

Effect of tin and potassium addition on the nature of platinum supported on silica[☆]

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Abstract

The effects of tin and potassium addition on the catalytic properties of Pt/SiO₂ catalysts were studied by diffuse reflectance UV–vis spectroscopy, temperature programmed reduction (TPR), CO chemisorption and isobutane dehydrogenation. Pt/SiO₂, Sn/SiO₂ and Pt–Sn/SiO₂ catalysts were prepared by incipient wetness impregnation with aqueous solutions of H₂PtCl₆ and SnCl₂. Pt–Sn/SiO₂ catalysts were prepared by coimpregnation and sequential impregnation. A part of these catalysts was then impregnated with an aqueous solution of KOH. Fresh and calcined catalysts were studied. [PtCl₂(SnCl₃)₂]²⁻ complex was only detected in (PtSn/SiO₂) and Sn(Pt/SiO₂) catalysts. The proximity between Pt and Sn species favoured the formation of Pt–Sn ensembles or alloys after the reduction treatment that provided stability and selectivity for the isobutane dehydrogenation. The addition of potassium to fresh Pt–Sn/SiO₂ did not change the activity, but it improved the dehydrogenation selectivity, which reached values of almost 100%. Surface Pt–Sn species changed by the calcination treatment, causing the segregation of Pt and Sn oxide species. This treatment caused a decrease of CO/Pt ratio, activity and selectivity of Pt–Sn catalysts. In calcined Pt–Sn–K catalysts, the activity seemed to be a function of K–Pt–Sn interactions.

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1. Introduction

Recently, the dehydrogenation of light paraffins has acquired importance due to the growing demand of light olefins such as propene and isobutene [1]. In these processes, supported Pt–Sn catalysts have shown advantages because of their lower deactivation rate and high selectivity for dehydrogenation reactions. The effect of tin has been explained in terms of geometric effects [2]: tin decreases the size of platinum ensembles; reducing hydrogenolysis and coking that require large ensembles of platinum. A second explanation is the modification of the electronic density of Pt, either due to a charge positive transfer from Snⁿ⁺ species or to the different electronic structures in Pt–Sn alloys [3].

Nowadays, several studies are being carried out to evaluate the modification of the stability, selectivity and activity of metallic catalysts by the addition of some alkali metals such as Li, Ba, K, Ca and others [4–9]. The use of alkaline ions has been reported for Pt/Al₂O₃ and PtSn/SiO₂, [4] Ni/SiO₂ [5], Pd/SiO₂ [6] and Cr/Al₂O₃ [7]. Siri et al. [8] studied isobutane dehydrogenation in a series of Pt and Pt–Sn catalysts, modified by the Li addition, prepared by incipient wetness impregnation and surface organometallic chemistry on metal (SOMC/M) techniques. The incorporation of Sn and Li improved light-paraffin dehydrogenation and inhibited isomerization and cracking reactions. Siri et al. [4] also found selectivities of 98% toward isobutene and a good performance in deactivation–regeneration cycles on Pt–Sn/Al₂O₃ catalysts modified with magnesium, calcium and barium.

The effect of potassium on Pt and Pt–Sn supported on silica, prepared by ion-exchange method, was studied by Cortright et al. [9] for isobutane dehydrogenation. They found that the addition of tin and potassium diminishes the size of the surface platinum ensembles, suppressing

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the hydrogenolysis, isomerization and coking reactions. In K–Sn–Pt/SiO₂ catalyst, dehydrogenation rate increased either due to an increase in the number of sites available for hydrogen removal from adsorbed isobutane or to the stabilization by potassium of molecular adsorbed isobutane.

This study aimed to examine the effects of tin and potassium addition on the catalytic properties of Pt/SiO₂. Temperature programmed reduction (TPR), UV–vis spectroscopy by diffuse reflectance (DRS) and CO chemisorption were used to characterize these catalysts. The activity of the catalysts was determined for the isobutane dehydrogenation.

2. Experimental

Pt/SiO₂, Sn/SiO₂ and Pt–Sn/SiO₂ catalysts were prepared by incipient wetness impregnation, using aqueous solutions of H₂PtCl₆ and SnCl₂ in 1 M HCl. Pt–Sn/SiO₂ catalysts were prepared by coimpregnation and sequential impregnation, adding first Pt and then Sn and vice versa. A commercial SiO₂ (Baker), crushed to a size of 60–80 mesh, was used as support. The volume of the impregnation solution was 2.4 cm³ g⁻¹ silica. A part of these catalysts was then impregnated with an aqueous solution of KOH. The metal contents in the catalysts were 0.5% Pt, 0.6% Sn and 0.3% potassium. Fresh and calcined catalysts were studied. The catalyst preparation methods are listed in Table 1.

The catalysts were studied by diffuse reflectance UV–vis spectroscopy at atmospheric conditions in a Perkin-Elmer model Lambda 2 spectrometer equipped with a diffuse reflectance accessory. The wavelength range varied from 190 to 700 nm. Temperature programmed reduction (TPR) was performed using a 5% H₂/Ar mixture at a heating rate of 10 °C min⁻¹ from 25 to 700 °C. Prior to the TPR experiments, samples were dried in Ar at 120 °C for 1 h; then calcined catalysts were obtained by heating in air at 500 °C for 1 h. The hydrogen consumption was monitored with a thermal conductivity detector (TCD). Dynamic CO chemisorption measurements were carried out by sending 46 μL pulses of CO at room temperature, the gas carrier was H₂ with a flow of 30 cm³ min⁻¹, samples were dried in Ar at 120 °C for 1 h, and then treated under H₂ flow at 500 °C for 2 h.

