

Influence of tin addition by redox reaction in different media on the catalytic properties of Pt-Re/Al₂O₃ naphtha reforming catalysts

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ABSTRACT

The influence of Sn addition by catalytic reduction method on the Pt-Re/Al₂O₃ properties for the *n*-C₇ reforming reaction was studied. The Sn addition was performed in different media (HCl and H₂O). It was found that trimetallic Pt-Re-Sn/Al₂O₃-Cl catalysts prepared in H₂O or HCl medium present a good interaction between Sn and the catalytically active species (Pt-Re). This strong interaction of Sn with the active phase correlates with the lower hydrogenolytic and dehydrogenating activity of the trimetallic catalysts. Total acidity and Brønsted acidity decrease with the addition of Sn. The catalysts prepared in HCl have both higher Brønsted and total acidity in comparison to those prepared in H₂O.

In the case of catalysts prepared in HCl medium, the production of C₂–C₄ gases in the *n*-C₇ reforming reaction also decreases upon Sn addition confirming that the cracking activity decreases when the acidity is decreased. In both trimetallic catalysts series a decrease in the toluene yield can be seen at high Sn contents. The production of toluene depends on the activity in dehydrocyclization reaction. Dehydrocyclization requires sites of lower acid strength than those needed for cracking. The addition of small amounts of Sn (≤0.2 wt%) would enable the step of sulfidation of Pt-Re/Al₂O₃ catalysts to be spared.

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1. Introduction

Catalytic naphtha reforming is a refinery process used for producing high octane gasolines, aromatics for the petrochemical industry, and hydrogen as a valuable subproduct. It is widely known that naphtha reforming requires bifunctional catalysts, normally Pt and another metal supported over an acidic carrier. First patents dealt with monometallic catalysts, such as those reporting Pt/Al₂O₃-Cl in 1949 [1,2]. The catalysts have however evolved towards multimetallic systems, like the classical Pt-Re/Al₂O₃-Cl [3] and other bimetallic alumina supported catalysts such as Pt-Sn, Pt-Ge, Pt-Ir, etc. [4–6].

Naphtha reforming catalysts are mainly deactivated by the deposition and accumulation of coke that blocks the active centers [7–10]. The addition of a second metal decreases coke formation and hence the reaction can be carried out at a lower hydrogen partial pressure and a lower H₂/HC ratio. This translates into an increase of the liquid yield and a higher production of the desired compounds.

More recently many patents and scientific articles have appeared that report the advantage of using trimetallic catalysts in processes with longer continuous operation periods [11–18]. These catalysts have very low coking rates and are therefore less prone to deactivation [17,19].

Most of the cited trimetallic catalysts have an active metal couple, like Pt-Re or Pt-Ir and a third inactive component like Ge, Sn or Pb. It has been reported that Pt-Re and Pt-Ir have high activity for the hydrogenolysis of hydrocarbons, producing methane and other light hydrocarbons of low value [20]. In the industrial practice this undesirable activity is suppressed by sulfidation. This is a costly operation that must be performed after each catalyst regeneration. For this reason the use of trimetallic catalysts aims primarily at the elimination of sulfidation. Sn is one of the most used elements among other inactive metals. It has been reported that the addition of Sn to Pt/Al₂O₃ catalysts prevents coke deposition on the Pt metal particles [21–25] and on the support [21–23,26,27]. It also enhances the selectivity to aromatics and the stability of Pt/Al₂O₃ [28].

We have recently studied the influence of the Sn addition on the catalytic properties of trimetallic Pt-Re-Sn/Al₂O₃-Cl catalysts prepared by the conventional coimpregnation method. These properties included: Pt resistance to sulfur poisoning, Pt metal

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activity and selectivity in metal-catalyzed reforming reactions, amount and distribution of acid strength, activity and selectivity in acid-catalyzed reactions [29,30]. In this work we are complementing these referred studies by studying the influence of the Sn content added by a surface redox reaction (the so-called catalytic reduction method) at different pH conditions on the catalytic activity and selectivity of trimetallic Pt-Re-Sn/Al₂O₃-Cl catalysts. In the course of the plurimetallic catalysts synthesis, the surface redox reactions are generally used in order to obtain a higher metallic interaction than by traditional preparation methods. The catalytic reduction method involves a redox reaction between adsorbed hydrogen on the base catalyst (i.e., Pt-Re/Al₂O₃-Cl in our case) and a precursor salt of the modifier (i.e., Sn in this work).

2. Experimental

2.1. Preparation of the Pt-Re/ γ -Al₂O₃ base catalyst

γ -Al₂O₃ (Cyanamid Ketjen CK-300, ground and sieved to 35–80 meshes, pore volume = 0.5 cm³ g⁻¹, specific surface area = 180 m² g⁻¹) was used as support and calcined at 500 °C for 4 h in air in order to eliminate organic impurities. HCl (0.2 M) was added (1.5 cm³ g⁻¹) and the slurry was let to rest for 1 h. H₂PtCl₆ and NH₄ReO₄ were added and the slurry was gently stirred for 1 h at room temperature. It was slowly dried at 70 °C until a dry powder was obtained which was further dried overnight at 120 °C. Finally the powder was calcined in air (60 cm³ min⁻¹, 300 °C) and reduced with H₂ (60 cm³ min⁻¹, 500 °C). The final content of Pt and Re on the catalyst was 0.3 and 0.3 wt%, respectively. This catalyst is named Pt-Re base catalyst.

