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PREPARATION, CHARACTERIZATION AND REGENERATION OF Pt-Re/Al_2O_3 NAPHTHA REFORMING CATALYSTS

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ABSTRACT

A review of some works related to preparation, characterization and regeneration of naphtha reforming catalysts, performed at the laboratories of INCAPE (Argentina) and Université de Poitiers (France) was undertaken. In the case of the preparation method the study was focused on the catalytic reduction method.

The reaction of Re deposition was performed by reduction with hydrogen adsorbed over the Pt particles of the base catalyst in two different ways. When the reaction was performed in an inert atmosphere (recharge method) the final content was limited by the maximum amount of hydrogen irreversibly adsorbed over Pt and the final Re content was small. When the reaction was performed in a H_2 atmosphere (catalytic reduction method) great amounts of Re could be deposited. The partial pressure of H_2, the temperature of reaction, the concentration and nature of the Re salt, and the dispersion of the base Pt catalyst, all of them were found to affect the kinetics and extent of Re deposition. The test reactions of cyclohexane dehydrogenation, cyclopentane hydrogenolysis and coke formation (from cyclopentane) showed that the activation of the catalysts influenced the degree of interaction between Pt and Re. It was found that calcination in air at 450 °C produces the segregation of Re, while direct reduction permits the obtention of a good Pt-Re interaction. The regeneration with O_2 diluted with N_2 adversely modified the interaction of the constituents of the metal phase and its dispersion while the regeneration with ozone at low temperature (125°C) eliminated the coke without modifying the metallic phase.

RESUMO

Uma revisão de alguns trabalhos relacionados com preparação, caracterização e regeneração de catalisadores reformas de nafta foram realizados nos laboratórios do INCAPE (Argentina) e Universidade de Poitiers (França). No caso do método de preparação o estudo foi focado no método de redução catalítica.

A reação de reposição de Re foi executada pela redução com hidrogênio adsorvido em partículas de Pt do catalizador em duas maneiras diferentes. Quando a reação foi feita em atmosfera inerte (método de recarga) o conteúdo final foi limitado pela quantidade máxima de hidrogênio adsorvido irreversivelmente sobre Pt e o conteúdo de Re final era pequeno. Quando a reação foi realizada em uma atmosfera de H_2(método de redução catalítica) grandes quantidades de Re puderam ser depositadas. A pressão parcial de H_2, a temperatura de reação, a concentração e a natureza de sal de Re, e a dispersão do catalisador de Pt, em conjunto afetaram a cinética e a extensão da deposição de Re. As reações testes de desidrogenação de ciclohexano, hidrogenólise e formação de coque (de ciclopentano) mostraram que a ativação do catalisador é influenciada pelo gráu de interação entre Pt e Re. Encontrou-se que a calcinação em ar a 450°C produz a segregação do Re, enquanto redução direta permite a obtenção de uma interação boa Pt-Re. A regeneração com O_2, diluído em N_2 modifica de forma adversa a interação dos constituintes da fase metálica a sua dispersão, enquanto a regeneração com ozone a baixa temperatura (125 °C) eliminou a formação de coque, sem modificações da fase metálica.

Keywords: Pt-Re catalysts, Cyclohexane dehydrogenation, Cyclopentane hydrogenolysis.
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INTRODUCTION

Catalytic naphtha reforming is one of the most important processes used in the industry of petroleum refining for the obtention of high octane naphthas and in the petrochemical industry for the obtention of aromatic compounds (benzene, toluene, xylenes). The catalysts used are bifunctional: they possess a metal function, Pt, usually modified by the addition of a second metal (Re, Sn, Ir, Ge, etc.), and an acid function (the support, chlorided alumina). The first bifunctional catalyst used was Pt/Al_2O_3, which was introduced in 1949 by the company Universal Oil Products [1]. The first patent concerning $Pt\text{-}Re/Al_2O_3$ catalysts appeared in 1968 [2]. Nowadays, these catalysts are most usually used due to their great stability and ease of regeneration.

The surface state of the bimetallic catalysts depends strongly on the preparation method and on the way the metal precursors are activated. The attempts for preparing these catalysts by coimpregnation are usually not reproducible. Other methods are therefore needed in order to optimize the interaction between the two metals. One of them, the method of catalytic reduction favors the deposit of the second metal on top of the first one. The mechanism is simple. The monometallic catalyst is modified by the surface reaction between the hydrogen chemisorbed over the first metal and the cation of the second metal, according to the following:

$$n\,H_{ads} + M^{n+} \longrightarrow M_{ads} + n\,H^{+} \qquad (1)$$

where:

H_{ads}: H_2 adsorbed over surface metal atoms
M^{n+}: cation of the second metal
M_{ads}: second metal adsorbed

There are two variations of the method: the "recharge" and the "catalytic reduction". In the recharge method a reaction is produced between the cation of the second metal and H_2 irreversibly chemisorbed on the first metal. The reaction of deposition is performed in an H_2-free atmosphere (e.g. N_2), and therefore the total amount of the second metal to be deposited is limited by the amount of H_2 adsorbed over the first metal (metal accessibility) and by the degree of oxidation of the second metal (the higher the state of reduction the higher the amount of consumed H_2 and the lower the amount of deposited atoms). In order to solve this problem, the salt of the second metal can be introduced in the presence of H_2. H_2 is continuously adsorbed over the first metal while it is being consumed by the reduction of the second metal. This is the basis of the "catalytic reduction" method.

