

Structural analysis of several commercial Pt-Re/Al₂O₃ catalysts deactivated through industrial Naphtha Reforming. DRIFT, TG-DTA, MS-TP analysis and test reaction with cyclohexane studies

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Abstract

Pt-Re/Al₂O₃ catalysts are commonly used in reforming naphtha, in this paper it is explained how to do a fast analysis and study about the origin and possible mechanism of deactivation for several catalysts from industrial reforming. Several studies using DRIFT, TG-DTA and MS-TP analysis were did, they showed as the coke is deposited over the acid and metallic centers of the catalysts. Test reaction using cyclohexane shows as the catalysts have less .for isomerization and more for dehydrogenation producing as principal product the benzene. The deactivation increases with the time and the amount of coke species over the catalyst (TG-DTA studies show clearly these results). Not paraffins were found over the catalyst (DRIFT and MS-TP results), only carbonaceous species which in first time are deposited over the acid centers. In our test reaction the deactivation is principally over the metallic centers because the acid places were deactivated before in the industrial reforming.

Keywords: Pt-Re/Al₂O₃; catalyst; deactivation; reforming; naphtha; coke; analysis; cyclohexane; dehydrogenation; activity.

1. Introduction

In the naphtha reforming the activity of the catalyst is decreasing gradually. This lost of activity is negative because of the low octane number of products and the less production of hydrogen. If the catalyst is too much deactivated we can increase the temperature of reaction to have the same octane number but at the same time we can have some production of other not suitable chemicals from coking, cracking, hydrocracking and hydrogenolysis [1-3] that definitively is not good for naphtha reforming.

The Pt-Re/Al₂O₃ is an important catalyst used commercially, this catalyst is the preferred for semi-regenerative units of reforming but it is sensible to the presence of sulfur and water (the water makes losing of Cl in the catalyst), iron from the corrosion in the tubes or the silica from the antifoaming [4].

Through the formation of different compounds the coke is the product more produced. At the same time the catalyst suffers sintering and is poisoned with some substances presents in the flowing raw material [5, 6]. The poisoning of the catalysts is limited by the use of adequate pretreatment. There are several heteroatom compounds like sulfured molecules [7], oxygen (in the regeneration the oxygen plays two roles, one regenerating and other like oxidation agent not good producing exothermic reaction positive for the sintering of the catalyst) [8] or nitrogen (the nitrogen oxides are contaminants) [9]. There are secondary negative substances for the catalyst like Hg, Cu, As, Si, Fe and other, they must be prevented.

In normal conditions the factory is stopped sometimes for the regeneration of the catalyst to recover the initial activity through controlled combustion of the coke and other not profitable products. At the same time the catalyst suffers a readjust of its level of chlorine [10], normal process for example for Pt-Re/Al₂O₃ chlorinated catalysts. Other regeneration described by G. J. Antos and col. or B. J. Cha and col. [4, 11] tell us about how in the

continuous catalytic regeneration the catalyst flow between the reactors and equipment, doing possible the reaction under similar conditions from the start of the reaction.

In the present paper our study explains about several deactivated catalyst Pt-Re/Al₂O₃ in naphtha reforming. To determinate de cause of their deactivation there were been used some specific structural analysis and a cyclohexane test reaction.

2. Experimental part

2.1.Catalysts reception and preparation

The catalysts studied were Pt-Re/Al₂O₃ deactivated in Naphtha Reforming during several days, they were kindly provided by the industry (REPSOL-YPF) with different deactivation degrees. They have between 0.1 and 20 % wt of coke

These solids were used under confidential conditions by the Company REPSOL-YPF for naphtha reforming. Our research work was focused into study how to know the origin and effect of the deactivation in the catalyst and the possible deactivation mechanism present in industrial naphtha reforming.

In the next table (Table.1) it is showed the nomenclature for each catalyst. The "F" is the fresh commercial catalyst. The other catalysts were reused in three closed cycles in the reactor n. 1 or n. 3. R1-0 is the catalyst with 0 days in the fourth cycle in reaction; R1-359S catalyst was recovered by Söxhlet extraction for to use it in the 4th cycle and then it was 359 days functioning in this cycle in reactor n. 1 and then; R3-128 is a catalyst which was 128 days in the reactor n. 3.

The catalysts were pre-treated before each test reaction with a reduction in a flow of dry hydrogen (pretreatment described in "TEST REACTION", the nomenclature used was exactly the same but only adding -P, F-P was the fresh pre-treated catalyst.

Table.1. Each catalyst was a specific number of days in the reaction.

Catalyst	N. days
F	0
R1-0	0*
R1-359S	359
R3-8	8
R3-128	128
R3-179	179
R3-310	310

* (not fresh, regenerated, 4th cycle, reactor n. 1)

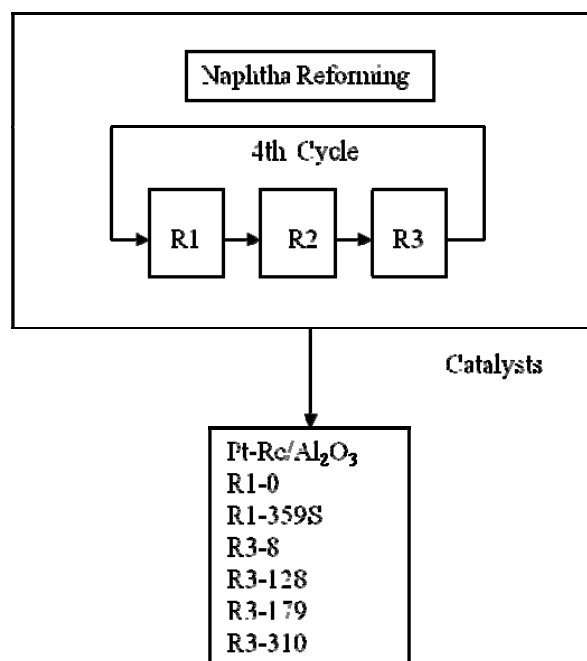


Figure 1. Representative scheme of the samples provided by REPSOL-YPF and assigned nomenclature for each one.

2.1.1. TG-DTA and MS-TP

Thermal analysis was performed by simultaneous TG-DTA measurement. Samples were heated at a heating rate of $5 \text{ K} \cdot \text{min}^{-1}$, in air (40 mL/min), in the temperature range 323-1273 K. System Setaram Setsys 12, with $\alpha\text{-Al}_2\text{O}_3$ a reference material; Pt/Pt-Rh(10%) temperature tester.

