

Effect of titania on the characteristics of a Tin-Platinum catalyst

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Abstract Pt-Sn bimetallic catalysts dispersed on alumina are commonly used for reforming and dehydrogenation reactions. In this research work, Pt and Sn were supported on titania. The resulting interactions between the components in the prepared samples, before and after treatment with hydrogen, were studied by Mössbauer spectroscopy, X-ray diffraction and Rietveld refinement. The results show the presence of Pt and SnO₂ after calcinations. After the reduction process, metallic Pt, PtSn, and Pt₃Sn alloys were identified. The Rietveld refinement analysis shows that some Ti⁴⁺ atoms were replaced by Sn⁴⁺ atoms in the titania structure. Finally, the Mössbauer spectroscopy and X-ray diffraction results indicate that metallic platinum and SnO₂ are encapsulated by a TiOx layer.

Keywords Mössbauer spectroscopy · Pt-Sn Catalyst · Dehydrogenation

1 Introduction

Bimetallic catalysts featuring Pt and Sn as active metals, dispersed on alumina, are commonly used for performing reforming and dehydrogenation reactions [1–6]. In this system the oxidation state and role of tin have become a matter of intense research. The conclusions obtained from the literature are concerned with the oxidation state of tin, i.e., Sn(IV),

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Sn(II) and Sn(0). The relative amounts of each species depend on the nature of the support, metallic precursor, preparation method and thermal history of the sample [7].

It has been reported that tin in the Pt-Sn system is stabilized in the +2 oxidation state on alumina [8] however, some studies indicate the possibility of alloy formation. Bimetallic Pt-Sn particles with Sn(0) have been prepared on alumina after specialized preparation routines [9] The characterization of Pt-Sn reforming catalysts has been done by means of several techniques, although the results have led to conflicting conclusions concerning the formation of Pt-Sn alloys and the reaction of tin with the support [10–14] Mössbauer spectroscopy has been used to study the interactions, oxidation and reduction processes in the pretreatment of iron, tin, ruthenium, europium and gold supported catalysts. In an attempt to have a better understanding of the role of tin in these catalysts, Mössbauer spectroscopy was used to study the oxidation states and structure in both the oxidized and reduced states of tin supported on titania with a relatively high tin loading. The study was complemented with X-ray diffraction.

2 Experimental

2.1 Preparation of samples

5.0 wt. % Pt and 5.0 wt. % Sn catalysts supported on commercial titania (166 m²/g) were prepared by using ethanol as solvent and the appropriate amount of salts (H₂PtCl₆·6H₂O and SnCl₂·2H₂O). The bimetallic systems were prepared by sequential impregnation (Sn first) dried for 12 h at 393 K and calcined at 773 K for 4 h between the impregnation steps.

The samples were reduced under hydrogen flow (50 ml/min) increasing slowly the temperature from ambient to 673 K, which was maintained constant for 4 h.

2.2 Characterization techniques

2.2.1 X-ray diffraction (XRD)

XRD patterns were obtained with a Siemens D500 diffractometer equipped with a copper anode X-ray tube and a diffracted beam monochromator ($K\alpha = 1.5405\text{Å}$). The XRD patterns of Pt-Sn supported on titania were refined by the Rietveld method, FULLPROF software [15], covering 2θ diffraction angles from 10° to 70°.

2.2.2 Mössbauer spectroscopy

Mössbauer spectra were obtained at 298 and 12 K by using a special cell to avoid the contact of the sample with the atmosphere. The spectrometer was operated in the constant-acceleration mode in transmission experiments with a 555MBq (15 mCi) single-line gamma-ray source of Ba^{119m}SnO₃. The source temperature was 298 K during the measurements. The detection of the 23.8 keV γ -rays was achieved with a Kr proportional counter. A 0.05-mm Pd foil was placed between the source and detector to filter 25.0 and 25.2 keV X-rays from the source. The source was moved by a loudspeaker drive with a sinusoidal velocity relative to the stationary absorber. Its velocity was regulated and the sine wave was followed within 0.1 %. The chemical isomer shift (δ) data are quoted relative to Ba^{119m}SnO₃. The absorption spectra were computer fitted by using the NORMOS software [16].