The main results obtained during the study of the preparation, regeneration and characterization of $Pt\text{-}Re/Al_2O_3$ naphtha reforming catalysts prepared by the method of surface reaction are summarized in this work.

EXPERIMENTAL

Support: the catalysts were prepared by Pt-Re loading of an γ-alumina base support (CK-300, Ketjien) with the following properties: specific surface area=180 m^2/g, density of solid phase=1.11 g/cm^3, pore volume=0.49 cm^3/g, apparent density=0,65 g/cm^3.

Catalysts: H_2PtCl_6 (Aldrich, 99%), NH_4ReO_4 (Carlo Erba, 98%) and $(NH_4)_2ReCl_6$ (Aldrich, 98%) were used as metal precursors. Pt/Al_2O_3 was prepared as described elsewhere [3] and then calcined in air (450 °C, 4 h) and reduced in hydrogen (500 °C, 8 h).

During preparation by the surface reaction method a portion of reduced Pt/Al_2O_3 was immersed in an HCl 0,20 M solution. The solution was then purged by a N_2 stream in order to eliminate dissolved O_2. Then H_2 was allowed to bubble for 2 hours. A solution containing the Re salt, previously purged by N_2 stripping, was introduced in the reacting vessel under continuous H_2 bubbling. The catalyst was finally washed with distilled water, filtered and dried in a stove at 120 °C overnight. Two different methods were used for the activation. In the first one, the material was reduced in hydrogen for 8 hours at 500°C. In the second one, the catalyst was first calcined (air, 4 h, 450°C) and then reduced (H_2, 8 h, 500°C).

Characterization: the catalysts were characterized by means of the test reactions of cyclohexane (CH) dehydrogenation, cyclopentane (CP) hydrogenolysis and cyclopentane (CP) coking. The reaction conditions are detailed in Table 1. Before the test the catalysts were reduced 2 h at 500 °C. Dispersion was assessed by chemisorption of O_2 and H_2 as described elsewhere [4]. Carbon content was determined in a TPO apparatus with a TCD detector [5].

TABLE 1

Reaction condition

Reaction variables	Hydrogenolysis of CP	Dehydrogenation of CH	Coking of CP
Temperature (°C)	290	270	500
H_2 flow rate (cc/min)	64.4	80.5	30
CP flow rate (cc/h)	1.61	-	2.68
CH flow rate (cc/h)	-	1.61	-
Catalyst mass (mg)	100	30	400

Regeneration: Coke-burning reactions were either performed in diluted oxygen (2.5 % in N_2) at 450°C or with ozone at 125°C (approximately 1% in air). Ozone was generated in an equipment similar to the one decrypted by My and Sahghal [6].

RESULTS AND DISCUSSION

Preliminary assay: the amount of Re deposited was determined under different operative conditions (pH, time, Re concentration, atmosphere) in order to assess the fraction corresponding to deposition by catalytic reduction and the fraction corresponding to deposition by simple adsorption on the alumina support. Selected results [7] are detailed in Table 2. A comparison between experiments A and B shows that the type of atmosphere does not modify the amount of Re deposited on alumina. On the other side, the amount of Re retained by the alumina is small compared to that present in the solution (theoretical Re percentage corresponding to complete deposition) and decreased when the amount of Re in solution was also decreased (experiments B and C). When the pH of the solution was increased from 3.54 to 7.50, the Re deposit over alumina diminished (experiments B and D). This trend is in accord with the isoelectric point of alumina that prevents the adsorption of anions at pH values greater than 7. At low pH values, ReO_4^- can be exchanged on the surface of alumina due to favorable electrostatic adsorption. The amount deposited also augmented slightly at reaction times between 30 and 60 min (experiments E and F). Comparison of experiments A and F show that in an inert atmosphere, Pt does not favor the deposition of Re and that its presence decreases the amount of Re deposited. Most probably Pt chemisorbs on the support and decreases the amount of sites accessible to Re.

The results of the previous assay can be summarized as follows: the amount of Re able of being deposited on the support is small if compared to the total content of the solution and it can be adjusted by means of a careful regulation of the reaction conditions.

