

Total metallic dispersion of sulfided Pt-Re/Al₂O₃ naphtha reforming catalysts

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Abstract

Catalysts with Pt, Re and Pt-Re supported on γ alumina were prepared by impregnation or catalytic reduction methods. The activation was performed by calcination–reduction or only direct reduction treatment. These catalysts and a commercial one were sulfided with H₂S at 500°C and characterized by chemical analysis, TPR, test reactions (cyclohexane dehydrogenation and cyclopentane hydrogenolysis), chemisorption of H₂ and O₂ and TEM. The test reactions were affected by S according to the interaction Pt-Re and metallic dispersion of the catalysts, which are functions of the preparation technique. The presence of S inhibits H₂ chemisorption, which cannot be used as a measure of the metallic dispersion. Nevertheless, sulfidation or Pt-Re alloying does not affect the O₂ chemisorption and this chemisorption can be used to calculate the total (Pt+Re) metallic dispersion with a stoichiometry ratio Pt or Re/O equal to 1. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Supported bimetallic catalysts have received considerable attention since the arrival of Pt-Re/Al₂O₃ catalysts to the market around 1968 [1,2]. The addition of a second metallic element such as Re or Sn greatly improved the stability and selectivity of traditional Pt/Al₂O₃ reforming catalysts. In the case of Re as promoter, such improvement is achieved only after passivation with S, which decreases the strong hydrogenolysis activity of Pt-Re ensembles [3]. Sulfur compounds normally present in the naphtha processed at commercial reforming units are converted to H₂S which is partially adsorbed on the catalyst metallic sites. S is more strongly adsorbed on Re than on Pt

[4,5]. The amount of S retained on the metallic function depends on both H₂S partial pressure and temperature, with an equilibrium relationship. S adsorption increases as P_{H₂S} increases and temperature decreases.

At the end of each operational cycle, the feed rate to the reforming unit is reduced so the HDS unit performs better and the amount of H₂S incoming to the reformer levels down. Some of the S adsorbed on the metals is then desorbed due to the equilibrium relationship already mentioned. After feed shutdown, hydrogen is circulated through the reformer causing a further S desorption. Chlorine is optionally added during this hydrogen treatment in order to enhance S desorption and increase the chlorine content of Al₂O₃ to avoid excessive SO₄²⁻ formation during the subsequent coke burning procedure. During this regeneration step S deposited onto the metals is removed as SO₂ and partially oxidized to SO₃ which readily reacts with Al₂O₃ to form Al₂(SO₄)₃. Low oxygen

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levels in the oxidative atmosphere avoid excessive SO_3 (and consequently SO_4^{2-}) formation. The presence of Cl in the support also decreases sulfate formation, as mentioned before, and the blocking of the Al_2O_3 sites.

During the subsequent step of regeneration (namely oxychloration and performed to redisperse the metal) the presence of Cl and H_2O in the circulating gases can also displace some of the previously formed SO_4^{2-} . Nevertheless, some sulfur remains as $\text{Al}_2(\text{SO}_4)_3$ at the end of the regeneration cycle.

Before reformer start-up, the oxidized metals must be reduced with H_2 . Some of the SO_4^{2-} on Al_2O_3 is also reduced to H_2S which in turn readily adsorbs onto the reduced metals [6], mainly on Re. Such $\text{SO}_4^{2-}/\text{H}_2\text{S}$ migration cycle makes the complete removal of S from the catalyst almost impossible. Barbier et al. [7] studied the determination of metal surface areas using unsulfided Pt-Re/ Al_2O_3 catalysts. It was found that oxygen chemisorption at room temperature may be used to calculate the total (Pt+Re) metallic dispersion. Hydrogen chemisorption at room temperature was found to occur only on accessible Pt atoms, being a measure of free Pt atoms (not alloyed to Re).

The presence of S on metal atoms hinders the chemisorption of H_2 . Pieck et al. [8] studied sulfided catalysts (0.02 and 0.07% S) that were regenerated and reduced with H_2 at 500°C and a measurable chemisorption of oxygen was observed.

Most of the research published in the open literature points out the impossibility of measuring metallic dispersion by chemisorption in Pt-Re/ Al_2O_3 catalysts due to S blocking of the metallic sites. A chemisorption technique to determine the metallic dispersion of such catalysts is presented in this work.

