Differences in coke burning-off from Pt–Sn/Al$_2$O$_3$ catalyst with oxygen or ozone

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Abstract

Pt–Sn/γ-Al$_2$O$_3$ catalysts with different Sn loadings were prepared by incipient wetness coimpregnation of γ-Al$_2$O$_3$ with H$_2$PtCl$_6$ and SnCl$_2$. The Pt–Sn interaction was tested by temperature-programmed reduction and the catalytic activity was measured by cyclohexane dehydrogenation. The catalysts were coked by cyclopentane at 500 °C and totally or partially decoked with O$_2$ at 450 °C or O$_3$ at 125 °C. Coke deposits were studied by TPO and the catalytic activity of coked catalysts, partially or totally regenerated, by cyclohexane dehydrogenation.

The TPO with O$_3$ shows that coke combustion with O$_3$ starts at a low temperature and has a maximum at 150 °C, that is a compensation between the increase of the burning rate and the rate of O$_3$ decomposition when increasing the temperature. Meanwhile O$_2$ burns coke with a maximum at 500 °C. When performing partial decoking with O$_3$ (125 °C) the remaining coke is more oxygenated and easier to burn than the coke that remains after decoking with O$_2$ (450 °C).

After burning with O$_3$ the dehydrogenation activity of the fresh catalyst is recovered, while after burning with O$_2$ the activity is higher than that of the fresh catalyst. The burning with O$_3$ practically does not change the original Pt–Sn interaction while the burning with O$_2$ produces a decrease in the interaction, producing free Pt sites with higher dehydrogenation capacity.

The differences in coke combustion with O$_3$ and O$_2$ are due to the different form of generation of activated oxygen, the species that oxidizes the coke. O$_3$ is activated by the γ-Al$_2$O$_3$ support at low temperatures firstly eliminating coke from the support while O$_2$ is activated by Pt at temperatures higher than 450 °C and the coke removal starts on the metal. Then, the recovery of the Pt catalytic activity as a function of coke elimination is faster with O$_2$ than with O$_3$.

1. Introduction

Pt–Sn/γ-Al$_2$O$_3$ is a very important catalyst in the petroleum refining and petrochemical industries. In the naphtha reforming process the main reactions, alkane isomerization and dehydrocyclization, occur by bifunctional metal-acid mechanisms that involve Sn promoted Pt (the metal function) and alumina promoted with chloride and SnO$_2$ (the acid function). In the alkane dehydrogenation process only the metal function is necessary and the acidity of γ-Al$_2$O$_3$ is neutralized by alkaline metals. In both processes a carbonaceous deposit, commonly named coke, is produced on the catalyst and causes its deactivation. The activity is recovered by burning-off the coke with diluted air, and in this process it is very important to maintain the Pt–Sn interaction.

The combustion of coke is very exothermal and its temperature must be controlled to avoid irreversible segregation of Sn from Pt and sintering of the alumina support. To fulfil these requirements the operation variables of the continuous catalyst regeneration (CCR) naphtha reforming process are such that the coke build up is smaller than in the classical semiregenerative platforming process and the combustion of this coke can be performed at a lower temperature. In the alkane dehydrogenation process the reaction temperature is limited but even so the simultaneous regeneration of the catalytic activity and of the Pt–Sn interaction by coke burning is difficult or not possible. In the literature, papers can be found that describe the elimination of coke with hydrogen [1,2] in a less exothermal reaction than the oxygen-assisted

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combustion. Also coke removal with carbon dioxide [3], that reacts with coke endothermally, has been attempted. These reactions are not practical because the coke elimination is only partial. The use of water as decoking agent is also unpractical; the reaction is endothermic, but water at high temperature accelerates the irreversible sintering of alumina. A more interesting approach is the use of comburents that burn-off the coke at lower temperatures. One of such comburents is ozone. It was used to burn-off coke from zeolite cracking catalysts [4], reforming Pt–Re/γ-Al$_2$O$_3$ catalysts [5–7] and SO$_4{}^{2-}$–ZrO$_2$ isomerization catalysts [8]. Nitrous oxide has also been used for the same purpose [9]. In the regeneration of Pt–Re/γ-Al$_2$O$_3$ catalysts it has been shown [5,6] that coke elimination with O$_3$ has a maximum at about 125–127 °C.

The objective of this paper is to compare the combustion of coke deposits of Pt–Sn/γ-Al$_2$O$_3$ catalysts with O$_2$ and O$_3$. The coke combustion patterns and the regeneration of the catalytic activity of the metal function when either O$_2$ and O$_3$ are used and the mechanisms of activation of these oxidizing agents are compared.

