Isobutane alkylation with C4 olefins: regeneration of metal-containing catalysts

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ABSTRACT

The activity, selectivity, stability, and regeneration of metal-containing zeolites, used in the isobutane alkylation with C4 olefins is studied. Platinum and palladium were impregnated on Y-zeolite catalysts that were previously ion-exchanged with lanthanum. The activity and stability of these catalysts are similar to the same catalysts without metal. The coke content after 40 minutes of reaction is also similar, between 10 and 13 % approximately. The regeneration was carried out in air, and hydrogen. It was found that in order to remove all the coke from the catalysts, high temperatures are needed.   Mild treatments either in hydrogen or in air do not allow a complete coke removal. Nevertheless, the regeneration with hydrogen at the reaction temperature, even though only eliminates a fraction of the coke, allows recovering also a fraction of the activity.

1. INTRODUCTION

The alkylation of isobutane with C4 olefins is currently carried out using liquid acids. In the last few years there was an increasing research effort in order to develop solid catalysts to replace the liquid acids. The major problem of the solid catalysts is a rapid deactivation due to coke deposition. Therefore, the development of a catalyst for this process requires the study of the regeneration and its optimization.

A detailed characterization of the coke has been previously carried out (1-4) both by our group (1,4) and by other groups (2,3). It has been shown that the coke deposited during the reaction on a zeolite catalyst requires temperatures well above 500°C to be fully removed (1), and that a pore mouth plugging also takes place during the reaction (1). The coke has an aliphatic structure after the reaction (2) and it gradually changes its structure as the temperature is increased (1,2), with a continuos decrease in the H/C ratio (4) what also shows the change in coke composition. The consequence of this continuous modification of the structure from the aliphatic to an aromatic one, is that the temperature has to be raised up to 550-600°C to completely eliminate the coke (1,3). An important characteristic of this system is that if an uncompleted regeneration is carried out at high temperatures, the coke left on the catalyst selectively poisons the more active acid sites for the alkylation reaction (1). Therefore, the regeneration should either be carried out at low temperatures, or at high enough temperatures to remove all the coke. To regenerate the catalyst at low temperature there are few options: ozone regeneration, solvent extraction, and adding a metal to catalyze the coke combustion decreasing the regeneration temperature, or to hydrogenate the coke at low

temperature. The ozone regeneration was studied in zeolites (4) and in heteropolyacids supported on silica (5), and it was shown to be an effective method to recover the activity and stability for isobutane alkylation. The solvent extraction was not fully effective, and it was not possible to recover the initial performance of the catalyst (4). The regeneration at mild conditions when Pt is incorporated in the zeolite has been previously suggested (6). Preliminary experiments using Pt/Y-zeolites coked during the isobutane alkylation reaction, indicated that it is not possible (4) to remove all the coke with oxygen or with hydrogen at low temperatures.

In this paper, lanthanum containing Y-Zeolites were impregnated with different amounts of metals. Platinum and palladium were used in this study. The catalysts were used in activity test in the isobutane-C4 olefins alkylation reaction, and several regeneration strategies were investigated. Oxygen containing carrier gas, or hydrogen followed by oxygen were used as regeneration procedures for these catalysts. Coke was analyzed by temperature programmed oxidation. The catalysts were characterized by temperature-programmed reduction (TPR), CO pulse chemisorption, BET and XRD analysis.

2. EXPERIMENTAL

2.1 Catalyst Preparation

Y-zeolite (UOP, Y-54) with a Si/Al ratio 5.3 was used. The sodium form of the zeolite was exchanged with $(NO_3)_3La$ 0.58 M, in reflux, for 4 h, drying at 100°C and calcining at 550°C. Then a second ionic exchanged 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. This sample is labeled LCH-Y. This support was impregnated with $(NO_3)_2(NH_3)_4Pt$ or with $PdCl_4Na_2$ in order to obtain 0.3, 0.5, 0.9 wt%. Pt and 0.5, 0.9 wt%. Pd. These catalyst will be name as Pt(x) or Pd(x), where ´x´ is the metal weight percent.