2.2. Preparation of trimetallic catalysts

The reactor used for this propose had means for degassing the Sn solution in order to eliminate dissolved oxygen. The base Pt-Re catalyst was first prerduced with H₂ (60 cm³ min⁻¹) for 1 h at 300 °C; then it was cooled down to room temperature under hydrogen. The solution of SnCl₂ was then added in amounts sufficient for obtaining samples with Sn theoretical mass percentages of 0.1, 0.3, 1.0 and 2.0 wt%. This Sn solution was further diluted by adding suitable solutions and taking a final volume of 25 cm³. These solutions were chosen in order to produce different pH values in the preparation medium: (i) H₂O medium; (ii) HCl medium (0.2 M). After the degassing step the solution was left in contact with the catalyst for 1 h and hydrogen was bubbled at a rate of 300 cm³ min⁻¹. Then the solution was removed and the catalyst was rinsed with distilled water. The catalyst was then dried in a hydrogen stream (60 cm³ min⁻¹, 100 °C) for 12 h. Finally it was reduced in this stream (60 cm³ min⁻¹) at 500 °C for 2 h. The solution of the Sn precursor was unstable and was prepared just before its use. It was first dissolved in deionised water and heated for 30 min at 70 °C. Then, 37% HCl was added until the solution became transparent.

These prepared catalysts were named Pt-Re-Sn(*x*, *y*) (*x*, number corresponding to the theoretical Sn content; *y*, impregnating medium). The Sn content represents the mass percentage of Sn actually deposited. Pt-Re-Sn(0.0, HCl) corresponds to the blank experiment, i.e., the preparation procedure was performed in HCl medium in the absence of SnCl₂.

2.3. Measurement of the Pt, Re, Sn and Cl contents

The composition of the metal function was determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES) after digestion in an acid solution and dilution. The chlorine content of the catalysts in their final state, i.e., after activation, was

determined by means of potentiometry. All these analysis were realized by the CNRS at the Service Central d'Analyse (Vernaison, France).

2.4. CO chemisorption

The tests were performed in a chemisorption equipment designed *ad hoc*. The catalyst was placed in quartz reactor and it was first reduced with hydrogen at H₂ at 500 °C (2 h, 60 cm³ min⁻¹). The adsorbed hydrogen was then stripped in a stream of nitrogen (1 h, 500 °C) and cooled down to room temperature. Then 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. 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. Repeatability assays have indicated that the variance of the dispersion value measured with this test is 2.2% (using a set of eight experiments) [31].

2.5. Temperature programmed reduction (TPR)

TPR tests were performed in an Ohkura TP2002 apparatus equipped with a thermal conductivity detector. At the beginning of each TPR test the sample was heated in air at 450 °C for 1 h. Then it was heated from room temperature to 700 °C at a heating rate of 10 °C min⁻¹ in a reducing gas stream (5.0% H₂ in argon).

2.6. Fourier transform infrared absorption spectroscopy (FTIR) of chemisorbed CO

FTIR spectra of chemisorbed CO for the prepared catalysts were recorded within a 4000–1000 cm⁻¹ wavenumber range. A Shimadzu Prestige-21 spectrometer, with a spectral resolution of 4 cm⁻¹ was used and spectra were recorded at room temperature. Self supported wafers with a diameter of 16 mm and a weight of 20–25 mg were used. Experimental procedure was as follows: catalyst samples were reduced under hydrogen flow at 400 °C (reached at a 10 °C min⁻¹ heating rate) during 30 min. Samples were then degassed at 2.7 × 10⁻³ Pa and 400 °C during 30 min. After the recording of a first (I) spectrum, the samples were exposed to a 4 × 10³ Pa CO atmosphere during 5 min and then a second (II) FTIR spectrum was recorded. Chemisorbed CO absorbance for each sample was obtained by subtraction of spectra (II) and (I).

2.7. Temperature programmed pyridine desorption

The amount of acid sites on the catalysts surface was assessed by means of temperature programmed desorption of pyridine. 200 mg of the catalyst was first immersed in a closed vial containing pure pyridine (Merck, 99.9%) for 4 h. Then the catalyst was taken out from the vial and excess pyridine was removed by evaporation at room temperature under a fume hood. The sample was then charged to a quartz microreactor and a constant nitrogen flow (40 cm³ min⁻¹) was set up. Weakly adsorbed pyridine was first desorbed in a first stage of stabilization by heating the sample at 110 °C for 2 h. The temperature of the oven was then raised to 600 °C at a heating rate of 10 °C min⁻¹. The reactor outlet was directly connected to a flame ionization detector to measure the desorption rate of pyridine. With respect to the error associated to the TPD experiments, the variance of the peak position and areas has been determined to be about 7% [17].