2. Experimental

2.1. Catalyst preparation

The catalysts were prepared by incipient wetness impregnation of a γ-alumina provided by Ketjen (200 m^2 g^{-1} specific surface area, 0.49 cm^3 g^{-1} pore volume, ground to 35–80 mesh) with a solution of SnCl$_2$·2H$_2$O and H$_2$PtCl$_6$·6H$_2$O acidified with HCl. The concentration and volume of the solution were regulated in order to yield final catalysts with the desired metal contents. Monometallic catalysts: 0.3% Pt or 0.3% Sn; bimetallic catalysts: 0.3% Pt and 0–0.6% Sn. The impregnated samples were dried for 10 h at 110 °C, calcined for 4 h at 450 °C and then reduced in hydrogen for 4 h at 500 °C. The chlorine content of the catalysts was determined by the Volhard–Charpentier method. The values were between 0.88 and 1.0% for all of them.

2.2. Coking of the catalysts

The coking agent was cyclopentane (CP), which was injected at a flow rate of 2.68 ml h^{-1} into a stream of hydrogen of 30 ml min^{-1} that flowed over 2.0 mg of catalyst maintained at 500 °C. The reaction was stopped after 8 h.

2.3. Coke burning

The coked catalysts were totally or partially regenerated with two different comburent streams and with different combustion time spans. (a) Oxygen–nitrogen mixture: pure N$_2$ was first allowed to flow over the sample until the temperature of 450 °C was reached. The N$_2$ flow was then stopped and the oxidizing mixture was injected (2.3% O$_2$ diluted in

N$_2$, 40 ml min^{-1}). (b) Ozone–air mixture: ozone was generated by passing a stream of air between two high-voltage electrodes; the equipment was similar to that used by My and Sahghal [10]. An air flow of 54 ml min^{-1} was used and the O$_3$ concentration at the ozonizer outlet was 1.1%. The ozone–air mixture was passed over the catalysts at a temperature of 125 °C. The ozonizer was turned-on only when the reaction temperature had stabilized.

2.4. Reaction test

The catalytic activity of the metal phase of the fresh and decoked catalysts was evaluated by means of the cyclohexane (CH) dehydrogenation reaction. The reaction was carried out in a fixed bed flow reactor at 270 °C, with 30 mg of the catalyst ground and sieved to 35–80 meshes, with flow rates of 1.61 ml h^{-1} of CH and of 80 ml min^{-1} of H$_2$ and at atmospheric pressure. The effluent was analyzed in an on-line chromatograph with a FID detector and a column packed with 15% FFAP on Chromosorb P.

2.5. Catalyst characterization

Temperature-programmed reduction (TPR) tests were performed in an Ohkura TP2002 S apparatus equipped with a thermal conductivity detector. The samples were heated from room temperature to 750 °C at 10 °C min^{-1} in a reducing gas stream (5% H$_2$ in Ar, of 45 ml min^{-1}).

Temperature-programmed oxidation (TPO) tests were carried out in an apparatus with intermediate methanation and with detection by flame ionization (FID). The catalyst sample was heated from room temperature to 700 °C at 12 °C min^{-1} in an oxidizing gas stream (30 ml min^{-1}, 2.3% O$_2$ in N$_2$). In one set of experiments and in order to see the burning pattern of coke with ozone, the oxidizing mixture was changed to 2.3% O$_2$ in N$_2$, and passed through the ozonizer before entering the TPO cell.

3. Results and discussion

The TPR tests indicate that the amount of hydrogen consumed during the reduction of the metal oxides and therefore yield information about the interaction between them. Fig. 1 shows the TPR plots of the monometallic (A) and bimetallic catalysts (B). Pt(0.3)/γ-Al$_2$O$_3$ has a main peak of hydrogen consumption that starts at 150 °C and has a maximum at 245 °C, which would correspond to the reduction of large Pt oxide or oxychloride crystals weakly interacted with the support [11]. A second peak at about 357 °C would correspond to the reduction of dispersed oxychloride species (PtCl$_x$O$_y$) in strong interaction with the alumina support. According to the TPR area, previously calibrated, the hydrogen consumption corresponds to the reduction of Pt(VI) to Pt(0). Sn(0.3)/γ-Al$_2$O$_3$ has a broad zone of reduction of Sn oxide, starting at 180 °C and ending at 550 °C, with two
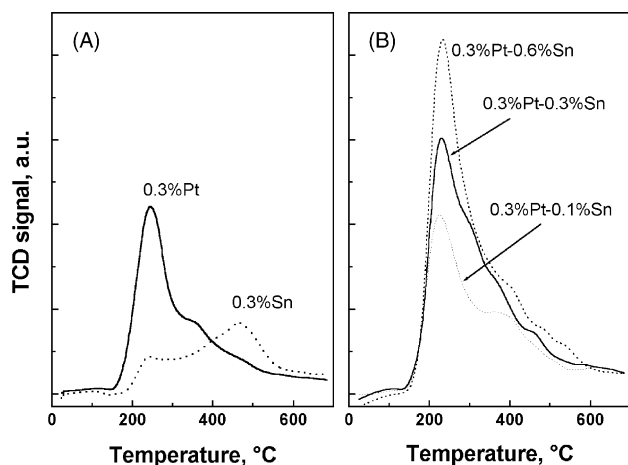
Fig. 1. TPR profiles: (A) monometallic Pt(0.3)/γ-Al₂O₃ and Sn(0.3)/γ-Al₂O₃ catalysts; (B) bimetallic Pt(0.3)–Sn(0.1)/γ-Al₂O₃, Pt(0.3)–Sn(0.3)/γ-Al₂O₃ and Pt(0.3)–Sn(0.6)/γ-Al₂O₃ catalysts.