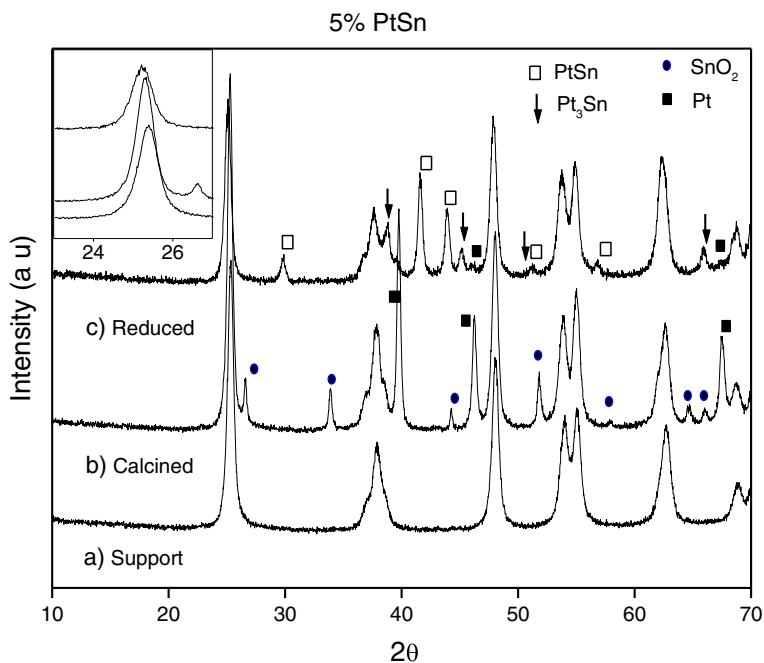


Fig. 1 XRD patterns of 5 % Pt-5 % Sn supported on TiO₂: **a** support, **b** calcined, and **c** reduced

3 Results

3.1 X-ray diffraction

XRD patterns of the support, calcined and reduced samples are shown in Fig. 1. Figure 1a shows the XRD pattern of the TiO₂ support (JCPDS No 21-1272). After calcination (Fig. 1b) besides TiO₂, two additional phases are observed: peaks at $2\theta = 39.8, 46.2$ and 67.5 are assigned to metallic Pt (JCPDS No 4-802) and peaks at $2\theta = 26.5, 33.9, 45, 64$ and 65 correspond to cassiterite (JCPDS No 21-1250, 3-1116). After reduction (Fig. 1c), the pattern shows the presence of three phases: peaks at $2\theta = 38.9, 45.2, 50.9$ and 65.9 are assigned to the Pt₃Sn alloy (JCPDS No. 35-1360) and peaks at $2\theta = 30.0, 41.8, 44.1, 51.5$ and 54.4 are assigned to the PtSn alloy (JCPDS No. 25-614); in addition the pattern shows low intensity peaks assigned to metallic Pt, which is still present after treatment with hydrogen.

3.2 Mössbauer spectroscopy

The Mössbauer spectra obtained at room temperature and at 12 K of both the calcined and hydrogen reduced samples are shown in Fig. 2 and the involved parameters can be seen in Table 1. The Line width (Γ) of the tin species was kept constant. For the calcined samples each spectrum shows a peak that could be deconvoluted into a doublet. The spectrum taken at 298 K of the calcined titania supported Pt-Sn material is shown in Fig. 2a. As expected, it consists of a peak near zero velocity ($\delta = -0.013$ mm/s and $\Delta = 0.410$ mm/s), which is attributed to the presence of SnO₂ ($\delta = 0.03$ mm/s, $\Delta = 0.61$ mm/s, $\Gamma = 1.2$ mm/s).

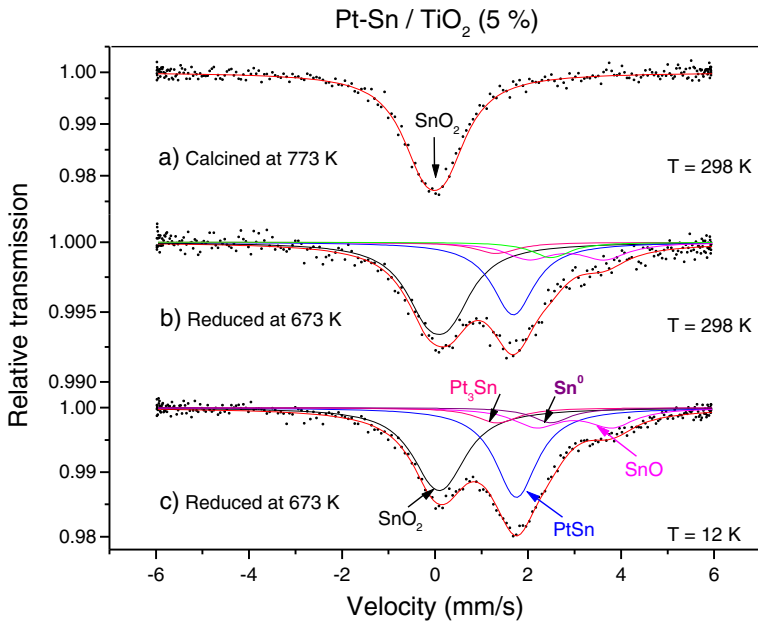


Fig. 2 Mössbauer spectra of 5 % Pt-5 % Sn supported on TiO_2 : **a)** calcined, **b)** reduced, taken at 298 K, and **c)** reduced, taken at 12 K