2.2 Catalyst characterization

Reaction conditions: The alkylation reaction was carried out in a fixed-bed reactor, at 30 kg/cm^2, 80 °C, a molar ratio isobutane/C4 olefins = 15, and a WHSV =1 h^{-1} (referred to olefins). Catalysts are pretreated in-situ, at 250°C in helium for 2 h, or in hydrogen at 300°C for catalyst containing Pd. After 40 minutes of time on stream, the catalyst is purged with helium at the reaction temperature for 30 minutes.

Catalyst Regeneration: metal containing catalysts were regenerated in oxygen containing carrier gas or in hydrogen. Different final temperatures and time were used. Selected samples were regenerated with hydrogen peroxide, at 50°C and 100°C, for different times.

Coke characterization: Coke was characterized by temperature-programmed-oxidation (TPO), or hydrogenation (TPHy). The detection of compounds is carried out after methanation of the gases coming out of the TPO cell, with a FID detector. Regeneration studies using different temperature programs with 6%O_2/N_2 or hydrogen were carried out. Additional details of the technique can be found elsewhere (7)

Temperature programmed reduction: TPR experiments were performed on fresh samples of Pt/LCH-Y and Pd/LCH-Y 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% H_2/Ar (45 cc/min) up to 600°C.

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 catalysts. The He used as a carrier and

to purge the catalyst was purified through a MnO trap before contacting the sample. A methanator reactor that quantitatively transforms CO in CH_4 was employed to increase the sensitivity of the CO analysis. An FID detector was used to continuously monitor the CH_4. 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 from the sum of the differences between the by-pass and each pulse.

X-ray diffraction (XRD) analyses: XRD analyses were performed with a Shimadzu XD-D1 instrument with a monochromator, CuK_α radiation and a scanning rate of 0.5° per minute.

Surface area and pore volume: BET surface area was determined from nitrogen adsorption isotherms, and pore volumes were estimated by means of t-plots. These determinations were carried out on fresh catalysts, using a Micromeritics Accusorb 2100 sorptometer. Samples were pretreated under vacuum at 250°C, for 3 h.

3. RESULTS AND DISCUSSION

3.1 Catalyst Characterization

The XRD spectra of the catalysts show that the impregnation of the metals, followed by the calcination either at 500°C or at 350°C, does not significantly modify the crystallinity degree of the LCH-Y support, which is 97%, taking the crystallinity degree of the original Y zeolite as 100%. In all cases the crystallinity degree was above 90%. This level of crystallinity was achieved both for supported Pt catalysts prepared from H_2PtCl_6 and from $(NO_3)_2(NH_3)_4Pt$ precursors.

The metal dispersion is a key factor for catalyst regeneration. If the metal dispersion is too low, the activity for coke combustion is correspondingly low, due to the long distance between the metal and the coke deposits. In our system this could be even more important, since coke deposition is not related to the metal, as is the case for example in other system like catalytic reforming, where coke precursors are produced on the metal particles, and then
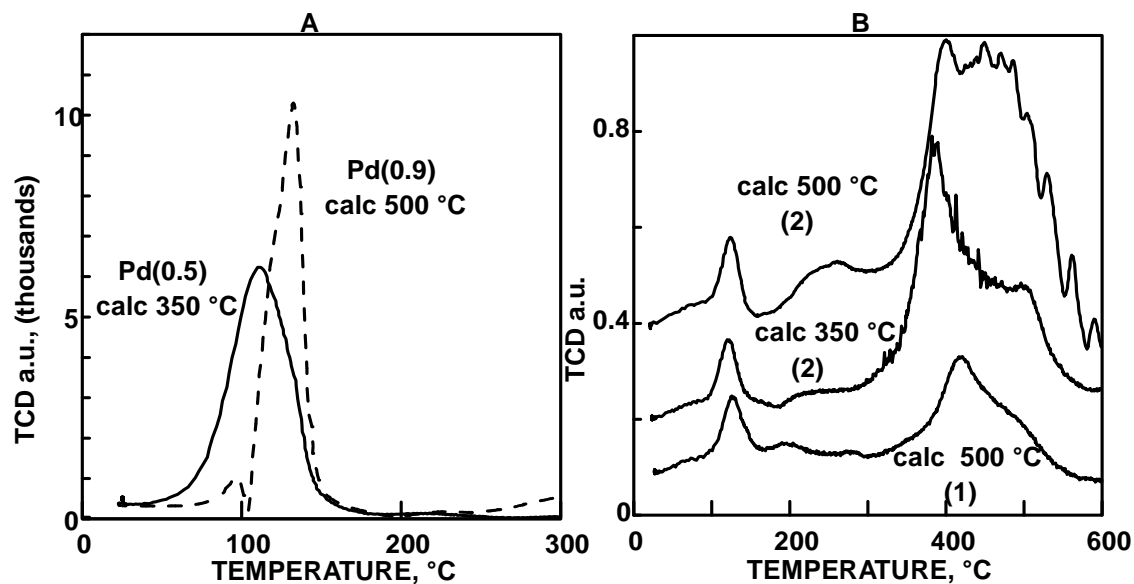