TABLE 2

Re content on different supports as a function of the conditions of operation [7]

Experiment	Atmosphere	Support	Time (min)	pH	Re Theoretical (%)	Re Deposited (%)
A	N_2	Al_2O_3	30	3.54	5.00	0.44
B	H_2	Al_2O_3	30	3.54	5.00	0.46
C	H_2	Al_2O_3	30	3.54	0.10	0.02
D	H_2	Al_2O_3	30	7.50	5.00	0.15
E	N_2	Pt/Al_2O_3	60	2.50	5.00	0.38
F	N_2	Pt/Al_2O_3	30	2.50	5.00	0.35
G	H_2	Pt/Al_2O_3	30	2.50	5.00	2.70

Re deposition by the recharge method: the amount of Re deposited by this technique is mainly due to reduction of the salt by the hydrogen irreversibly adsorbed over Pt. The maximum amount that could be deposited in one step over 0.6% Pt/Al_2O_3 (56 % de dispersion) is 0.048% in the case of the Re^{7+} salt and 0.084% for the Re^{4+} salt (Table 3) [7]. Therefore, it is necessary to increment the number of recharges in order to obtain meaningful amounts of Re, like those present in commercial catalysts (1 ≤ Re/Pt ≤ 2). The values of Table 3 also show that it is possible to deposit Re by successive recharges. In any case the amounts are inferior to the theoretical ones, specially in the case of Re^{7+}.

TABLE 3

Percentage of deposited Re as a function of the number of charges [7]

Number of charges	NH_4ReO_4 Theor.	NH_4ReO_4 Depos.	$(NH_4)_2ReCl_6$ Theor.	$(NH_4)_2ReCl_6$ Depos.
1	0.048		0.084	0.08
2			0.168	0.14
3	0.144	0.12		
4			0.336	0.25
6	0.288	0.20	0.504	0.34
8			0.672	0.42
9	0.432	0.20		
13	0.624	0.23		

Deposition of Re by catalytic reduction: in order to solve the problem of the scarce deposition of Re by the method of the recharge, the exchange was performed with continuous supply of H_2. It was verified [7] that Re^{4+} y Re^{7+} salts used in this work are not reduced by H_2 dissolved in the solution because the reduction potential of Re is superior to that of H_2. Comparing the amount of Re deposited on different samples (Al_2O_3, Re/Al_2O_3, Pt/Al_2O_3) an important catalytic effect of Pt over the deposition of Re can be clearly seen (Table 2, experiments D, E y G).

Figure 1 shows the variation of the Re content as a function of time for different initial Re concentrations [7]. A rapid initial deposition of Re can be seen but the deposition rate between 5 and 30 minutes is slower. The amount of Re deposited increased with the concentration of Re in the impregnating solution. The amounts deposited at 30 min are lower than the theoretical ones. In this case it must be pointed out that the number of deposited Re atoms was always superior to the number of surface Pt atoms. The little amount of Re deposited over alumina and the fact that Re poorly catalyzes its own reduction (see Table 2) indicate that a portion of Pt atoms is still accessed by H_2 after Re loading. If this were not the case the amount of Re would be limited to a monolayer. One possible explanation to the effect is that Re accumulates over some sites of Pt and/or the interphase between Pt and Al_2O_3.

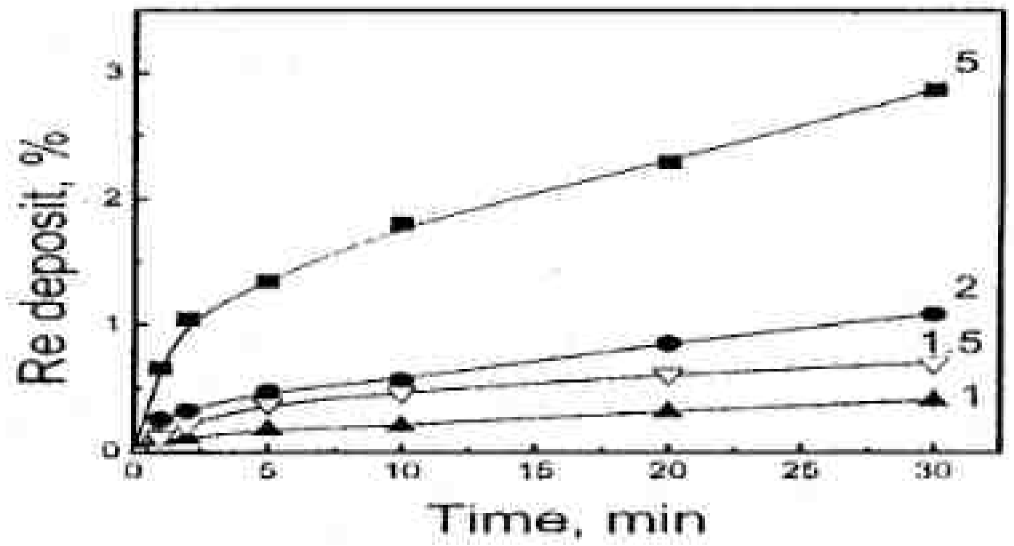

FIG. 1 - *Re deposit (in weight) as a function of reaction-time for different concentrations of Re in solution [7].*