The results obtained in the analysis TG-DTA were confirmed through de utilization of programmed mass spectrometry (MS-TP) "VG Prolab instrument" in line with a continuous flow reactor heating the sample in the range 323-873 K; flow rate (air), $50 \text{ mL} \cdot \text{min}^{-1}$. The spectrometer was working in "multiple ion monitoring" mode; selected products were (air), H_2O (18), paraffin (43), CO_2 (44), benzene (78), toluene (92), SO_2 (64), methylhexane (100) and CO (30). Using argon were selected to be object of the analysis the next compounds; CO (30), H_2O (18), benzene (78), SO_3 (80), SO_2 (64), NO_2 (46), paraffin (43) and CO_2 (44).

2.1.2 DRIFT

The Diffuse Reflectance Infrared by Fourier Transformed (DRIFT) spectra were measured in a Bomem MB-100 spectrometer equipped with one diffuse reflectance collector Spectra Tech, P/N 0030-100. The resolution was 8 cm^{-1} between $4000\text{-}400 \text{ cm}^{-1}$. In each step were used 256 repetitions added continuously by Fourier transformed equations. The place for the sample was at 573 K of temperature. Te samples are diluted to 15 % wt. with KBr.

2.1.3 TEST REACTION

All catalysts received were pre-treated before the test reaction with cyclohexane with a reduction in a flow of dry hydrogen ($50 \text{ cm}^3 \cdot \text{min}^{-1}$) and 2 h. with 723 K of temperature and a heating rate of $5 \text{ K} \cdot \text{min}^{-1}$ in the range 293-723 K. For each treatment it was used a micro-catalytic stainless steel reactor "MICROACTIVITY-PRO" of 30 cm length and 1.3 cm external diameter was used. The catalyst bed contains 0.1 g of catalyst.

The reactor was electrically heated and electronically thermostated. The microreactor was fixed at the inlet of a gas chromatograph type 3400 Varian for direct analysis of the reaction effluents using a separation column (fused silica capillary column) of 100 m length capillary with 0.25 mm internal diameter and $0.50 \mu\text{m}$ film thickness. The reaction products were analyzed by gas chromatography with flame ionization detector (FID) using a Supelco capillary column (Petrocol DH). The chromatographic oven temperature during testing was 318 K.

The reaction conditions were as follows: reaction temperature 673 K and 773 K, flow rate of H_2 , $50 \text{ cm}^3 \cdot \text{min}^{-1}$, 1 bar pressure and reactant pulse (cyclohexane (Aldrich, 99.5%)), $50 \mu\text{L} \cdot \text{min}^{-1}$. The conversion of cyclohexane was carried out for all Pt catalysts Re/ Al_2O_3 in a continuous flow catalytic reactor. The space velocity (WHSV) for the experiments was 23 h^{-1} , approximately.

The characterization of the reaction products was performed using chromatographic patterns and mass spectrometry. The starting order of the different reaction products, under the above conditions were: methylcyclopentene (MCPeno, 26.5 min), methylcyclopentane (MCP, 29.3 min), benzene (B, 32.9 min), cyclohexane (CH, 34.5 min) and cyclohexene (Chen, 37.4 min).

3. Results, discussion and conclusion

3.1 Thermal analysis and MS-TP

The TG-DTA analysis and MS-TP spectrometry were used to optimize the proceeding of standardization of the analysis for the catalysts Pt-Re/ Al_2O_3 ;

1. Allowing us to avoid the elimination of some possible substances adsorbed (physical or chemically) or deposited on the deactivated catalyst.
2. Knowing the nature of the adsorbed species (physically, chemically and/or deposited over the catalyst).

There were carried out some analysis TG-DTA for the catalyst fresh and pretreated (as pretreated catalysts for test reaction, with a reduction in a flow of dry hydrogen ($50 \text{ cm}^3 \cdot \text{min}^{-1}$) and 2 h. with 723 K of temperature and a heating rate of $5 \text{ K} \cdot \text{min}^{-1}$ in the range 293-723 K) (Figure 2.) taking all of them (four experiences showed) similar results. Thus, it is shows in the Figure 2 that there is a first weight loss (around 2 %) at temperatures below 498 K, accompanied by a DTG maximum in the curve and one endothermic band centered at 411 K showed in the DTA graphic; this corresponds to the desorption and removal of

water physically adsorbed on the catalyst surface. The second weight loss ($\sim 3.8\% \sim 1.2\%$ for catalysts F and F-P, respectively), which covers the temperature range 498 to 1273 K, is related to the removal of water generated in the dehydroxylation of Al-OH adjacent groups. The difference in weight loss, at this late stage, between F and F-P indicates that in the pretreatment has occurred partial dehydroxylation of the alumina used as support.

Also, in the experiments, as expected, there were not significant differences between the different atmospheres applied in the analysis represented in the Figure 2.

MS-TP experiments carried out with these catalysts has been detected only H₂O.