The isobutane dehydrogenation activity was carried out in a stainless steel apparatus designed to work either by pulses or continuous flow. The reactor was a U-shaped Vycor tube, 6 mm OD. The switching of gases was done without mixing or access of air. The reaction was done at atmospheric pressure and 500 °C. Eighty milligrams of catalyst were used for each reaction test, samples were dried in Ar at 120 °C for 1 h and then reduced in H₂ at 500 °C for 2 h. The reaction mixture contained H₂, i-C₄H₁₀, and He, with a 3:1 hydrogen:isobutane ratio. A total flow of 100 cm³ min⁻¹ and a WHSV of 28.8 h⁻¹ was used. The exit gases were analyzed in a Perkin-Elmer GC, equipped with an Alumina F1 packed column and a flame ionization detector (FID).

3. Results and discussion

3.1. UV–vis

Diffuse reflectance spectra of Pt/SiO₂, PtSn/SiO₂, Sn/SiO₂ and SiO₂ catalysts are shown in Fig. 1. The spectrum of calcined silica (Fig. 1a) presents a band at 226 nm, which also has been reported by other authors [10,11]. The absorption band at 220 nm observed in the spectrum of the Sn/SiO₂ sample is mainly attributed to the contributions of the silica.

In the Pt/SiO₂ spectra, the three bands at 260, 353 and 460 nm have been attributed to the (PtCl₆)²⁻ anion adsorbed on the support [12], which could be anchored on the surface by a ligand exchange of silanol (OH)⁻ groups of the silica. Due to the low OH⁻ density of the silica, a large fraction of (PtCl₆)²⁻ could be mobile on the support surface.

Jackson et al. [13] by NMR found that Pt adsorbs on alumina both as (PtCl₆)²⁻ and [PtCl₅(OH)]²⁻, the latter species is produced by the deprotonation of [PtCl₅(H₂O)]⁻ present in the initial solution. The ratio of (PtCl₆)²⁻/[PtCl₅(OH)]²⁻ depends on the pH of the impregnating solution, the support pretreatment and impregnation time [14]. Lietz et al. [12] and Alerasool et al. [15] proposed that the reaction of ligand exchange begins with the water adsorbed on the support. Choren et al. [10] proposed the following scheme for the

Table 1
Precursor and preparation method of the Pt/SiO₂, Sn/SiO₂ and Pt–Sn/SiO₂ catalysts

Catalyst nomenclature	Precursors	Preparation method
Pt/SiO ₂	H ₂ PtCl ₆ ·6H ₂ O	Incipient wetness impregnation
Sn/SiO ₂	SnCl ₂ ·2H ₂ O	Incipient wetness impregnation
(Pt–Sn)/SiO ₂	H ₂ PtCl ₆ ·6H ₂ O + SnCl ₂ ·2H ₂ O	Coimpregnation
Sn–(Pt/SiO ₂)	H ₂ PtCl ₆ ·6H ₂ O/SnCl ₂ ·2H ₂ O	Successive impregnation 1st Pt, 2nd Sn
Pt–(Sn/SiO ₂)	SnCl ₂ ·2H ₂ O/H ₂ PtCl ₆ ·6H ₂ O	Successive impregnation: 1st Sn, 2nd Pt
K–/SiO ₂	KOH	Impregnation
K–Pt/SiO ₂	H ₂ PtCl ₆ ·6H ₂ O + KOH	Successive impregnation: 1st Pt, 2nd K
K–(Pt–Sn)/SiO ₂	(H ₂ PtCl ₆ ·6H ₂ O + SnCl ₂ ·2H ₂ O) + KOH	Coimpregnation and then addition of K
K–Sn(Pt/SiO ₂)	H ₂ PtCl ₆ ·6H ₂ O/SnCl ₂ ·2H ₂ O/KOH	Successive impregnation: 1st Pt, 2nd Sn, 3rd K
K–Pt(Sn/SiO ₂)	SnCl ₂ ·2H ₂ O/H ₂ PtCl ₆ ·6H ₂ O/KOH	Successive impregnation: 1st Sn, 2nd Pt, 3rd K

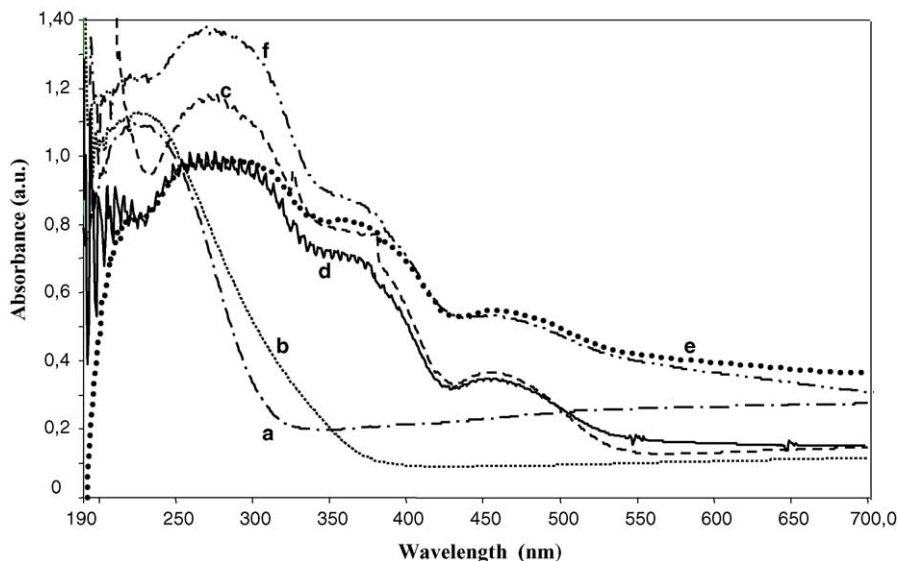
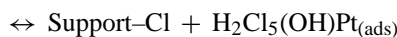
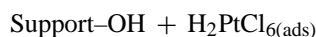