Fig. 2. Catalytic activity (conversion) in the dehydrogenation of CH at 270 °C.

peaks at 235 and 462 °C. In the absence of Pt, Sn(IV) is reduced only to Sn(II) [12]. The TPR area indicates that nearly 80% of Sn(IV) is reduced to Sn(II).

Fig. 1B shows the TPR plots of the bimetallic Pt–Sn catalysts. For the three catalysts the hydrogen consumption starts at 150 °C and has a sharp peak at 218 °C. The H₂ consumption increases compared to the monometallic catalysts because of the simultaneous reduction of Pt and Sn oxides. Additional Sn oxides are reduced due to the catalytic action of Pt(0). In Pt(0.3)–Sn(0.1)/γ-Al₂O₃ the number of Pt atoms almost doubles the number of Sn atoms; then many Pt atoms are not interacted with Sn and the TPR of this catalyst has the peak of Pt at 375 °C. In Pt(0.3)–Sn(0.1)/γ-Al₂O₃ and Pt(0.3)–Sn(0.3)/γ-Al₂O₃ catalysts, practically all the reducible Sn oxides are interacted with Pt(0) and the reduction ends at 500 °C, while in the case of the monometallic Sn(0.3)/γ-Al₂O₃ catalyst the reduction of the oxides continues up to 550 °C. This means that there is a good interaction between Pt and Sn oxides and that Pt catalyzes the reduction of the Sn oxides. In Pt(0.3)–Sn(0.6)/γ-Al₂O₃ due to the great excess of Sn (3.3 atoms of Sn per Pt atom) some amount of Sn oxide is separated from Pt and needs higher temperatures to be reduced. The catalysts were prepared by coimpregnation of the support with a solution of the metal precursors and in this solution the complex PtCl₂(SnCl₃)₂ is formed. This complex on reduction leaves Pt and Sn in good interaction [13].

The presence of Pt(0) is necessary to reduce Sn(IV) up to Sn(0) [12], but according to Lieske and Volter [14] only a minor part of Sn(IV) is reduced to Sn(0), which combines with Pt(0) to form "alloy clusters". The major portion of Sn(IV) is reduced to Sn(II) which interacts with the γ-Al₂O₃ support. The amount of alloy increases with the increase of tin content. Several Pt–Sn alloys can be formed, rich in Pt or rich in Sn, according to the metal concentrations. According to the literature [15–18] the main alloy is 1:1 Pt:Sn. The alloys have very low dehydrogenation activity [19]. It can be
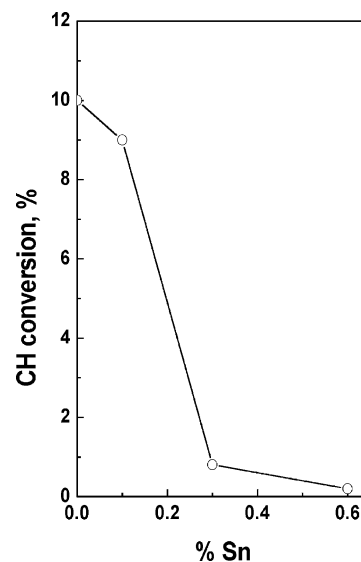
considered [16,20] that there is an electronic transfer from Sn to Pt in the alloy, due to the smaller electronegativity of Sn, and that the electronic character of the alloy $Pt^{\delta-}$–$Sn^{\delta+}$ produces a decrease in the hydrogenation–dehydrogenation activity of Pt.

Fig. 2 shows catalytic activity results of the fresh catalysts in the CH dehydrogenation reaction test. At the temperature of the test this reaction is perfectly selective, only benzene is produced and no cracking products are observed. The activity drops markedly when increasing the Sn content. This reaction is a non-demanding one in the sense of Boudart et al. [21], meaning that the catalytic activity of each exposed Pt atom is always the same, irrespective of a particular structure or size of the ensemble of Pt atoms. Comparing Pt(0.3)/γ-Al₂O₃ with Pt(0.3)–Sn(0.3)/γ-Al₂O₃, we can see that the activity drops to one-tenth. This decrease is not due to a great increase in the size of the metal particles (great decrease in dispersion) because the mean particle size measured by TEM was 1.6 nm for both catalysts. The reason of the decrease would be an electronic effect (alloy formation) together with a geometric effect produced by the blocking of Pt atoms by Sn.

