH-Y catalyst

Fig. 7 shows preliminary results obtained with a Pt(0.5%)/LCH-Y catalyst. The activity of this catalyst (not shown) is somewhat lower than the one obtained with the LCH-Y catalyst [16]. The crystallinity degree of the platinum-containing catalysts

is lower than the LCH-Y zeolite used to prepare it. It is not clear which is the reason for this, since the catalyst was calcined after the impregnation with Pt at 500°C, temperature that should not affect the structure. The amount of coke is also lower than for the LCH-Y zeolite. The TPO profile (Fig. 7) shows that Pt is catalyzing the coke burning, represented by the sharp peak at 250°C approximately. The effect of Pt is not relevant in decreasing the maximum temperature needed to burn the coke. The TPO profile finishes above 600°C, similarly to the temperature found with the LCH-Y zeolite, without Pt. It is possible that the mobility of Pt is not enough to catalyze the combustion of coke that is located far away from the metal particles. It has been suggested that the catalyst containing Pt could be regenerated at low temperatures with H₂ [24]. Experiments using H₂ to remove the coke from the Pt(0.5%)/LCH-Y catalyst were carried out. Fig. 8A shows the hydrogenation of coke (TPHy), increasing the temperature up to 700°C. After this treatment, only 0.1% C is left on the catalyst, what is lower than the 2% left after helium stripping [16]. To avoid this treatment at high temperature, an experiment was carried out heating up to 190°C, holding this temperature for 2 h, increasing the temperature up to 285°C, holding for 3 h, and finally increasing up to 380°C and holding the temperature for 2 h. The objective is to allow the hydrogenation of the coke at

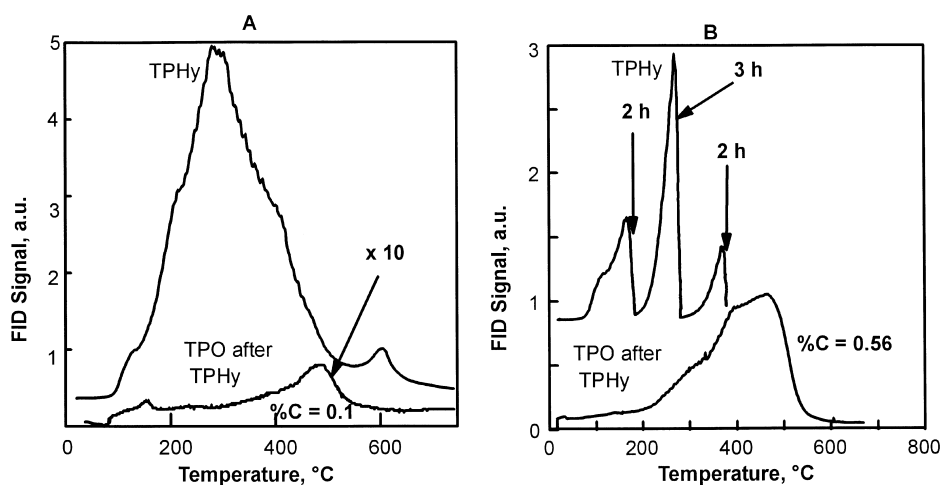


Fig. 8. Temperature-programmed profiles during the hydrogenation of coke on Pt/LCH-Y catalyst. (A) Heating from 20 to 700°C in H₂, and TPO profile of coke after this treatment; (B) temperature-programmed hydrogenation: from 20 to 190°C, 2 h at 190°C, heating up to 285°C, 3 h at 285°C, heating up to 380°C, 2 h at 380°C. TPO profile after this treatment.

mild conditions. Fig. 8B shows the TPhy profile, and the TPO of the coke left after this treatment. Again, it is not possible to remove all the coke using H_2 , in spite of the long times used in the treatment. Therefore, the addition of Pt does not allow the removal of alkylation coke neither with O_2 nor with H_2 at low temperatures.