Fig. 1. UV-vis diffuse reflectance spectra of: (a) SiO₂; (b) Sn/SiO₂; (c) Pt/SiO₂; (d) Pt(Sn/SiO₂); (e) Sn(Pt/SiO₂); and (f) PtSn/SiO₂.

ligand exchange:



The UV-vis spectra of Pt(Sn/SiO₂) and Sn(Pt/SiO₂) catalysts show absorption bands at 210, 270, 381 and 460 nm, similar to those of the coimpregnation solution. The band at 210 nm corresponds to Sn(IV) species while the other three bands have been assigned to [PtCl₂(SnCl₃)₂]²⁻ complex adsorbed on the support [16]. The spectrum of Pt(Sn/SiO₂) has absorption bands at similar wavelengths to that of Pt/SiO₂. This is an indication that the [PtCl₂(SnCl₃)₂]²⁻ complex was not formed, probably due to the oxidation of Sn(II) to Sn(IV) during the drying step [17]. Baronetti et al. [16] assigned the

band at 210 nm to Sn (IV) species and the other bands to Pt(IV) species.

Fig. 2 shows the UV-vis spectra for Pt, Sn and Pt-Sn catalysts modified with potassium. In the spectrum of K/SiO₂, a band is observed at 210 nm, similar but smaller in intensity than the corresponding to the silica without K. The spectra of the Pt and Pt-Sn catalysts modified by the addition of K have absorption bands at the same wavelengths of the catalysts without potassium (see Fig. 3).

3.2. Temperature programmed reduction

Fig. 1 shows TPR profiles of the fresh catalysts without K; the TPR diagram of Pt/SiO₂ showed a broad peak at 210 °C attributable to the reduction of Pt(IV) to Pt(0) [10,18]. Two

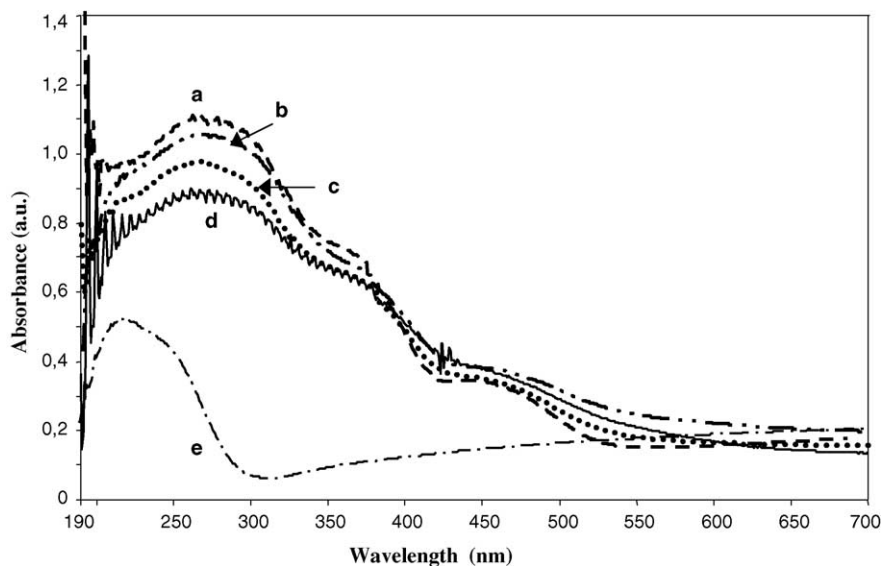


Fig. 2. UV-vis diffuse reflectance spectra of: (a) K-Pt/SiO₂; (b) K-(PtSn/SiO₂); (c) K-Sn(Pt/SiO₂); (d) K-Pt(Sn/SiO₂); and (e) K-SiO₂.