When the Sn concentration is low (0.1%) the drop in catalytic activity is small. Probably the low amount of Sn produces an alloy rich in Pt that still has catalytic activity. In the Sn(0.3%) catalyst the alloys formed must be richer in Sn and very likely of the Pt:Sn 1:1 kind, that is catalytically inactive, as quoted above. Another possibility is the difference in the spillover of activated hydrogen from Pt due to the different composition and concentration of the γ-Al₂O₃-Sn-oxide species of the support.

Fig. 3 shows the TPO profiles of coke on the catalysts, using as oxidant the mixture 2.3% O₂ in N₂. For Pt/γ-Al₂O₃ coke combustion starts at 350 °C and ends at approximately 550 °C with a maximum at 520 °C. An in-
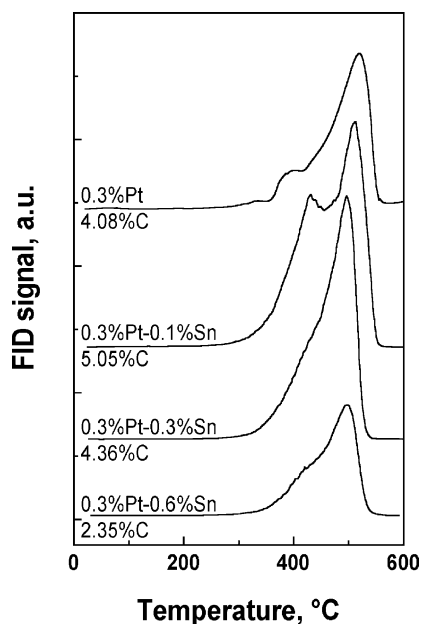
Fig. 3. TPO profiles of coke deposited on the catalysts using an oxidizing mixture of 2.3% O_2 in N_2.

Fig. 4. TPO profiles of coke on a Pt(0.3)–Sn(0.3)/γ-Al$_2$O$_3$ catalyst with 4.36% carbon content: O_2 = 2.3% O_2 in N_2; O_3 = 2.3% O_2 in N_2 passed through the ozonizer.

crease in the Sn concentration decreases the coke deposition and the temperatures of the start of coke combustion, of the peak maximum and of the end of combustion. These facts can be due to the lower dehydrogenation activity of the bimetallic catalysts and to the decrease of the acidity of the support produced by Sn oxides [22]. Pt(0.3)/γ-Al$_2$O$_3$ and Pt(0.3)–Sn(0.1)/γ-Al$_2$O$_3$ have a small zone or peak at low temperatures. It is accepted that the coke that burns in this zone is deposited on the metal and on its neighborhood [23] and that in bimetallic catalysts the fraction of coke deposited on the metal is very small [24].

In order to see the temperature at which O_3 is able to burn the coke and to compare this with O_2 burning, two TPO tests were performed. The first used oxygen as oxidant (2.3% O_2 in N_2) and the other used ozone (same mixture passed through the ozonizer). Fig. 4 shows both TPO profiles. On the catalyst surface O_3 is adsorbed and decomposed to O_2 and atomic oxygen [25]. Atomic oxygen has a great oxidizing activity and is capable of oxidizing coke at low temperatures. The TPO shows that coke elimination with O_3 has a maximum, as in the case with Pt–Re/γ-Al$_2$O$_3$ [5,6]. In Fig. 4, this maximum is located at 150–160 °C and can be due to a compensation of two phenomena. When the temperature is augmented, the rate of oxidation by atomic oxygen increases and the same occurs with the rate of O_3 decomposition to O_2 at the reactor walls, homogeneously and in contact with the catalyst particles [6]. At temperatures higher than 200 °C O_3 is completely decomposed before reaching the coked catalyst and the only oxidizing gas in contact with coke is O_2, that is inert at this temperature. Nevertheless the oxidation to CO_2 is higher than in the case of the mixture without O_3 because at low temperatures atomic oxygen oxidizes the coke to oxygen-rich intermediates that are more
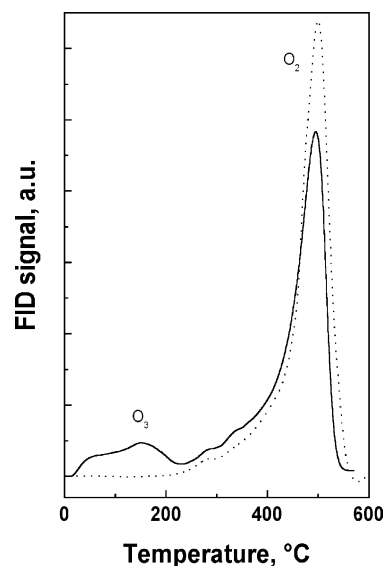
easily burned by O_2 at these temperatures. For this reason the combustion of O_3-treated coke with O_2 ends before the combustion of coke not treated with O_3.