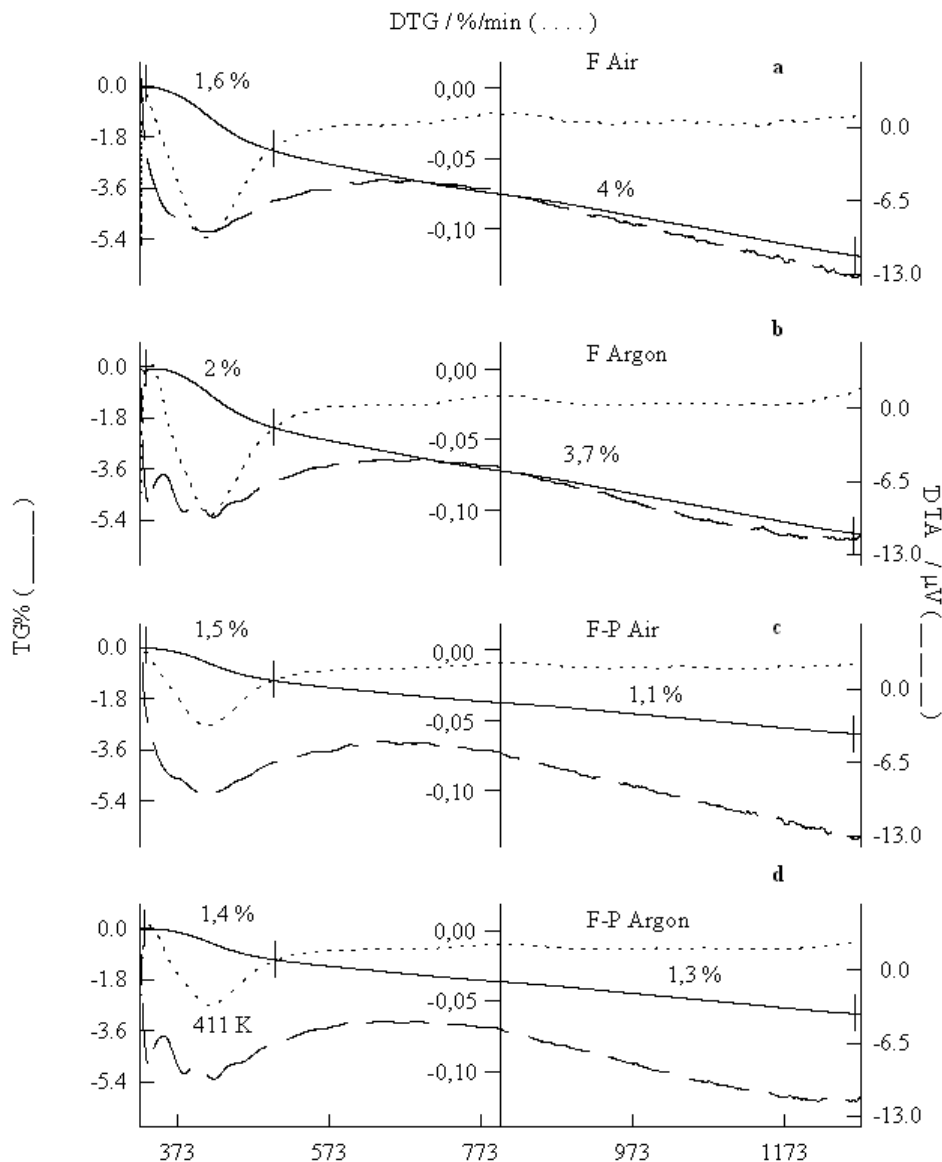


Figure 2. TG/DTA Curves TG, DTG and DTA of materials: a) F with air, b) F with argon, c) F-P air and d) F-P argon.

The TG curves and their differentials DTG and DTA analysis of the deactivated R1 and R3 catalysts, show similar profiles with the exception of the catalyst R1-0. However, the catalyst R1-0 shows similar results like F catalyst. The R1-0 catalyst comes from a stage of regeneration prior to use in the 4th cycle in a zero time (regenerated-“clean” to use other time) with not weight loss assigned to carbonaceous species (confirmed by MS-TP analysis).

For samples R1-359S and R1-359S-P are four different stages in the TG-DTA analysis, in oxidizing atmosphere (air) and inert gas (argon) (Figure 3) the first stage with a weight loss around 3% ($T < 498$ K) and it is associated to a peak in the DTG curve and endothermic band centred in the DTA at 383 K. Moreover at this temperature (383 K) is showed a peak in the MS profile for the H₂O TP (Figure 4), allowing us to assign this first stage to the removal of water physically adsorbed. The second weight loss occurs in the temperature range 598-698 K ($\sim 1.8\%$) and it is related to the disposal of water generated by condensation of adjacent Al-OH groups.

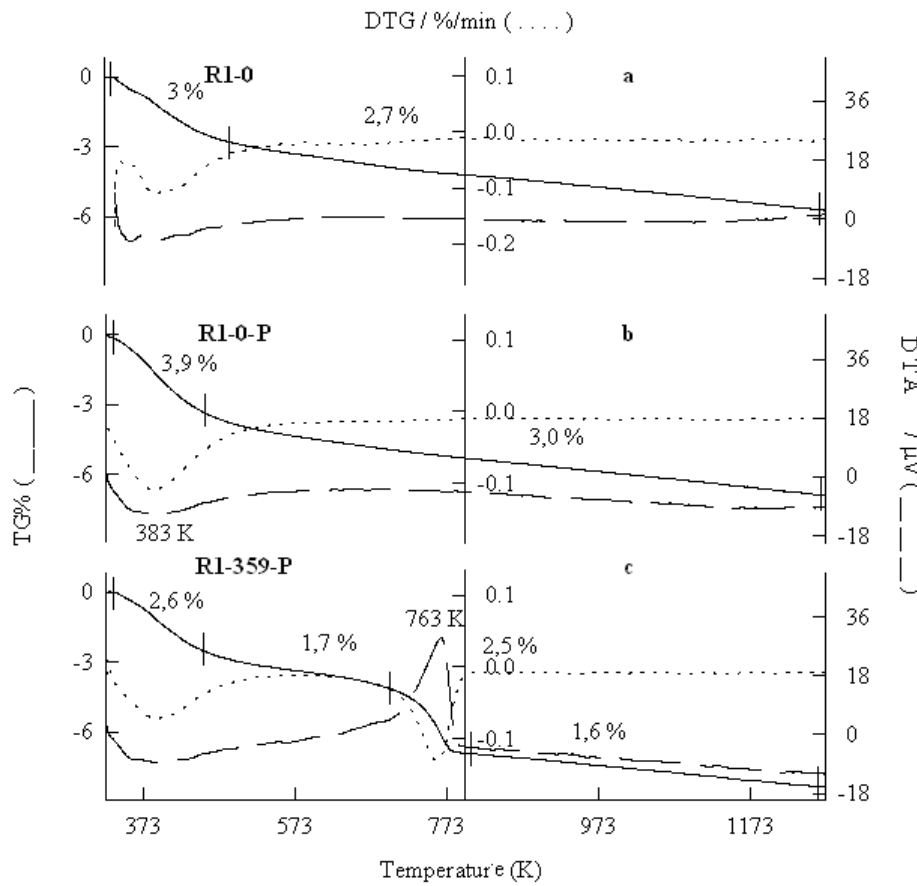


Fig. 3. Curves TG, DTG and DTA in air for pretreated materials: a) R1-0, b) R1 0 P y b) R1-359S-P.