2.8. Isomerization of 3,3-dimethyl-1-butene (33DM1B)

The reaction was performed in a microreactor of U shape (length = 20 cm, diameter = 0.6 cm). The feed was generated by passing a nitrogen stream through a saturator contactor containing the liquid reagent and immersed in an ice bath at 0 °C. The catalyst (100 mg) was pretreated in situ, being first reduced with H₂ (60 cm³ min⁻¹, 500 °C) and then calcined in air (300 °C, 60 cm³ min⁻¹) to deactivate the metal phase. The sample was then cooled in N₂ (30 cm³ min⁻¹) to the reaction temperature (250 °C). Then the feed from the saturator was injected. The reagent partial pressure and flowrate were 20.9 kPa and 15.2 mmol h⁻¹, respectively. The products were analyzed with a gas chromatograph connected on-line. The error associated to the test of 33DM1B isomerization was determined by calculating the variance of the conversion in a set of seven experiments (variance = 6.5%)

2.9. Cyclohexane dehydrogenation (CH)

The reaction was performed in a glass reactor (length = 10 cm, diameter = 1 cm) with the following conditions: catalyst mass = 50 mg, temperature = 300 °C, pressure = 0.1 MPa, H₂ flow rate = 36 cm³ min⁻¹, cyclohexane flow rate = 0.727 cm³ h⁻¹. The CH was introduced into the reactor using a Sage Instruments 341B syringe pump. Before the reaction was started, the catalysts were treated in H₂ (60 cm³ min⁻¹, 500 °C, 1 h). The reaction products were analyzed in a gas chromatograph connected on-line. All points reported are mean values obtained averaging 12 consecutive measurements equally spaced along the run. No significant catalyst deactivation was observed in any run. The average error was less than 3%. The cyclohexane dehydrogenation rate was determined from the conversion value according to the following formula:

$$\text{rate}(\mu\text{mol g}^{-1}\text{s}^{-1}) = \frac{\text{conversion} \times n}{m_{\text{cat}}} \quad (1)$$

where n is the molar quantity of cyclohexane injected per second and m_{cat} is the catalyst mass.

2.10. Cyclopentane hydrogenolysis (CP)

The reaction was performed in a glass reactor (length = 10 cm long, diameter = 1 cm) with the following conditions: catalyst mass = 150 mg, temperature = 350 °C, pressure = 0.1 MPa, H₂ flow rate = 40 cm³ min⁻¹, cyclopentane flow rate = 0.483 cm³ h⁻¹. Cyclopentane was fed to the reactor using a Sage Instruments 341B syringe pump. Before the reaction was started, the catalysts were treated in H₂ (60 cm³ min⁻¹, 500 °C, 1 h). The reaction products were analyzed in a gas chromatograph connected on-line. The cyclopentane hydrogenolysis rate was determined from the conversion value according to formula (1). The error of the conversion value in the CP hydrogenolysis test is about 8%. Only values of initial conversion at 5 min time-on-stream are reported. Additional values until 1 h time-on-stream were also obtained but they are not reported. They were only used to test the validity of the value of initial conversion.

2.11. *n*-Heptane reforming reaction

The reaction was performed in a continuous flow reactor with the following conditions: catalyst mass = 1 g, temperature = 500 °C, pressure = 0.5 MPa, H₂ flow rate = 60 cm³ min⁻¹, *n*-C₇ flow rate = 3 cm³ h⁻¹ (i.e., H₂/*n*-C₇ gas mixture = 7.5:1). The stainless steel reactor had a length of 40 cm and a diameter of

1.3 cm. The *n*-C₇ was fed to the reactor using a Gilson 307 piston-pump system. Effluent products were analyzed by an on-line chromatograph (Varian 3400) using a FID and equipped with a CP-Sil 5 capillary column. Product yields were obtained from the chromatographic data. The yield of product i is the percentage of *n*-heptane converted into this product and is calculated as:

$$C_i \text{Yield} = \frac{\%C_i 100X}{\sum \%C_i} \quad (2)$$

where X is the total conversion, C_i the i compound concentration in the reaction products, $\sum \%C_i$ the sum of C_i products of reaction (*n*-heptane is not included). For each experiment, the sum of all the C_i yields was in agreement with the *n*-C₇ conversion, pointing out an adequate carbon balance. Moreover, the repetitiveness of the *n*-C₇ reforming reaction test was quite good with a variance lower than 4%.

In order to avoid the initial hyperactivity of the Pt-Re/Al₂O₃ catalysts which causes excessive hydrocracking, sometimes referred to as "runaway hydrocracking", before the *n*-C₇ reforming reaction test, bimetallic Pt-Re blank catalysts were sulfided under a 5% H₂S/H₂ mixture for 1 h at 500 °C, followed by a treatment under H₂ for 8 h at the same temperature. Catalysts with Sn were not sulfided because in this case Sn addition is supposed to produce an inhibition of the hydrocracking hyperactivity so the sulfiding step should be unnecessary. Moreover one objective of this work was to see whether Sn doped catalysts can be used without any kind of sulfidation pretreatment.

The absence of mass transfer limitations was assessed by calculating the modulus of Weisz-Prater and the Damköhler number for all the reactions involved: 3,3-dimethyl-1-butene isomerization, CH dehydrogenation, CP hydrogenolysis and *n*-C₇ reforming. In all cases the Weisz-Prater modulus was found to be much smaller than 0.1 while the Damköhler number was smaller than 0.01. Mass transfer problems were thus disregarded.

3. Results and discussion

In previous works we reported that the addition of Ge by the catalytic reduction method influences the properties of the Pt-Re/Al₂O₃ base catalyst and that these modifications depended on the pH of the preparation solution [32,33]. Also, it was observed that the immersion of the base catalyst in the solution without introduction of the ions of the additive (blank catalyst) may induce a modification of the catalytic properties. It was found that at high pH values the blank catalysts retain less chlorine and the metals are reduced at a lower temperature due to the low metal-support interaction. The opposite effect is obtained when HCl medium is used in the preparation. The Brønsted acidity decreases as the pH is increased while the Lewis acidity of the catalyst is not substantially modified by either preparation medium. Catalysts with higher Pt-Re interaction are obtained at high pH values of the preparation solution. For these reasons, we report in the present work the catalytic properties of the Pt-Re-Sn and the corresponding blank catalysts, i.e., the catalysts treated by the catalytic reduction method but with no tin addition.