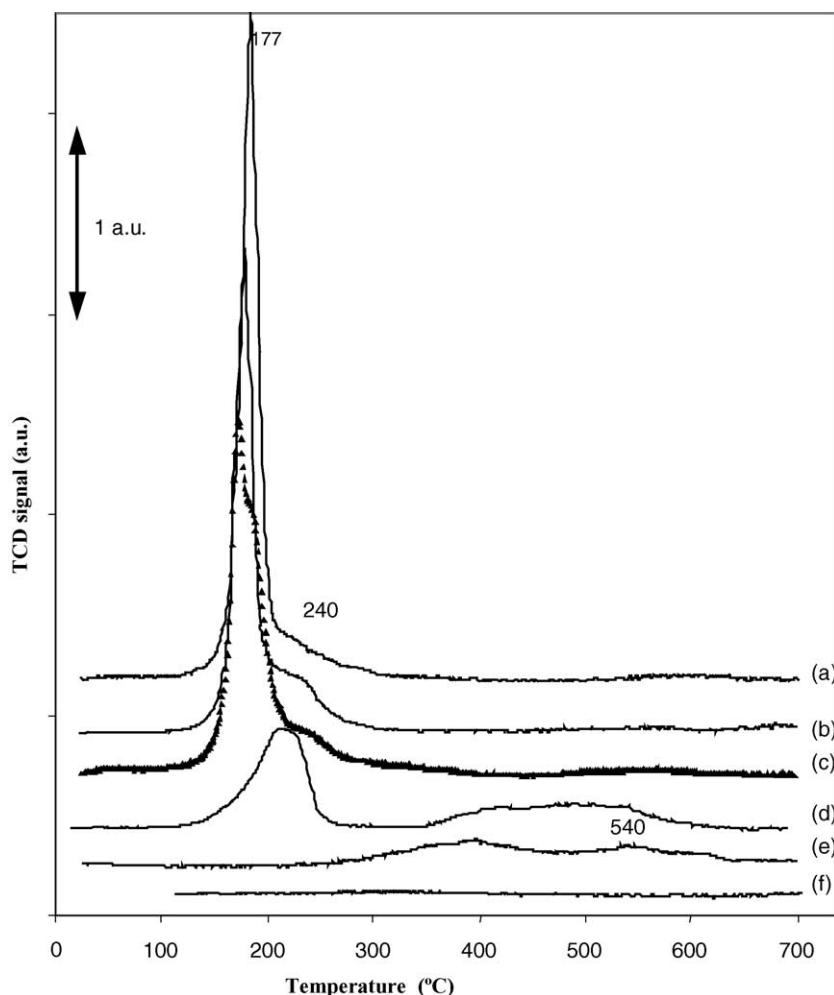
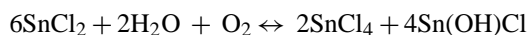


Fig. 3. TPR profiles for fresh catalysts without potassium: (a) Pt(Sn/SiO₂); (b) Sn(Pt/SiO₂); (c) (PtSn/SiO₂); (d) Pt/SiO₂; (e) Sn/SiO₂; and (f) SiO₂.

peaks at 400 and 540 °C appear in the reduction profile of Sn/SiO₂, indicating that there are tin species interacting in different ways with the support. These peaks can correspond to Sn(II) and Sn(IV). The Sn(IV) species could have been formed during the drying step by the following oxidation reaction [19]:



The Pt–Sn/SiO₂ profiles show a common peak at 177 °C, indicating that the simultaneous reduction of Pt and Sn species occurs [20] with the formation of Pt–Sn ensembles or alloys [17]. The shoulder observed at 240 °C for the (PtSn/SiO₂) and Sn(Pt/SiO₂) catalysts can be due to Sn species located very close to the Pt.

In the TPR profiles of the calcined catalysts illustrated in Fig. 4, Sn/SiO₂ shows a broad reduction band with two peaks at 440 and 540 °C. Considering that tin is present as Sn(IV) after the calcination step, then after reduction, tin could be present as Sn(II) and/or Sn(0) [21]. The Pt/SiO₂ catalyst shows a single peak at 100 °C that can be assigned to the reduction of Pt(IV), mainly PtO₂, to Pt(0) [22].

The segregation of Pt and Sn caused by the calcination of the Pt–Sn catalysts was due to a weak interaction with the support [23,24]. The single peak around 100 °C can be attributed to the reduction of Pt species, as PtO₂ [25,26] or PtO_xCl_y, assisted by Pt(0) formed during the calcination step [25]. The second peak at 545 °C corresponds to the reduction of tin oxides species, probably SnO₂. In spite of that, the TPR profiles for the calcined Pt(Sn/SiO₂) and Sn(Pt/SiO₂) catalysts do not suggest the formation of some Pt–Sn alloys, it can not be discarded that a part of Sn has been deposited on or dissolved in the platinum particles. The shoulder at 210 °C for the catalyst prepared by coimpregnation could correspond to the reduction of Sn species near to the reduced platinum particles. This proximity between the Pt and Sn can be related to the deposition of the bimetallic [PtCl₂(SnCl₃)₂]²⁻ complex formed during the impregnation step [16].

Fig. 5 shows the TPR profiles of the fresh catalysts modified with potassium. The profile of K–Pt/SiO₂ shows a broad peak at 245 °C, indicating the simultaneous reduction of the different species of Pt and K. In that region, the reduction of K₂PtCl₆ may occur, which is formed during the preparation

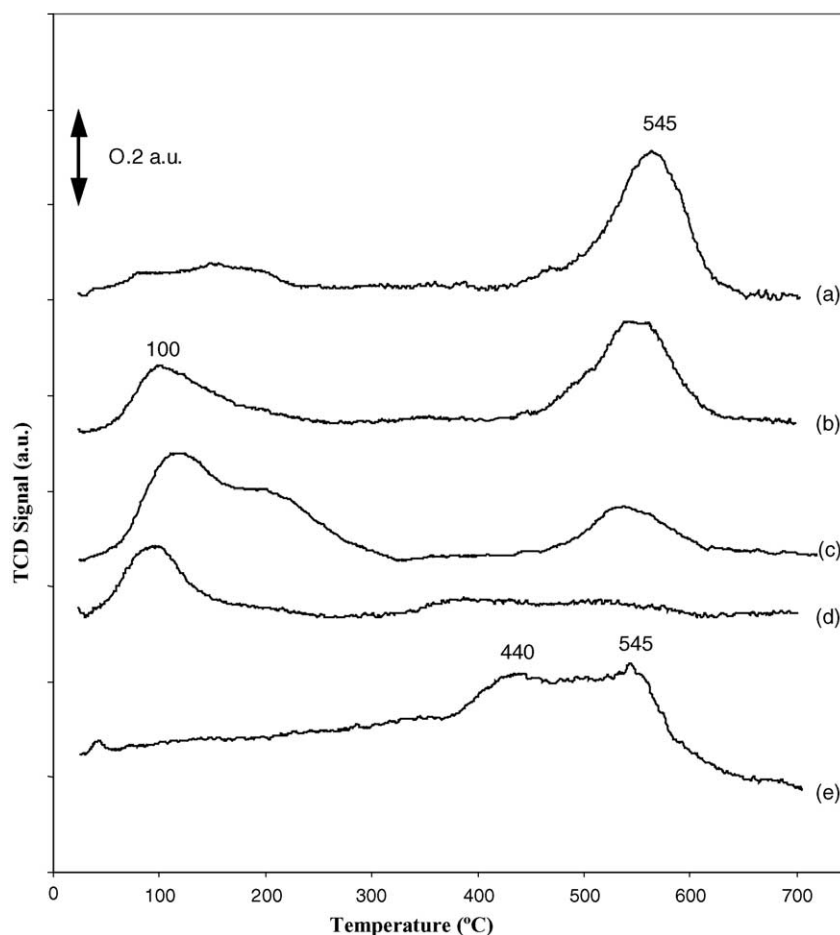
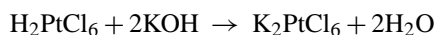