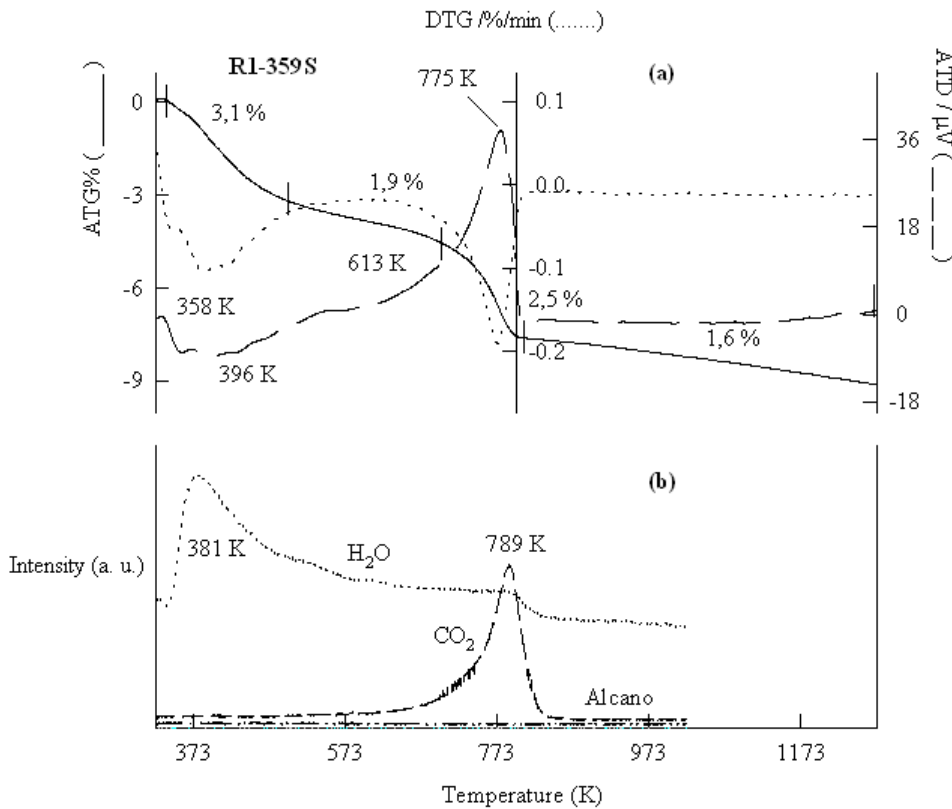


Figure 4. (a) TG-DTG-DTA curves in air and (b) MS TP for R1-359S.

The next stage takes place in the temperature range 698-823 K and 698-973 K for the R1-359S catalyst in air and argon respectively. For the pretreated catalyst the temperature range is narrow (698-798 K and 698-823 K in air and argon)

In all cases, this weight loss is accompanied by a peak in the DTG curve, and a DTA exothermic band, more intense, as expected for DTA analysis carried out in air. Moreover if we consider the results obtained by MS-TP, we can make the following considerations:

- In the MS-TP spectra of the sample R1-359S in an oxidizing atmosphere (air) are detected exclusively CO_2 and H_2O from the exothermic combustion of carbonaceous adsorbed species and/or deposited on the catalyst. The results also in an inert atmosphere confirmed the removal of carbonaceous species by desorption and exothermic decomposition (exothermic peak in DTA curve).
- Logically, the total elimination of carbonaceous species in argon requires higher temperatures from the order of 25-50 K higher compared to oxidation in air.
- Pretreatment with H_2 of the catalyst R1-359S is a change in the nature of the adsorbed species and/or deposited on the catalyst, favoring its elimination in both air and argon, being much more pronounced change in the latter case (narrowing of the temperature range in the third weight loss).

The fourth stage, which involves a progressive weight loss (< 2%) to the end of the analysis temperature TG-DTA (1273 K) is attributed to the removal of water generated in the dehydroxylation of the support (alumina).

All the results for all of the catalysts are really similar because of the same nature of them and the same process in the industry.

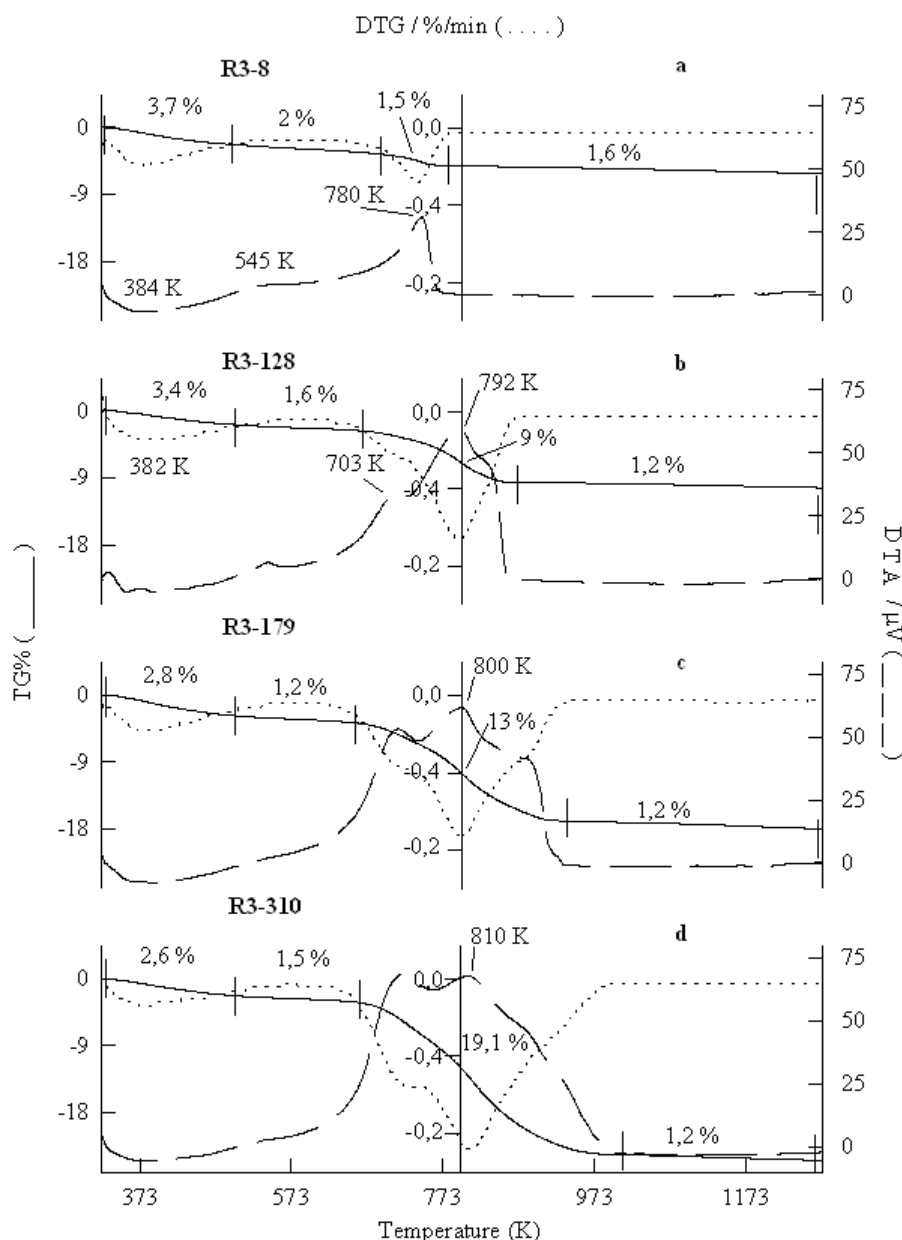


Figure 5. TG, DTG and DTA curves in air for catalysts: a) R3-8, b) R3-128, c) R3 179 and d) R3-310.