Figure 1: TPR profiles: (A) Pd catalysts (B) Pt(0.5) catalysts (1) prepared from $PtCl_6H_2$; (2) prepared from $Pt(NH_3)_4(NO_3)_2$

deposited on the acid function. During the isobutane alkylation, the coke is deposited independently of the presence of metal particles, and therefore, the metal dispersion should be as high as possible in order to increase the contact between the metal and the coke, which is deposited on all the acid sites of the support. With the preparation method we used in this study, we obtained different values of dispersion depending mainly on the calcination temperature. In the case of the Pt(0.9), prepared from $(NO_3)_2(NH_3)_4Pt$, and calcined at 550°C, the dispersion was 13%. In the case of the catalyst Pt(0.5), prepared using the same precursor, but calcined at 350°C, the dispersion was 36%, what is a good dispersion for this metal loading.

Figure 1 shows the TPR profiles of Pd and some of the Pt supported catalysts. Palladium supported catalysts reduce at low temperature. The hydrogen consumption is much higher than in the case of the Pt catalysts. The latter display, in all cases the peak between 100 and 150 °C approximately, and a second reduction zone between 350°C and 550°C, as usually found for this type of materials. This second reduction zone represents a higher proportion of the metal than the first peak.

The BET surface area of the Pt(0.5) catalyst was 400 m^2/g, similar to the support before the metal impregnation.

3.2 Activity

Figure 2 shows the results of activity experiments, with LCH-Y and the supported metal catalysts Pt(0.5) and Pd(0.5). The product distribution is very similar with the three catalysts. The selectivity towards trimethylpentanes (TMP) is 50% approximately, being the main type of component of the C5+ fraction. At about 25 minutes on oil, the selectivity to this type of compound decreases, and increases towards the dimethylhexenes (DMH=). This is due to coke deposition that deactivates the acid sites, decreasing the hydrogen transfer
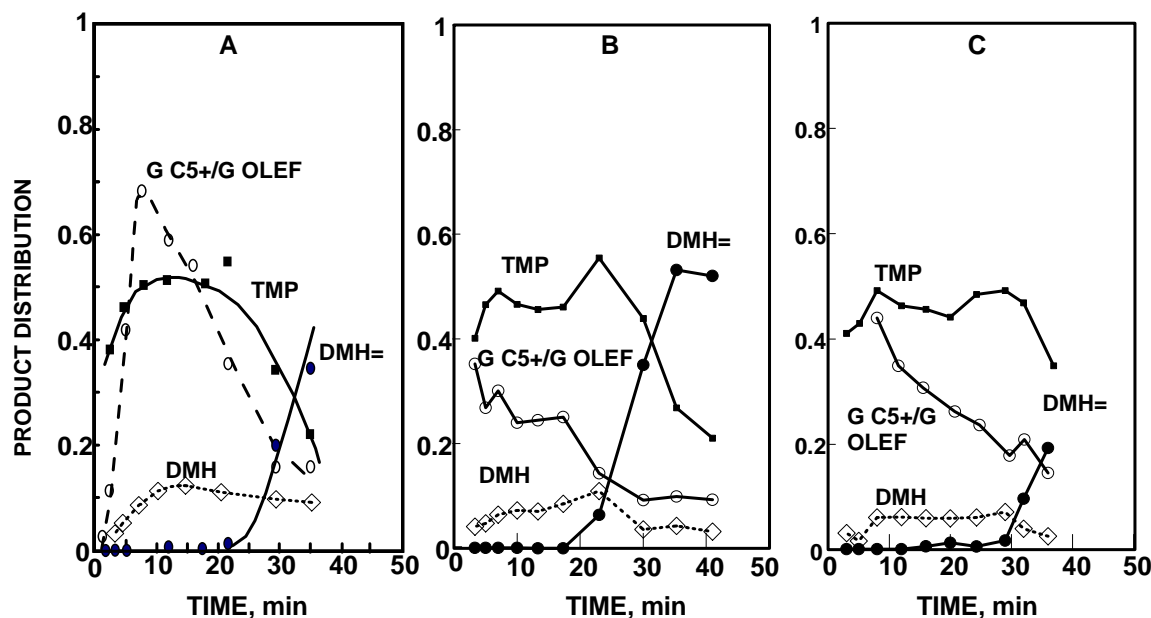

