Preparation and characterization of bifunctional Pt-Sn/H[Al]ZSM5 catalysts

Ricardo Morales[a,b], Luis Melo[b,*], Aura Llanos[c], Joaquín Brito[d], Yraida Díaz[d], Luis Albornoz[d], and Delfín Moronta[e]

[a]*Departamento de Química, Universidad Simón Bolívar, Baruta, Edo. Miranda, Venezuela*
[b]*Facultad de Ingeniería, Universidad Central de Venezuela, P.O. Box: 48.057, Caracas, 1041-A, Venezuela*
[c]*Departamento de Química, IUT Región Capital, Caracas, Venezuela*
[d]*Centro de Química, IVIC, Caracas, Venezuela*
[e]*Facultad de Ciencias, Universidad Central de Venezuela, Caracas*

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Bifunctional monometallic Pt/H[Al]ZSM5, Sn/H[Al]ZSM5 and bimetallic Pt-Sn/H[Al]ZSM5 (tin atomic fraction, X_{Sn}, of 0.46) catalysts were prepared and characterized by means of XPS, EPR, TEM and toluene hydrogenation. The species on their surface as well as the presence of an effect of the electronic and/or geometric type between Pt and Sn in the bimetallic catalyst, which would result in the existence of reduced tin species (Sn^0 and/or Sn-Pt), were determined. These species were determined through XPS and would explain the decrease in the hydrogenating activity in the toluene hydrogenation reaction.

KEY WORDS: Pt-Sn/H[Al]ZSM5 catalysts characterization; toluene hydrogenation; XPS; EPR; TEM.

1. Introduction

The use of heterogeneous catalysis for the selective synthesis of fine chemicals is currently of great interest [1]. With this purpose, the use of bifunctional bimetallic catalysts has been developed owing to their higher selectivity and stability toward some kinds of reactions. The effects produced by the presence of a second metal besides platinum are characteristic and depend on the nature of this second metal, on the M/Pt atomic reaction (where M is the second metal), on the method used to prepare these catalysts, on the conditions and on the reaction itself [2]. For instance, in the Pt-Cu/H[Al]ZSM5 bifunctional bimetallic catalysts, evidence has been reported of an electronic effect between copper and platinum when the copper atomic fraction ($X_{\mathrm{Cu}} = \mathrm{Cu}$ moles n°/(Pt moles n° + Cu moles n°)) in the catalyst is below 0.4, as well as of the presence of an electronic effect combined with a geometric one for those catalysts with $X_{\mathrm{Cu}} > 0.4$ [3].

According to a previous work, bimetallic Pt-Sn/H[Al]ZSM5 catalysts ($X_{\mathrm{Sn}} \sim 0.5$) exhibit more activity, stability and selectivity in the methyl isobutyl ketone (MIBK) synthesis from acetone than the monometallic Pt/H[Al]ZSM5 catalyst. This behavior has been basically attributed to the presence of an electronic effect between Pt and Sn [4]. In this regard, this work is aimed, among other things, at contributing to elucidate the presence of this effect by means of the characterization of bifunctional Pt-Sn/H[Al]ZSM5 catalysts using the XPS, EPR and transmission electronic microscopy (TEM) techniques and the test reaction of toluene hydrogenation.

2. Experimental

Using a zeolite of the MFI type (Si/Al = 15) as a support, three bifunctional catalysts were prepared as described below: two monometallic catalysts (0.5% Pt/H[Al]ZSM5 and 1.0% Sn/H[Al]ZSM5) using the exchange-impregnation method and the third one, a bimetallic catalyst (Pt-Sn/H[Al]ZSM5 ($X_{\mathrm{Sn}} = 0.46$)), using the simultaneous exchange-impregnation method.

These catalysts, once calcinated for 6 h under dry airflow (Pt/H[Al]ZSM5 at 300 °C [5], Sn/H[Al]ZSM5 and Pt-Sn/H[Al]ZSM5 at 500 °C [6]) and reduced under hydrogen atmosphere for 6 h at 500 °C, were characterized by means of the XPS, EPR and TEM techniques. The XPS analysis was carried out in a VG scientific X-ray photoelectronic spectrometer, ESCALAB 220i-XL model, equipped with an Al/Mg source. The reduction treatment was carried out *in situ* by heating the fresh samples under a hydrogen flow at 500 °C for 2 h, to avoid any contact with air. Spectra of the reduced catalysts were taken, avoiding any contact with air, under vacuum of the 10^{-8} to 10^{-11} mbar order and using as a reference the Si 2p signal at 102.9 eV [7]. Analysis through EPR was conducted at room temperature using an X-band Varian E-line spectrometer with a rectan-