Table 1 Mössbauer parameters taken at 298 and 12 K for Pt-Sn supported on TiO_2

T(K)	δ (mm/s)	Δ (mm/s)	Γ (mm/s)	Tin States	Contribution area (%)
Calcined					
298	-0.013	0.410	1.200	SnO_2	100.0
Reduced					
298	0.069	0.497	1.200	SnO_2	47.0
	1.327	0.000	1.100	Pt_3Sn	4.5
	1.683	0.000	1.100	PtSn	29.0
	2.820	1.630	1.200	SnO	13.8
	2.500	0.000	1.000	Sn^0	5.7
12	0.069	0.340	1.200	SnO_2	38.0
	1.270	0.000	1.100	Pt_3Sn	5.9
	1.748	0.000	1.100	PtSn	35.0
	2.990	1.620	1.200	SnO	15.5
	2.500	0.000	1.000	Sn^0	5.6

Error: $\delta = \pm 0.01$ mm/s; $\Delta = \pm 0.01$ mm/s, $\Gamma = \pm 0.01$ mm/s, Contribution area ± 2 -3 δ isomer shift given relative to $\text{Ba}^{119\text{m}}\text{SnO}_3$ at RT; Δ Quadrupole splitting; Γ line width

After treatment with hydrogen at 673 K, Mössbauer spectra were obtained at 298 and at 12 K. The Mössbauer spectrum taken at 298 K (Fig. 2b) could be fitted with five lines, which

Table 2 Refined parameters

	a (Å)	c (Å)	Occupation Factor	Substitution (%)
Pt-Sn/TiO ₂ *	3.78586(0.00051)	9.51797(0.00149)	0.117(1)	5.6
Pt-Sn/TiO ₂ **	3.78473(0.00020)	9.51425(0.00067)	0.118(1)	6.4
TiO ₂ (pure)	3.78570(0.00104)	9.50188(0.00278)	0.12500	—

*Calcedined **Reduced

suggests the distinction between tetravalent, divalent and metallic tin, respectively [17] The leftmost intense peak with $\delta = 0.069$ mm/s and $\Delta = 0.497$ mm/s is assigned to SnO₂ The interaction of Sn⁴⁺ ions with the titania sites decreases the quadrupole splitting to 0.497 mm/s. The second weak peak with $\delta = 1.327$ mm/s and $\Delta = 0.00$ mm/s corresponds to the Pt₃Sn alloy. The third singlet with $\delta = 1.683$ mm/s and $\Delta = 0.00$ mm/s corresponds to the PtSn alloy. The fourth doublet with $\delta = 2.820$ and $\Delta = 1.630$ mm/s corresponds to the SnO phase. The last singlet with $\delta = 2.500$ and $\Delta = 0.000$ mm/s is assigned to metallic tin. The Mössbauer spectrum taken at 12 K shows a similar behavior to the one at 298 K; only the spectral contribution is different for each tin species due to the Lamb-Mössbauer factor [18].

The catalytic activity was tested in the cyclohexane dehydrogenation to benzene reaction, where in spite of the high platinum load almost no activity was observed.

4 Discussion

The XRD pattern of the calcined sample indicates the presence of both metallic Pt and SnO₂ phases, and as for the reduced sample Pt, PtSn and Pt₃Sn alloy phases are observed.

The XRD pattern in the 2θ range = 24-26° for the calcined and reduced samples shows a progressive shift towards lower 2θ values with respect to unsupported TiO₂ which suggests some type of interaction between TiO₂ and Sn⁴⁺ atoms.

In order to obtain additional information about the TiO₂ and Sn⁴⁺ structures, the Rietveld refinement was carried out. The Rietveld refinement pattern of the reduced sample and cell parameters such as a, c, occupation factor and substitution percentage are shown in Fig. 3 and Table 2, respectively.

As it can be seen in Fig. 3 and Table 2, after calcinations, 5.6 % of Ti⁴⁺ atoms are replaced by Sn⁴⁺ atoms and after hydrogen treatment this substitution is increased to 6.4 %, which causes a distortion of the lattice parameters. The observed changes for a and c are significant in comparison with the cell parameters of pure TiO₂; these changes are due to the substitution of Sn⁴⁺ atoms in the titania structure. Apparently the unit cell suffers a shrinkage in the a direction.

