

# Mössbauer spectroscopy in catalysis

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**Abstract** Application of in situ Mössbauer spectroscopy for studying catalysts and catalytic processes is discussed. Examples are presented to illustrate the potentials of the method by describing studies on supported heterogeneous catalysts performed with  $^{119}\text{Sn}$  and  $^{57}\text{Fe}$  spectroscopies in cases with certain metals and alloys, oxides and porous substances. The results are interpreted in comparison to the catalytic performance.

**Keywords** In situ spectroscopy · Supported catalysts

## 1 Introduction

In general, catalysis is connected to molecular level processes. In case of homogeneous catalysis the reaction partners and the catalyst are single molecules interacting in the same gas or liquid phase. In the case of heterogeneous catalysis the catalyst phase is usually a suitable solid phase (e.g. noble metal) dispersed on some convenient support (oxide, active carbon, etc.) In the latter instance the catalytic promotion of the reaction takes place on the surface of the highly dispersed solid catalysts. Regarding these conditions, it is not obvious at the first glance how Mössbauer spectroscopy can contribute to the study of catalytic processes.

The answer is related to three aspects. First, usually not the catalytic process itself but the substance of catalyst is studied by the tool of Mössbauer spectroscopy. Second, the studied substances are stabilised in high dispersion state, thus significant portion of them is on the surface or in the close vicinity of it, and consequently their properties can be related to and modified by the catalytic processes. The third point is the advantageous application of the in situ technique. The studied reactions can be

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performed in appropriate in situ cells which are transparent to gamma rays carrying the information. The catalyst supports are usually oxides of light metals ( $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{MgO}$ ) which are practically transparent to gamma rays, consequently the information can be obtained primarily from the catalysts phase itself.

The usual limitations of Mössbauer spectroscopy are valid in the case of studying catalysts, as well. The most severe one among these is the limited number of conveniently applicable Mössbauer isotopes ( $^{57}\text{Fe}$ ,  $^{119}\text{Sn}$  for transmission studies and  $^{57}\text{Co}$  for emission spectroscopy). Most of catalysts are noble metal based ( $\text{Pt}$ ,  $\text{Pd}$ ,  $\text{Ir}$ , etc.), thus these elements cannot be analysed easily. Some of them have Mössbauer transitions which usually need low temperature (liquid He) conditions for detection, thus, the in situ technique is less accessible for them ( $^{193}\text{Ir}$ ,  $^{197}\text{Au}$ ). On the other side, those alloys of noble metals which contain any of the previously mentioned “conventional” Mössbauer elements (iron and tin) can conveniently be studied by the in situ technique.

The number of publications related to catalysis with using the tool of Mössbauer spectroscopy is huge, e.g. 1740 communications of this kind are filed in the database of Mössbauer Effect Data Center (MEDC) for the 1966–2007 period [1]. Related overviews can also be mentioned. First, the Catalysis Handbooks compiled and published regularly by the MEDC should be referred [2]. Further, excellent reviews were also published earlier (e.g. [3–8]), and in the recent years as well [9, 10].

Various substances may exert catalytic effects. Some of the catalysts can provide advantageous preformed adsorption sites for the reaction partners (e.g. metals). Other catalysts may directly supply reaction partners (e.g. oxides). Further possibility is the interaction with reaction partners by modifying the acidic properties e.g. by forming Lewis or Bronsted acidic sites capable for transferring electrons or protons in the process. In the present contribution a selection of examples is provided to illustrate the potentials of the in situ Mössbauer spectroscopy by obtaining unique informations on a few of the mentioned metallic, oxidic and porous catalysts.

## 2 Experimental

As mentioned in the introduction, in situ Mössbauer cells can conveniently be constructed for studying catalysts. Various experimental aspects can be considered. The first obvious condition is that the catalyst sample should be heated, and treated among reaction conditions (with gaseous reactants). An advantage is if the catalysts can be measured at lower temperatures (cooling preferably with liquid nitrogen or even with liquid helium) at the very same place where the preceding treatments had been performed [11]. Another important condition can be that the catalytic process and analysis of the reaction products can be performed on the very same sample which is measured by the Mössbauer analysis. This condition can be fulfilled by using chemically inert metals for constructing the sample holder and heating mantle which do not exert any catalytic activity (titania, molybdena, etc.) [12]. Another possibility is using sealable quartz vessels, in which the samples can be treated and the corresponding Mössbauer measurement can be performed after the treatments [13]. A further aspect is whether the sample reacts homogeneously with the treating gases or not. If the reaction mixture flows evenly through in the whole cross section the homogeneity of the sample can be provided [14]. The orientation of the sample

holder may play also a role, e.g. on horizontal sample holders at low temperatures (typically with liquid nitrogen) frozen slurries of liquid reaction mixtures with catalysts can also be measured [15]. An additional option is the provision of pressurizing the sample chamber, since catalytic reactions usually proceed at elevated pressures [16]. A further option is using the “quasi” in situ arrangement, where the locations of the treatment and the measurement are different, and the sample transfer between the two positions can be performed in a protecting atmosphere [17–19].

### 3 Catalysis by metals

#### 3.1 Alloys of tin

Various bimetallic alloys of tin formed with noble metals are extensively studied among the alloys used for catalysis. An essential point in these studies is that the isomer shift of tin linearly depends on the composition of the bimetallic alloys (for Au, Pt [20], and Ir [21]). Thus, analysis of the in situ spectra may provide information on the composition of the active catalyst. Selection can be made among the existing bimetallic crystalline phases by comparing the isomer shift values with the phase diagrams, their catalytic role can be estimated (cf. some examples for PtSn [22, 23], RhSn [24], PdSn [25] and AuSn [26]). Having identified the presence of the different active bimetallic phases even the role of their various crystal facets can also be proposed in the catalytic process [27].