2. Experimental

2.1. Support

Catalysts were prepared starting from a extruded commercial sample of gamma alumina with $180\text{ m}^2/\text{g}$ of surface area, a total porous volume of $0.50\text{ cm}^3/\text{g}$, porosity 55% and 0.3 ppm S. This support was ground and then sieved in order to retain those particles with sizes between 35 and 80 mesh.

2.2. Pt and Re monometallic catalyst

A certain amount of the support was dipped in a solution of HCl 0.2 M. After the addition of the desired amount of a solution of the precursor salt, Pt (H_2PtCl_6) or Re (NH_4ReO_7), the sample was slowly evaporated. The catalyst was then oven dried at 120°C overnight. Finally, it was activated by calcining in flowing air at 450°C for 4 h and then reduced with flowing H_2 at 500°C for 8 h.

2.3. Bimetallic Pt-Re catalysts

They were prepared by the catalytic reduction methods [9,10]. The deposition of the second metal is performed in the presence of hydrogen. A known amount of the prerduced monometallic Pt/ Al_2O_3 catalyst was introduced into a closed vessel and covered with a solution of HCl 0.2 M. A nitrogen stream purged the solution in order to eliminate the dissolved oxygen and then hydrogen bubbling was done for 2 h. The necessary quantity of the Re salt (NH_4ReO_4) was introduced into another vessel and purged by bubbling nitrogen; then, this Re solution was transferred to the first vessel and left to react for 1 h. Solids were then filtered and washed. After heating in an oven at 120°C overnight, the sample was activated by two thermal treatments: one part was directly reduced (H_2 , 8 h, 500°C) and the other was first calcined (air, 4 h, 450°C) and then reduced (H_2 , 8 h, 500°C). In all cases, a solution of HCl 0.2 M and a base Pt/ Al_2O_3 catalyst with 0.30% Pt and 1.0% Cl were used.

2.4. Commercial catalysts

A trilobe unsulfided and nonreduced commercial catalyst with $192\text{ m}^2/\text{g}$ of surface area and $0.42\text{ cm}^3/\text{g}$ of pore volume was ground to 35–80 mesh and its composition can be seen in Table 1.

2.5. Catalyst sulfidation

It was performed in a continuous flow reactor at atmospheric pressure using a flowing mixture of 1% H_2S in H_2 at 500°C for 2 h. After this treatment, catalyst samples were maintained under pure hydrogen flowing at 500°C for 5 h in order to eliminate all the S reversibly adsorbed. Non-sulfided catalysts were

Table 1
Chemical composition of the catalysts and preparation methods

Catalysts	Preparation methods	Activation	Pt (%)	Re (%)	S (%)
1	Impregnation	Calcination–reduction	0.30	0.00	0.000
1-S	Impregnation	Calcination–reduction	0.30	0.00	0.014
2	Impregnation	Calcination–reduction	0.00	0.59	0.000
2-S	Impregnation	Calcination–reduction	0.00	0.59	0.020
3	Catalytic reduction	Reduction	0.30	0.58	0.000
3-S	Catalytic reduction	Reduction	0.30	0.58	0.024
4	Catalytic reduction	Calcination–reduction	0.30	0.58	0.000
4-S	Catalytic reduction	Calcination–reduction	0.30	0.58	0.035
5	Commercial	Calcination–reduction ^a	0.27	0.28	0.001
5-S	Commercial	Calcination–reduction ^a	0.27	0.28	0.011

^a Calcined in commercial preparation and reduced in laboratory.

treated with H₂ at 500°C for 7 h in order to reproduce as closely as possible the procedure used for sulfided catalysts.

2.6. Test reactions

The dehydrogenating properties were assessed by the test reaction of dehydrogenation of cyclohexane. This reactant was injected in a hydrogen stream, temperature of reaction=270°C; WHSV=10 h⁻¹; H₂/HC=30, mass of catalyst=30 mg and atmospheric pressure. The hydrogenolysis capacity was tested by cyclopentane hydrogenolysis at 290°C; WHSV=5.3 h⁻¹; H₂/HC=10, mass of catalyst=100 mg and atmospheric pressure. Previously to the test reactions, the catalysts were reduced at 500°C for 2 h.