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[*] To whom correspondence should be addressed.
E-mail: melol@camelot.rect.ucv.ve

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gular cavity operating under TE_{102} mode. The study by TEM was carried out in a Phillips electronic microscope, CM-10 model, operated at 120 kV. The samples for this analysis were treated as follows: a suspension was prepared combining 30% ethanol, the catalyst to be analyzed; then ultrasound was applied for 5 min, and when the suspension was homogeneous, one drop was placed over a copper grid that had been previously covered with collodion and coal.

In addition, the series of bifunctional monometallic and bimetallic catalysts prepared was analyzed by means of the toluene hydrogenation reaction under atmosphere pressure, at 110 °C, $PH_2/Ptoluene = 4$ and $WHSV[AQ4] = 21.5\,h^{-1}$.

3. Results and discussion

3.1. Toluene hydrogenation

Since the toluene hydrogenation reaction is sensitive to the density of metallic centers and to the nature of the supported phase [3], in this work this test reaction was used to correlate hydrogenating activity per gram of platinum extrapolated at zero time (AH_0) with the population of metallic centers present in these catalysts, as well as to evidence possible disturbances resulting from the presence of effects of the electronic and/or geometric type in the supported metal particles.

In this sense, according to table 1, AH_0 is considerably influenced as Sn is introduced into the catalyst, to such an extent that hydrogenating activity decreases around seven times from Pt/H[Al]ZSM5 ($X_{Sn} = 0.00$) to Pt-Sn/H[Al]ZSM5 ($X_{Sn} = 0.46$). This phenomenon could be due to several reasons: (a) a remarkable decrease in the dispersion of the platinum metallic phase; (b) an effect of the electronic type between platinum and tin; (c) an effect of the geometric type, owing to which Pt particles are covered by tin species; and (d) a combination of an electronic and a geometric effect.

As a consequence, the kind of effect existing in the bimetallic catalyst under study will be determined by means of the characterization techniques described below.

3.2. TEM analysis

Figures 1(a) and 2 show micrographs for the Pt/H[Al]ZSM5 and Pt-Sn/H[Al]ZSM5 catalysts. The histogram in figure 1(b) shows the frequency of the platinum particles as functions of the particle size (in nm). The surface mean diameter, d_s, is calculated using the same expressions used in a previous article [8]. Table 1 presents the approximate value of the dispersion, D, of the metallic phase for both catalysts, determined by means of TEM. According to this table, dispersion is of the 50% order for each catalyst (figures 1 and 2); this means that the suppression of the hydrogenating activity shall depend on the presence of another factor rather than on the decrease in the dispersion of the Pt metallic phase caused by the presence of Sn. In the authors' opinion, this is the result, in this case, of electronic and/or geometric effects; however, since the specific hydrogenating activity substantially decreases from the catalyst with $X_{Sn} = 0.00$ to the solid with $X_{Sn} = 0.46$ (table 1), the phenomenon influencing this catalyst would be basically an electronic effect, by means of which tin would give up electronic density in favor of platinum.

3.3. XPS analysis

This analysis was conducted to determine the kind of chemical species present on the surface of the different catalysts. The XPS spectra obtained for the Pt/H[Al]ZSM5, Sn/H[Al]ZSM5 and Pt-Sn/H[Al]ZSM5 catalysts are shown in figure 3. Each spectrum was deconvoluted, evidencing a number of signals in each one of the studied spectra. These signals correspond to the different chemical species present on the catalyst surface. Table 2 shows the binding energy (BE) values belonging to the chemical species in the different catalysts analyzed, which are referred to the Si 2p signal located at 102.9 eV; this is a reference value used for a

Table 1

Physical–chemical characteristics of the series of bifunctional monometallic and bimetallic catalysts. Pt (%), Sn (%), wt% of platinum and tin determined by means of ICP[AQ5]-AES[AQ6]. X_{Sn}: Sn atomic fraction in the catalysts; SSA: specific surface area; D (%): platinum dispersion determined by TEM; AH_0: activity per gram of platinum in the toluene hydrogenation extrapolated at zero time

Catalysts	Pt (%) exp.	Sn (%) exp.	X_{Sn}	SSA (m^2/g)	AH_0 ($mmol/h^a gPt$)	D (%)
H[Al]ZSM5	—	—	—	380	—	—
0.50% Pt/H[Al]ZSM5[a]	0.47	—	0	375	3300	48.0
0.50% Pt–0.30% Sn/H[Al]ZSM5[a]	0.49	0.26	0.46	373	470	49.0
1.0% Sn/H[Al]ZSM5	—	0.80	1.0	375	0	—

[a] Catalysts assessed by means of TEM.