Finally, the TG DTA curves of the catalysts from the reactor R3 and with different times of use are similar to those described for the R1-359S catalyst showing, therefore, four main weight losses. However, this series of catalysts was observed several characteristics in the third stage of elimination of coke, which follow:

- The coke content increases with the number of days of use of the catalyst, from a loss of 1.5 wt% for the catalyst R3-8 to 19.1 wt% for the catalyst R3-310, in an atmosphere of air (Figure 5).
- Furthermore, in air, there is clearly an increase in the temperature range for the removal of carbonaceous species adsorbed and deposited on the catalyst with the degree of deactivation, and this interval 650-780, 870, 937 and 1010 K for catalysts R3-8, R3-128, R3-179 and R3-310, respectively.
- The results obtained in air pretreated catalysts coincide practically with the above for non-pretreated catalysts. Consequently, in the standardization process (pretreatment before test reaction) has not changed the nature of carbonaceous species on the catalyst fixed.
- The analysis of the results in argon ATG ATD is more complex, since it is difficult to establish the final temperature of the third stage of removal of coke. However, this analysis shows that the removal of carbonaceous species in an inert atmosphere takes place through processes of desorption and exothermic decomposition.
- Similar to the results obtained for the ATG ATD R1-359S catalyst, the results have confirmed MS TP assignments carried out.

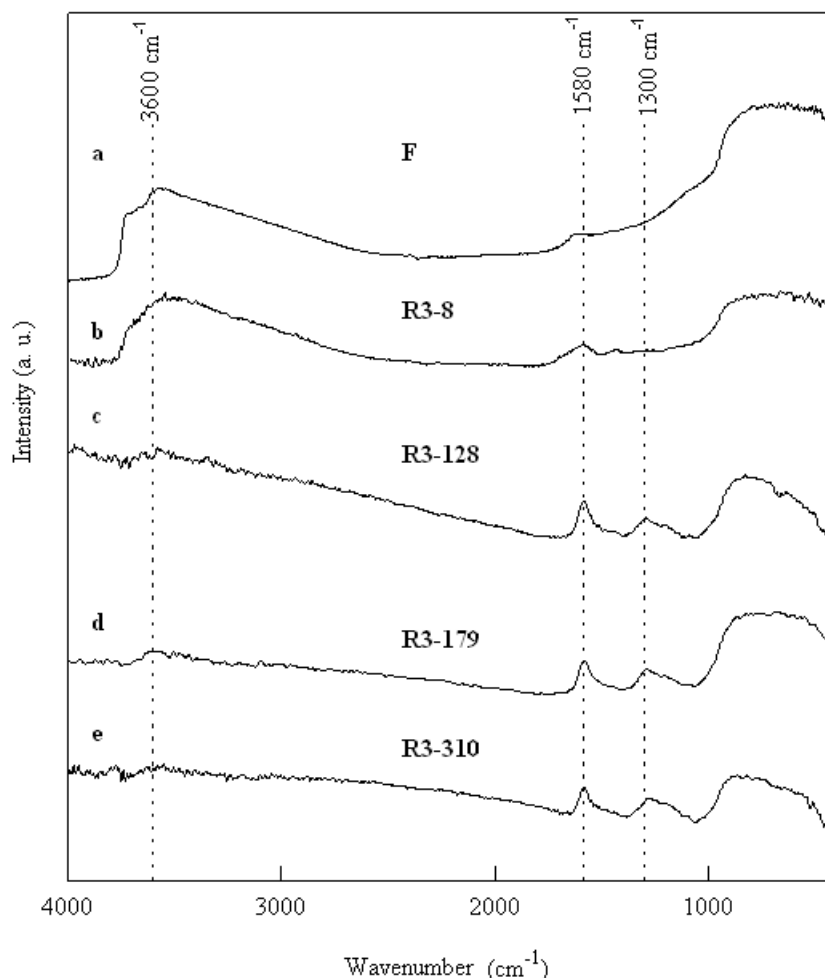


Figure 6. DRIFT spectra (4000 400 cm^{-1}) for Pt Re/ Al_2O_3 catalysts: a) F, b) R3 8, c) R3 128, d) R3 179 and e) R3 310.

3.2 Drift

The infrared spectra of diffuse reflectance obtained for the different catalysts investigated are similar (Figures 6, 7). Thus in the fresh catalyst and less deactivated catalysts (F, R3-8, R1-0, R1-359S an pre-treated catalysts) shows clearly in the region of OH stretching vibration a broad band centered at 3600 cm^{-1} , approximately, characteristic of the surface hydroxyl groups (Al-OH) influenced by the hydrogen bonds in the alumina ^[12]. In addition,

the deactivated catalysts in the reforming factory shows the decrease of the band at 3600 cm^{-1} compared to the fresh catalyst (R3-8, R1-0, R1-359S and its pre-treated analogues), disappearing in the most heavily deactivated catalysts (R3-128, R3-179, R3-310 and their respective pre-treated catalysts). Simultaneously, there are two bands at 1580 and 1300 cm^{-1} attributed to bending vibrations and torsional olefinic C-H, respectively [4].

Moreover, there are no characteristic bands of polycyclic aromatic compounds to 774 and 871 cm^{-1} , along with two other less intense bands in the range $700\text{-}900\text{ cm}^{-1}$. Also do not detect the bending vibration bands of C-H bond of $-\text{CH}_2-$ groups (bands at 2846 and 2912 cm^{-1} approximately) [13].