Figure 2 shows the evolution of deposited Re as a function of time, for two different Re precursor salts, Re^{7+} (NH_4ReO_4) and Re^{4+} ($(NH_4)_2ReCl_6$), and two different values of hydrogen partial pressure (1 atm, 0.10 atm). Comparing the values for Re^{7+} and Re^{4+} it can be seen that for the same reaction time, the Re content is greater for Re^{4+} than for Re^{7+}. The difference in reaction rate is in accord with the amount of H_2 needed for the reduction of each salt. Comparison of the curves at 1 atm and 0.1 atm shows that the diminution of the H_2 partial pressure leads to a decrease in the Re deposition rate. This may indicate that the reaction rate is limited by the rate of diffusion of H_2 from the solution to the Pt interface. These and the previous results stress the important role played by the H_2 adsorbed over Pt in the deposition of Re. The little difference in the initial deposition rate of Re at 1 and 0.1 atm can be explained by the existence of a initial stage of H_2 accumulation before the deposition of Re, which can take place during the 2 h H_2 bubbling step before the introduction of the Re salt.

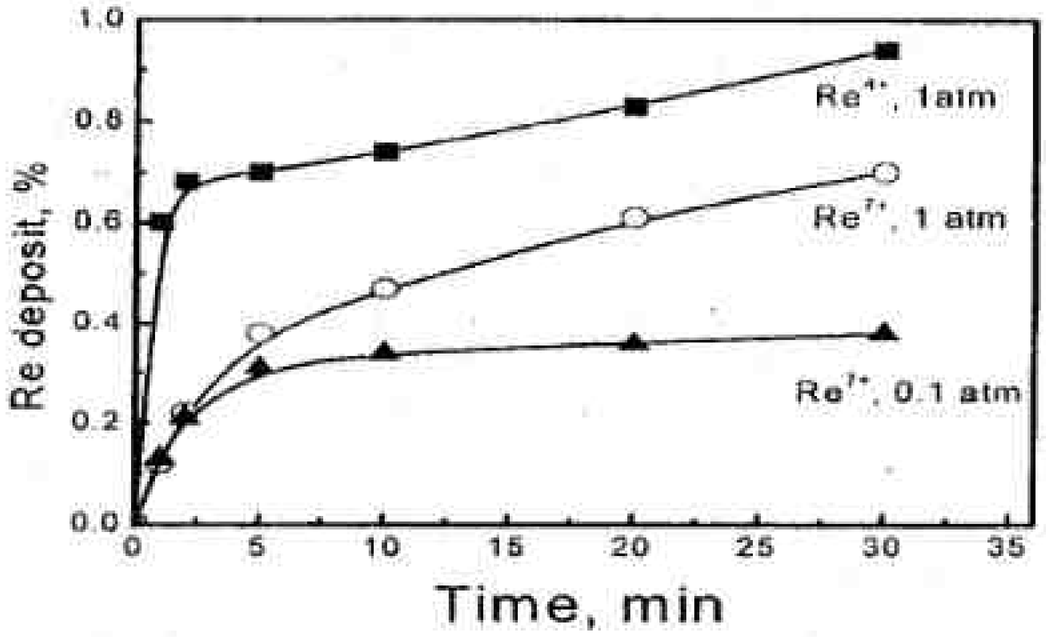

FIG. 2 - *Re deposit (in weight) as a function of reaction-time for different Re salts and pressure of hydrogen [7].*

The variable-temperature Re deposition experiments showed that the initial deposition rate increases with temperature and that at 30 min the Re deposit formed at 20°C is bigger than those obtained at 50 and 80°C. The increase in the initial rate with the temperature can be explained considering a greater mobility of H_2 over the Pt surface at high temperatures (it must be recalled that 7 hydrogen atoms are needed to reduce one Re atom). The relation between the amounts loaded at 30 min reaction-time would be related to the lower solubility of H_2 in aqueous medium at high temperatures.

Another effect is that of Pt dispersion. The initial rate of deposition per atom of accessible Pt, increases with the crystal size, indicating that the reaction of catalytic reduction of ReO_4^- is structure sensitive. The reaction rate increases over big particles. The sites preferred for reaction would be the planes (with atom with high coordination) rather than the edges and corners (with atoms of low coordination).