Table 1 shows the percentage of Sn deposited, the amount of Cl and the CO/Pt ratio obtained by CO chemisorption of the trimetallic catalysts prepared using two different aqueous medium (HCl and H₂O). It can be seen that the amount of deposited Sn either for the catalysts prepared in H₂O medium or those prepared in HCl medium differs notably from the theoretical one for nominal percentages of Sn higher than 0.3 wt%. At lower Sn nominal percentages the difference between the real and the nominal Sn% is not important. It can also be seen that in this case the same amount of Sn is deposited whatever the preparation medium used. For the

Table 1
Values of Sn content, Cl content and CO/Pt atomic ratio.

Theoretical Sn (wt%)	Catalyst					
	Sn (wt%)		Cl (wt%)		CO/Pt	
	HCl	H ₂ O	HCl	H ₂ O	HCl	H ₂ O
0.00	0.00	0.00	1.32	1.10	0.33	0.36
0.10	0.10	0.10	1.45	0.97	0.31	0.28
0.30	0.20	0.23	1.36	1.00	0.30	0.26
1.00	0.62	0.65	1.50	1.18	0.27	0.25
2.00	0.69	0.71	1.52	1.25	0.26	0.24

two catalysts series, the percentage of Cl increases with the amount of Sn. This is due to the incorporation of Cl from the precursor salt (SnCl₂). It can be seen that the CO/Pt ratio decreases as the Sn content increases. These results are as expected because Sn has no capacity for chemisorbing CO and its addition should decrease the CO chemisorption capacity of Pt.

Fig. 1 shows the TPR patterns of all the studied catalysts. In a previous work, we reported that the base catalyst has three reduction peaks being the first one (located at 250 °C) due to the reduction of Pt and a part of Re in strong interaction with Pt. The second peak at 350 °C was attributed to the reduction of Re enhanced by the catalytic action of Pt and the third peak at 570 °C was likely due to the reduction of segregated Re [34,35]. TPR patterns for blank catalysts prepared either in H₂O or HCl medium showed that both samples have two reduction peaks. The first was placed at 234 °C and the second at 471 °C for the catalyst prepared in pure H₂O medium while the catalyst treated in HCl medium has these peaks shifted to 297 and 542 °C, respectively. This higher temperature shifting was attributed to the increase of the chlorine concentration on the catalysts and leading to a stronger metal–

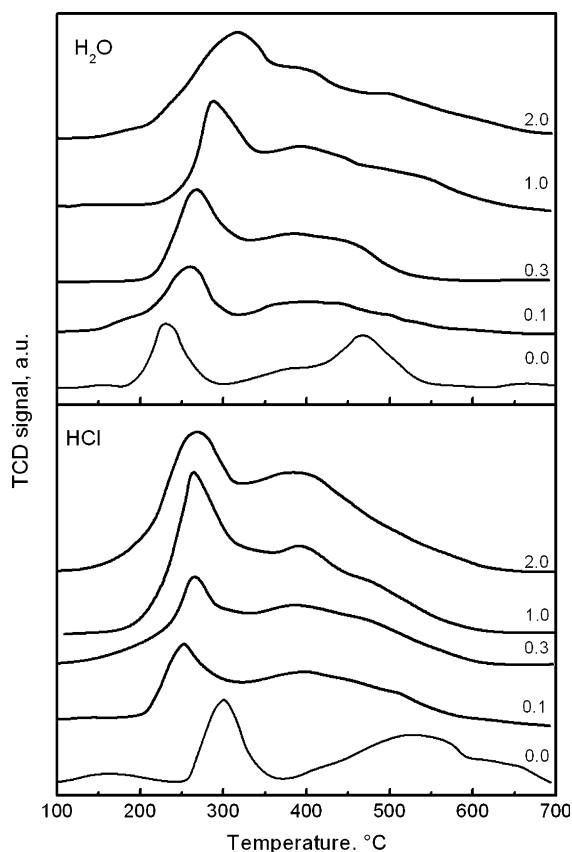


Fig. 1. TPR traces of the trimetallic Pt-Re-Sn catalysts prepared in H₂O and HCl medium as a function of the Sn content.

support interaction. Higher levels of metal–support interaction would demand a higher reduction temperature.

For the trimetallic catalysts, the Pt reduction peak is shifted to higher temperatures as the Sn content is increased. This effect occurs on both series of catalysts and is more marked in the case of the catalysts prepared in H₂O medium. The shift of the first reduction peak to higher temperatures (257 °C in the case of the 0.1 wt% catalysts and 314 °C for the Pt-Re-Sn(2, H₂O)) can be attributed to a delay of the reduction of the Pt oxides by Sn which interacts with the base catalyst. Since this effect increases with the Sn content, the quantity of Sn in interaction with Pt must increase with the Sn loading of the trimetallic catalysts. The growth of the intermediary reduction zone (300–500 °C) as the Sn content is increased in both series is in accordance with the reduction of Sn species in this temperature range [13].