Figure 2: Product distribution in the C5+ fraction; (A) LCH-Y; (B) Pd(0.5)/LCH-Y; (C) Pt(0.5)/LCH-Y. Reaction conditions: 80°C, 25 kg/cm^2, iC4/Olefins: 15

activity, which is essential for the alkylation reaction. This is a typical behavior found with solid catalysts for the isobutane alkylation reaction (8,9). Figure 2 shows that the addition of the metal to the LCH-Y catalyst does not modify the catalytic behavior of the support. The coke deposition does not only decreases the activity, but what is even worse, it changes the selectivity, what consumes isobutane and olefins to form DMH=.

3.3 Coke characterization

Figure 3 shows results of the TPO analyses of the supported Pt catalysts (Fig. 3 A), and the supported Pd catalysts and the unpromoted zeolite LCH-Y (Fig. 3 B). The TPO profiles of the metal containing catalysts display a distinctive feature, compare to the Y-zeolite without metal. A sharp peak appears between 200 and 250°C, due to the catalytic effect of the metal on the coke combustion rate. In both cases, platinum and palladium promoted catalysts, the peak comes out at the same temperature approximately. The total amount of coke deposited in each case is between 11 and 14% C. This means, as also indicated by the activity results, that there is no a significant change in acidity upon metal addition. As it has been previously proposed (1), the level of coke formation is strongly related to the catalyst acidity. Similar levels of coke, indicate a similar acidity of the catalysts. The most important observation in the results shown in Figure 3, is that even though the catalysts contain a metal active for coke combustion, the coke still needs high temperatures to be fully remove with air heating at 12°C/min. A reason for this, is that some coke is not very close to the metal particles and the burn-off is unaided by the metal. Unfortunately, when the temperature is increased to eliminate the coke, changes in its structure from aliphatic to aromatic take place (1,2). This modified coke needs higher temperatures to be eliminated. The major problem associated with the change in structure is that the more polymerized coke is formed on the strongest acid sites, since these sites catalyses the transformation of the coke structure. Therefore, when the catalyst is partially
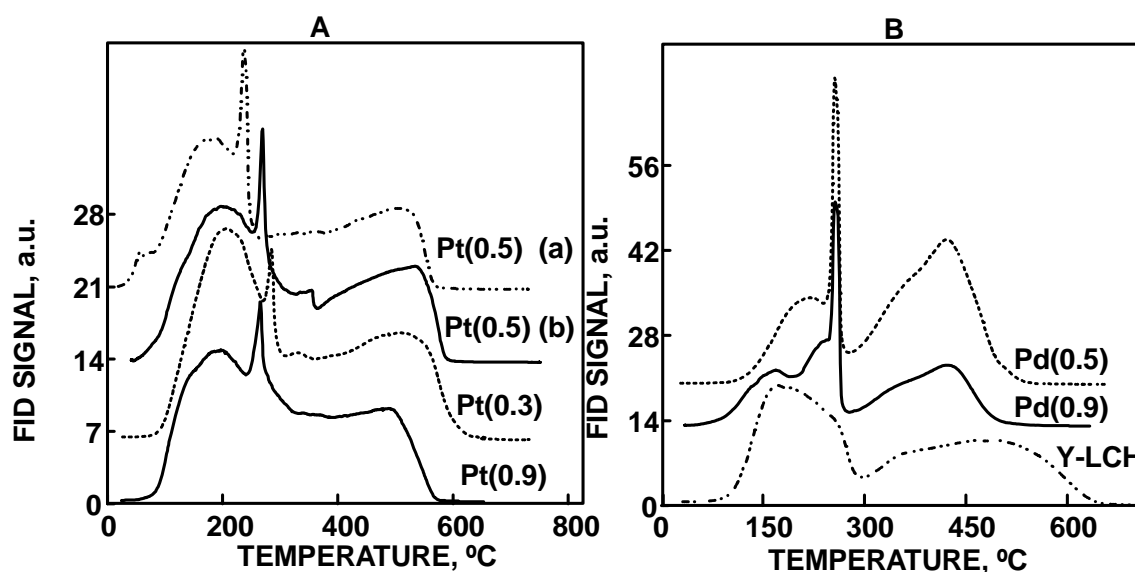