The curves shown in Figure 3 indicate that the amount of Re deposited by catalytic reduction reaches a maximum for an optimum amount of acid [8]. The reaction of total reduction of ReO_4^- (see equation 2) dictates that the pH decreases the rate of Re deposition must increase. However a maximum in the amount of deposited Re is found and the effect was consistently repeated for same molar concentration independently of the acid used. The drop in the amount of deposited Re at high concentrations of acid could be explained in terms of a strong adsorption of Cl^- and NO_3^- ions over Pt, thus inhibiting the adsorption of H_2, or over the support (inhibiting the approach of the ReO_4^- ions). Another possible explanation is that perrhenic acid is formed, which is more difficult to reduce than ReO_4^- [8].

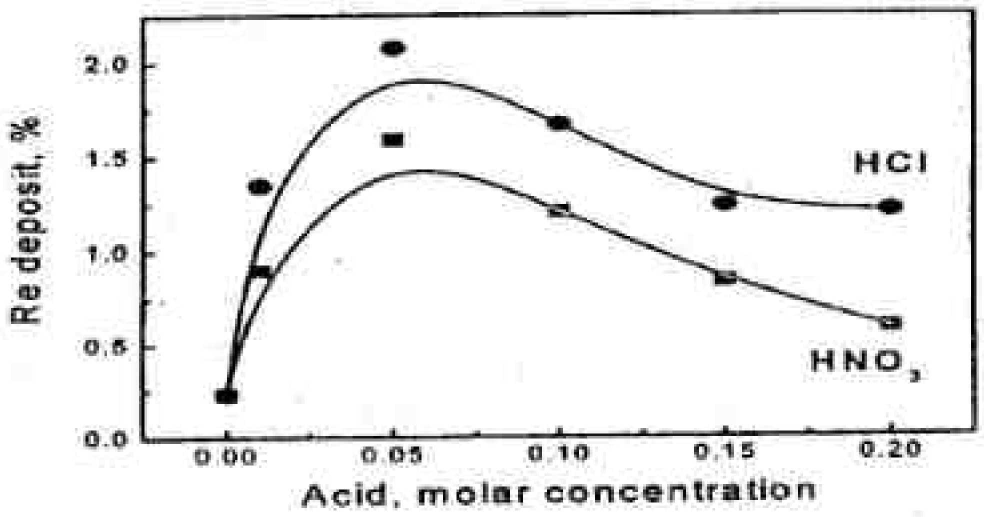

FIG. 3 - *Re deposit (in weight) as a function of the concentrations of the mineral acid in the mother solution (before introduction the Re salt) [8].*

$$7\,(\text{Pt-H} \longrightarrow \text{Pt} + H^+ + e^-)$$
$$ReO_4^- + 8H^+ + 7e^- \longrightarrow Re^\circ + 4\,H_2O$$

$$7\,\text{Pt-H} + ReO_4^- + H^+ \longrightarrow 7\,\text{Pt} + Re^\circ + 4\,H_2O \qquad (2)$$

Figure 4 contains values of conversion of CP at 5 min time-on-stream for the reaction of hydrogenolysis of CP [9]. It can be seen that at equal Re percentages, the catalysts activated by direct reduction possess a hydrogenolytic activity superior to that of the catalysts activated by calcination-reduction. The reaction of hydrogenolysis is a demanding one, and in the case of Pt and Re there exists a synergic effect. The heat of adsorption of the precursors of hydrogenolysis over an ensemble of Pt atoms have a low heat of adsorption, but this will be fairly high in the case of the ensembles of pure Re and will have an intermediate value in the case of the ensembles of Pt-Re. For this reason a Pt-Re ensemble have higher hydrogenolytic activity and the conversion in this reaction can be taken as an indirect measure of the Pt-Re interaction [10]. The destruction of the Pt-Re interaction is addressed to the formation of oxychlorinated species of Pt and Re during the calcination. These species would be strongly bonded to alumina and would not be able to migrate and be correduced [11].

