

changes in the chemical composition of Pt_xSn from Pt_3Sn to PtSn . As y increases, more Sn oxides are in a weak interaction with alumina, and Pt-Sn alloying becomes possible with higher tin atomic concentration in the formed alloys.

The presence of indium in Pt-Sn-In/ Al_2O_3 -Cl catalysts, obtained by SI of metals, leads to the formation of $\text{Pt}_x\text{Sn}(\text{O})$ oxo-metallic phases [75]. The Mössbauer spectrum obtained for 0.11 wt% of In can be fitted to four subspectra that can be assigned to unreduced “Sn(IV) 1” oxide, “Sn(II) 2a” and “Sn(II) 2b” oxides, and oxo-metallic $\text{Pt}_x\text{Sn}(\text{O})$ phase (Figure 1.20). The other spectra obtained for 0.31, 0.41, and 0.55 wt% of In also show oxo-metallic phases that represent 16, 17, and 22% of the Sn species, respectively. The isomer shift of $\text{Pt}_x\text{Sn}(\text{O})$ decreases with increasing In content, which indicates that x increases. Such a decrease in the Sn atomic concentration agrees with the substitution of Sn by In and proves the close Pt-In proximity in these catalysts.

Improving the formation of Pt_xSn alloyed clusters on γ -alumina with a high $\text{Sn}(\text{O})/\text{Pt}$ ratio represents a crucial step toward more selective heterogeneous

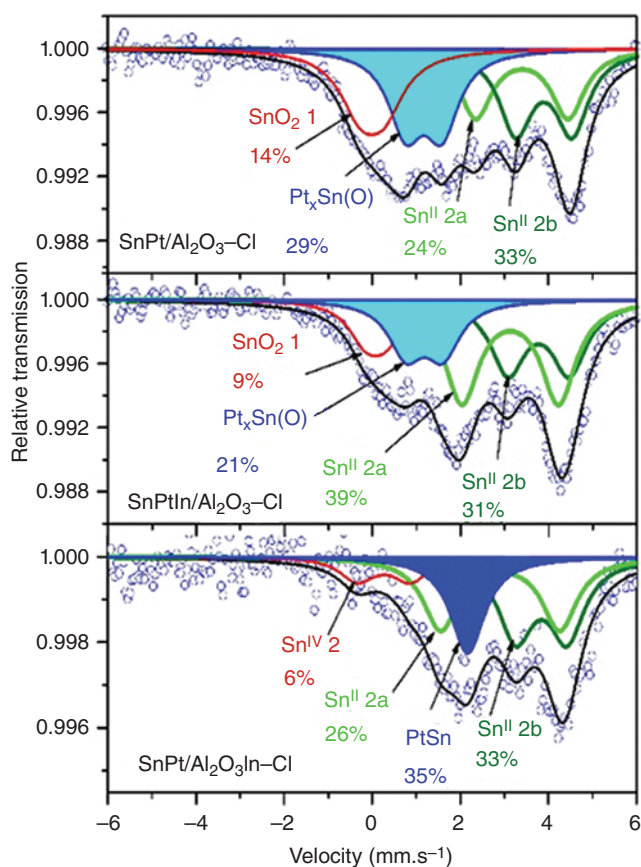


Figure 1.21 ^{119}Sn Mössbauer spectra of reduced catalysts obtained by SOMC: Sn-Pt/ Al_2O_3 -Cl, Sn-Pt-In/ Al_2O_3 -Cl (In by SI), and Sn-Pt/ Al_2O_3 In-Cl (In by CP). Source: Reproduced from Ref. [76]/with permission from American Chemical Society.

catalysts [76]. For that purpose, bimetallic Sn-Pt and trimetallic Sn-Pt-In-based catalysts were prepared by SOMC on monometallic Pt and bimetallic Pt-In-based catalysts, respectively. The ^{119}Sn Mössbauer spectra of reduced Sn-Pt/ Al_2O_3 -Cl, Sn-Pt-In/ Al_2O_3 -Cl (In added by impregnation), and Sn-Pt/ Al_2O_3 In-Cl (In added by CP with alumina source) are shown in Figure 1.21. The spectra of Sn-Pt/ Al_2O_3 -Cl and Sn-Pt-In/ Al_2O_3 -Cl show the contribution of $\text{Pt}_x\text{Sn}(\text{O})$ species but not of Pt_xSn alloys, in contrast to Sn-Pt/ Al_2O_3 In-Cl. Pt-Sn alloying is favored in the latter case, when In is introduced in the support via CP. This can be explained by the existence of In(III) species to stabilize Pt_xSn at the interface with the alumina support.

The application of ^{119}Sn Mössbauer spectroscopy to ternary Pt-Sn-In based systems provides some explanations about the effect of indium as a function of its introduction method, its loading, and the introduction method of the other elements (Pt, Sn). The CP catalysts have higher Sn(0)/Pt ratios than 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_xSn alloys in CP catalysts only and to the substitution of Sn in $\text{Pt}_x\text{Sn}(\text{O})$ by surface indium in SI catalysts. The observed differences in the activity and selectivity of the two differently prepared Pt-Sn-In systems can be related to the Sn(0)/Pt ratio [77].

1.4 Conclusion

In this chapter, we have presented different applications of ^{57}Fe and ^{119}Sn Mössbauer spectroscopies to energy materials, including electrode materials for Li-ion and Na-ion batteries and tin-based catalysts.

The Mössbauer spectroscopy can be used for the characterization of pristine electrode materials but also as an operando technique to follow electrochemical reactions. The examples considered here have been selected to illustrate the three main types of reactions encountered in electrode materials for batteries. The first one is referred to as an alloying reaction where x Li atoms react with a p-block atom M to reversibly form Li_xM . About 4 Li can react with Sn ($x \approx 4$), which explains the high specific capacity of Sn-based electrode materials although they contain a heavy element. However, alloying reactions are associated with strong volume variations that limit the cycle life of batteries. Tin intermetallics have been proposed to overcome this problem. In that case, the first lithiation is a conversion reaction that transforms the pristine material into a nanocomposite for cycling. This is the second type of reaction that also occurs for tin oxides and composites. For both alloying and conversion reactions, the Mössbauer spectroscopy has been mainly used to identify the electrochemically formed species that are often nanosized and poorly crystallized. Finally, the insertion reactions involve Li^+ diffusion on the vacant sites of a host material as often encountered in positive electrode materials containing transition metals. Such reactions go along with the reduction and oxidation of metal ions due to lithiation and delithiation, respectively. In the case of iron-based electrode materials, the ^{57}Fe Mössbauer spectroscopy has been mainly used to detect changes in the oxidation state of Fe or of other metal elements in its environment.

Some examples of supported alumina bimetallic Pt-Sn and trimetallic Pt-Sn-In catalysts have been discussed. In that case, in situ Mössbauer spectroscopy has been used for the identification of tin species formed during the oxidation and reduction steps. The proposed approach, based on the use of an isomer shift – quadrupole splitting correlation diagram, has allowed to identify the most interesting tin species with improved performance and to optimize the synthesis methods.

Mössbauer spectroscopy provides reliable information on complex reaction mechanisms observed in electrochemistry and catalysis. However, an accurate analysis of such mechanisms often requires to combine different in situ measurements, as shown in this chapter for XRD and Mössbauer spectroscopy. Undoubtedly, the use of synchrotron radiation could also be of great interest to expand the field of applications to other elements apart from Fe and Sn and to reduce the measurement time.

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