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Mössbauer Spectroscopy: an elegant tool for the active sites identification and quantification in Pt-Sn-In based naphta reforming catalysts

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Abstract Trimetallic PtSnIn/Al_2O_3-Cl catalysts have been synthesized by successive impregnations (SI) of metals and characterized by ^{119}Sn Mössbauer Spectroscopy (MS). Various Sn-species have been identified thanks to the use of a Δ (Quadrupole Splitting) – δ (Isomer shift) diagram. ^{119}Sn MS results show that addition of different amounts of In (0.11 to 0.55 wt.%) lead to the formation of $Pt_xSn(O)$ oxo-metallic phases. As the In loading increases these $Pt_xSn(O)$ oxo-metallic phases are richer in Pt. The preferential formation of a given Sn phase in these catalysts is directly related to the preparation method.

Keywords Naphtha-reforming catalysts · Pt-Sn-In Mössbauer Spectroscopy · $Pt_xSn(O)$ oxo-metallic phases

1 Introduction

Alumina supported Pt-Sn heterogeneous catalysts are widely employed in the catalytic naphtha reforming industry [1]. Trimetallic catalysts are considered to be superior to their bimetallic counterparts in terms of stability and resistance to deactivation by coke. However, little information about these materials can be found in the literature. Few examples exist on the promotion of Pt-Sn systems by another metal such as indium [2].

^{119}Sn Mössbauer Spectroscopy (MS) is a powerful tool to fully classify Sn species as a function of their hyperfine parameters in these systems [3, 4] as shown on Fig. 1.

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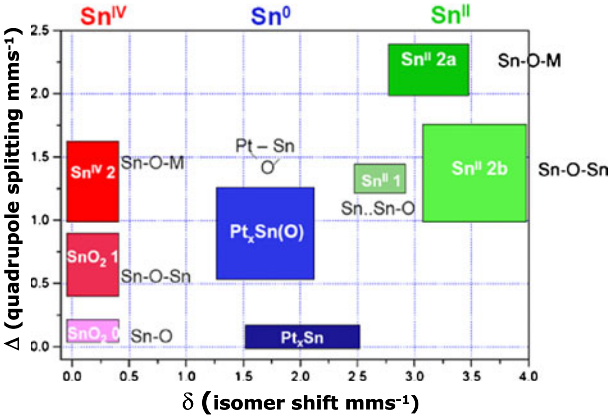
Fig. 1 Classification of the Sn species [3] observed on Sn-based catalysts and of model compounds as a function of their Mössbauer parameters



Using this diagram we have previously shown that the presence of In in Pt/Al_2O_3SnIn-Cl catalysts obtained by co-precipitation of Sn and In with the alumina precursor following a sol-gel method (CP samples) favours the formation of Pt_xSn alloys [5, 6]. In the absence of indium, a Sn^0 unalloyed phase was rather identified. The consequent activity and selectivity differences have been interpreted on the basis of these results [5]. In this paper we present an ^{119}Sn Mössbauer characterization for PtSnIn based catalysts obtained by successive impregnations (SI) of metals.

2 Preparation of catalysts by SI and characterization by ^{119}Sn MS

The calcined γ-alumina support was first impregnated with In using the proper amount of $In(NO_3)_3$, $5H_2O$ to yield 0.10, 0.30, 0.40 and 0.55 wt.% of In relative to support's mass. After this, each of the obtained supports was impregnated with $SnCl_2$, $2H_2O$ (0.30 wt.% of support's mass). Finally the obtained bimetallic supports were impregnated with H_2PtCl_6 (0.30 wt.% of support's mass). The chlorine content of the catalysts was adjusted to approximately 1 wt.% by injecting distilled water to the catalyst at 520° in dry air flow.

^{119}Sn Mössbauer spectra were recorded at room temperature in the transmission mode on a standard spectrometer using a $Ca^{119m}SnO_3$ source of 370 MBq nominal activity. All isomer shifts are given with respect to the room temperature spectrum of $BaSnO_3$. All catalysts were characterized in the reduced form (500°C, 2 h in 1 l/h/g H_2 stream). The reduction was performed in special-U shaped reduction cells adapted for MS measurements. Once reduction was completed, the cell was neutralized and sealed under vacuum.