The interaction between the metals was studied by FTIR-CO. CO chemisorbs on metallic Pt but not on metallic Re or Sn [31,32]. On the other hand, CO is adsorbed on Pt particles in the linear and bridged forms. In Fig. 2 only the wavenumber region corresponding to linear CO is shown, i.e., the 1950–2250 cm⁻¹ region. The band at 2070 cm⁻¹ which predominates on the Pt-Re base catalyst corresponds to the adsorption of linear CO on Pt [36–39]. Such band is observed at the same frequency level for the blank catalyst prepared in pure water medium. This band is shifted to higher

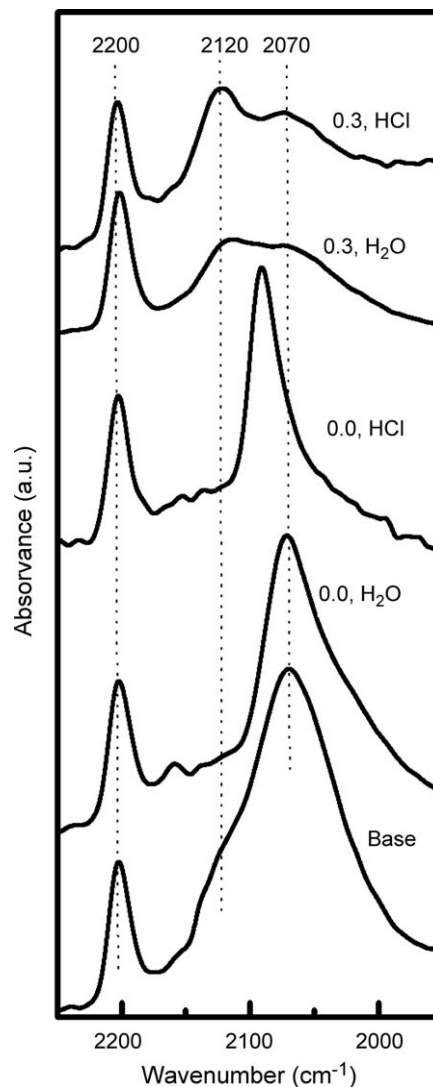


Fig. 2. IR spectra of CO adsorbed. Trimetallic Pt-Re-Sn(0.3, HCl) and Pt-Re-Sn(0.3, H₂O) catalysts, Pt-Re base and blank catalysts.

frequency for the blank catalyst prepared in aqueous HCl medium. It has been found that Pt-CO absorption peak is shifted to higher frequencies when the electron density of Pt diminishes [40]. The base catalyst and the blank (pure water) catalyst have the same Cl content (1.10 wt%), but the blank (aqueous HCl) catalyst has a higher Cl level (1.32 wt%). It is therefore expected that the effect of Cl on the electronic state of Pt to be more profound for this later.

The band at 2200 cm^{-1} observed on the five samples can be assigned to the interactions between CO and Al_2O_3 [41,42]. It is specifically associated to adsorption on acid sites of alumina, Al^{3+} ions with tetrahedral coordination [43–46].

The size of the Pt-CO adsorption peak is noticeably reduced upon the addition of Sn both on pure H_2O or aqueous HCl medium as compared with the catalysts which have no Sn. Moreover on the trimetallic catalysts, a shift of this peak is observed to higher frequencies. Del Angel et al. [47] have attributed the shift of the Pt⁰ band (2070 cm^{-1}) to higher frequencies to the interaction of the Pt atoms with SnO_x and La_2O_3 where Pt is stabilized in its oxidized state (Pt^{2+}) as a result of the decrease of the retrodonation $d\pi \rightarrow 2\pi^*$ from the metal to the antibonding orbitals of CO. In the case of the Pt-Re-Sn trimetallic catalysts under study, it can be deduced that this effect is produced by the Sn oxides that have not been reduced during the treatment preceding the adsorption of CO (reduction at 400°C). Other authors have found that on $\text{Pt}/\text{Al}_2\text{O}_3$ the bands between 2145 and 2120 cm^{-1} can be assigned to stable $\text{Pt}^{2+}\text{-CO}$ [37] or $\text{Pt}^+\text{-CO}$ complexes [48]. It is possible that Sn oxides in the vicinity of Pt generate an electronic transfer from Pt to Sn species, thus justifying the apparition of a band at 2120 cm^{-1} . At a closer distance from the Pt oxides greater modifications on the CO adsorption are expected. The trimetallic catalyst prepared in HCl medium would have a higher Sn-(active phase) interaction than the one prepared in H_2O medium. On the other side, the presence of the adsorption band at about 2120 cm^{-1} was assigned to the effect of chlorine [47]. In the case of the studied catalysts this band is merged into the broad main peak and is more marked in the case of the catalyst prepared in HCl medium.

Fig. 3 contains values of the reaction rate for cyclopentane hydrogenolysis at 5 min of time-on-stream as a function of the real amount of deposited Sn. The reaction of cyclopentane hydrogenolysis is structure sensitive and it is known that the addition of Sn destroys the Pt-Re ensembles and inhibits the hydrogenolytic activity [49,50]. It can be seen that small Sn amounts are enough to destroy or decrease the effective size of the Pt-Re ensembles responsible for the breaking of the C–C bonds. This inhibition of the hydrogenolytic activity occurs both for the H_2O and HCl medium.