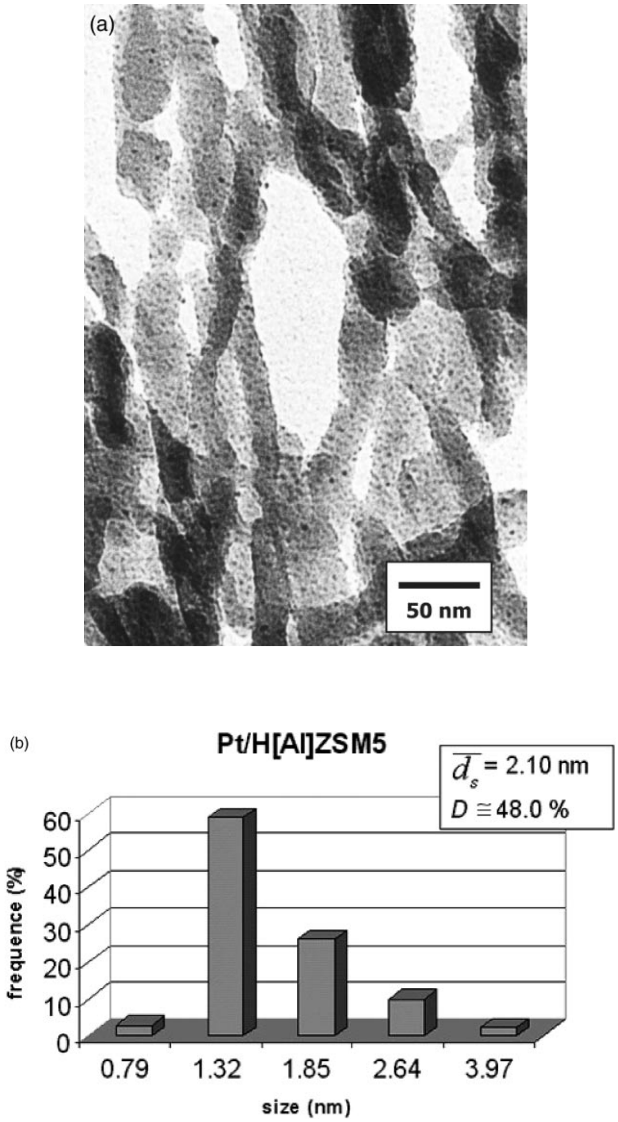

Figure 1. (a) TEM micrograph of the Pt/H[Al]ZSM5 catalyst and (b) histogram showing the particle size distributions for the Pt/H[Al]ZSM5 catalyst.

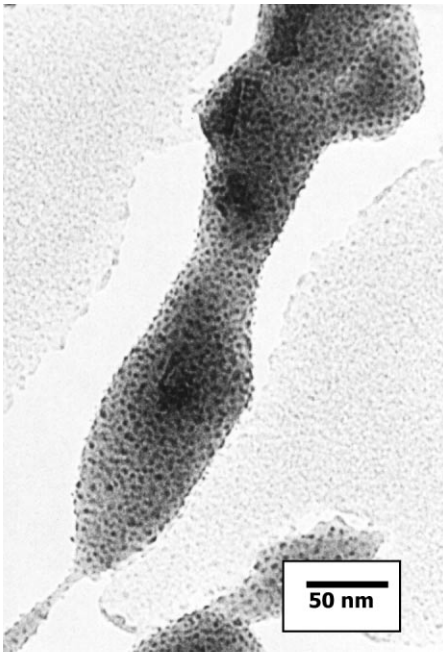

Figure 2. TEM micrograph of the Pt-Sn/H[Al]ZSM5 catalyst ($X_{\mathrm{Sn}} = 0.46$).

support of the crystalline aluminosilicate type such as that employed in this work [7].

Figure 3(a) shows the XPS spectrum for the support, where only one peak appears at 74.5 eV, which corresponds to the Al 2p signal. The Pt $4f_{7/2}$ signal in the XPS spectrum for the Pt/H[Al]ZSM5 catalyst (figure 3(b)) appears overlapped with the one corresponding to Al 2p; this undoubtedly makes it difficult to take advantage of this spectrum. However, once it is deconvoluted, signals at 70.9 and 72.2 eV are identified that correspond to the Pt^0 and PtO_{ads} species respectively, as indicated in table 2.