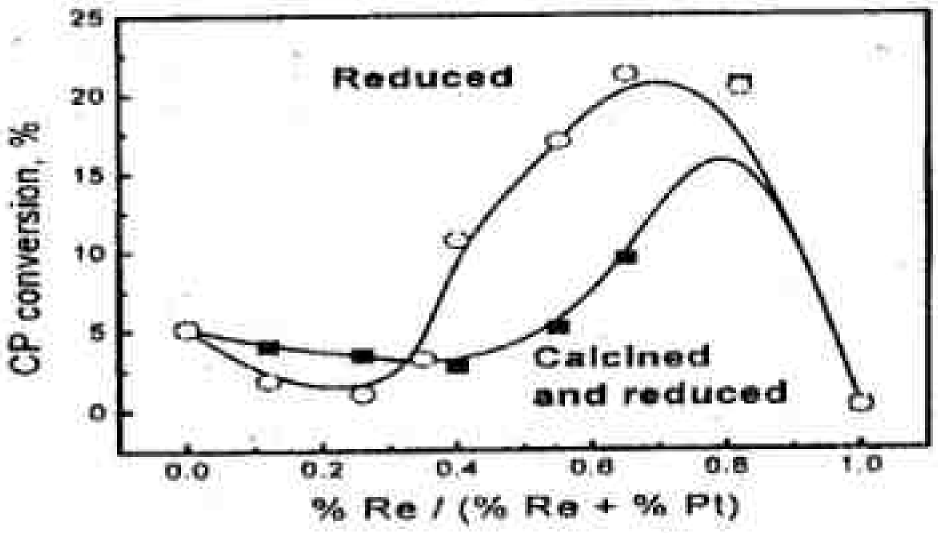

FIG. 4 - *CP conversion in hydrogenolysis reaction as a function of Re content for the calcined-reduced and the reduced catalysts [9].*

In Figure 5 we can see that the activities in CH dehydrogenation are high for the catalysts activated by calcination-reduction and low for the catalysts activated by direct reduction [9]. These results are in accord with the results of metal dispersion (not presented) and the previous results of Figure 4 just discussed. The greater metal accessibility of the catalysts activated by calcination-reduction is likely caused by the calcination at 450 °C which leads to the formation of oxychlorinated compounds of Pt and Re strongly bonded to alumina. Migration necessary for correduction is therefore impeded and therefore the formation of big "bimetallic crystals" is inhibited [11].

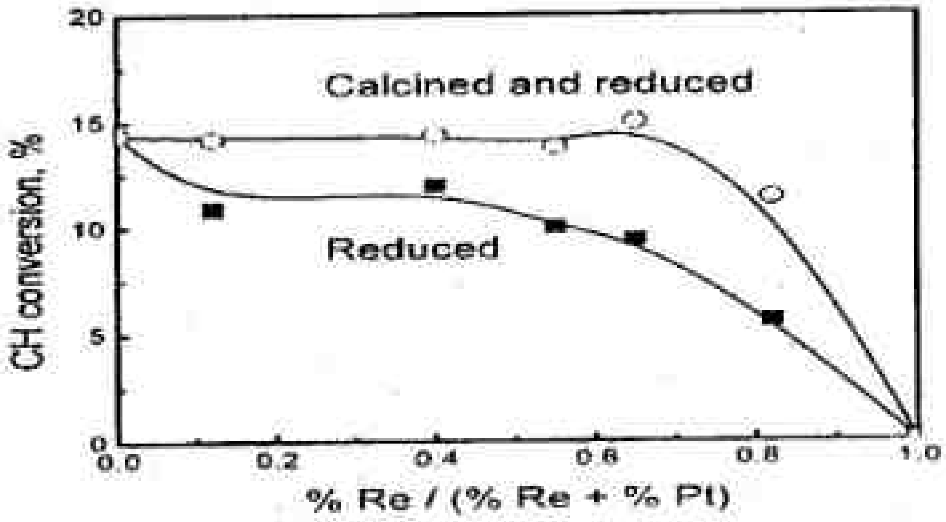

FIG. 5 - *CP conversion in dehydrogenolysis reaction as a function of Re content for the calcined-reduced and the reduced catalysts [9].*

The effect of pressure on the coking reaction over the sulfided catalysts was also studied [12]. Some the results are indicated in Table 4 being the reaction performed at 1 and 15 atm. At 15 atm, the amount of coke deposited was fairly similar on the catalysts activated by calcination-reduction and on those activated by direct reduction. However, the detrimental effect of the coke as measured by the reaction of CH dehydrogenation was lower for the catalysts activated by direct reduction. At atmospheric pressure, the catalysts activated by direct reduction have a smaller coke deposit than those activated by calcination-reduction [12,13]. Deactivation of the bifunctional catalysts is a consequence of the deposition of coke over the acid function and over the metallic one. Coke formation is a complex phenomenon because the metal promotes the formation of coke by producing dehydrogenated compounds and at the same time we can eliminate coke precursors by means of the hydrogenolysis reaction [14]. The results presented here showed that deactivation strongly depends on activation conditions [12].

Values of conversion of CP for the catalysts regenerated with air and ozone can be seen in Figure 6 (data from [15]). As indicated by the extent of hydrogenolysis we can see that the regeneration with ozone (performed at 125 °C) does not destroy the Pt-Re interaction and conversely this interaction is destroyed to a great extent by oxygen treatment at high temperatures (450 °C). Figure 7 [16] contains results of activity in dehydrogenation of CH for the catalysts activated by direct reduction and regenerated partially with oxygen or ozone, as a function of the percentage of remaining coke. Catalysts regenerated with O_3 recover the activity proportionally to the amount of eliminated coke thus indicating that coke is not selectively eliminated. Conversely for the catalysts regenerated with O_2 the elimination of coke is selective because a little elimination of coke produces a great recovery of the metal activity [15-18].