Fig. 4. TPR profiles for calcined catalysts without potassium: (a) Pt(Sn/SiO₂); (b) Sn(Pt/SiO₂); (c) (PtSn/SiO₂); (d) Pt/SiO₂; and (e) Sn/SiO₂.

of the catalysts by the reaction:



A TPR experiment of K₂PtCl₆ showed a reduction peak around 240 °C. The K–Pt–Sn/SiO₂ profiles show a single reduction peak around 240 °C, this peak can be associated to the simultaneous reduction of platinum, tin and potassium species. The platinum can assist the potassium and tin reduction.

TPR diagrams of K–Pt–Sn/SiO₂ calcined catalysts are shown in Fig. 6. The TPR profile of K–Pt/SiO₂ shows a peak at 130 °C attributable to a reduction of a fraction of Pt, as PtO₂ [26]. The peak at 235 °C can be due to a reduction of K₂PtCl₆ that did not decompose during the calcination step, and the peak at 410 °C could correspond to the reduction of KO_x species by hydrogen activated in the Pt(0) particles. Three hydrogen consumption regions are observed in the K–Pt–Sn/SiO₂ profiles. The first region is around 130 °C and could be attributed to the reduction of platinum oxide segregated on the silica surface. The second region of hydrogen consumption is observed at 240 °C, the same temperature of the simultaneous reduction of Pt, Sn and K species than in the fresh catalyst. The third peak at 540 °C indicates the

segregation of the Sn in the same way that in the calcined Pt–Sn/SiO₂ catalysts. K–Pt–Sn interactions were stronger in the catalyst prepared by coimpregnation. Park et al. [27] by CO TPD experiments found that the addition of Sn and K to Pt(111) leads to a direct interaction between these three metals, with the possible formation of a surface Pt–K–Sn alloy.

3.3. CO chemisorption

The CO/Pt ratio of each catalyst is shown in Table 2. It is observed that the incorporation of Sn to the Pt/SiO₂ catalyst

Table 2
CO/Pt ratios on reduced Pt/SiO₂, Pt–Sn/SiO₂ and K–PtSn/SiO₂ catalysts

Catalyst	(CO/Pt) _F	(CO/Pt) _C
Pt/SiO ₂	0.25	0.15
Pt(Sn/SiO ₂)	0.09	0.04
Sn(Pt/SiO ₂)	0.08	0.03
(PtSn/SiO ₂)	0.08	0.04
K–Pt/SiO ₂	0.23	0.12
K–Pt(Sn/SiO ₂)	0.07	0.03
K–Sn(Pt/SiO ₂)	0.07	0.04
K–(PtSn/SiO ₂)	0.06	0.03

(F) Fresh and (C) calcined catalysts.