3.6. Low temperature oxidation with hydrogen peroxide

In our previous work [16], we showed that both Cl_2CH_2 and a mixture of benzene plus methanol are not effective for coke removal. This was associated also with the difficulty of extracting the bulky coke molecules from inside the pores of the zeolites. Additional experiments were carried out using hydrogen peroxide. In this case, the objective is to oxidize the coke with the oxygen generated upon heating the coked catalyst in this oxidizing agent. At room temperature, it was found that there is no coke removal due to the hydrogen peroxide. When carrying out the treatment at $90^\circ C$, a large fraction of the coke can be removed with the hydrogen peroxide. Results are shown in Fig. 9. However, it takes a long time, 20 h, to decrease the coke from the initial value down to 0.62% C. The catalyst used in these experiments, was run in a 4-cycle experiment, having the TPO profile shown in Fig. 6. It has to be pointed out that this coke requires higher temperatures to be removed than the coke left

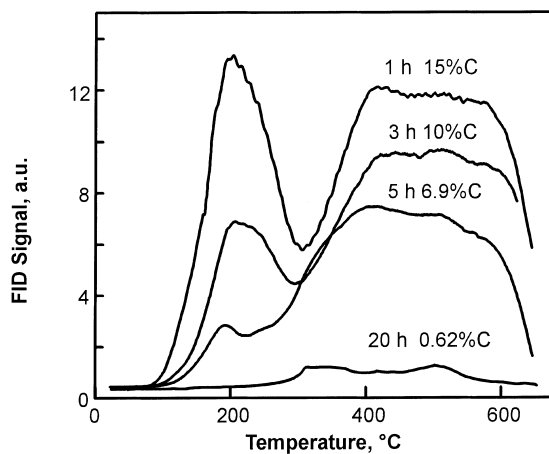


Fig. 9. TPO profiles of samples regenerated in hydrogen peroxide, at $90^\circ C$, for different times (see labels).

on the catalyst after only one reaction cycle. Comparing with the ozone, the hydrogen peroxide is somewhat less active, but the main difference, is the main feature of the coke left on the catalyst after the treatment. Both with ozone and hydrogen peroxide, the coke left after the treatment can be removed at lower temperatures than the original coke, the effect being much more noticeable in the case of using ozone as oxidizing agent.

4. Conclusions

The coke formed during the isobutane alkylation with C4 olefins is highly hydrogenated. Upon heating at low temperatures, this coke desorbs as hydrocarbons and simultaneously changes from an aliphatic structure to an aromatic one. This modification is the reason of the difficulty found in completely removing the coke from these types of catalysts. To burn the coke with an oxygen-containing gas, it is necessary to increase the temperature well above $200^\circ C$, and this leads to the aromatization of the coke and consequently, to the need of a further increase in temperature. Therefore, $600^\circ C$ for long times or higher temperatures are needed to fully remove the coke with air. The extraction with solvents was shown to be ineffective for coke removal, both after the reaction, as previously reported, or during the reaction under supercritical conditions. This behavior seems to be related to the microporosity of the catalyst, which prevents the bulky coke molecules to be extracted.

If platinum is added to the zeolite catalyst, a slight modification in the TPO profile is found, with a sharp peak around $250^\circ C$. This peak corresponds to the catalytic effect of Pt in burning the coke. However, the effect is not enough in order to decrease the maximum temperature needed to fully regenerate the catalyst. Either with an oxygen-containing gas or with pure H_2 , the addition of Pt to the zeolite catalyst was not effective for the regeneration. The hydrogen peroxide is active for coke oxidation at $90^\circ C$. Most of the coke can be eliminated from the catalyst if enough time is allotted for the treatment. The shortcoming of this procedure is that the coke left on the catalyst still requires high temperatures. Using ozone, it is possible to develop a regeneration strategy by combining a first treatment in ozone followed by a treatment either in H_2 or in He to complete the operation.

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