

Metal dispersion and catalytic activity of trimetallic Pt-Re-Sn/Al₂O₃ naphtha reforming catalysts

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Abstract

The chemisorption of CO over mono-, bi- and trimetallic naphtha reforming catalysts containing Pt, Re and Sn in the metallic function was studied. The temperature-programmed reduction (TPR) results show that there are important interactions among the metals. The CO chemisorption experiments were performed in a pulse equipment. Pulses of the adsorbate (CO) were successively injected to the system until saturation and the exposed Pt was determined from the amount of adsorbate irreversibly adsorbed. The exposed or accessible Pt obtained was compared with that one determined by the classical static method and it was also correlated with the results of catalytic activity of the metal function (cyclohexane dehydrogenation at 400 °C, 0.1 MPa, H₂/CH = 30).

The CO chemisorption results indicate that it is possible to determine in an easy way the metallic dispersion of Pt/Al₂O₃ monometallic catalysts and that the same method can be applied to measure the exposed Pt on bimetallic Pt-Re and Pt-Sn catalysts and trimetallic Pt-Re-Sn catalysts. The values obtained from CO adsorption have very good repeatability and are proportional to the dehydrogenating activity of the catalyst. The latter correlation has a few outliers which were attributed to the electronic effects exerted by Sn and Re over Pt that modify differently the metal activity and the capacity to chemisorb CO.

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1. Introduction

Catalytic naphtha reforming units are at the heart of many modern refineries. They are the main producers of high octane naphtha (approximately, 40% of the world production comes from catalytic reforming units) and aromatic hydrocarbons and they are a very important source of hydrogen. The reactors of naphtha reforming units are loaded with bifunctional metal-acid catalysts. The metal function is provided by Pt, which is supported over the acid function, chlorinated gamma alumina [1]. The catalytic properties of Pt can be improved by the addition of another metal, such as Re [2], Sn [3] or Ge [4]. These additives

modify the activity, selectivity and stability of the catalyst [5,6]. The mechanisms of the main bifunctional reactions of naphtha reforming (paraffins isomerization and dehydrocyclization) are controlled by the acid function. The metal function in these reactions determines both the selectivity and the stability of the catalysts. The effects of the additives on these functions are multiple. (i) They decrease the deep dehydrogenation capacity of Pt and thus decrease the formation of unsaturated coke precursors. (ii) They decrease the hydrogenolysis capacity and therefore also decrease the formation of light gases. (iii) They modify the concentration of surface hydrogen. This has an effect on the relative production of different reaction intermediates and therefore on the final reaction selectivity. (iv) A portion of the additives remains oxidized on the surface and modifies the amount and strength of the acid sites of the support.

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The accessibility to reactants and reactivity of Pt is modified by the additives and it is important to measure them. There are many reports exist that highlight the intimate relation that exists between the catalytic activity and the metal dispersion or accessibility to reactants, being proportional in the case of non-demanding reactions (hydrocarbons dehydrogenation or hydrogenation) on Pt/Al₂O₃ [7,8]. Generally, the Pt dispersion in this catalyst is measured by hydrogen chemisorption. However, there are no robust and precise methods available to measure the accessibility of Pt on particles of the multimetallic catalysts. Neither there are correlations between this structural parameter and the activity of the naphtha reforming catalyst operating under industrial conditions.

The catalytic activity of the metallic function of the most common naphtha reforming catalysts (Pt/Al₂O₃, Pt-Re/Al₂O₃, Pt-Sn/Al₂O₃, Pt-Ge/Al₂O₃ and Pt-Re-Sn/Al₂O₃) is due to the exposed Pt atoms. The methods of indirect determination of the catalytic activity are attractive because they are faster and cheaper than the direct determination methods. The chemisorption of probe molecules as a tool for measuring the Pt accessibility is a strong candidate because of its easiness of implementation, the test rate, its robustness and its repeatability.