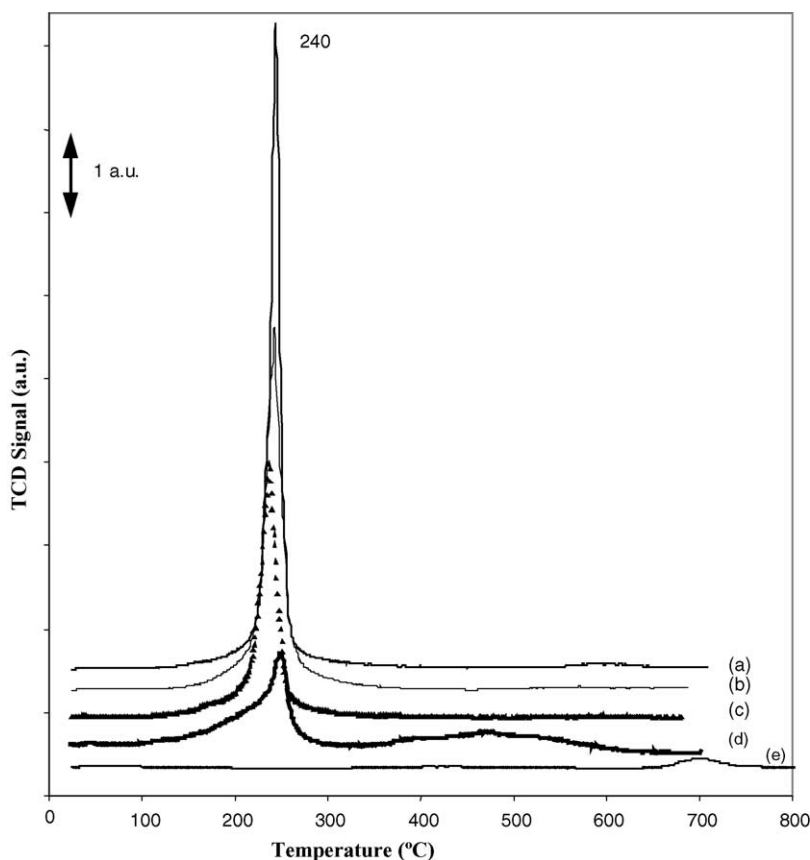


Fig. 5. TPR profiles for fresh catalysts modified with potassium: (a) K–Pt(Sn/SiO₂); (b) K–Sn(Pt/SiO₂); (c) K–(PtSn/SiO₂); (d) K–Pt/SiO₂; and (e) K–SiO₂.

caused an appreciable decrease of the CO/Pt ratio, and therefore the Pt dispersion [28]. This decrease can be due to the formation of Pt–Sn ensembles or alloys that do not adsorb CO [25]. The interaction between Pt and Sn is favored by the silica [29], and that could be affecting the strength of the CO–Pt binding. Tin affects more those Pt sites that adsorb CO more strongly [30].

The fresh Pt–Sn/SiO₂ catalysts exhibited a similar CO/Pt ratio; that is, the preparation method did not have a marked effect on the amount of surface Pt atoms. According to the UV–vis and TPR results, Pt and Sn could form bimetallic ensembles that are favored by the close contact between Pt and Sn, due to the formation of the [PtCl₂(SnCl₃)₂]^{2–} complex in the Sn(Pt/SiO₂) and (PtSn/SiO₂) catalysts.

The decrease of CO/Pt ratio in the calcined catalysts indicates a lower dispersion of Pt, probably due to sintering of the Pt particles [31]. The addition of potassium to the Pt–Sn catalysts did not have a marked effect on the Pt dispersion of the fresh catalysts. According to these results, and those of the TPR and UV–vis experiments, the potassium is mainly deposited on the support and the K–Pt–Sn interactions show weakness under fresh conditions.

Except for calcined K–Pt/SiO₂ catalyst, the calcined K–Pt–Sn/SiO₂ catalysts did not show an appreciable difference in their CO/Pt ratios compared to the free potassium calcined catalyst. The decrease of CO/Pt ratio in K–Pt/SiO₂

probably indicates the loss of some active sites due a blocking with potassium or by formation of K–Pt ensembles.

3.4. Dehydrogenation of isobutane

The effects of Sn and K additions in the fresh and calcined catalysts is showed in Figs. 7 and 8. The Pt/SiO₂ catalyst shows a lower activity than Pt–Sn/SiO₂ catalysts. The lowest activity of the Pt catalyst could be due to a blockage of active sites by coke deposition at the beginning of the reaction. The conversions in the Pt–Sn catalysts were higher than that in the Pt catalyst because Sn could hinder or reduce coke poisoning of the active Pt sites. This effect is favoured by the presence of chlorine in the prepared catalysts [31]. Sn, as shown in the TPR results, could be forming alloys with Pt, which have small capacity of coke formation [32]. Several authors have pointed out that tin facilitates the transport of coke from the Pt sites to the support [33].

The isobutane dehydrogenation activities in the Pt–Sn catalysts indicate the marked influence of the preparation method on the catalytic properties. The lower conversion obtained for the Pt(Sn/SiO₂) catalyst could be due to fast deactivation, because there is a higher Pt surface fraction not alloyed than in the rest of the Pt–Sn catalysts. The formation of Pt metal particles could be due to the Pt–Sn complex not being formed during the impregnation step.