Figure 3(d) presents the XPS spectrum for the bifunctional Sn/H[Al]ZSM5 catalyst, which shows only two peaks located at 487.6 and 488.6 eV; these signals are attributed to oxidized tin species (Sn(II) and/or Sn(IV)). Now, since a discrimination between Sn(II) and Sn(IV) is not possible by means of the XPS studies [9,10], it is possible to state that tin exists only in its oxidized form in the catalyst, although before their XPS analysis these samples were treated for 6 h under hydrogen atmosphere at 500 °C; this means that it is difficult to reduce this metal to Sn^0 over a support of the H[Al]ZSM5 type.

A possible explanation for the difficulty in completely reducing the tin supported over the H[Al]ZSM5 zeolite could be the presence of a strong interaction between Sn and structural oxygen and/or between this metal and the aluminum in the zeolite, which could result in the formation of a bond between aluminum and tin [11]. Of course, these interactions do not take place when solids such as SiO_2 or carbon black are used as support, because these are catalysts over which the XPS analysis detected a signal at 485.3 eV that was attributed to Sn^0 [9,10].

However, three signals in the Pt 4f region in the XPS spectrum (figure 3(c)) are observed for the bimetallic Pt-Sn/H[Al]ZSM5 catalyst. These signals are located at the following binding energies (BE): 70.4, 71.3, and 72.3 eV, which could be attributed to those platinum species forming a Pt-Sn alloy, Pt^0 and PtO_{ads} respectively. This would imply that a large part of the reduced platinum would be gaining electronic density from tin, as has been reported by Stagg *et al.* [12], which could be the fundamental reason the new Pt $4f_{7/2}$ signal would be produced at lower binding energies (70.4 eV). Now, if a displacement of the platinum signal occurs, forming the Pt-Sn alloy, toward lower binding energies as a result of

