

Identification and quantification of Sn-based species in trimetallic Pt-Sn-In/Al₂O₃-Cl naphtha-reforming catalysts

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Abstract Trimetallic Pt/Al₂O₃SnIn–Cl naphtha-reforming catalysts were prepared via co-precipitation route. Platinum and chlorine were introduced by the incipient wetness technique on the alumina support already doped with about 0.3 %wt of Sn to obtain about 0.3 %wt of Pt and 1.5 %wt of Cl. For the same Pt, Sn and Cl composition, indium loading ranged from 0.06 to 0.6 wt.%. The obtained catalysts were investigated by ¹¹⁹Sn Mössbauer spectroscopy between 95 and 300 K. Two Sn(IV), Sn(II) and Sn(0) environments have been identified and well characterized by their hyperfine parameters. The Lamb-Mössbauer factors have been determined for each environment and found to be 0.53, 0.27 and 0.31 for Sn(IV), Sn(II) and Sn(0) respectively. The addition of indium has been found to favour the formation of Pt_xSn alloys. ¹¹⁹Sn Mössbauer spectroscopy results show that addition of even small amount of In (0.06 wt.%) leads to the formation of a Pt₃Sn alloy. At higher indium loadings, higher amounts of Pt_xSn alloys of almost equal Pt and Sn atomic concentrations were detected. The increasing formation of Pt_xSn alloys with higher indium loading is in good correlation with a decrease of catalyst's overall conversion and selectivity to C1 and C3–C4 paraffins and increase of isomerization selectivity.

Keywords Naphtha reforming catalysts · Pt-Sn-In · ¹¹⁹Sn Mössbauer spectroscopy · Pt-Sn alloys

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1 Introduction

Catalytic reforming is a major petroleum refining process for the production of hydrogen, high-octane gasoline, fine chemicals and one of the largest users of catalysts in the chemical industry. In particular, catalytic reforming is a chemical process used to convert naphtha (produced during petroleum refining) into high octane number gasoline. If Pt/Al₂O₃ was the first naphtha-reforming catalyst, great progress has been achieved with the introduction of supported bimetallic-reforming catalysts in which Pt is promoted by another metal (Re, Sn, Ge, Ir). Among these the Pt-Sn based catalysts are particularly selective at low pressure and highly resistant to Pt sintering [1]. The presence of a second metal, like tin, reduces considerably the catalyst deactivation by coke formation and coalescence of the metallic particles during the reaction and regeneration steps, respectively. The role played by tin seems to depend on several factors like the nature of the support, the pre-treatment the support has undergone, the preparation method and the precursors used. Some of these parameters influence the particle size and the accessibility of the noble metal, which, in turn, determine the way tin acts on the catalytic performances.

More recently the addition of a second promoter as In [2] leading to a significant selectivity improvement has been evidenced. During the catalyst preparation and activation, the catalysts undergo more or less complex redox processes. For the characterization of such catalysts by ¹¹⁹Sn TMS, specific reaction cells have been developed in our laboratory to allow both thermal treatments under controlled atmosphere and TMS. In this way the evolution of the catalyst during a oxidation/reduction cycle can be followed by “*in situ*” TMS by stopping the cycle and sealing the cell after any reaction step of the cycle.

2 Identification diagram of Sn-based species

A detailed study by ¹¹⁹Sn TMS of monometallic Sn/Al₂O₃ and bimetallic PtSn/Al₂O₃ samples has allowed to identify a number of species of Sn^{IV}, Sn^{II}, and Sn⁰ occurring after oxidation or reduction under various conditions [3]. It has been shown that the numerous species can be classified into a few categories on the basis of their hyperfine parameters and characteristic structural features could be derived for each of these categories as shown in Fig. 1. Tin phases in contact with the support or with platinum have been identified and the results have been used to establish a model describing the phase transformations occurring in PtSn particles under oxidising or reducing conditions [3]. The reaction mechanisms between Sn-(n-C₄H₉)₄ and alumina surface sites have been studied and the results applied to the controlled preparation of PtSn/Al₂O₃ catalysts [4]. A structural model has been proposed describing at an atomic scale the morphology of the bimetallic particles and their evolution under various heat treatments.