2.7. Temperature-programmed reduction

TPR diagrams were recorded in an Ohkura TP-2002 S. All samples were previously oxidized with oxygen (2% in argon) at 400°C. At lower oxidation temperatures hydrogen uptake signals were low due to an incomplete oxidation of the metallic particles. On the other hand, higher oxidation temperatures would favor a great segregation of the metal oxides. The reducing gas was hydrogen (4.8% in argon) and the temperature ramp was 10°C/min.

2.8. Metallic dispersion

Metal accessibility was determined by selective chemisorption (O₂ and H₂). Chemisorbed amounts

were measured by static volumetry using a Micromeritics Accusorb 2100 equipment with an attainable vacuum level of ca. 10⁻⁵ mmHg. Degassing and H₂ reduction temperatures were performed at 500°C and the double isotherm method was used for H₂ and the chemisorption for O₂.

2.9. TEM

Supported metal particles were observed in a Jeol Model JEM-1200 EX II operated at 100 kV and the samples were prepared by extractive replica.

3. Results and discussion

The experimental techniques we used for metallic phase characterization of Pt-Re/Al₂O₃ catalysts were the chemical analysis, test reactions (dehydrogenation and hydrogenolysis), temperature programmed reduction (TPR) and chemisorption of probe molecules (metal accessibility).

3.1. Chemical composition

The chemical composition of catalysts used in this work are shown in Table 1. It must be pointed out that after the reduction treatment with H₂ at 500°C, that is the final part of the sulfidation procedure, only strongly bounded S remains on the metallic phase. This is due to the total elimination of reversibly adsorbed H₂S and the adsorption on Al₂O₃ is totally reversible [11,12]. It can be observed that monometallic catalysts retain

lower amounts of S than the bimetallic ones, being the S retention for Re/Al₂O₃ higher than for Pt/Al₂O₃. The bimetallic catalyst activated by direct reduction (3-S) retain lower S amounts than the one activated by calcination–reduction (4-S).

3.2. Metallic phase characterization by catalytic activity tests

Conversion values for cyclohexane and cyclopentane test reactions are presented in Table 2. It can be seen that the bimetallic catalyst prepared in the laboratory that was only reduced has a higher activity for CP hydrogenolysis than the one calcined and reduced. In the catalysts with Pt and Re, there is a synergetic effect related to the heat of adsorption of the hydrogenolysis precursors over the ensembles. An ensemble containing both Re and Pt would have a higher hydrogenolytic activity than ensembles with only one metal [13]. Therefore, the lower activity of the calcined and reduced catalysts can be explained considering that, during the calcination step the Pt-Re ensembles were destroyed or their formation was inhibited. These results are in accordance with previous findings [9,10,14].

It can also be seen in Table 2 that the bimetallic catalyst that was calcined and reduced have a greater cyclohexane dehydrogenating capacity than the catalyst which was only reduced. This could be due to the fact that the calcination, while inhibiting Pt-Re interaction, also leads to a larger metallic dispersion, mainly of segregated Pt. The comparison between catalytic activities of sulfided and unsulfided catalysts

in Table 2 indicates that the presence of S is more harmful for cyclopentane hydrogenolysis than for cyclohexane dehydrogenation, as it could be expected because S adsorption destroys the big metallic ensembles. The reaction of hydrogenolysis is a demanding reaction [15], i.e. it needs big metallic ensembles in order to proceed, while dehydrogenation is a non-demanding reaction and its deactivation is proportional to the number of Pt atoms deactivated.

3.3. Characterization by TPR

TPR spectra for Pt/Al₂O₃ and Re/Al₂O₃ are shown in Fig. 1. A small reduction peak at about 130°C followed by a broader main peak centered at 230°C were observed for Pt/Al₂O₃. Size and position of the reduction peaks depend on crystallite size and strength of metal/support interaction. The reduction of Re oxide begins at about 400°C, with a sharp major peak at 480–490°C and a broader minor peak at 600°C.

The location of reduction peaks for Pt-Re/Al₂O₃ catalysts depends on the degree of interaction between Pt and Re. The influence of the type of activation method (calcination–reduction or direct reduction) employed is shown in Fig. 2 for a Pt-Re/Al₂O₃ catalyst prepared by catalytic reduction and activated using both activation procedures. The catalyst activated by calcination–reduction, with a moderate degree

Table 2
Activity of the catalysts previously reduced at 500°C

Catalysts ^a	CH dehydrogenation (%)	CP hydrogenolysis (%)
1	18	4.8
1-S	13	0.9
2	0	0.2
2-S	0	0.0
3	13	21.3
3-S	6	2.5
4	16	12.4
4-S	7	2.0
5	11	5.4
5-S	7	1.4

^a Nomenclature as in Table 1.