TABLE 4

Sulfided catalysts. % carbon deposited at 15 atm and conversion values of CH [12]

X	%C	CH	CH(1)	Activation
0.50	0.12	12.2	2,19	Reduction
0.50	0.14	15.0	1.65	Calcination-reduction
0.61	0.12	10.0	1.60	Reduction
0.61	0.10	12.8	1.41	Calcination-reduction
0.67	0.12	9.4	2.16	Reduction
0.67	0.11	15.0	1.80	Calcination-reduction
0.00	2.47	14.4	0.10	Monometallic (Pt)

X: %Re / (%Re + %Pt);

CH - dehydrogenation of CH, fresh catalyst;

CH(1) - dehydrogenation of CH, coked catalyst.

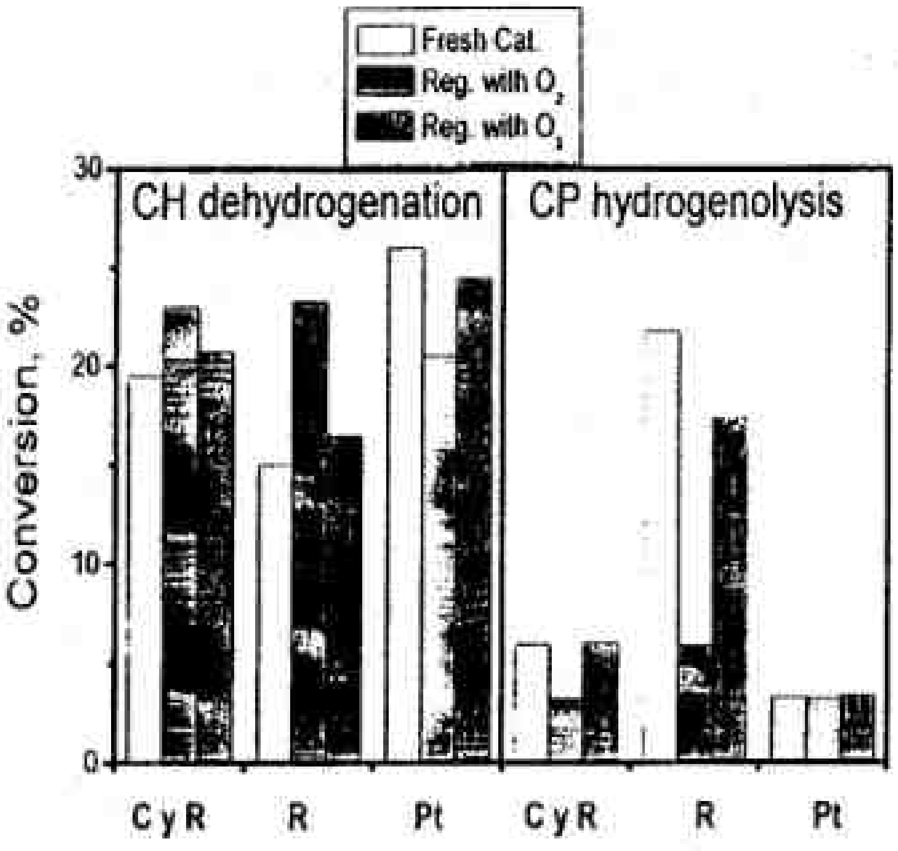

FIG. 6 - *CP and CH conversion of fresh and regenerated catalysts activated by direct reduction and by calcination-reduction [15].*