Figure 3: TPO profiles of: (A) Pt/LCH-Y catalysts, (a) calc 500 °C, (b) calc 350°C; (B) Pd/LCH-Y and LCH-Y catalysts

regenerated by any means that requires an increment in the temperature above 250-300°C, either the catalyst is completely regenerated by elimination of all the coke at high enough temperature, or the catalyst does not recover the initial activity. For this reason, regeneration strategies at low temperature have been studied.

3.4 Regeneration studies

In the literature, the only method presented for full regeneration at low temperature was using ozone (5,10). The use of solvent extraction is not effective enough (4). In a Mobil patent (11), a BF_3/resin catalyst is regenerated by extraction with alcohol, but a second step is necessary, in which additional BF_3 is added to the catalyst, what indicate that the first step is not enough to recover the activity. The objective of including a metal in the catalyst formulation in the isobutane alkylation reaction, is to decrease the regeneration temperature. However, Figure 3 shows that the temperature needed to burn the coke off is exactly the same in the case of the platinum containing catalysts as compared to the unpromoted support. In the case of the catalysts with palladium, the temperature at the end of the TPO profile is 100°C lower than in the LCH-Y catalyst or in any of the Pt/LCH-Y catalysts. In the latter, the final temperature does not depend on the metal loading, or the preparation procedure, or in the dispersion. The palladium seems to be much more effective for coke combustion than the Pt. Nevertheless, in a dynamic analysis as in the case of the TPO, the temperature needed to burn the coke is very high. In the patent issued to Union Carbide (6), the regeneration with hydrogen for long times is proposed, at pressures in the range of 1 to 30 atm, and a temperature of 150 F. In this case, regeneration of 12 hours was used, being possible to recover the catalyst activity with this treatment. It has to be emphasized that the regeneration temperature is low enough to avoid the modification in the coke structure, what is the cause of a selective deactivation of the active sites, as explained above. It has to be also noted, that the coke left after this treatment was not measured, and most probably there is still a certain amount of hydrocarbon left on the catalyst. Nevertheless, the time consumed to regenerate
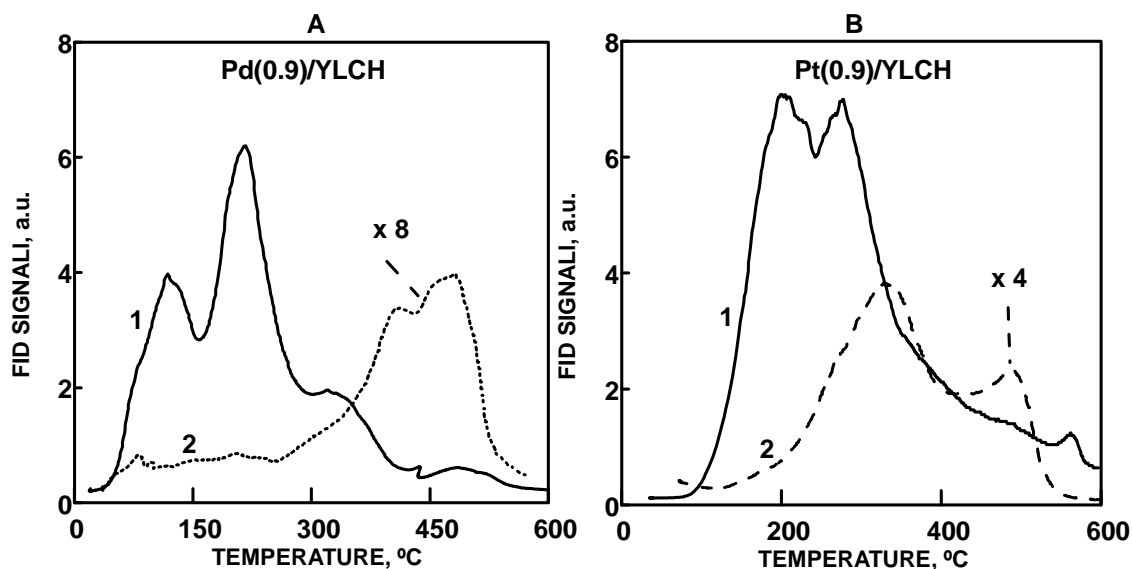