Thus, the decrease in the quadrupole splitting to 0.41 mm/s can be attributed to the fact that some Sn⁴⁺ atoms occupy some sites in the titania structure [19] The Mössbauer parameters show the presence of SnO₂ after calcination and SnO₂, Pt₃Sn, PtSn, SnO and Sn⁰ phases after reduction Note that the f-factors are found to be insensitive to Sn loading and that Sn(0) shows similar variations with temperature.

We consider that the formation of PtSn alloys inhibits the catalytic activity as it has been pointed out in our earlier work. The absence of activity can be attributed to the fact

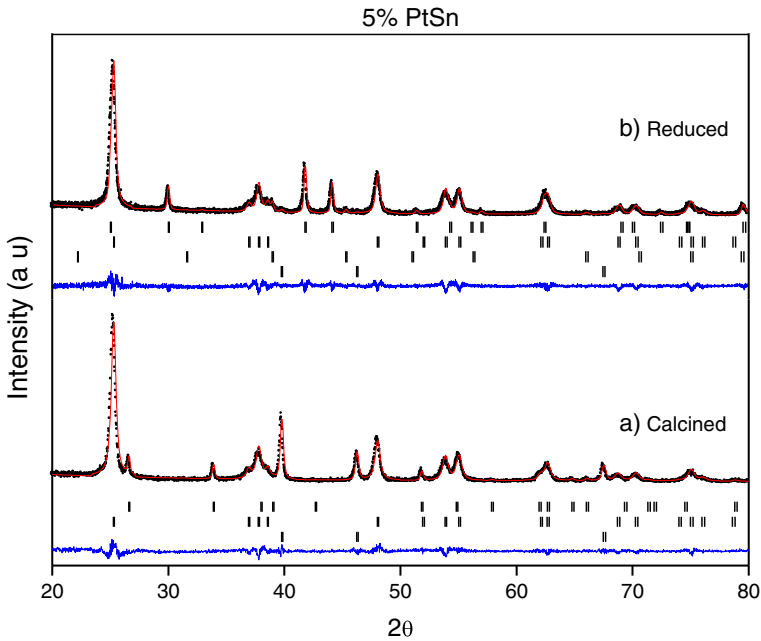


Fig. 3 Rietveld refinement patterns of 5 % Pt-5 % Sn supported on TiO_2 : a) calcined, and b) reduced

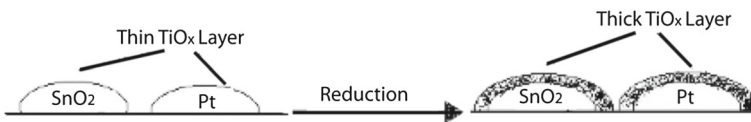


Fig. 4 Schematic formation of a thin TiO_x layer after the calcination process, and subsequent formation of a thick TiO_x layer after the reduction process

that Pt atoms have been encapsulated partially by the titania support after both calcination and hydrogen treatments, forming TiO_x .

The encapsulation of metals has been widely studied [21] and one of the most analyzed systems has been the one corresponding to Pt/ TiO_2 [20]. Abhaya et al. [21] found encapsulation evidences by TEM and observed the formation of an amorphous layer around platinum; this layer grows after a reduction treatment at high temperature and it is difficult to analyze by EDS due to the fact that the support contributes to the final signal. This layer is a sublayer of TiO_x formed around platinum after reduction conditions.

A proposed model scheme is shown in Fig. 4, where it can be observed that tin oxide and platinum particles are covered by a thin TiO_x layer after the sample calcination; after the reduction step, a sublayer of TiO_x is formed around these phases, producing a poor interaction between them and blocking different platinum active sites, producing no catalytic activity.

5 Conclusions

The conclusions from this work are as follows:

After calcination, the XRD spectra show the presence of SnO₂ and metallic Pt, and after reduction, Pt₃Sn and PtSn alloys and metallic platinum are shown. The Rietveld analysis shows that some Ti⁴⁺ atoms are replaced by Sn⁴⁺ atoms in the titania structure after calcination and reduction, respectively.

The Mössbauer spectra indicate that SnO₂ is present after calcination; after reduction SnO₂, Pt₃Sn, PtSn, SnO and metallic Sn⁰ are present.

The amount of each tin species obtained after reduction play an important role when controlling the type of interaction between platinum and tin and between Pt-Sn and the support. The observed absence of activity confirms that metallic platinum is encapsulated by a sublayer of TiOx after the reduction process.

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