In this work, the chemisorption of probe molecules is applied to the assessment of the metal dispersion or accessibility of Pt in naphtha reforming catalysts of the monometallic (Pt/alumina), bimetallic (Pt-Re/alumina and Pt-Sn/alumina) and trimetallic (Pt-Re-Sn/alumina) kind and its relation to a typical Pt reaction in the process, dehydrogenation of cyclohexane.

2. Experimental

2.1. Catalysts preparation

All catalysts were prepared using an industry grade gamma alumina support (Cyanamid Ketjen CK-300, $V_p = 0.5 \text{ cm}^3 \text{ g}^{-1}$, $S_g = 180 \text{ m}^2 \text{ g}^{-1}$). Some catalysts were prepared by the method of coimpregnation, i.e. the salts of each metal were impregnated simultaneously, while others were prepared by the method of successive impregnations. In the last case, after each impregnation, the catalyst was calcined at 500 °C for 4 h in an air stream and then reduced at 500 °C for 4 h in H₂. With this procedure, mono-, bi- and trimetallic Pt, Re, Sn catalysts were prepared. The concentration and volume of the impregnating solution were adjusted to achieve a final content of 0.3% of each metal. The metal precursor salts used were: H₂PtCl₆, SnCl₂ and NH₄ReO₄. During the impregnation step, 1.5 cm³ g⁻¹ of HCl 0.2 M were added to the solution. The solution was then left unstirred at room temperature for 1 h in order to let the metals to distribute homogeneously inside the particles. Then, the solution was evaporated at 70 °C while stirring gently. Then, the catalyst was dried at 120 °C overnight. The

catalysts were finally calcined in air (500 °C, 4 h) and reduced in H₂ (500 °C, 4 h).

For conciseness, the catalysts are named only by its metallic components. In the case of those prepared by successive impregnations, the metal order is the one in which they were impregnated (e.g. in Pt-Re, Pt was impregnated first). In the case of the coimpregnated catalysts, the suffix “coimp” is added.

2.2. Dehydrogenation of cyclohexane

The reaction was performed in a glass reactor. The operation conditions were: catalyst mass = 40 mg, reaction temperature = 400 °C, pressure = 0.1 MPa, hydrogen flow rate = 80 cm³ min⁻¹, molar ratio H₂/CH = 30. Previously, they were reduced at 500 °C for 2 h in hydrogen. The products were analyzed in a gas chromatograph connected on-line.

2.3. Temperature-programmed reduction (TPR)

The TPR tests were performed in an Ohkura TP-2002S equipment. The operation conditions were: heating rate 10 °C min⁻¹, reducing mixture H₂ (5%): air, carrier flow rate 45 cm³ min⁻¹. The temperature was raised from room temperature to 700 °C in each experiment.

2.4. CO chemisorption

The tests were performed in a chemisorption equipment designed ad hoc. The catalyst was placed in quartz reactor and was first reduced with hydrogen at H₂ at 500 °C (2 h, 60 cm³ min⁻¹). The adsorbed hydrogen was then stripped with a stream of nitrogen (1 h, 500 °C) and cooled down to room temperature. The 0.25 cm³ pulses of a mixture of CO in N₂ (3.5%) were sent to the reactor. The CO that was not chemisorbed was quantitatively transformed into CH₄ over a kieselguhr-supported Ni catalyst and detected downstream in a flame ionization detector.

2.5. H₂ chemisorption

H₂ chemisorption was performed in a Micromeritics Accusorb 2100 equipment with 10⁻⁵ mmHg residual pressure. The amount of hydrogen irreversibly adsorbed was calculated by means of the double isotherm method and then the metal dispersion was calculated.