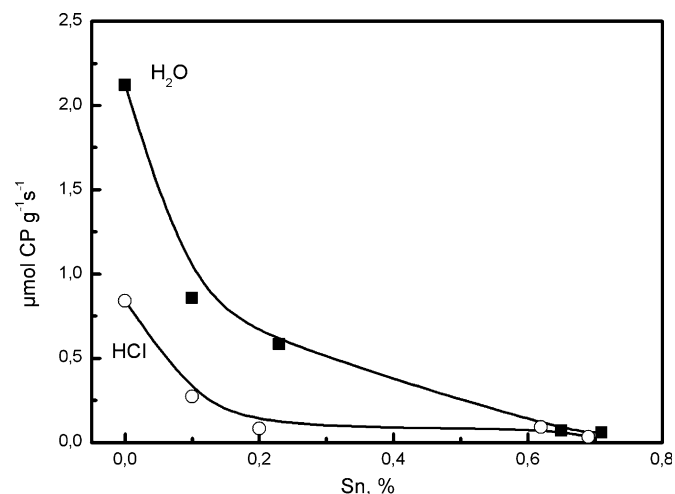


Fig. 3. Cyclopentane hydrogenolysis reaction rate at 5 min of time-on-stream and as a function of the Sn content. Catalysts prepared in H_2O and HCl medium.

At high Sn contents ($\geq 0.6\text{ wt}\%$) the activity of the catalysts is almost null because Sn blocks almost completely the Pt-Re active phase.

Fig. 4 is a plot of the cyclohexane dehydrogenation rate and the turnover number as a function of the Sn amount. From Fig. 4a, it is evident that the catalyst activity decreases with the increase of the Sn content. Sn has no dehydrogenating activity under the reaction conditions reported in the experimental section. This reaction is catalyzed by the metal function and the reaction rate is proportional to the number of surface active atoms because this is a non-demanding reaction. From these results it can be seen that at low Sn contents the decrease of the conversion with the addition of Sn is almost linear. The trimetallic catalysts prepared in HCl medium are the most affected. At higher Sn percentages ($>0.2\text{ wt}\%$) the activity drop is not linear in the case of the HCl catalysts. This can be due to Sn being preferentially deposited over the active metal phase. In the case of the catalysts with higher than $0.6\text{ wt}\%$ Sn the activity is almost null. Fig. 4(b) shows that in the case of the catalyst prepared in aqueous medium the TON is practically constant at Sn contents lower than 0.23% . At higher Sn values the activity drastically decreases. The catalysts prepared in HCl have a different behavior; the TON is decreased when Sn is increased from 0% to 0.20% and for higher Sn contents the TON is almost constant. These results are in agreement with literature reports that indicate that tin addition decreases the TON of the active sites [51]. The lower activity of the catalysts could be explained by geometrical and electronic effects. The geometrical effect involves the blocking of Pt active sites by Sn, precluding in this way the adsorption of the reactant. The electronic effect takes into account the modification of the electronic structure of Pt by Sn deposit in its vicinity. Studies by Carvalho et al. [40] indicated that the electronic effect is more important than the geometrical one. Fig. 4 shows that Sn is deposited in greater interaction with the active (Pt-Re) metal phase in the case of the trimetallic catalysts prepared in HCl medium, especially at low Sn content.

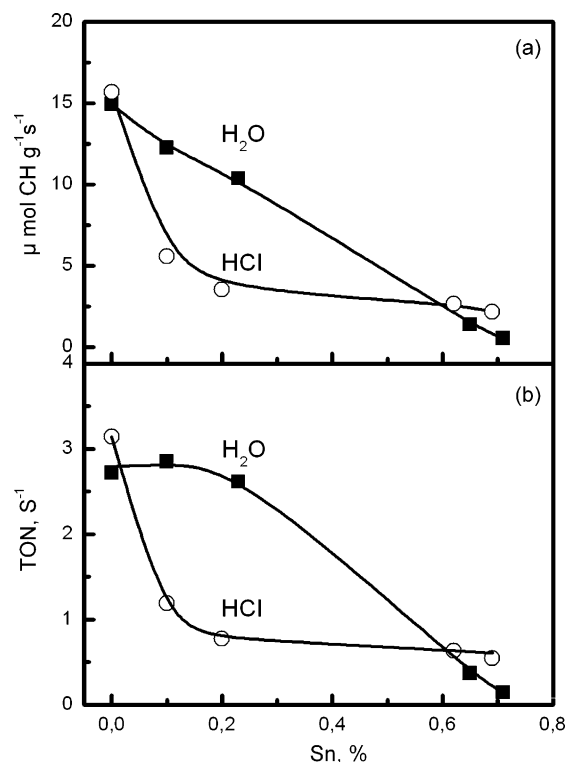


Fig. 4. Cyclohexane dehydrogenation rate as a function of the Sn content. Catalysts prepared in H_2O and HCl medium.