3 Trimetallic Pt/Al₂O₃SnIn-Cl catalysts

Recently trimetallic naphtha-reforming catalysts comprising the Pt-Sn system modified by the addition of a second promoter as In have received close attention

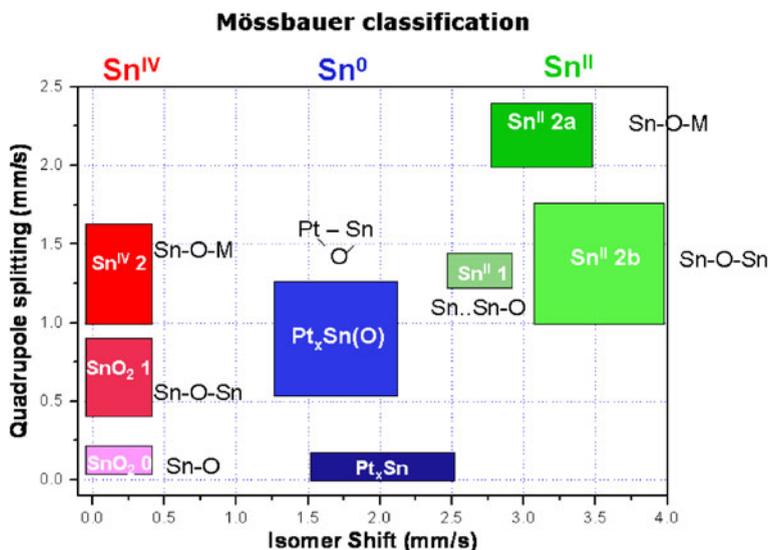


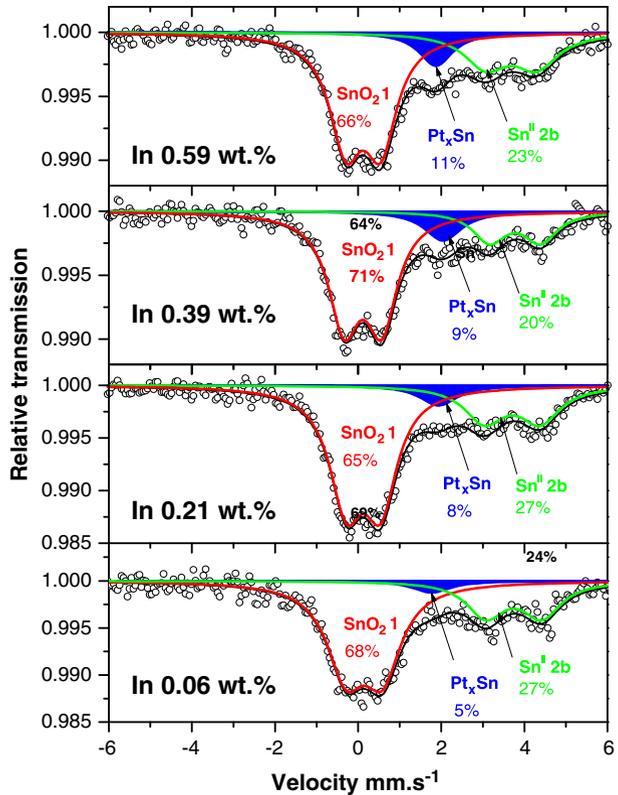
Fig. 1 Classification of the Sn species observed on Sn-based catalysts and of model compounds as a function of their Mössbauer hyperfine parameters

due to a higher selectivity [2]. A detailed study on the effect of indium in alumina supported trimetallic PtSnIn-based naphtha reforming catalysts synthesized by co-precipitation (CP) has been investigated using ^{119}Sn TMS. The various Sn-based species have been identified using the diagram shown in Fig. 1.

The Pt/Al₂O₃SnIn-Cl catalysts have been obtained by CP of Sn and In with the alumina precursor following by a sol-gel method [5]. Figure 2 shows the ^{119}Sn TMS spectra of reduced trimetallic catalysts (500 °C under H₂), Pt/Al₂O₃SnIn_y-Cl with different amounts of In ($y = 0.06, 0.21, 0.39$ and 0.59 wt.%). In all cases the presence of a singlet at $\delta \sim 1.67 - 1.93$ mms⁻¹ demonstrates the formation of Pt_xSn alloys during reduction step. For simplicity, only SnO₂1 and Sn^{II} 2b subspectra are represented since Sn^{IV} 2 and Sn^{II} 2a contributions vary similarly upon changing temperatures.

The presence of indium is found to favour Pt_xSn alloys [6]. For Pt_xSn alloys in the absence of indium, the isomer shift of the Pt_xSn depends linearly on x [3]. An electronic effect of indium on the alloy is expected to modify the isomer shift of the alloy. For the catalysts loaded with 0.06 to 0.39 wt.% of In, infrared spectroscopy monitoring of the CO adsorption showed no electronic modification on platinum. On Mössbauer spectra, in absence of electronic modifications, the positions of the alloy signals in these catalysts indicate that they are Pt₃Sn, Pt_{2.6}Sn and PtSn for 0.06, 0.21 and 0.39 wt.% In, respectively. IR experiments showed however that Platinum was electronically modified at higher In loadings (0.59 wt.%). The Mössbauer isomer shift of this catalyst may therefore result from the alloy signal and the electronic modification. Given that the quadrupole splitting of the alloy signal is 0, we tend to consider that the perturbation induced by indium is minor and that the alloy must be close to a PtSn alloy.