Fig. 5 compares the TPO profiles of Pt(0.3)/γ-Al$_2$O$_3$ partially decoked with O_2 and with O_3. In the TPO experiment the oxidant was the standard O_2 mixture (2.3% in N_2). It can be seen that in 1 h O_3 at 125 °C can eliminate more coke from the catalyst than O_2 at 450 °C. The TPO shows that the coke remaining after the partial elimination with O_3 can be totally eliminated with the standard O_2 mixture at a lower temperature than that required in the case of the partial elimination with O_2. Fig. 5 shows that the coke remaining after a 1 h O_2 treatment has a TPO maximum at 500 °C, and at 400 °C after a 2 h treatment. Meanwhile the coke remaining after a 1 h O_3 treatment has a TPO maximum at 285 and 257 °C after a 2 h treatment. After 2 h the same amount of coke (0.16% C) burns completely at a temperature lower than 400 °C in the case of the partial regeneration with O_3, while in the case of the partial regeneration with O_2 the maximum burning rate occurs at 400 °C. O_3 regeneration leaves oxidized residual coke that can be burned with O_2 more easily than the original coke.

From Fig. 5 it can be deduced that O_3 is superior to O_2 in the initial part of coke elimination: in 1 h O_3 decreases the carbon content from 4.08 to 0.34%, while O_2 decreases it from 4.08 to 1.19%. But in the second hour O_3 decreases the carbon content from 0.34 to 0.16% while O_2 decreases it from 1.19 to 0.15%. Because of the great reactivity of O_3 there are diffusional effects that retard the burning in the particle center. Burning with O_3 the outer part of the particle is white (rapid burning) while the center is still black. When using O_2 all the particle is cleared off simultaneously (non-diffusive or chemical control).
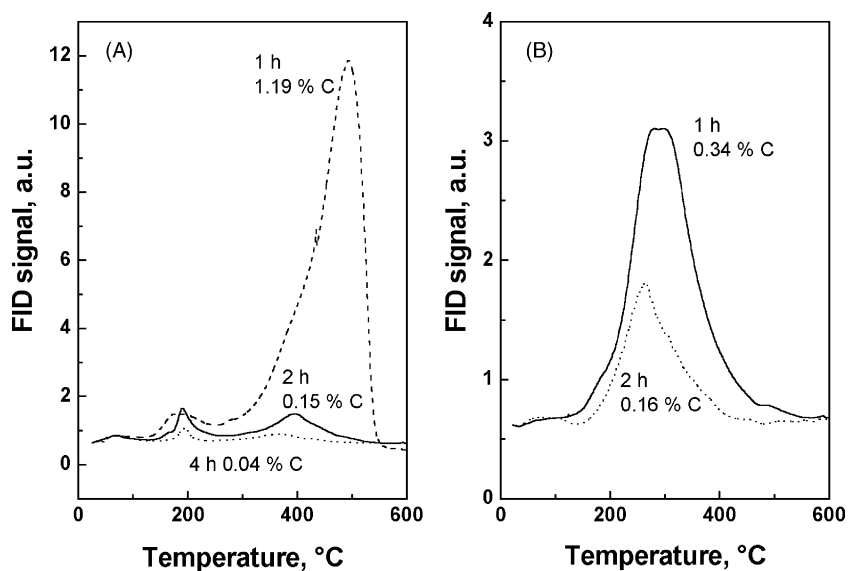
Fig. 5. TPO profiles obtained with an oxidizing mixture of 2.3% O_2 in N_2 and a partially decoked Pt(0.3)/γ-Al$_2$O$_3$ catalyst: (A) partially decoked with O_2–N_2 at 450 °C; (B) partially decoked with O_3–O_2–N_2 at 125 °C.

Fig. 6 confirms for Pt(0.3)–Sn(0.1)/γ-Al$_2$O$_3$ that partial coke elimination with O_2 leaves a residual coke that requires high temperatures for total removal, 500 °C, as in the case of the original coke without any treatment. Fig. 6 also shows that in the case of O_3 partial decoking the residual coke needs lower temperatures in order to be eliminated with O_2.