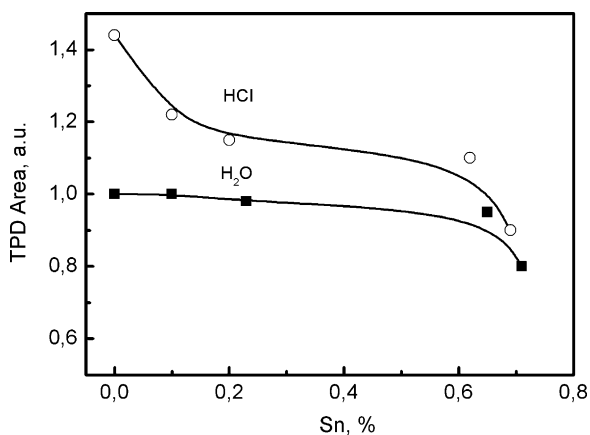


Fig. 5. Area of the pyridine TPD trace as a function of the Sn content. Catalysts prepared in H₂O and HCl medium. Area of the TPD trace of Pt-Re(base) = 1.00.

Fig. 5 is a plot of the area under the pyridine TPD curves as a function of Sn loading. It can be seen that the two series of catalysts have different curve shapes. The catalysts prepared in HCl medium have continuous decrease in the total acidity as Sn content is increased while the catalysts prepared in H₂O medium show a nearly constant acidity zone between 0 and 0.65 wt% of Sn content. At higher Sn content (0.71 wt%) the acidity decreases. In the case of catalysts prepared in HCl medium the results can be easily explained when the basicity of the Sn oxides is recalled. These oxides would neutralize the acid sites of the support. On the other hand, for the series of catalysts prepared in H₂O medium the effects of tin oxides on the acidity could be compensated by the increase of Cl contents. The Cl level is increased about 30% when the Sn content is increased from 0.10 to 0.65 wt% in the H₂O medium series (Table 1). For the same Sn loading range the catalysts prepared in HCl have an increase of Cl content of only 5%. It can also be seen in Fig. 5 that the series of catalysts prepared in HCl medium have a higher total acidity than catalysts prepared in H₂O medium. The TPD traces of the catalysts (not shown) display a slight shift of the maximum of the desorption peak to lower temperatures as the Sn content increases. This means that Sn addition produces a decrease of the strong acid sites. This behavior can be found in the case of all the catalysts, regardless of the preparation medium.

Fig. 6 shows the conversion values obtained in the reaction of isomerization of 3,3-dimethyl-1-butene (33DM1B) as a function of the Sn content for both catalyst series. The extent of this reaction was taken as a measure of the concentration of Brønsted acid sites. With the exception of the blank (pure H₂O) catalyst, the variation

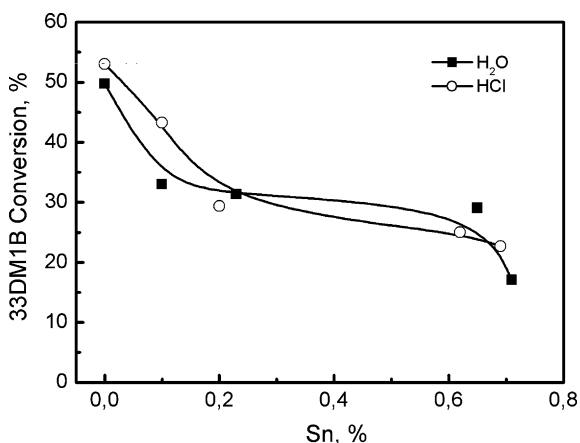


Fig. 6. Conversion of 33DM1B as a function of the Sn content. Catalysts prepared in H₂O and HCl medium.

of Brønsted acidity (measured as 33DM1B conversion) closely resembles the pattern obtained with TPD of pyridine (Fig. 5). Similar results were previously reported for Pt-Re/Al₂O₃ catalysts [32] where it was found that Lewis acidity (measured by pyridine FTIR) does not depend on the pH of the impregnating solution of Ge loading. Then it can be safely concluded that the modification of total acidity is only due to the variation of Brønsted acid sites.

The results of Fig. 6 show that the catalysts prepared in HCl medium with the lower Sn content have a greater activity in 33DM1B isomerization than those prepared in H₂O medium, i.e., they have a greater Brønsted acidity. This can be related to a higher amount of chlorinated species on the surface of alumina [52]. These species have an inductive effect over the hydroxyl groups.

The *n*-C₇ reforming reaction allows an analysis of both the metal and acid functions of the catalyst because it proceeds through a bifunctional mechanism [53–57]. It is a typical reaction occurring in naphtha reforming units. Due to the importance of toluene production in the petrochemical industry, a high and stable selectivity to this product is very much desirable. Another objective is to minimize the formation of C₁–C₄ light gases of low commercial value.

Table 2 contains values of *n*-C₇ conversion and yield to toluene, C₇ isomers, C₁ and C₂–C₄ at 6 and 20 h time-on-stream, for the blank Pt-Re(H₂O) and the blank Pt-Re(HCl) catalysts previously sulfided, and for the Pt-Re-Sn catalysts (0.1, 0.3, 1, 2; H₂O, HCl). It can be seen for each catalyst series that the conversion on the trimetallic catalyst with low Sn content (<0.2 wt%) is greater than that obtained with the corresponding sulfided catalyst. As the Sn doped catalysts lose less activity in the course of the reaction it can be concluded that these trimetallic catalysts are more stable than the bimetallic sulfided samples. At high Sn contents the acidity decreases and the decrease of the dehydrogenating capacity of the metal function makes these catalysts less active.