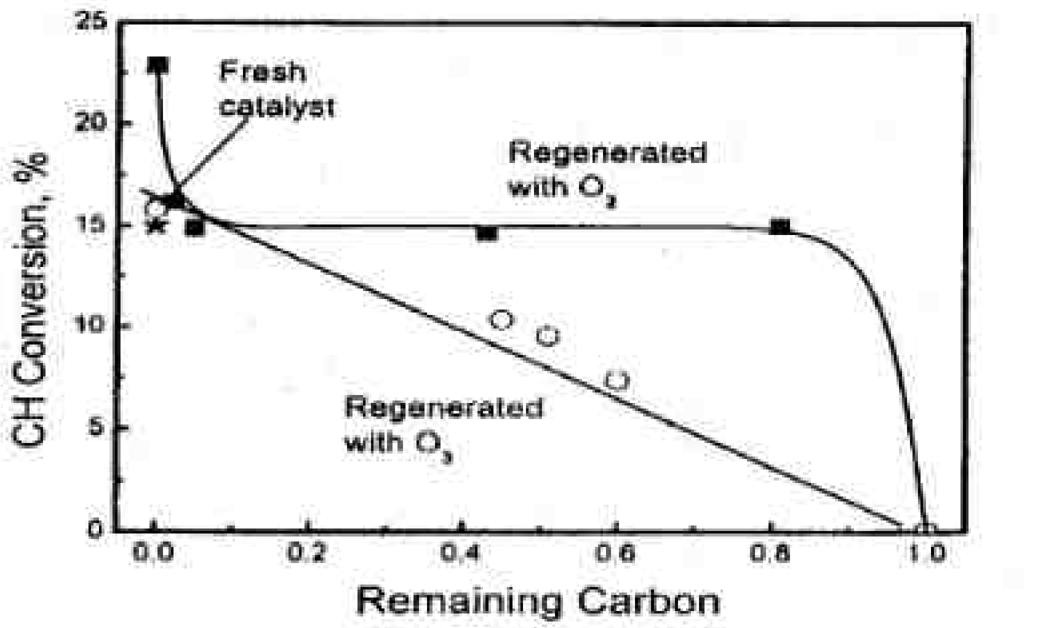

FIG. 7 - *CH conversion as a function of the coke remaining on the catalyst surface. Catalyst regenerated with oxygen and ozone [16].*

CONCLUSIONS

-From the inspection of the results found it can be concluded that multiple charges are necessary in order to obtain high Re contents like those found in commercial catalysts (1 < Re/Pt < 2) if recharge method is used. The method of catalytic reduction enables to obtain catalysts with a strong Pt-Re interaction and in only one step of preparation.

-Calcination in air (450°C) leads to catalysts with lower Pt-Re interaction.

-Catalysts with a high Pt-Re interaction are more resistant to deactivation by coke at atmospheric pressure and at high pressure.

-Regeneration with oxygen partially destroys the Pt-Re interaction and is selective: the coke on the metal is burned first. Regeneration with ozone is not selective and permits to recover the activity with noticeable modifying the Pt-Re interaction..

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REFERENCES

1. V. Haensel, 1969. U.S. Patents, 2, 479, 109 and 2, 479, 110.
2. H. E. Kluksdahl, 1968. U.S. Patents, 3, 415, 737.
3. J. Barbier, P. Marecot & C. L. Pieck, Catalyst Deactivation 1997, C. H. Bartholomew & G. A. Fuentes (Eds), Studies in Surface Science and Catalysis, 1997 Elsevier Science B.V., vol. III, pp. 327.
4. C. L. Pieck, M. B. González & J. M. Parera, 2000. XVII Simp. Iberoam. Catal., Porto, Portugal.

5. J. Barbier, E. Churin & P. Marécot, 1987. Bull. Soc. Chim. France, N° 6.

6. N. L. My & P. N. Sahghal, 1989. Chem. Eng. J. 40, 15.

7. C. L. Pieck, P. Marécot & J. Barbier, 1996. Appl. Catal. A: General 134, 319.

8. C. L. Pieck, P. Marécot & J. Barbier, 1996. Appl. Catal. A: General 143, 283.

9. C.L.Pieck, P.Marécot, J.M. Parera & J. Barbier, 1994. Actas XIV Simp. Iberoam. Catal., Concepción, Chile, Vol I, pp. 263.

10. S. M. Agustine & W. M. H. Sachtler, 1987. J. Catal. 106, 417.

11. P. Malet, G. Munuera & A. Caballero, 1989. J. Catal. 115, 567.

12. C. L. Pieck, P. Marecot & J. Barbier, 1996. Appl. Catal. A: General, 145, 323.

13. C. L. Pieck, C.A. Querini, J. M. Parera, P. Marecot & J. Barbier; 1995. Appl. Catal. A: General 133, 281.

14. P. Marécot & J. Barbier, 1995. "Catalytic Naphtha Reforming. Science and Technology", G. J. Antos et al. (eds) Marcel Dekker, New York, p.279.

15. C. L. Pieck & J. M. Parera, 1997. Catalyst Deactivation, C. H. Bartholomew & G. A. Fuentes (Eds), Stud. Surf. Scie. and Catal., 1997, Elsevier Science B.V., vol. III, pp. 433

16. C. L. Pieck, C. A. Querini & J. M. Parera, 1997. Appl. Catal. A: General 165, 207.

17. C.L.Pieck, E.L.Jablonski & J.M.Parera, 1993. Proc. 10th Inter. Congress on Catal., Budapest, Hungary, L.Guzci et al.(Eds), Elsevier Scie Pu B.V., Vol.III, pp. 2535.

18. C.L.Pieck, E.L.Jablonski & J.M.Parera, 1991. Appl. Catal. 70, 19.