Fig. 7 shows the TPO profiles of the bimetallic catalysts with 0.3 and 0.6% Sn after partial coke elimination with O_3. After 4 h treatment the carbon contents of the catalysts are 0.18 and 0.07%, respectively. In both cases the TPO results show that the combustion with O_2 of the residual coke occurs between 200 and 400 °C. Therefore this is a

Fig. 6. TPO profiles obtained with an oxidizing mixture of 2.3% O_2 in N_2 and a partially decoked Pt(0.3)–Sn(0.1)/γ-Al$_2$O$_3$ catalyst. Combustion with O_2 only (450 °C) and with O_3 (125 °C).

confirmation that an alternative method for removing the coke from these catalysts could be the partial elimination of coke with O_3 at 125 °C and a final combustion with diluted O_2 at a temperature lower than 400 °C. One indication from Figs. 5–7 is that adding Sn to Pt/γ-Al$_2$O$_3$ the rate of coke burning is decreased. Probably Sn decreases the ability of Pt to produce activated oxygen by dissociation and for equal regeneration time spans more coke remains on the Sn-rich catalysts.

Figs. 8 and 9 show the catalytic activity in CH dehydrogenation after coke elimination with O_2 and O_3. The catalytic activity increases with the time of decoking. In general, after the treatment with O_2 for 2 h the new catalytic activity is even greater than the original one of the fresh catalyst. In the case of Pt(0.3)/γ-Al$_2$O$_3$ (Fig. 8) the greater catalytic activity after regenerating with O_2 can be due to the greater dispersion of Pt because for this non-demanding reaction the activity is proportional to the amount of exposed Pt. It was shown [26] for Pt/γ-Al$_2$O$_3$ that the treatment with O_2 at around 500 °C produces a redispersion of Pt, obtaining a metallic dispersion greater than that of the original catalyst. In the case of the bimetallic catalysts shown in Fig. 9 the higher conversion can be due to the partial segregation of Sn from Pt. During combustion Sn is converted to Sn oxide which cannot be totally reduced back to Sn(0) upon H_2 reduction. Then only a fraction of Sn can get alloyed to Pt and the amount of free Pt crystals increases. We saw in Fig. 2 that the greater the amount of Sn interacted with Pt the lower the dehydrogenation activity. After this treatment with O_2, the greater the Sn segregation the greater the catalytic activity. An O_3 treatment of the same length produces a catalyst with an activity close to that of the fresh catalyst because the Pt–Sn interaction is preserved more. Therefore O_3 decoking of the metal function is effective in recovering
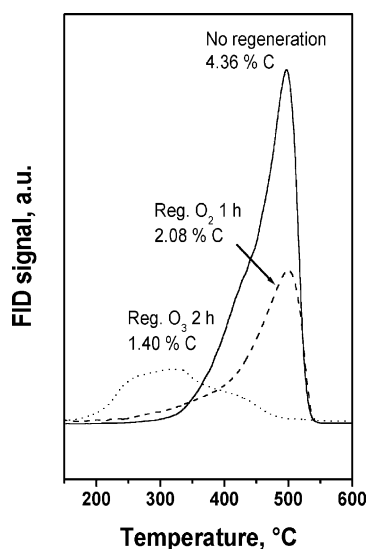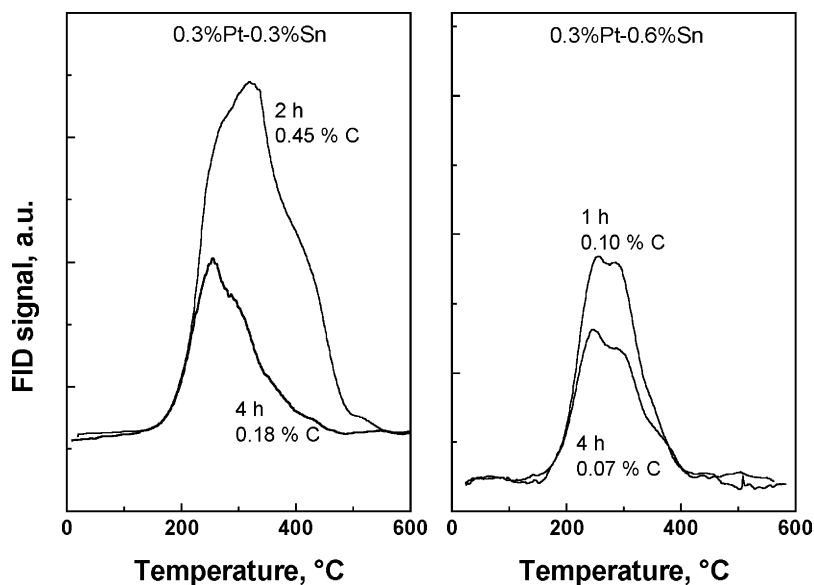
Fig. 7. TPO profiles of two bimetallic catalysts partially decoked with O_3.

the activity without changing too much the Pt–Sn interaction or the metal particle size (constant size, about 1.6 nm, according to TEM measurements).