3. Results and discussion

The TPR of the Pt/Al₂O₃, Re/Al₂O₃ and Sn/Al₂O₃ monometallic catalysts and of the bimetallic Pt-Re and Pt-Sn were shown in Ref. [5]. It was found that Pt oxides are reduced at lower temperature than Re oxides. In both monometallic catalysts, there is more than one peak of

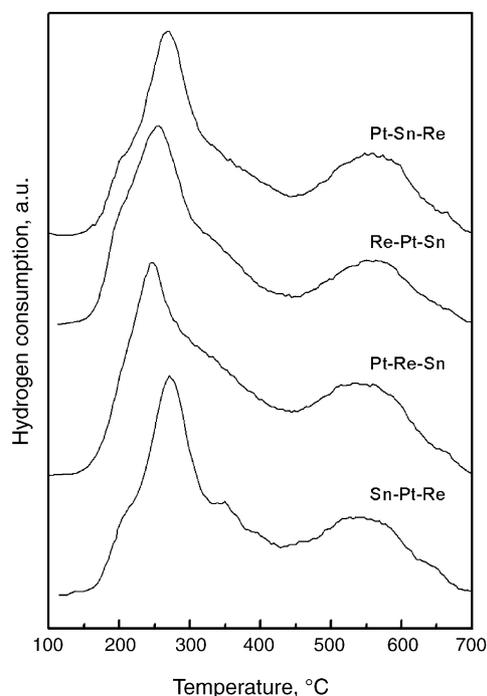


Fig. 1. TPR curves of the trimetallic catalysts prepared by the method of successive impregnations.

reduction. This phenomenon was attributed to Pt and Re in different interactions with the support. According to Bacaud et al. [9], it was also reported that Sn^{4+} is reduced only to Sn^{2+} in monometallic $\text{Sn}/\text{Al}_2\text{O}_3$ catalyst and that there are Sn species with different degree of interaction with the alumina. The TPR of bimetallic catalysts showed that part of Re and Sn oxides are reduced together with Pt oxide, indicating an interaction between Pt and the second metal. The interaction between Pt and other metals is reflected in the merging of reduction peaks and the shift of the Pt peak. The TPR traces of the trimetallic catalysts can be seen in Fig. 1. All of them are similar and have a great peak at 250 °C due to the reduction of Pt oxide and the reduction of a small fraction of Re and Sn oxide species. A second reduction zone at 300–450 °C might be attributed to the reduction of Re and Sn oxides catalyzed by Pt particles. A third peak at 450–700 °C is due to the reduction of segregated Re and Sn oxide particles. Some portions of these oxides might be strongly bonded among themselves or with the support and might fail to get reduced during the TPR experiments.

There is some controversy in the literature about the reduction state of Re in bimetallic Pt-Re/ Al_2O_3 catalysts. Some authors proposed that Re is not reduced to zero state in commercial reforming conditions [10], other authors found that part of Re is reduced to zero state while other part remains as oxide [11,12]. Finally, some studies pointed out the total reduction to zero state of Re [13–15]. Huang et al. [16–18], in a series of studies employing TEM and energy dispersive X-ray analysis, investigated alloy formation in Pt-

Re, Pt-Sn and Pt-Ge/alumina. They found that after reduction at 400 °C, the second metal was present mainly as a highly dispersed oxide. They also detected that during reforming of hydrocarbons at 500 °C, alloy formation and an increase of the reduction degree of Sn and Ge occurred. However, no alloy could be detected in the case of Pt-Re and Re remained as a highly oxidized dispersed phase. In Section 2, the catalysts were reduced in H_2 at 500 °C for 2 h at atmospheric pressure before the reaction tests.

During the preparation of the catalysts, the amount of each metal precursor was adjusted in order to obtain the same concentration (weight%) of each metal. Therefore, for each Pt atom, there are 1.05 Re atoms and 1.64 Sn atoms. In order to reduce Re_2O_7 to the metal state, 3.5 H_2 molecules are needed for each Re atom, while during the reduction of PtO_2 and SnO_2 , 2 H_2 molecules are necessary. If all the oxides were reduced to the metal state, the relative amount of H_2 consumed by each metal would be: Pt = 1, Re = 1.84 and Sn = 1.64. The total reduction of the trimetallic catalysts would demand 4.48 times the amount of H_2 consumed by the Pt monometallic catalysts. However, the total area under the TPR trace of the trimetallic catalysts is about 3.5 times the area of the Pt monometallic catalyst. It must, therefore, be concluded that not all the oxides are reduced and that not all the reduced oxides are in interaction. As it has been pointed out early, the H_2 is consumed to reduce the whole SnO_2 into SnO , but only a small fraction of the SnO is reduced to metallic Sn forming a Pt–Sn alloy. The TPR curves show that there is a certain amount of segregated Re and Sn oxides which are reduced at higher temperatures and that do not interact with Pt.