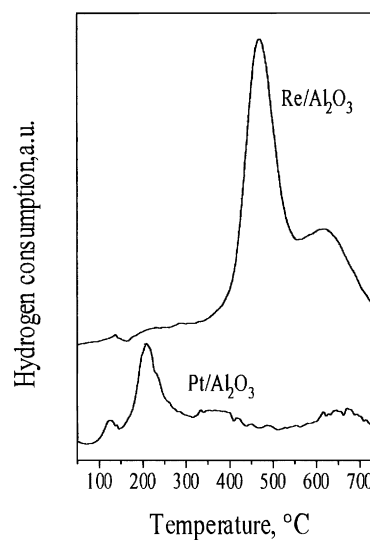


Fig. 1. TPR spectra of Pt/Al₂O₃ and Re/Al₂O₃ catalysts.

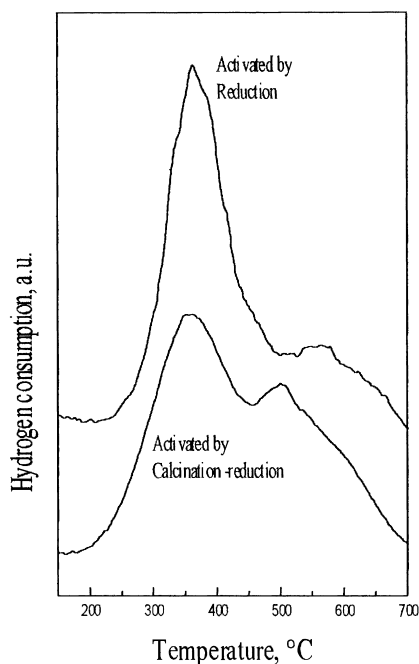


Fig. 2. TPR spectra of Pt-Re/Al₂O₃ catalysts prepared by catalytic reduction and activated by calcination–reduction and direct reduction methods.

of Pt-Re interaction as pointed out before, has two reduction peaks. The first peak at 350°C is due to reduction of Pt and part of Re oxides. The second peak at about 500°C corresponds to the reduction of segregated Re oxide. PtO₂ is reduced to Pt⁰ which catalyzes the reduction of Re₂O₇ [16,17] at a lower temperature than that found for Re alone. The peak at 500°C corresponds to the reduction of Re₂O₇ located so far from Pt that its catalytic effect is not possible.

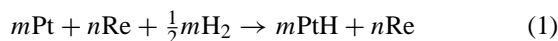
In the sample activated by direct reduction the first reduction peak at 350°C is greater, than in the sample calcined-reduced. This peak is due to the co-reduction of Pt and Re and shows the higher degree of Pt-Re interaction. On the other hand, the second reduction peak is smaller and occurs at higher temperatures for this catalyst.

3.4. Characterization by O₂–H₂ chemisorption

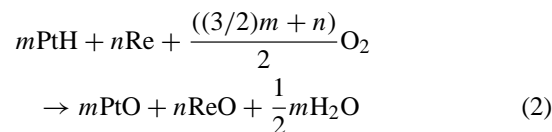
The following stoichiometric equations were postulated by Pereira and co-workers [7,18] and Isaac and Petersen [16] for unsulfided Pt-Re/Al₂O₃ catalysts,

where m and n are the number of Pt and Re surface atoms

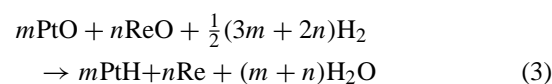
- direct H₂ chemisorption at 25°C (HC)₂₅



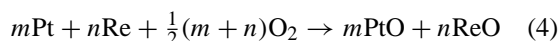
- titration with oxygen (OT)₂₅ of adsorbed hydrogen at 25°C



- titration with hydrogen (HT)₂₅ of adsorbed oxygen at 25°C

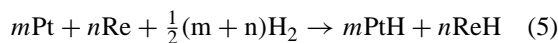


- direct oxygen chemisorption (OC)₂₅

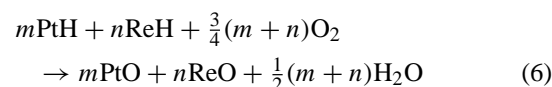


Adsorption/titration steps may be carried out also at 500°C. In this case the gases are introduced at room temperature, being the reactor then heated up to 500°C, with the temperature maintained for 10 min. After cooling to room temperature, pressure measurements are made. Stoichiometries are as follows:

- direct hydrogen adsorption (HC)₅₀₀



- adsorbed hydrogen titration with oxygen at room temperature (OT)₅₀₀



Metallic dispersion values calculated from direct hydrogen chemisorption at room temperature, (HC)₂₅ are usually very low. This fact has been explained by an electronic effect of Re on Pt or by a decrease in the amount of surface neighboring Pt atoms due to the dilution effect of Re atoms [7,19]. For this reason, the values of dispersion calculated from (OT)₂₅ or (HT)₂₅ would be very low. On the other hand, it has been demonstrated that values of dispersion calculated from high temperature titration data (HT)₅₀₀ are too high

due to an excessive hydrogen chemisorption [7]. This results were interpreted as a consequence of spillover, which could reach a maximum at ca. 60% Re [7]. Finally it was concluded that only $(OC)_{25}$, $(HC)_{500}$ and $(OT)_{500}$ values are comparable, leading to the proper number of accessible metal atoms [7].

Chemisorptive properties of the catalyst are changed when S is present. Sulfur can be on the metal and on the support. Sulfur is present as SO_4^{2-} on the support and at certain temperature its reduction and migration of H_2S towards metal sites (Pt or Re) is produced. In this paper a study of oxygen chemisorption on the commercial (sulfided and unsulfided) catalyst reduced at different temperatures was done. The commercial catalyst was provided unsulfided and nonreduced. The values of the total metallic dispersion of this catalyst (sulfided and without S) from oxygen chemisorption data as a function of reduction temperature are shown in Fig. 3. It can be seen that for both samples metallic dispersion (oxygen chemisorption) values increase as reduction temperature increases. In the case of the sample without S it can be speculated that, at higher temperatures, more Re_2O_7 is reduced to Re, thus being able to chemisorb oxygen during the dispersion measurement. In the sulfided sample, the values of dispersion are smaller because the S-metal bond is stronger and needs higher temperature for reduction to metal than the bond O-metal. At 500°C the metallic phase is

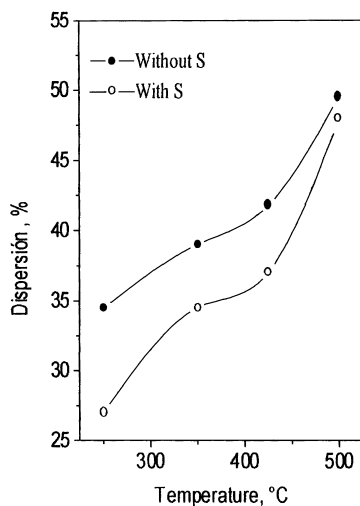


Fig. 3. Total metallic dispersion of the commercial catalyst, sulfided and without S as a function of reduction temperature.

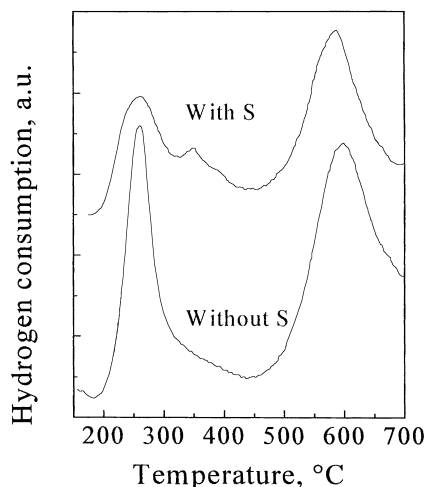


Fig. 4. TPR spectra of the commercial catalyst sulfided and without S.

reduced similarly on both catalysts, and S that is on the metal does not interfere in O_2 chemisorption at 25°C. This is the reason for accepting 500°C as the reduction temperature previous to oxygen chemisorption.