In Fig. 9, the regeneration profiles of Pt(0.3)–Sn(0.3)/γ-Al$_2$O$_3$ (the catalyst with the highest Sn content among the catalysts shown in Figs. 8 and 9) are different from those of the other catalysts. This occurs mainly in the regeneration with O_3. As shown in the next sections below, the decomposition of O_3 on the Lewis acid sites of γ-Al$_2$O$_3$ produces active nascent oxygen. Very likely at high values of Sn concentration, Sn oxide clusters block former Lewis acid sites and the rate of O_3 decomposition is decreased. Then longer

treatments would be required for the regeneration of Sn-rich catalysts.

In the case of Pt(0.3)–Sn(0.6)/γ-Al$_2$O$_3$ the catalyst activity is very low (Fig. 2) and its recovery practically null. This catalyst has a great excess of Sn compared to Pt and most Pt sites should be covered by Sn.

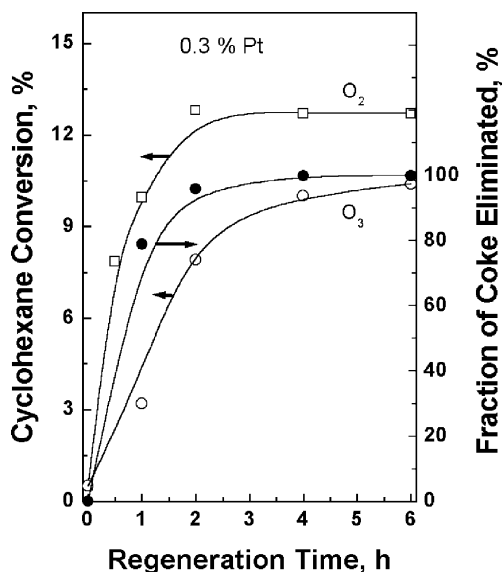All the former results show the advantages of regenerating Pt–Sn/γ-Al$_2$O$_3$ with O_3 in order to maintain the nec-

Fig. 8. Catalytic activity in CH dehydrogenation of Pt(0.3)/γ-Al$_2$O$_3$ samples decoked with O_2 or O_3. Fraction of coke eliminated as a function of the length of the regeneration step.
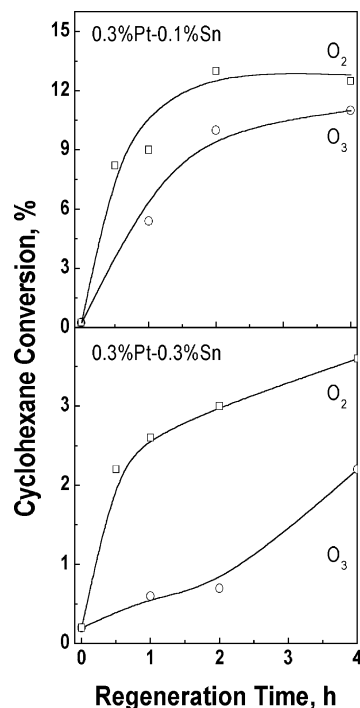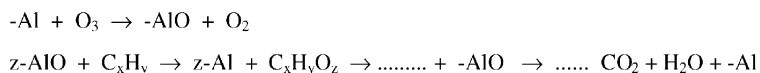

Fig. 9. Catalytic activity in CH dehydrogenation of Pt(0.3)–Sn(0.1)/γ-Al$_2$O$_3$ and Pt(0.3)–Sn(0.3)/γ-Al$_2$O$_3$ catalysts after being regenerated with O_2 or O_3.

$$-Al + O_3 \rightarrow -AlO + O_2$$

$$z\text{-AlO} + C_xH_y \rightarrow z\text{-Al} + C_xH_yO_z \rightarrow .... + -AlO \rightarrow ...... \; CO_2 + H_2O + -Al$$

Scheme 1. Ozone dissociation and oxidation of coke deposits.

essary Pt–Sn interaction. These results are similar to those obtained with Pt–Re/γ-Al$_2$O$_3$. However in the case of the Pt–Sn/γ-Al$_2$O$_3$ catalysts this advantage is even more important because the Pt–Sn interaction is difficult to keep due to the irreversible segregation of the metals at high temperatures in an oxidizing atmosphere. The Pt–Re interaction segregation is reversible in Pt–Re/γ-Al$_2$O$_3$ catalysts.

3.1. Differences in the mechanisms of coke combustion with ozone and oxygen

According to our results and others from the literature it is possible to deduce the way O$_3$ and O$_2$ eliminate coke by oxidation from the catalyst surface. Though the temperature of some experiments reported in the literature is different from ours, the results have been extrapolated to build working hypotheses.