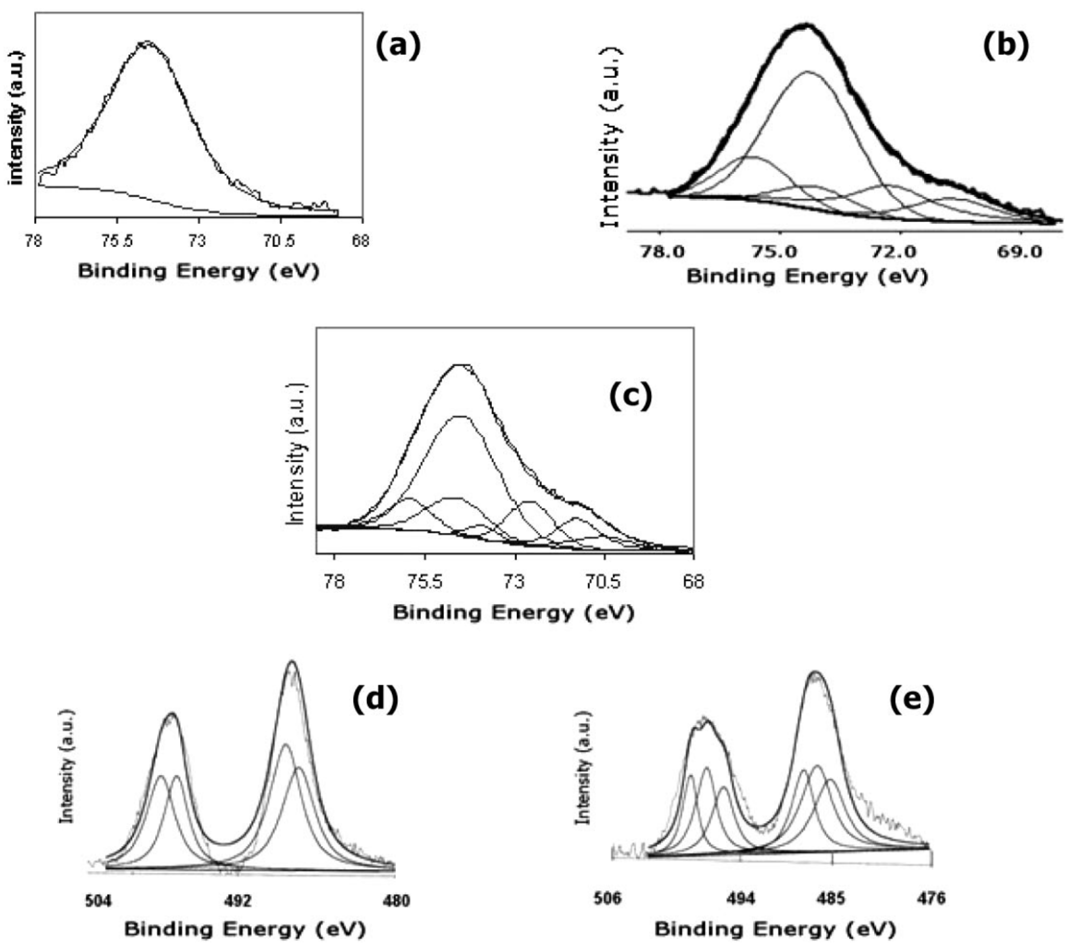

Figure 3. XPS spectra for (a) H[Al]ZSM5 in the Al 2p zone, (b) Pt/H[Al]ZSM5 in the Pt 4f zone, (c) Pt-Sn/H[Al]ZSM5 ($X_{\mathrm{Sn}} = 0.46$) in the Pt 4f zone, (d) Sn/H[Al]ZSM5 in the Sn 3d zone and (e) Pt-Sn/H[Al]ZSM5 ($X_{\mathrm{Sn}} = 0.46$) in the Sn 3d zone.

the charge density admission effect, a similar effect should also take place but in the opposite direction for the tin signal of the Pt-Sn alloy. Therefore, in the Sn 3d region in this catalyst spectrum (figure 3(e)), three peaks are observed at 485.9, 487.3, and 488.5 eV, which are attributed to species of reduced [Sn^0] and oxidized (Sn(II) and/or Sn(IV)) tin. It can be seen that the signal attributable to Sn^0 is a little displaced toward binding energies higher than the one reported by Coloma *et al.* [9,10]; this displacement suggests that this metal would be giving up electronic density and the authors think that this phenomenon would be taking place from tin toward platinum, which would mean that they are forming a Pt-Sn alloy. On the other hand, it is necessary to indicate that the presence of the oxides of platinum and tin in high proportions could be due to interactions between the metallic phases and the zeolitic support, as were reported by Mallmann *et al.* [13].

3.4. *EPR analysis*

The catalysts prepared were assessed by EPR to demonstrate the existence of an electronic effect between

Table 2
Binding energies determined by XPS (in eV)

Catalyst	Si 2p	Al 2p	Pt $4f_{7/2}$	Sn $3d_{3/2}$
H[Al]ZSM5	102.9	74.5	—	—
Pt/H[Al]ZSM5	102.9	74.5	70.9–72.2	—
Sn/H[Al]ZSM5	102.9	74.5	—	488.6–487.6
Pt-Sn/H[Al]ZSM5 ($X_{\mathrm{Sn}} = 0.46$)	102.9	74.5	70.4–71.3–72.3	488.5–487.3–485.9

Note: All BEs are referred to Si 2p = 102.9.

Pt and Sn on the bimetallic Pt-Sn/H[Al]ZSM5 catalyst. The spectra of the support, the Pt and Sn monometallic catalysts and the Pt-Sn bimetallic catalyst are shown in figure 4. It is worth mentioning that all EPR spectra will be represented with a 5×10^4 gain for comparative purposes.

Figure 4(a) presents the spectrum of the aluminosilicate of the MFI type used as a support in all of the catalysts prepared, once it was reduced under hydrogen atmosphere. No signal is observed in this spectrum, indicating the presence of paramagnetism. However, as figure 4(b) shows (spectrum of the reduced bifunctional Pt/H[Al]ZSM5 catalyst), a signal is observed around a magnetic field at 3300 gauss ($g = 2.04$), which would imply the presence of non-paired electrons in this solid and would be indicative of the existence of different magnetic environments between H[Al]ZSM5 and Pt/H[Al]ZSM5. Notwithstanding, considering that the PtO_{ads} species could be diamagnetic, it should then be considered that Pt^0 is the species provoking the paramagnetism detected in the Pt/H[Al]ZSM5 catalyst.