The temperature-programmed reduction curve of the monometallic Re/ Al_2O_3 catalysts shows that at 500 °C, only a fraction of Re has been reduced. TPR is a dynamic test and it could be considered that an increase in the amount of reduced Re could occur when the heating at 500 °C is maintained for 2 h. In the case of the Pt-Re and Pt-Re-Sn catalysts, the degree of reduction could be further increased due to the catalytic effect of Pt. However, direct measurements like TEM and EDAX indicate that despite its influence on Pt, Re is not completely reduced to Re^0 and remains oxidized to a great extent [19,20]. As a conclusion, it is expected from the TPR results that during the cyclohexane dehydrogenation and CO chemisorption experiment used in this work, the whole Pt is in metallic state alloyed with Re and Sn partially reduced to zero state, some fraction of Sn or Re can remain segregated as oxides. Moreover, all the TPR data show that there is an interaction between the metals in the bi- and trimetallic catalysts. Pt is alloyed or in close interaction with the other metals, then its chemisorption capacity and catalytic activity should be affected.

The catalytic activity test used for catalyst comparison was the reaction of dehydrogenation of cyclohexane. This reaction was chosen because it is very important in naphtha reforming, it is the only reaction of the process that needs

only the metallic function, it is very fast and is the main reaction occurring in the first reactor of the reforming plants. Pt is very selective, producing only benzene. The addition of Sn or Re to the catalyst decreases the dehydrogenating activity of Pt and the high selectivity is maintained. The values of cyclohexane conversion [5] are shown in Fig. 3, where they are compared with the CO/Pt ratio. For all the tested catalysts, the conversion is high (more than 70%) and this conversion can be taken as the catalytic activity because the reaction has zero-order kinetics [21]. In the experimental conditions, mass transfer limitations are absent, as shown by calculating the Weisz-Prater criterion for internal mass transfer ($\Phi \ll 0.01$) and the Damköhler number ($Da \approx 0$) for external mass transfer. Sn has the highest inhibiting effect. The decrease of the dehydrogenating activity of Pt that occurs upon addition of a second metal can be attributed to a geometric or an electronic one. Though both factors contribute, it has been proposed that the most important one is the electronic one [5].

Preliminary tests of CO pulse chemisorption indicated that Re, Sn and the support do not chemisorb CO and the chemisorption of CO on Pt does not vary when the temperature fluctuates in the 30–50 °C range. Additionally, repeatability assays indicated that the variance of the method is 2.2% (using a set of eight experiments). Finally, an experiment was made in order to verify reversibility of CO chemisorption. After CO saturation, the catalyst was maintained under nitrogen flow for 3 h and then new pulses were injected. No adsorption was observed indicating that the CO chemisorptions was irreversible. Also, the experiments were repeated with different interval between injections and no difference was obtained.

The results obtained with the CO pulse dynamic chemisorption method on Pt/Al₂O₃ were compared with those obtained in chemisorption of H₂ in a static adsorption apparatus. Table 1 shows the gas chemisorption obtained with both methods on the monometallic Pt catalyst that was subjected to two sintering pretreatments at high temperature. There is a close agreement between the results obtained by each method. This agrees with the accepted concept that CO or H₂ chemisorption and static or dynamic procedures can be used to measure the metallic dispersion and calculate the Pt particle size on monometallic Pt/Al₂O₃. This is not valid for bi- or trimetallic catalysts. It has been shown that the addition of Re, Sn or both [5] or W [22] to Pt produces a great decrease of the chemisorption of H₂ while the mean particle size as measured by TEM remains practically

constant. Then, the calculation of the metal particle size from chemisorption data is only valid for monometallic Pt/Al₂O₃.