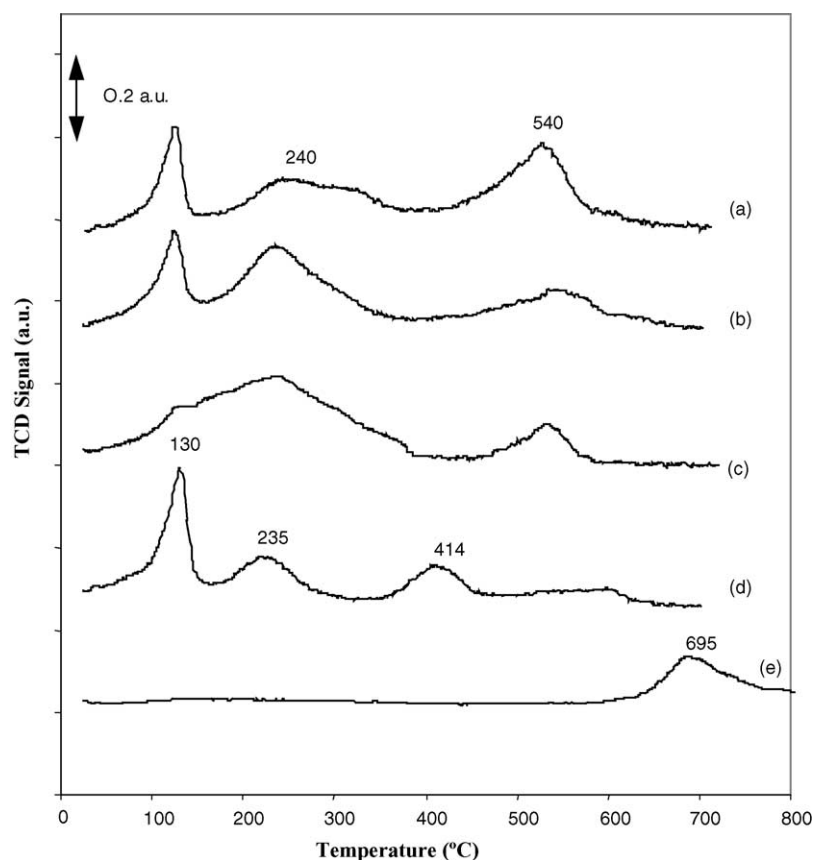


Fig. 6. TPR profiles for calcined catalysts modified with potassium: (a) K–Sn(Pt/SiO₂); (b) K–Pt(Sn/SiO₂); (c) K–(PtSn/SiO₂); (d) K–Pt/SiO₂; and (e) K–SiO₂.

In the case of Sn(Pt/SiO₂) and (PtSn/SiO₂) catalysts, the conversion seems to maintain relationship with the formation of the [PtCl₂(SnCl₃)₂]²⁻ complex, because the Pt dispersion of these catalysts is the same. Sn(Pt/SiO₂) catalyst presents a higher conversion than the (PtSn/SiO₂) catalyst, in which the complex is formed in a larger proportion.

The increase of the selectivity on Pt/SiO₂ catalyst at the beginning of the reaction can also be explained by geometric effects. The coke deposited during the first minutes reduces the size of Pt ensembles, inhibiting undesirable reactions [25,34,35].

Although geometric effects of the Pt for the addition of the Sn can explain many of the changes observed, it is also possible that certain ligand effects could be present. This electronic modification of Pt has been explained in terms of electron transfer from Sn to Pt, modifying the intrinsic catalyst properties of Pt [36,37].

The presence of tin increased the selectivity towards isobutane dehydrogenation, and reduced the hydrogenolysis and isomerization reactions; this may be due to the dilution of the Pt ensembles by Sn [2,38].

The calcination treatment diminished both the conversion and selectivity in the free potassium catalysts; this effect is more pronounced in the Pt–Sn catalysts. The TPR results indicated that in these bimetallic catalysts, after the calcination

step, there were Sn, Pt and Pt–Sn species. Due to the fast deactivation of Pt, this does not keep the activity in these catalysts at steady conditions [25]; consequently, the activity would be determined by the nature of the Pt–Sn alloys formed during the reduction of the catalysts. The lower conversion in the calcined Pt/SiO₂ against the fresh Pt/SiO₂ can be due to the formation of large ensembles of Pt surface atoms, as is shown by the reduction of CO adsorption after calcinations. It is probable that due to a lower dispersion in the calcined Pt/SiO₂ catalyst, its initial activity was smaller; however, its true initial activity is difficult to measure due to the fast deactivation of this catalyst.

The addition of potassium to the fresh Pt–Sn/SiO₂ does not change the activity, but improves the dehydrogenation selectivity, which reaches values of almost 100%. This seems to corroborate that under fresh conditions, potassium interacts weakly with the platinum active phase. This increase in dehydrogenation selectivity could be due to the deposition of potassium on the support, thus diminishing the little acidity of silica. However, in the calcined K–Pt–Sn catalysts, the activity seems to be a function of the K–Pt–Sn interactions. The lower conversions in these catalysts in comparison to those of the fresh catalysts were probably due to the calcination treatment that caused a superficial enrichment of K and Sn species. This would block the active sites for the reaction. The

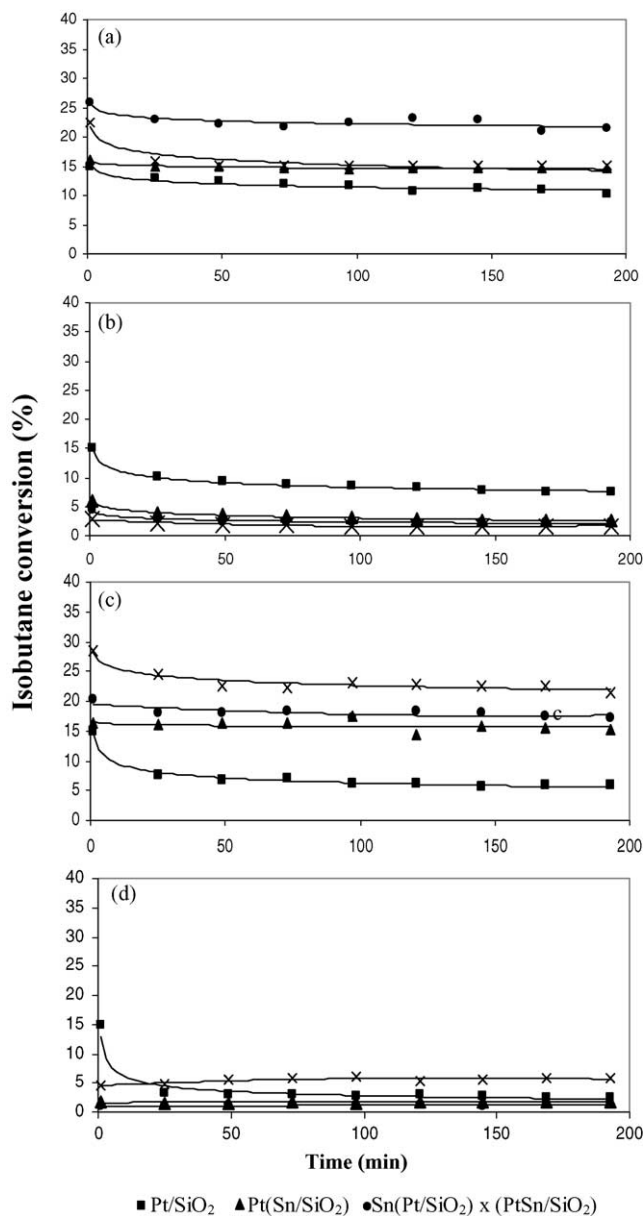


Fig. 7. Isobutane conversion for: (a) fresh catalysts without K; (b) calcined catalysts without K; (c) fresh catalysts modified with K; and (d) calcined catalysts modified with K.