Fig. 2 ^{119}Sn TMS spectra of reduced trimetallic catalysts Pt/Al₂O₃SnIn-Cl with different indium loadings



4 Quantification of Sn-based species

Relative amounts of Sn formed species can be estimated from the contributions of their sub-spectra corrected using their different f factors (Lamb Mössbauer factors). Experimentally these f factors have been determined using the thermal variation of the absorption areas which are known to be related to f in the case of thin absorber approximation by $A(T) = c \cdot f(T)$ where A is the area under the resonance curve and the constant c depends on physical parameters that are unchanged during the acquisition of Mössbauer spectra between 95 and 300 K. It is common to use Debye model for solid permitting the determination of the factor from the following equation [7]:

$$f = \exp \left[\frac{-3E_R}{2k_B\theta_D} \left(1 + 4 \left(\frac{T}{\theta_D} \right)^2 \right) \int_0^{\frac{\theta_D}{T}} \frac{y dy}{\exp(-y) - 1} \right]$$

Where $E_R = 2.572$ meV is the recoil energy for ^{119}Sn , θ_D is the Debye temperature of the solid and k_B is the Boltzmann constant. Typical variation of absorption area

Fig. 3 Experimental (circles) and Debye model fit (line) of the thermal variation of the relative spectral absorption

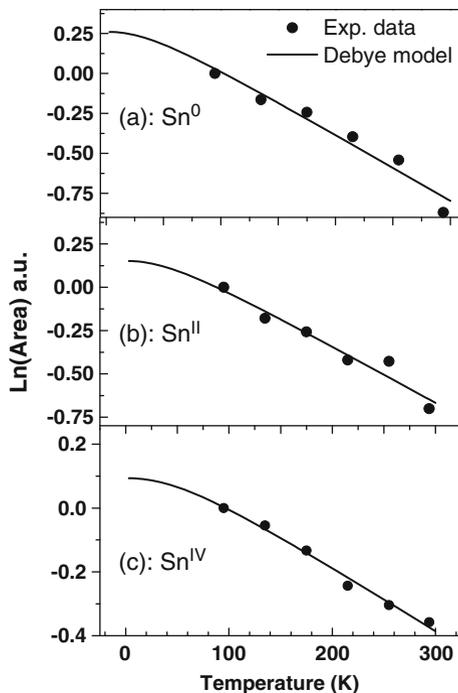


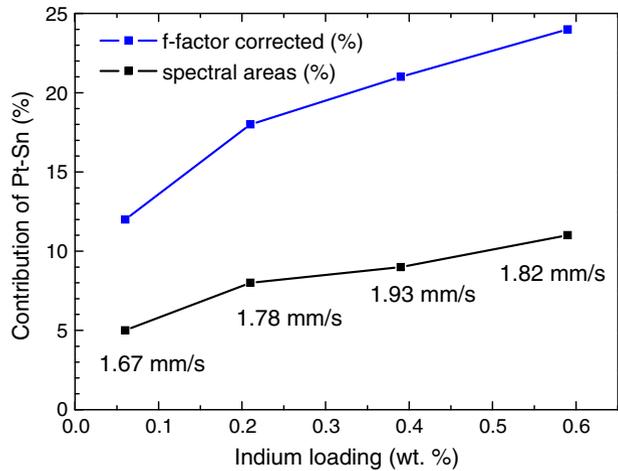
Table 1 Fitted Debye temperatures and Lamb-Mössbauer factors for Sn⁰, Sn^{II} and Sn^{IV} environments

	θ_D (K)	f_{300K}
Sn ⁰	206(10)	0.27(4)
Sn ^{II}	231(12)	0.36(4)
Sn ^{IV}	295(8)	0.53(3)

with temperature is given in Fig. 3 for the alloy containing 0.59 wt.% In. The obtained Debye temperatures and f -factors (Table 1) are in the range of reported data for Sn compounds [8]. Unlike what is generally accepted for iron compounds, significant differences of the Lamb-Mössbauer factors are observed between the different tin environments involved in the catalytic reaction. As it can be seen, the direct use of the relative absorption areas leads to an underestimation of Sn⁰ and Sn^{II} amount. Note that the f -factors are found to be insensitive to In loading and that Sn^{IV} 1 and Sn^{IV} 2 as well as Sn^{II} a and Sn^{II} b show similar variations with temperature.