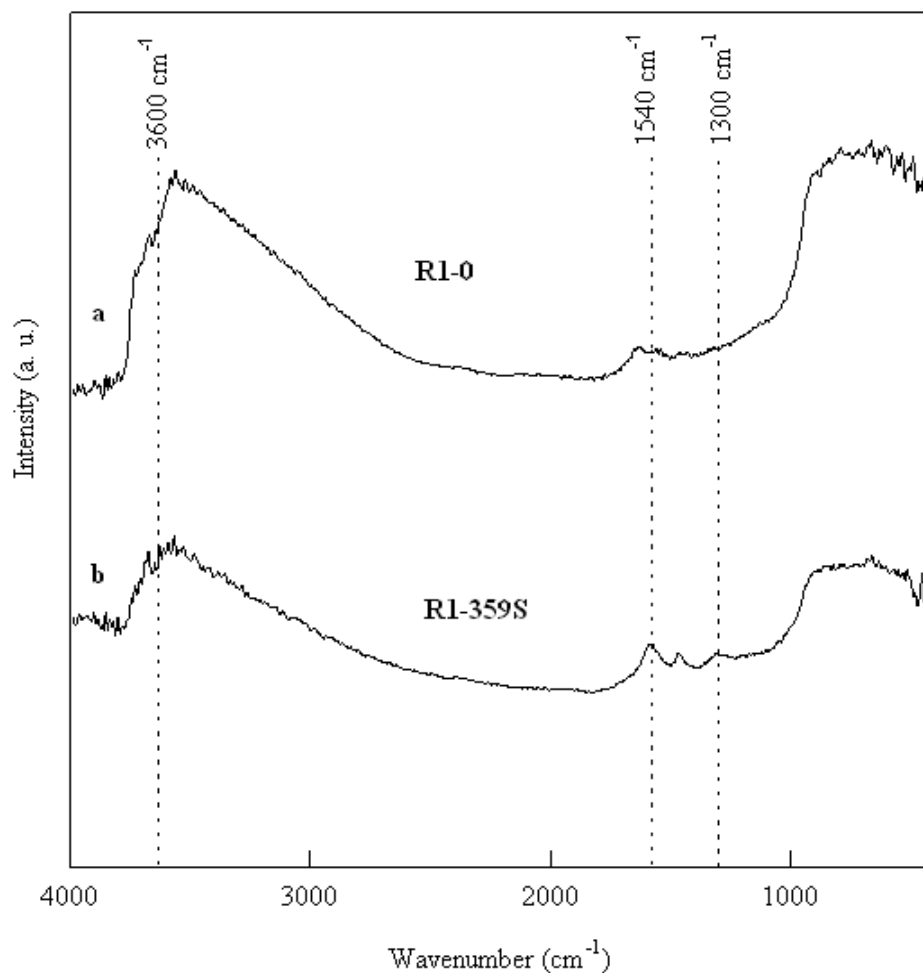


Figure 7. DRIFT spectra ($4000\text{--}400\text{ cm}^{-1}$) of Pt Re/ Al_2O_3 catalysts: a) R1 0 and b) R1 359S.

3.3 Test reaction

3.3.1 Dehydrogenation of cyclohexane over Pt/Re/ Al_2O_3

The dehydrogenation of cyclohexane over transition metals has been widely studied because of its great importance in the process of refining and petroleum reforming [14]. The dehydrogenation of cyclohexane produces benzene and it can desorb or decompose to form coke.

Specifically, the conversion of cyclohexane interaction allows us to evaluate if the interaction is between the coke with the metallic or with the acid support, because of the insensitive reaction relation with the structure of the metal particle [15]. Therefore, the relative activity of the modified catalyst by coke deposits can be related to the amount of coke deposited on the active phase. Furthermore, the selectivity is related to the type of the active phase which have deposited coke. Thus, a decrease in the values of selectivity to dehydrogenation or isomerization process, we will indicate the presence of coke on the metal or acid function, respectively.

Moreover, in Figure 8 are shown schematically the reactions concerning for the conversion of cyclohexane in the catalytic reforming under working conditions of industrial reforming, proposed by Menon et al. [16] and adapted recently by Marcos Gonzalez et al. [17].

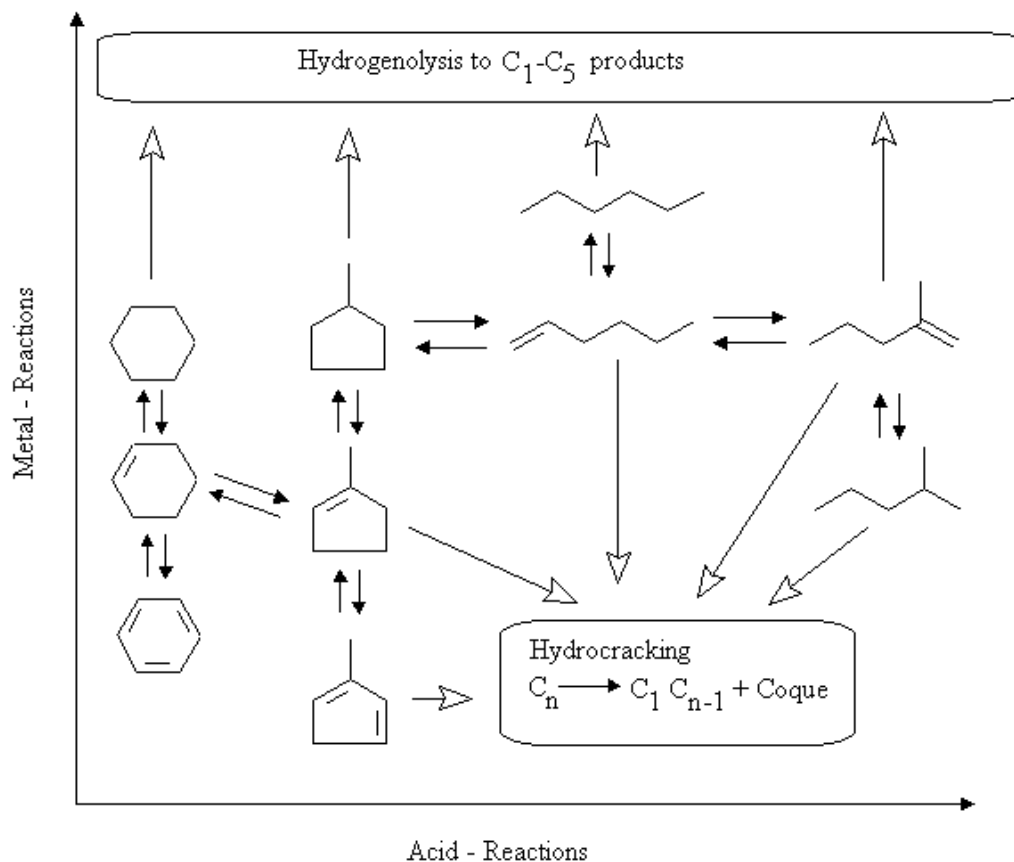


Figure 8. Conversion of cyclohexane in Catalytic Industrial Reforming [17].

The values of total conversion (X_T) and selectivity to products, reaction times of 5, 10 and 15 h are shown in the Table 2 for 673 K (temperature of reaction) in the process of conversion of cyclohexane on Pt-Re/ Al_2O_3 catalysts. They are too showed the results for 773 K in Table 3.

Except for strongly deactivated catalysts (R3-179, R3-310), no deactivation is observed or changes in the selectivity to products with the reaction time. However, in the more strongly deactivated catalysts the deactivation of the reaction is more than the 20 % (catalyst R3-310 at 673 and 773 K) and it is accompanied by a decrease of the selectivity to benzene (dehydrogenation). This result shows that in the catalysts more strongly deactivated, the produced coke in the reaction is more deposited over the metallic function (Table 2, 3).

As expected at reaction times of ≥ 2 h, there is a clear decrease in the catalytic activity (X_T) with the increasing number of days of use for the Pt catalyst in the reforming. This less activity is due to the increasing amount of coke over the catalyst. Furthermore, this decrease in catalytic activity is accompanied by a decrease in selectivity to benzene, indicating that the coke formed on the catalyst in the industrial catalytic reforming is deposited initially on the acid function (selectivity zero or near zero for isomerization processes in the catalysts less disabled) as it does on the metal function with increasing degree of activation (S_B , decreases). At this point, we must make clear that the observed decrease in selectivity to benzene and the consequent increase in the selectivity to metylcyclopentenes, along with the decrease in catalytic activity, does not in any case, an increase in catalytic activity toward isomerization processes, but only a decrease in the activity of the metal function on the processes of dehydrogenation. Thus, the results of activity and selectivity in the conversion of cyclohexane, are entirely consistent with the measures obtained in the structural analysis for catalysts Pt Re/ Al_2O_3 investigated.