activity of these catalysts seems to be inversely related to the amount of Sn segregated as shown in the TPR results. Tin and potassium species could be very near on the catalyst surface, perhaps alloyed or forming ensembles. It is possible that also an electronic effect between platinum and potassium takes place. The potassium can be acting as donor of electrons or inducing a polarization of electrons in the Pt particles [39].

Both a higher selectivity and dehydrogenation activity were obtained in the K-(Pt-Sn/SiO₂) catalyst. Both of them were diminishing as the amount of the $(\text{PtCl}_2(\text{SnCl}_3)_2)^{2-}$ complex decreased in the catalysts prepared by sequential impregnation.

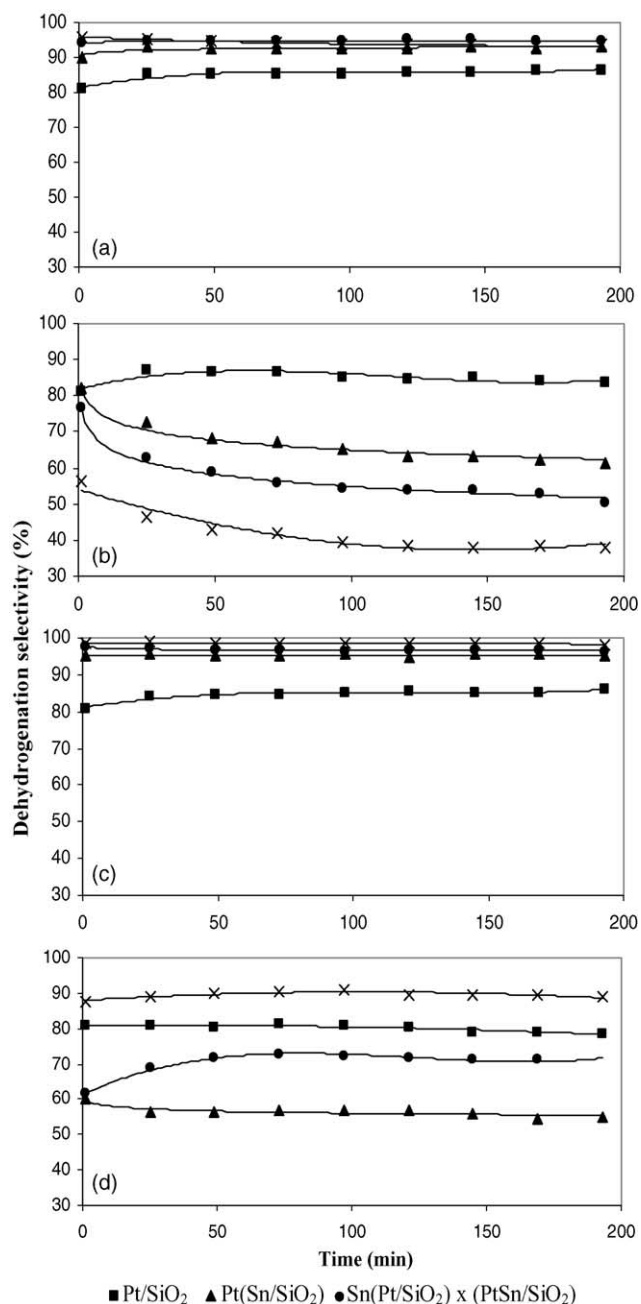


Fig. 8. Dehydrogenation selectivity for: (a) fresh catalysts without K; (b) calcined catalysts without K; (c) fresh catalysts modified with K; and (d) calcined catalysts modified with K.

4. Conclusions

The $[\text{PtCl}_2(\text{SnCl}_3)_2]^{2-}$ complex was only detected in (PtSn/SiO₂) and Sn(Pt/SiO₂) catalysts. In Pt(Sn/SiO₂), the Pt and Sn species formed, are located very near on the catalyst surface. The proximity between the Pt and Sn species favors the formation of Pt-Sn ensembles or alloys after the reduction treatment that provides stability and selectivity for the isobutane dehydrogenation. The addition of potassium to Pt-Sn/SiO₂ did not have a marked effect in the Pt dispersion

nor the activity of the fresh catalysts; however, this improved the dehydrogenation selectivity, which reached values of almost 100%. Potassium is deposited mainly on the support, affecting reactions there. The surface Pt–Sn species were affected by the calcinations, causing the segregation of Pt and Sn oxide species. In addition, there was a decrease of the CO/Pt ratio, activity and selectivity of the Pt–Sn catalysts. The low values of conversion for the calcined Pt–Sn catalysts, in comparison with the fresh catalysts, emphasize the effect of the calcination treatment on the distribution and interaction of Pt and Sn. In the calcined Pt–Sn–K catalysts, the activity is related to the K–Pt–Sn interactions.

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