With the determined Lamb-Mössbauer factors Pt-Sn amounts in the reduced catalysts (blue curve in Fig 4) can be obtained from the spectral areas (black curve in Fig. 4). As the indium loading increases, more Sn oxides are in a weaker interaction with alumina, and Pt-Sn alloying becomes possible with more tin atomic concentration in the formed alloys.

Fig. 4 Composition of Pt_xSn alloys and their signal contribution to the total TMS absorption of trimetallic catalysts Pt/Al₂O₃SnIn-Cl as a function of indium loading



5 Catalytic properties

The n-heptane conversion test was carried out in the continuous flow mode in a fixed bed tubular reactor at 470 °C and total pressure of 8 bar, with a hydrogen-to-hydrocarbon molar ratio H₂:HC equal to 3 and a WHSV of 2 h⁻¹. Prior to the test, catalysts (about 2 g each) were reduced *in situ* under hydrogen flow (500 °C, 2 h). Total conversion (X) and the yields to each reaction product (Y_i) were calculated on carbon basis. Conversion was defined as:

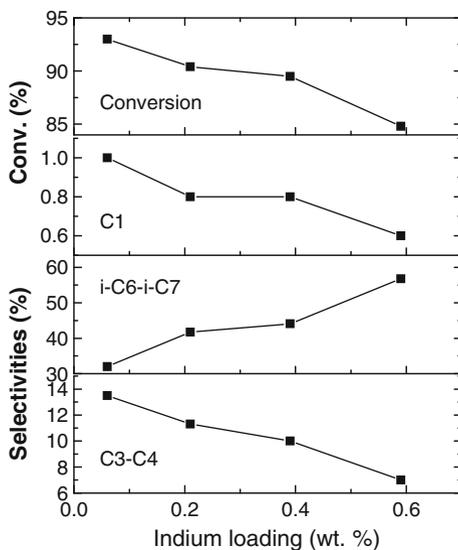
$$X = \frac{HC^i - HC^0}{HC^i}$$

where HCⁱ is the concentration of the fed hydrocarbon at the reactor inlet, and HC⁰ is the concentration of the non-reacted hydrocarbon at the reactor outlet. Selectivity (S_i) to product i was calculated as follows:

$$S_i = \frac{Yield(i)}{X} = \frac{A_i f_i n_i}{X M_i \sum A_i f_i n_i / M_i}$$

where A_i is the area of the chromatographic peak of the product i; f_i is its response factor; n_i is the number of carbon atoms of i, and M_i is its molecular weight. Hydrogenolysis selectivity only includes the selectivity to methane formation. Selectivity to isomerization includes only selectivities to i-C7 and i-C6 hydrocarbons, while hydrocracking selectivity includes selectivity to C3 and C4 hydrocarbons. Figure 5 summarizes the main observations on the catalytic behaviour of the trimetallic catalysts. The total conversion is found to decrease with In loading. This fact may be explained by the physical blockage of Pt atoms by indium and also by the loss of acid sites. By contrast, the trimetallic catalysts have better selectivity to C5+ reformat since hydrogenolysis is decreased while isomerization is increased. The hydrogenolysis decrease is consistent with the increasing formation of Pt_xSn alloys (and possibly

Fig. 5 Evolution of the total conversion and the selectivities to hydrogenolysis, isomerization and hydrocracking as a function of In loading



Pt_xIn) since the reaction is structure sensitive and necessitates contiguous Pt atoms. The hydrocracking decrease shows that the presence of oxidized Sn (and In) in the alumina support as evidenced by TMS has an impact on the surface acidity.

6 Conclusions

TMS is a powerful tool to characterize the local electronic structure around the probed element in crystalline, glass, amorphous or nano-structured materials by the determination of oxidation state, local coordination and bonding. It allows identification of redox processes, characterisation of intermediate phases and makes possible the study of reaction mechanisms thanks to a diversity of experimental facilities.

In the field of catalysis ¹¹⁹Sn TMS has been applied not only for the characterisation of surface and bulk species of supported catalysts but also for the identification of redox reaction during the catalytic cycle (*in situ* measurements). TMS is an elegant analytical tool which provides valuable complementary information to other techniques (such as XAS or XPS) on the fundamental properties of tin in complex Sn-based multimetallic catalysts. The obtained results in the framework of supported trimetallic PtSnIn catalysts on γ alumina, demonstrate new potential for the technique to the definition of phase analysis and local cationic arrangements in complex system of real and industrial importance.

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