Table 2 also shows that sulfidation is effective in inhibiting the hydrogenolytic activity of the Pt-Re ensembles as expected. The unsulfided Pt-Re (base) catalyst (not reported here) has a methane yield of 11.9% and 10.6% at 6 and 20 h time-on-stream, respectively. The addition of Sn produces an effect similar to the effect of sulfidation. The effect is stronger as the Sn content is increased. The trimetallic catalysts prepared in HCl medium produce less methane than those prepared in H₂O. The hydrogenolysis results in the course of the *n*-C₇ reforming are in agreement with the values of Fig. 3 that revealed a lower hydrogenolytic activity of the HCl catalysts.

In order to analyze the formation of light gases C₁–C₄, it must be taken into account that C₁ is produced mainly from a hydrogenolysis reaction catalyzed by the metal sites while the C₂–C₄ gaseous hydrocarbons are formed by a bifunctional mechanism controlled by the acid function of the catalyst. It is convenient to discuss the two series of catalysts separately. For the catalysts prepared in HCl medium the production of C₂–C₄ light gases decreases as Sn content increases. This result is in agreement with the acidity variation of these catalysts. For the H₂O series, the C₂–C₄ yield does not have a well defined tendency as Sn content varies. This different behavior could be due to differences between the acid sites formed in each catalyst series, as discussed previously. The results in Table 2 also indicate that the toluene yield passes through a maximum for 0.2 wt% Sn (0.3 wt% Sn nominal) in both catalyst series. This can be explained by recalling that the dehydrocyclization reaction is bifunctional. The limiting step is the acid-catalyzed cyclization on the acid sites. The main difference between the cracking and dehydrocyclization reactions is that the latter requires sites of lower acid strength. Therefore as the Sn content is increased the proportion of mild acid sites is increased and the dehydrocyclization reactions are favored. In the same way, cracking is disfavored.

Table 2
n-C₇ reforming reaction. Percentages of conversion and yields to toluene, *i*-C₇, C₁, C₂–C₄, at 6 and 20 h time-on-stream.

Catalysts	Time (h)	Conversion (%)	Yield (%)			
			Toluene	<i>i</i> -C ₇	C ₂ –C ₄	C ₁
Pt-Re(H ₂ O), sulfided	6	93.6	30.1	6.6	31.8	1.0
	20	88.5	25.1	7.2	31.2	1.0
Pt-Re-Sn(0.1, H ₂ O)	6	95.3	37.6	8.5	27.0	1.9
	20	93.7	37.4	8.8	27.3	1.4
Pt-Re-Sn(0.3, H ₂ O)	6	95.5	39.7	6.3	31.2	2.0
	20	94.8	34.1	7.4	30.4	1.2
Pt-Re-Sn(1, H ₂ O)	6	97.9	35.8	5.2	35.2	1.1
	20	96.5	32.8	5.6	33.8	0.9
Pt-Re-Sn(2, H ₂ O)	6	85.4	21.4	11.0	26.1	0.6
	20	83.0	19.9	10.5	26.2	0.6
Pt-Re(HCl), sulfided	6	87.4	39.5	6.5	22.6	0.8
	20	76.3	21.7	6.4	27.4	0.8
Pt-Re-Sn(0.1, HCl)	6	93.2	23.1	7.1	38.6	1.0
	20	88.9	19.9	7.7	37.1	0.8
Pt-Re-Sn(0.3, HCl)	6	97.9	33.8	6.2	35.8	1.1
	20	96.5	31.4	7.6	33.8	0.9
Pt-Re-Sn(1, HCl)	6	81.1	18.3	9.2	29.0	0.6
	20	75.1	16.0	9.1	27.0	0.6
Pt-Re-Sn(2, HCl)	6	74.0	14.1	9.1	28.1	0.5
	20	66.7	12.1	8.7	26.0	0.5

C₂–C₄: C₂ + C₃ + C₄.

Finally it is interesting to remark that for the two catalysts series in the case of the trimetallic sample with 0.1 wt% Sn the yield to C₇ isomers is greater than that of the corresponding blank catalyst. This could be due to a decrease of the acid strength that inhibits the cracking and favors the isomerization. In spite of obtaining a higher yield in isomers with the catalysts containing 0.6 and 0.7 wt% Sn (2.0 wt% Sn nominal), these catalysts display a low activity and for this reason are considered as not convenient.

4. Conclusions

The FTIR-CO and TPR results show that trimetallic Pt-Re-Sn/Al₂O₃-Cl catalysts prepared in H₂O or HCl medium present a good interaction between Sn and the catalytically active species (Pt-Re). This strong interaction of Sn with the active phase correlates with the lower hydrogenolytic and dehydrogenating activity of the trimetallic catalysts than those of the bimetallic catalysts.

The total acidity and the Brønsted acidity decrease with the addition of Sn. The catalysts prepared in HCl have both higher Brønsted and total acidity in comparison to those prepared in H₂O.

In the case of catalysts prepared in HCl medium, the production of C₂–C₄ gases in the *n*-C₇ reforming reaction also decreases upon Sn addition confirming that the cracking activity decreases when the acidity is decreased. In both trimetallic catalysts series a decrease in the toluene yield can be seen at high Sn content. The production of toluene depends on the activity of dehydrocyclization. Dehydrocyclization requires sites of lower acid strength than those needed for cracking.

In the two preparation media (H₂O and HCl), the addition of small amounts of Sn (≤0.3 wt%) would enable the step of sulfidation of Pt-Re/Al₂O₃ catalysts to be spared. Sn decreases hydrogenolytic capacity of the metal function and the Sn doped catalyst has a greater stability than the sulfided Pt-Re catalyst.

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