Figure 4: temperature programmed analysis of coked catalysts: (A) Pd(0.9); (B) Pt(0.9); (1): temperature programmed hydrogenation (TPHy); (2) TPO after TPHy.

the catalyst at this temperature is very high.

Figure 4 shows results obtained heating the coked catalyst in hydrogen, while increasing the temperature up to 620°C (TPHy), both in the case of the Pt(0.9) and in the case of Pd(0.9). In both cases, there is an important amount of coke left in each catalyst after this treatment. The TPO carried out after the TPHy are shown in Fig. 4 A for Pt(0.9) and in the Fig. 4 B for Pd (0.9). After this treatment, and even though the amount of coke was substantially reduced, the activity recovery is very poor. Therefore, another set of experiments was carried, trying to regenerate the catalyst either with oxygen or with hydrogen, but at lower temperatures and for longer times. In the case of the Pt(0.9), an experiment was carried out heating in hydrogen from room temperature up to 110°C, holding this temperature for 1 h, then increasing the temperature 25 °C, and holding again the temperature for 1 h. The steps are continued up to a final temperature of 260°C, with a total time of treatment of 7 h. The amount of coke left on the catalyst was more than 1%, what shows that the coke is not fully remove even with this long treatment.

In the experiments described above, the catalyst was not reduced. Therefore, during the regeneration with hydrogen, there is no catalytic effect for hydrogenation or hydrocracking at low temperature, where the metal is not reduced yet. To test the regeneration in hydrogen, with the reduced metal, an experiment was carried out with the Pd(0.9), with a reduction step before the activity test. The catalyst was reduced in flowing hydrogen, heating in 4 h from room temperature up to 300°C, and holding this temperature for 1 h. Then, the temperature was adjusted to the reaction temperature (80°C). Figure 1 A shows that the Pd is fully reduced at 300°C. The activity of the catalyst is the same as when it was not reduced. After the reaction, the catalyst was treated in-situ, in pure hydrogen at 120 psig for 12 h at 80°C. Then, a sample was discharged from the reactor, and characterized by TPO. The profile is shown in Figure 5. The amount of coke left after this treatment was 5%, which is almost the half of the coke left after the run. The TPO profile obtained with the reduced catalyst after the treatment with H_2 is different than th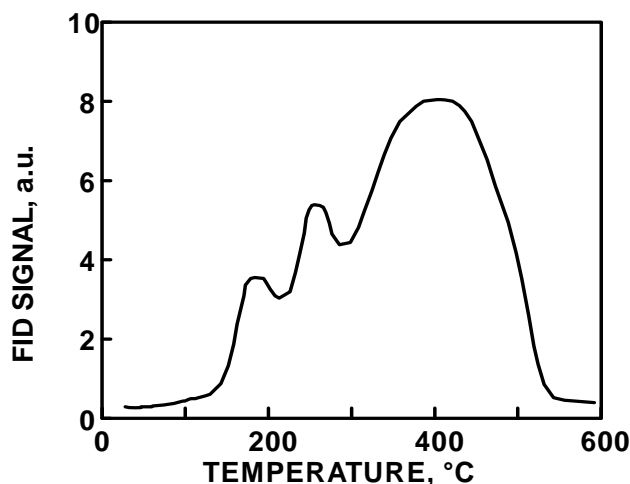e one obtained without catalyst reduction. The contribution of the first peak is much smaller in the former; besides, the sharp peak related to the combustion of coke deposited directly on top or very close to the metal particles, is not any longer observable. This means that the treatment in hydrogen has eliminated preferentially the coke that is located very close to the metal particles. The coke that is removed between 80 and 150°C is also eliminated with the H_2 treatment. A large amount of coke was anyway left on the catalyst. The reason for this is that the elimination of coke with hydrogen involves the hydrocracking besides the hydrogenation of olefinic species. The latter occurs at low temperatures, but the former does not.