No paramagnetic signal is observed for the bifunctional Sn/H[Al]ZSM5 catalyst (see figure 4(c)), once this was subjected to a reduction process under H_2 atmosphere at 500 °C over 6 h. This could be due to the presence of oxidized species of Sn (Sn(II) and/or Sn(IV)) that cannot be reduced under the aforementioned conditions, as already reported in the XPS analysis. This would mean the absence of non-paired electrons in the supported phase in the Sn/H[Al]ZSM5 catalyst.

Figure 4(d) shows the spectrum of the bifunctional bimetallic Pt-Sn/H[Al]ZSM5 catalyst, obtained after calcination and reduction. No visible signals are observed in this catalyst according to the EPR test. Therefore, the magnetic environment in this catalyst suggests that the species on its surface are basically diamagnetic or that their proportion is much larger than that of the paramagnetic ones. This result suggests that the metallic phase of the platinum could be passivated by the transference of the electronic density from tin to platinum, as was stated in XPS analysis. A similar effect was reported by Melo *et al.* in a previous work [8].

In this regard, it can be observed that the EPR analysis is perfectly compatible with the results obtained by XPS, since by means of this technique the presence of PtO_{ads}, Pt^0, Pt-Sn and Sn in the form of oxides (II and/or IV) was demonstrated. Since most of the platinum and tin species detected on the surface of the catalyst are apparently diamagnetic, we consider that the paramagnetic signal generated by Pt^0 in this solid would be hardly detectable owing to the small fraction of this species in the bimetallic Pt-Sn/H[Al]ZSM5 catalyst.

4. Conclusions

The presence of Sn in the bimetallic Pt-Sn/H[Al]ZSM5 catalysts results in an electronic effect for a tin atomic fraction ≤ 0.46. This effect has been evidenced by a decrease in the hydrogenating activity of the Pt/H[Al]ZSM5 catalysts and the formation of Sn reduced species from its oxidized forms owing to the presence of platinum, suggesting the electron transfer

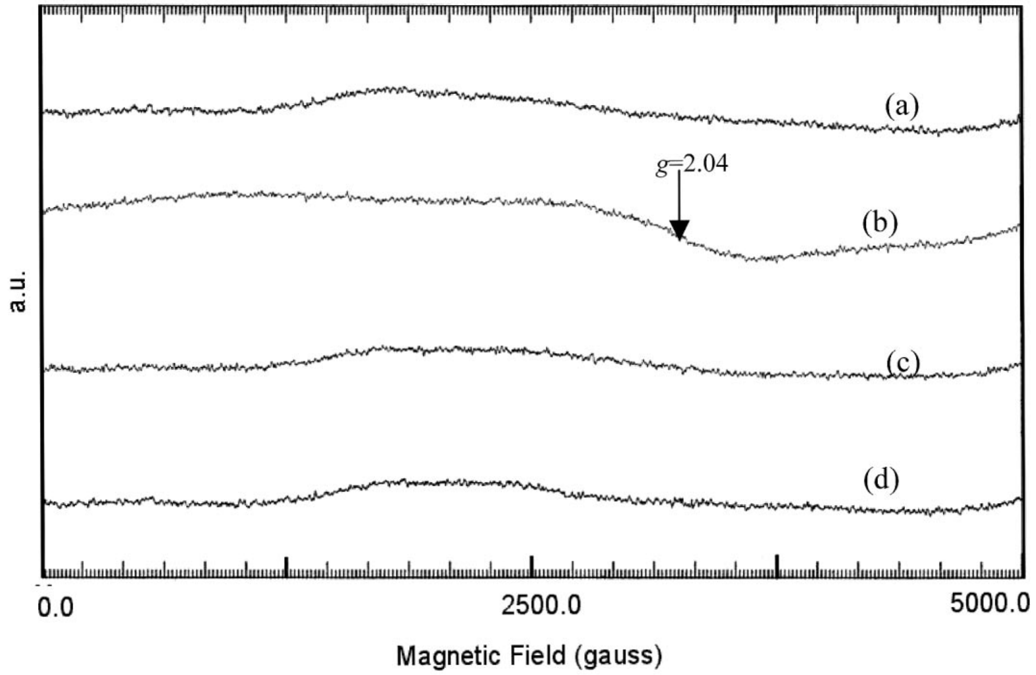

Figure 4. EPR spectra for (a) the support, (b) Pt/H[Al]ZSM5, (c) Sn/H[Al]ZSM5 and (d) Pt-Sn/H[Al]ZSM5 ($X_{Sn} = 0.46$).

from tin to platinum to give rise to the $Pt^{\delta-}$–$Sn^{\delta+}$ alloy, which was evident from the XPS and EPR analysis.

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