Thomas et al. [25] by quantum chemistry calculations found that the terminal atoms of O$_3$ have a net negative charge, whereas the central atom has the compensating net positive charge. The negative oxygen atoms are Lewis bases that are easily attached to the Al^{3+} Lewis acid sites of γ-Al$_2$O$_3$. This strong O–Al bond produces the dissociation of O$_3$, giving O$_2$ that is desorbed and a nascent oxygen atom which remains on the surface. This oxygen atom, or activated oxygen, has an extraordinary oxidizing capacity and can oxidize coke deposits at room temperature. According to our TPO tests the residual coke after O$_3$ partial decoking contains oxidized components that can continue being oxidized in a step by step fashion until total elimination, as it is shown in Scheme 1.

Mul et al. [27] studied the formation of [carbon-(surface oxygen)] complexes and considered that the formation of the complexes could be due to the migration of activated oxygen from the oxide surface to the carbonaceous substrate. They also concluded that lattice oxygen of the oxides is not directly involved in the oxidation. During its migration over the surface the activated oxygen first eliminates coke on the support and then coke on the metal function.

In Ref. [5] O$_3$ was passed through an empty reactor and through the reactor charged with a fresh Pt–Re/γ-Al$_2$O$_3$ catalyst (without coke) at different temperatures. In all cases the concentration at the reactor outlet depended only on temperature, irrespective of the reactor charge. At room temperature the outlet concentration was similar to that of the inlet but decreased when the temperature was increased. The greatest decrease occurred at about 125 °C corresponding to the maximum in coke elimination with O$_3$ [5]. Therefore this maximum must be a compensation between the increase in the rate of coke burning with O$_3$ and the increase in O$_3$ decomposition. Both are activated processes which are ac-

celerated when the temperature is increased. As the decomposition of ozone is not affected by the presence of the catalyst, this decomposition should be homogeneous:

$$2O_3 \rightarrow 3O_2 \tag{1}$$

At higher temperatures activated oxygen also recombines to O$_2$ and leaves the surface:

$$2AlO \rightarrow 2Al + O_2 \tag{2}$$

O$_2$ is inert at low temperatures. Temperature values between 350 and 400 °C are necessary to activate it. The activation occurs upon dissociation over the metal:

$$2Pt + O_2 \rightarrow 2PtO \tag{3}$$

These activated oxygen atoms eliminate the coke on the metal function and can also spill over the support eliminating its coke [28].

In summary, the differences in activation and coke burning of O$_3$ and O$_2$ are the following: (i) O$_3$ is activated on the γ-Al$_2$O$_3$ support at low temperatures. Coke burning starts on the support and can continue on the metal function due to oxygen spillover. Upon an increase of the temperature the burning capacity disappears due to rapid and homogeneous decomposition of O$_3$ into inactive O$_2$. (ii) O$_2$ is activated on Pt at high temperatures and the coke burning starts on the metal. The combustion continues with coke on the support by means of spilt-over activated oxygen. Increasing the temperature always increases the burning capacity of O$_2$.

The former assertions justify the curves of activity recovery shown in Figs. 8 and 9. The activity recovery is rapid with O$_2$ because the metallic active sites get free of coke first. With O$_3$ the recovery is slower because these sites are the last to get free of coke. In the case of Pt(0.3)/γ-Al$_2$O$_3$ (Fig. 8) if we consider that at 4 h all the coke (4.08% C) was eliminated from the catalyst surface and if we take the data of %C of Fig. 5A, the fraction of carbon eliminated can be calculated as a function of the regeneration time. These data were introduced in Fig. 8 (dotted line). The curve clearly shows how the metal activity is recovered more selectively with O$_2$.

4. Conclusions

The preparation of Pt–Sn/γ-Al$_2$O$_3$ catalysts by coimpregnation produces a good Pt–Sn interaction. A fast drop of the dehydrogenating capacity occurs upon increasing the Sn content, due to the increase of the Pt–Sn alloying and the decrease of free non-alloyed Pt.

The TPO of coked catalysts with O$_2$ and with O$_3$ showed that O$_3$ is able to burn coke at near room temperature with

a maximum rate at 150–160 °C, that is a balance between the growth of the oxidation rate and the O_3 decomposition at higher temperatures. The TPO with O_2 starts at about 350 °C, and has a sharp maximum at 520 °C and ends at 550 °C.

The regeneration of the coked catalyst with O_2 at 450 °C produces metal segregation, with an increase of the concentration of unalloyed Pt and of the metal catalytic activity. The regeneration with O_3 at 125 °C preserves better the Pt–Sn interaction. In this case the coke is oxygenated step by step producing intermediates that are easier to burn with O_3 or O_2. The coke elimination with O_2 starts on the metal function while the coke elimination with O_3 starts on the alumina support.

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