Figure 5: TPO profile of Pd(0.9), reduced before the activity test, and treated with H_2 after the test at 80°C, 120 psig, for 12h.

Another set of experiments was carried out with hydrogen peroxide. We previously showed that at 90°C, the hydrogen peroxide decreases the amount of coke as function of time (4). During the decomposition the hydrogen peroxide provides atomic oxygen, which in the presence of a metal oxide could accelerate the oxidation of the hydrocarbon deposits. However, at 50°C the amount of coke removed was rather low (result not shown). At 100°C, in a treatment carried out for 3.5 h, the coke was decreased from 13% to 8.5%, what is similar to the effectivity found on the LCH-Y catalyst without metal.

4.CONCLUSIONS

The catalyst based on the Y zeolite, containing metals like platinum or palladium, are as active and stable as the zeolite without metal promotion. Also, the amount of coke deposited is very similar in both types of materials.

The palladium is more effective to remove the coke in an oxygen-containing carrier gas. The TPO profile finishes at approximately 100°C lower temperature in the case of the palladium compared to the platinum. In both cases, the catalytic effect of the metal is displayed as a sharp peak that appears in the TPO profile at 250°C approximately. The amount of metal only slightly modifies these TPO profile.

The elimination of the hydrocarbonaceous deposits with hydrogen at low temperature only occurs is the metal is reduced before the activity test. In this case, the coke that is deposited on top of the metal or very close to it, is eliminated at 80°C, but almost half of the coke still remains on the catalyst after a 12 h treatment at 120 psig.

5. ACKNOWLEDGEMENTS

REFERENCES
1- C.A. Querini, E. Roa,Appl. Catalysis A: General 163 (1997)199.
2- C. Flego, I. Kiricsi, W.O.Parker, M.G.Clerici, Appl. Catal. A: General 124 (1995) 107
3- T. Rorvik, H. Mostad, O.H. Ellestad, M. Stocker, Appl. Catal. A: General 137(1996)235.
4- C.A. Querini, Catalysis Today, 62(2000)135
5- G. Baronetti, H. Thomas, C.A. Querini, Applied Catalysis A: General, in press
6- C.L. Yang, US Patent 3,893,942 (1975)
7- S.C. Fung, C.A. Querini, J. Catal. 138 (1992)240
8- A.Corma, A. Martínez, C. Martínez, J. Catal. 149(1994)52
9- A.Corma, A. Martínez, C. Martínez, Catal. Lett. 29 (1994)187
10- C.A. Querini, E. Roa, C. Pieck, J.M. Parera.; Studies in Surface Science and Catalysis, 111(1997)407
11- US Patent 3 855 343 (Mobil Oil) (1974)