Table 2. Conversion of cyclohexane (X_T , % molar) and selectivities (% molar) to methylcyclopentane (S_{MCP}), cyclohexene (S_{CHeno}) y benzene (S_B) for catalysts Pt-Re/ Al_2O_3 . ($T_{reac.}$: 673K).

t (h)	Catalyst	X_T	S_B	S_{MCP}	S_{CHeno}
5	F	82,9	99,8	0,2	0,0
	R1-0	70,0	100,0	0,0	0,0
	R1-359S	47,0	100,0	0,0	0,0
	R3-8	42,0	99,2	0,5	0,3
	R3-128	14,5	98,8	0,2	1,0
	R3-179	15,7	95,4	3,2	1,4
	R3-310	5,6	86,3	8,6	5,1
10	F	83,0	99,9	0,1	0,0
	R1-0	75,2	100,0	0,0	0,0
	R1-359S	49,6	100,0	0,0	0,0
	R3-8	40,0	99,1	0,6	0,3
	R3-128	16,9	94,9	3,8	1,3
	R3-179	12,7	98,7	0,0	1,3
	R3-310	5,8	83,5	12,1	4,4
15	F	83,2	99,8	0,2	0,0
	R1-0	66,6	100,0	0,0	0,0
	R1-359S	44,7	100,0	0,0	0,0
	R3-8	41,3	99,0	0,7	0,3
	R3-128	17,6	94,9	3,6	1,5
	R3-179	12,3	91,6	6,4	2,0
	R3-310	4,4	78,8	14,6	6,6

Table 3. Conversion of cyclohexane (X_T , % molar) and selectivities (% molar) to methylcyclopentane (S_{MCP}), cyclohexene (S_{CHeno}), benzene (S_B), methylcyclopentenes (S_{MCPeno}) and products of cracking (S_{Otros}) for catalysts Pt-Re/ Al_2O_3 . ($T_{reac.}$: 773 K).

t (h)	Catalyst	X_T	S_{MCP}	S_B	S_{CHeno}	S_{MCPeno}	S_{Otros}
5	F	92,4	0,8	98,9	0,0	0,0	0,3
	R1-0	96,6	1,3	98,7	0,0	0,0	0,0
	R1-359S	87,4	2,2	97,6	0,1	0,0	0,0
	R3-8	76,4	3,3	95,7	0,3	0,3	0,4
	R3-128	56,2	10,7	85,8	0,8	1,1	1,6
	R3-179	16,5	25,2	54,0	4,5	9,9	6,5
	R3-310	9,6	15,3	64,1	9,1	7,3	4,2
10	F	91,3	1,2	98,5	0,0	0,0	0,3
	R1-0	96,2	1,4	98,2	0,0	0,1	0,4
	R1-359S	87,7	2,3	97,6	0,2	0,0	0,0
	R3-8	76,8	3,2	96,3	0,3	0,2	0,0
	R3-128	54,9	10,1	86,5	0,9	1,1	1,4
	R3-179	14,9	24,7	53,0	4,8	10,8	6,7
	R3-310	8,4	14,8	63,4	10,4	8,1	3,3
15	F	90,9	1,5	98,1	0,0	0,0	0,4
	R1-0	95,5	1,4	98,6	0,0	0,0	0,0
	R1-359S	88,1	2,4	97,0	0,2	0,1	0,3
	R3-8	77,1	3,3	96,2	0,3	0,2	0,0
	R3-128	54,3	9,6	87,0	0,9	1,1	1,4
	R3-179	14,1	24,2	52,6	5,0	11,3	6,8
	R3-310	7,8	14,4	62,5	11,1	8,5	3,5

In the Figures 9, 10 are represented graphically, the results discussed previously for the fresh reactor and catalysts from reactor R3. Thus, there is likewise a decrease in catalytic activity and selectivity to benzene, both the increase in the degree of catalyst deactivation as the reaction time in the conversion of cyclohexane. However, some of the catalysts shows an initial increase (reaction time <2 h) of the catalytic activity with reaction time, related probably to a cleaning effect of the reactant (cyclohexane) to act as a solvent of coke deposited on the catalyst. This effect is more pronounced at higher reaction temperatures (773 K, Figure 9).

Finally, we conclude, based on the results in the conversion of cyclohexane on Pt catalysts Re/Al₂O₃ deactivated in industrial reforming process of naphtha:

The coke is deposited on the metal function both as on acid, if well, preferably on the support makes acid to use shorter times in the reforming unit.