3 Results and discussion

The different Sn species (Table 1) have been identified using the diagram reported on Fig. 1. Ratios with which Sn species are formed have been estimated from the contributions of their sub-spectra corrected using their different *f* factors (Lamb

Table 1 ^{119}Sn hyperfine parameters δ (mms^{-1}), Δ (mms^{-1}) of species and their corrected contribution CC (%) to spectra of reduced SI samples recorded at room temperature

Sample	δ	Δ	FWHM[a]	CC [b]	Attribution	Absorption (%)
PtSnIn$_{0.11}$Al$_2$O$_3$-Cl	0.36(0)	1.48(6)	0.88(2)	4	Sn^{IV} 2	0.88
	3.10(3)	2.17(3)	0.88(6)	26	Sn^{II} 2a	
	3.86(2)	1.32(2)	0.88(3)	50	Sn^{II} 2b	
	1.95(6)	1.48(6)	0.88(2)	20	Pt$_x$Sn(O)	
PtSnIn$_{0.31}$Al$_2$O$_3$-Cl	0.02(0)	0.68(1)	1.07(2)	8	SnO$_2$ 1	0.63
	3.15(3)	2.49(4)	1.07(3)	36	Sn^{II} 2a	
	3.55(3)	1.18(4)	1.07(7)	40	Sn^{II} 2b	
	1.46(0)	1.35(3)	1.07(2)	16	Pt$_x$Sn(O)	
PtSnIn$_{0.41}$Al$_2$O$_3$-Cl	−0.20(0)	0.30(1)	1.01(2)	4	SnO$_2$ 1	0.59
	3.26(5)	2.34(5)	1.01(1)	36	Sn^{II} 2a	
	3.61(5)	1.14(6)	1.01(5)	43	Sn^{II} 2b	
	1.25(9)	1.08(9)	1.01(2)	17	Pt$_x$Sn(O)	
PtSnIn$_{0.55}$Al$_2$O$_3$-Cl	3.16(5)	2.08(6)	1.07(6)	44	Sn^{II} 2a	0.74
	3.73(7)	1.34(9)	1.07(2)	34	Sn^{II} 2b	
	1.05(6)	1.28(7)	1.07(2)	22	Pt$_x$Sn(O)	

[a] Full Width at Half Maximum, [b] Corrected Contribution (quantitative)

Mössbauer factors). Experimentally these *f* factors have been determined as 0.55 (SnO$_2$ 1 and Sn^{IV} 2), 0.18 (Sn^0/alloys), 0.34 (Pt$_x$Sn(O)), 0.35 (Sn^{II} 2a) and 0.31 (Sn^{II} 2b) [7].

At 0.11 wt% In, the obtained spectrum is composed of 4-subspectra: an unreduced "Sn^{IV} 2" oxide, the two "Sn^{II} 2a" and "Sn^{II} 2b" oxides and a metallic Sn phase (δ = 1.95 mms^{-1} and Δ = 1.48 mms^{-1}). The hyperfine parameters of this phase thus lie at the lower limit of isomer shifts of Sn-rich Pt$_x$Sn alloys (Fig. 1), but its relatively high quadrupole splitting indicates that this phase is rather an oxo-metallic Pt$_x$Sn(O) phase. Higher In loadings (0.31, 0.41 and 0.55 wt%) also lead to a comparable formation of these oxo-metallic phases (16, 17 and 22% respectively). More importantly, the isomer shift of the formed Pt$_x$Sn(O) phase in trimetallic catalysts decreases when the In content increases. The Pt and Sn relative atomic concentrations in these formed Pt$_x$Sn(O) phases can be estimated starting from the isomer shift at which the phase is observed in the spectrum and following the same rule applied for Pt$_x$Sn alloys, i.e. phases with lower isomer shifts are richer in Pt and those with higher isomer shifts are richer in Sn [3]. This implies that in trimetallic catalysts, as the In loading increases, less Sn is engaged in the observed Pt$_x$Sn(O) phase. Such a decrease in the Sn atomic concentration is in accordance with the substitution of Sn by the added In, which is also an evidence of the close Pt-In proximity in these catalysts. The effect of indium in the ternary PtSnIn based system is therefore qualitatively understood as a function of its introduction method, its loading, and the introduction method of the other elements, *i.e.* Pt and Sn. The CP catalysts have surprisingly higher Sn^0/Pt ratios compared to SI catalysts, where the elements were initially thought to be closer to Pt due to the preparation method. This is attributed to the presence of Pt$_x$Sn alloys in CP catalysts only and to the replacement of Sn in Pt$_x$Sn(O) by surface indium in SI catalysts. The interpretation of activity and selectivity differences for the two differently prepared PtSnIn systems is mostly based on these Sn^0/Pt ratios [7].

4 Conclusions

This study represents a solid basis for the profound understanding of complex metallic interactions that exist in PtSnIn based systems. MS is an elegant analytical tool which provides valuable complementary information to other techniques such as EXAFS and XPS. Thanks to MS it has been shown that the preferential formation of a given Sn phase in these catalysts is directly related to the preparation method, as well as the presence (or not) of other promoters.

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