Chemisorption of CO and H₂ on Sn-Pt-Re/Al₂O₃ were performed in the static adsorption apparatus and the results were CO/Pt = 0.26 and H₂/Pt = 0.10. This result with a trimetallic catalyst agrees with the literature related to bimetallic ones. Many authors have found that the addition of Sn to Pt decreases more the chemisorption of H₂ than the chemisorption of CO [23,24]. Verbeek and Sachtler [25] studying Pt and Pt-Sn alloys indicated that “dissociative adsorption of hydrogen is likely to require two Pt atoms; moreover, it may be necessary for these to be adjacent”. They also indicated that this adsorption becomes an activated process when the distance between the Pt atoms is enlarged or alternatively when due to electronic effects, a drastic lowering of the heat of H₂ adsorption is produced. These possibilities occur with the Sn addition to Pt. Rajeshwer et al. [26] verified that H₂ chemisorption on Pt alloyed to Sn is suppressed at 25 °C even when the catalyst is still active in dehydrogenation. This geometrical adjacency of Pt atoms is not necessary for the linear adsorption of CO that needs only one Pt atom. Similarly, in the case of Pt-Re/Al₂O₃, the addition of Re decreases much more the H₂ chemisorption than the catalytic activity [5] or they vary differently [27,28]. For this reason, the chemisorption of CO is preferred over that of H₂ for the assessment of the exposition or availability of Pt. Furthermore, determination of CO can be done easily and with great sensitivity in a flame ionization detector, while the determination of H₂ requires a less sensitive and less accurate thermal conductivity detector.

There are methods using direct chemisorption and titration of chemisorbed H₂ and O₂ that allow the calculation of the exposed fraction of each metal on Pt-Sn/Al₂O₃ [26,29,30] and Pt-Re/Al₂O₃ [27,31], but the only important metallic fraction is that of Pt because it supplies the metal function activity. Then a simple method, like the dynamic chemisorption of CO, provides enough information on the metallic function of the catalyst.

Fig. 2 shows the trace of the FID signal as a function of the time (or pulse number) during a CO chemisorption experiment. It can be seen that as the number of injected pulses is increased, the area of the CO peaks (detected as CH₄ in the FID) increases until a stable, constant value of area is reached. Equal CO pulses reach the detector because they pass through the catalyst without being adsorbed, i.e. the Pt sites are saturated and are unable to chemisorb additional amounts of CO. The first part of the experiment (peak growth) is due to the adsorption of CO over Pt sites.

Fig. 3 shows the conversion of cyclohexane on the bimetallic and trimetallic catalysts as a function of the CO/Pt ratio. A linear fit between the values of dehydrogenating activity (cyclohexane conversion) and the number of surface Pt atoms (as measured by CO chemisorption) can be seen.

Table 1

Chemisorption of CO and H₂ by a Pt/Al₂O₃ catalyst subjected to different thermal treatments

Treatment	CO/Pt (dynamic method)	H/Pt (static method)
None	54	52
600 °C, 2 h, air	40	44
600 °C, 6 h, air	10	11

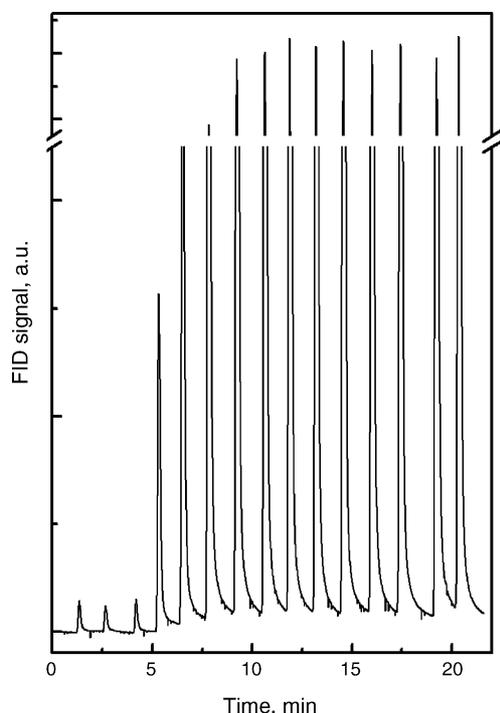


Fig. 2. CO chemisorption in the pulse chemisorption apparatus. FID signal evolution as a function of time (pulse number).