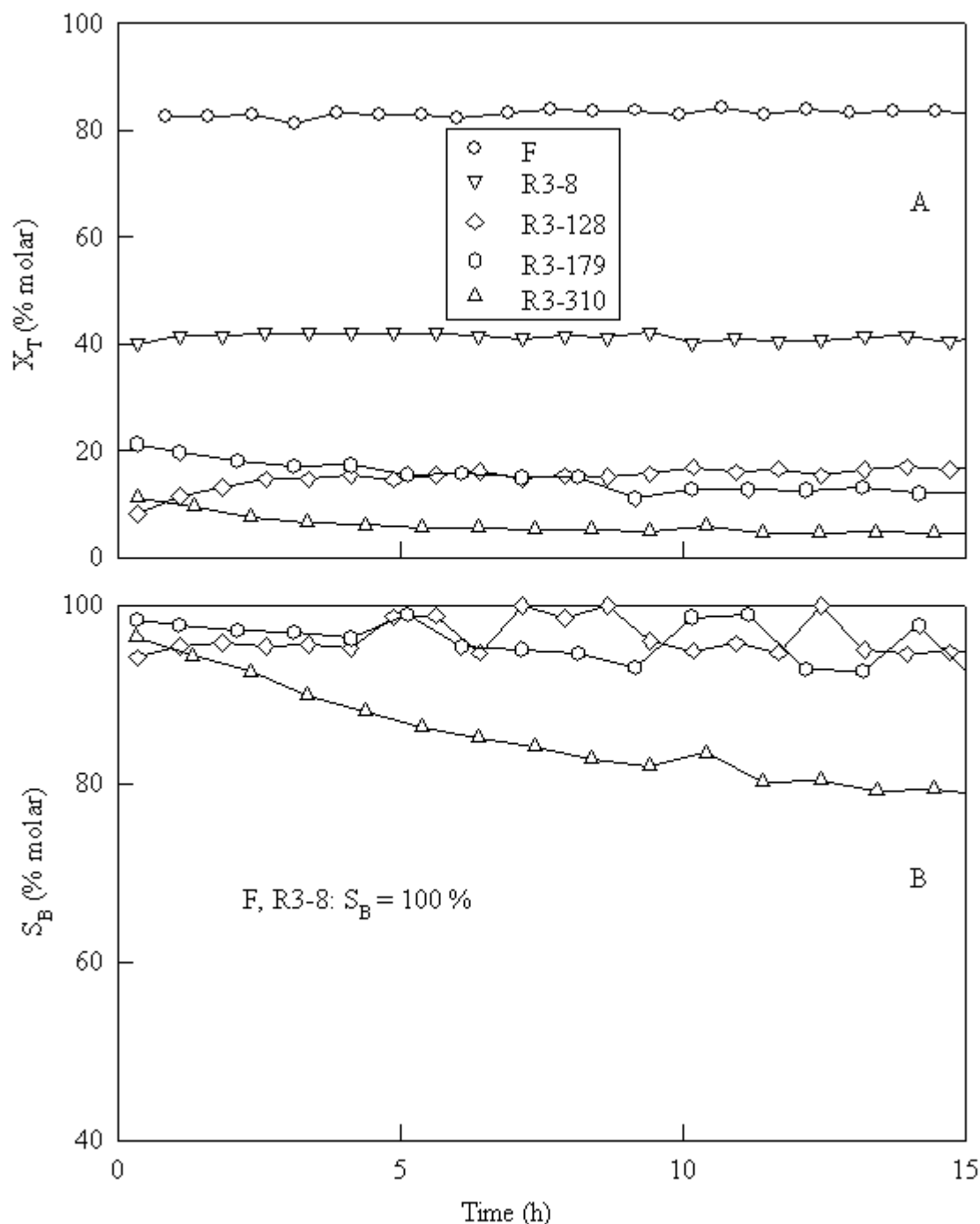


Figure 9. (A) Total Conversion (X_T) and (B) molar selectivity to benzene (S_B) for the conversion of cyclohexane (673 K) over the Pt Re/Al₂O₃ catalysts, from reactor R 3 y and fresh catalyst.

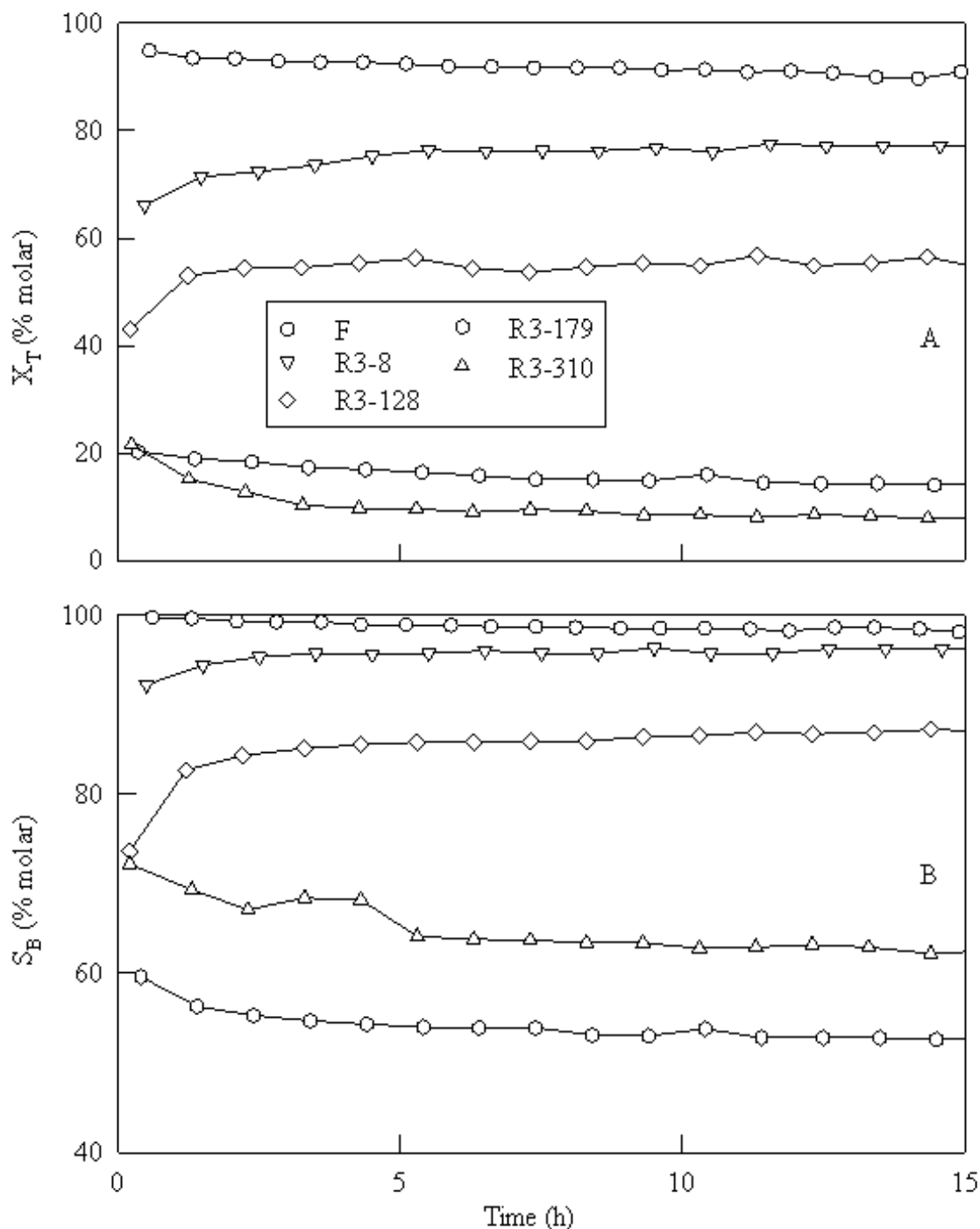


Figure 10. (A) Total Conversion (X_T) and (B) molar selectivity to benzene (S_B) for the conversion of cyclohexane (773 K) over the Pt Re/Al₂O₃ catalysts, from reactor R 3 y and fresh catalyst.

4. Conclusion

Analysis using TG-DTA experiments and mass spectrometry temperature-programmed (MS-TP) has managed to optimize the standardization procedure of the catalysts and know the nature of species adsorbed physically or chemically, and / or Pt catalysts deposited on deactivated Re/Al₂O₃.

DRIFT spectra show characteristic bands of hydrogen-poor carbonaceous species and the decrease in the intensity of the bands of the hydroxyl groups of alumina, with increasing the degree of contamination of the catalysts of the reactor R 3.

The model reactions of conversion of cyclohexane show that coke is deposited on the metal function both as the acid medium, preferably on the acid centers on the use of the catalyst periods shorter.

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