Fig. 4 shows the TPR diagrams of the commercial catalyst, sulfided and without S. In this catalyst Pt and Re are segregated, as can be deduced comparing Fig. 4 with Figs. 1 and 2. The sulfided catalyst is more difficult to reduce (smaller H_2 consumption) than the catalyst which is only oxidized. As quoted before, the reason should be the stronger S-metal bond. At 350°C the sulfided catalyst presents a peak of H_2 consumption. This consumption can be due to the reduction of SO_4^{2-} located on the support surface, producing H_2S that is adsorbed on the metallic surface. The SO_4^{2-} on the support was produced during the oxidation step previous to the TPR determination: part of the S on the metal is oxidized to SO_3 , which produces $Al_2(SO_4)_3$ by reaction with the Al_2O_3 surface.

Total dispersion values from hydrogen and oxygen chemisorption are presented in Table 3. It can be observed that monometallic Re catalysts do not chemisorb hydrogen at room temperature, as previously found by many authors. Hydrogen chemisorption on bimetallic catalysts leads to very low values of metallic dispersion as pointed out earlier. The presence of S greatly diminishes H_2 chemisorption. The values of oxygen chemisorption of catalysts prepared and activated by the same method are equal, independently of the

Table 3
Total metallic dispersion of the catalysts

Catalysts ^a	Total dispersion by H ₂ (%)	Total metallic dispersion by O ₂ (%)
1	58	61
1-S	25	60
2	No adsorption	18
2-S	No adsorption	17
3	9.4	44
3-S	1.2	45
4	7.3	69
4-S	2.4	69
5	18.1	48
5-S	8.1	49

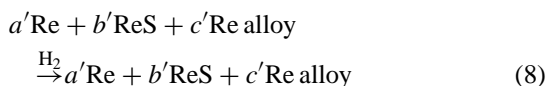
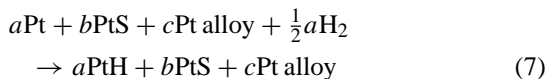
^a Nomenclature as in Table 1.

S content, this behavior was observed for mono or bimetallic catalysts and for catalysts with different interaction degree Pt-Re.

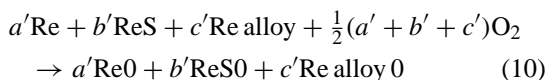
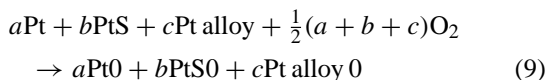
In other words, it seems possible to determine metallic dispersion of the different catalysts by oxygen chemisorption.

In the commercial catalyst Pt and Re can be free (segregated), alloyed or sulfided, and according to what was discussed above, and to a reference that Pt alloyed does not adsorb H₂ [17], the following reactions are possible:

- direct H₂ chemisorption at 25°C



- direct O₂ chemisorption at 25°C



According to these stoichiometries, at 25°C O₂ chemisorpts on all exposed metal atoms and the measurement of O₂ chemisorption allows the calculation of the total (Pt+Re) metallic dispersion.

3.5. Metallic particle size by TEM

The data provided by TEM allowed to verify the total metallic dispersion by O₂ shown in Table 3. For instance for the commercial catalyst the crystal size distributions have the average values of 1.2 and 1.4 nm for the sulfided and the nonsulfided catalysts, respectively, accepting the average value. The value of the metallic dispersion as number of particle surface atoms divided the total number of particle atoms was calculated. The surface area occupied by one metal atom depends on the atom packing and we used the values of Kubicka [20] which depend on the lattice structure and crystallographic plane of Pt and Re. The atomic volume values of $9.10 \times 10^{-3} \text{ nm}^3$ for Pt and $8.85 \times 10^{-3} \text{ nm}^3$ for Re were used. Calculating the metallic dispersion considering the cubic and the spherical model of particles and the different values of atom surface area given in [20] different values were obtained. The average value gives a dispersion of 43%, relatively close to the ones of Table 3.

Other verification is the calculation of metallic particle size from data of metallic dispersion, considering that the metallic particles are cubes with a face in contact with the support surface and five exposed faces. For catalyst 4 with metallic dispersion 0.69 the particle size results 1.3 nm and the average value by TEM is 1.7 nm.

4. Conclusions

Hydrogen is chemisorbed only on unsulfided and nonalloyed Pt and (HC)₂₅ is a measure of free (segregated) Pt.

Oxygen is adsorbed on all surface metallic Pt and Re, sulfided or not, alloyed or not and the oxygen chemisorption at 25°C, (OC)₂₅, is a measure of all exposed Pt and Re atoms. Values of (OC)₂₅ can be used to calculate the total metallic dispersion of Pt-Re/Al₂O₃ catalysts.

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