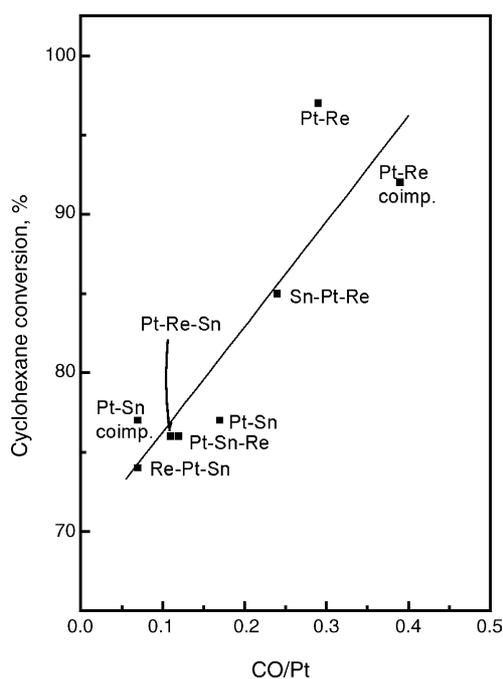


Fig. 3. Activity during dehydrogenation of cyclohexane as a function of the CO/Pt ratio. Stable conversion value all throughout the time span of the reaction. Regression coefficient, $R^2 = 0.934$. Coimp., catalysts prepared by coimpregnation of metal precursors; Suc., catalysts prepared by successive impregnations of metal precursors in the order indicated. Temperature = 400 °C, pressure = 0.1 Mpa, H_2/CH molar ratio = 30.

This linear relation occurs in spite of the catalysts having different composition, different reduction state and different metal–metal interaction.

The latter phenomenon can be explained after recalling that the reaction of cyclohexane dehydrogenation is “non-demanding” [7] and therefore, it does not require a specific ensemble of Pt atoms in order to take place. All the Pt atoms have the same activity, independent of the adjacency of other Pt atoms. The conversion level in this reaction is then approximately proportional to the amount of surface Pt atoms measured during the selective adsorption of CO. The deviation from the linear pattern in the case of some catalysts can be due to the differences in electron density of Pt in these solids. The electronic density is affected by the addition of Sn and Re. There is an electronic transfer from Re and Sn to Pt and the resulting $Pt^{\delta-}$ adsorbs less H_2 , CO and hydrocarbons than Pt^0 . The bond $Pt^{\delta-}-H_2$ is weaker than the bond Pt^0-CO or the Pt^0 -cyclohexane bond and when Pt is electronically enriched, the weakening of these bonds produces the inability of $Pt^{\delta-}$ to adsorb H_2 . This electronic factor could act together with the geometrical factor noted above. If all the exposed Pt atoms have the same electronic state, CO/Pt measures the fraction of Pt that is exposed to CO and to the reactants. If there are different electronic states of exposed Pt atoms, the linearity indicates that the changes in CO adsorption of each atom are similar to the changes in cyclohexane dehydrogenation activity.

4. Conclusions

The measurement of the metal dispersion of Pt/Al_2O_3 catalysts can be performed with the aid of a simple dynamic method of CO chemisorption that has great repeatability (a variance of 2%) and that yields similar values to those obtained in more costly and complex static adsorption equipments.

The method used for the Pt/Al_2O_3 catalyst can also be used with no modifications to measure also the exposed Pt in bi- and trimetallic catalysts, where H_2 chemisorption cannot be used.

Despite the different composition of the catalysts used (mono-, bi- and trimetallic), there exists a good correlation between the dehydrogenating activity in “non-demanding” reactions and the metal dispersion as measured by the CO chemisorption method. This fact backs the usefulness of the method for measuring the metallic activity in naphtha reforming catalysts.

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