Tin has a low melting point (505 K), thus it is rather mobile in the alloys during catalytic reactions which usually take place at temperatures in this range. The change of the content of tin in the bimetallic alloys is particularly expressed in catalytic processes connected to reduction/oxidation. Tin is easily removed from the bimetallic alloys by oxidative reaction partners (oxygen or chlorine) and forms oxidised species on PtSn/SiO<sub>2</sub> [28, 29]. The formed Sn(IV) species may even remain directly on the surface of metal [30]. The latter reversible process can even be observed at room temperature oxidation of carbon monoxide [31]).

#### 3.2 Iron and alloys of iron

Pure iron without alloying can also be used as catalyst in synthesis of ammonia [32] and in Fischer-Tropsch reactions [33]. In these reactions, the non-metal elements, nitrogen and carbon, can easily be dissolved in the metal phase [34]. Thus other stabilising metal (usually Co) is added preferably to retard the carbide and nitride formation during the processes.

In the case of iron alloys not only the isomer shift but the ferromagnetic properties (value of hyperfine field) is also influenced considerably in most cases by the alloy formation, which provides an additional tool for the distinction between the pure iron and bimetallic phases.

Recently iron and iron base alloys are used also for synthesis of carbon nanotubes. The process starts with the decomposition of the gaseous carbon source (acetylene or methane) at high temperature (e.g. 1000 K) the carbon atoms dissolve in the metallic phase then at a preferred surface geometry the tubes can grow fast. Pure iron is less preferred since mostly amorphous carbon is formed on it during 30 min exposure

to the reaction mixture. Addition of Co in 1:1 atomic ratio improves significantly the yield of synthesis of nanotubes on 2.5/2.5 wt% (Fe,Co)/Al<sub>2</sub>O<sub>3</sub> catalysts. The corresponding Mössbauer spectra show that the dominant component is  $\ominus$ -Fe<sub>3</sub>C on the spent Fe/Al<sub>2</sub>O<sub>3</sub> catalyst, whereas the bimetallic FeCo alloy is the major component in the spent (Fe,Co)/Al<sub>2</sub>O<sub>3</sub> without any presence of iron carbide [35].

Iron may also form alloys with noble metals. Ruthenium can also be used for stabilizing iron in Fischer-Tropsch reaction. A particular method, based on the decomposition of coimpregnated carbonyl clusters of Fe<sub>3</sub>(CO)<sub>12</sub>/hexane and Ru<sub>3</sub>(CO)<sub>12</sub>/ether was used to prepare RuFe/SiO<sub>2</sub> catalysts in excess of Ru (Ru:Fe = 6.5). The coimpregnated complexes were decomposed by heating in hydrogen at 650 K, the obtained supported catalyst was studied whether FeRu bimetallic components can also be formed or iron and ruthenium phases remain separated. The decomposition of Fe<sub>3</sub>(CO)<sub>12</sub> results mostly in oxidation of iron probably due to the presence of silanol groups. However, a certain extent of iron was present in a component with isomer shift (IS)  $\sim$  0.0 mm/s at 4.3 K measurements. To obtain more information on this component spectra were collected at 1.5 K without external magnetic field and in 6 T field as well. The previous, central IS  $\sim$  0.0 mm/s component exhibited a splitting proportional to the applied field proving thereby the paramagnetic behaviour of that component. The iron-ruthenium alloys above 23 % Ru content have hcp structure and are paramagnets. Thus formation of bimetallic RuFe alloy in a certain amount could be proven on the RuFe/SiO<sub>2</sub> catalyst prepared by decomposing the suitable impregnated carbonyl clusters of the two metals [36].

Another noble metal is Pd which may form alloys with iron. Pure palladium can also be used to catalyse synthesis of hydrocarbons from CO + H<sub>2</sub> mixtures, the reaction usually proceeds to full hydrogenation resulting in formation of methane. Minor amounts of additives, e.g. iron, may change the reaction path, and more valuable methanol can also be produced in high selectivity. In particular, addition of 0.2 or 0.5 wt % Fe to 2 wt% Pd supported on silica may provide excellent yields for methanol [37]. Metallic iron and the palladium-iron alloys (PdFe and Pd<sub>3</sub>Fe) can suitably be distinguished by their internal magnetic fields. Corresponding in situ Mössbauer studies reveal that FePd<sub>3</sub> and Pd phases are present on these preferred catalysts. Furthermore, iron is converted to carbides whereas FePd<sub>3</sub> is stable in the CO + H<sub>2</sub> conversion to methanol [38].

#### 4 Catalysis by oxides

Oxides of transition metals can also be used as catalysts. The ability of transition metals to change their valency is utilized in the catalytic processes. In most of cases mixed oxides of them are applied. For instance, (Cu<sub>1-x</sub>Co<sub>x</sub>)Fe<sub>2</sub>O<sub>4</sub> ferrosphenel can be used for gas phase alkylation of phenol to 2,6-xyleneol. In these catalysts copper may change its valency most easily among the transition metal constituents. On the other side, cobalt may provide stabilisation of the structure. Performance of catalysts with various compositions were compared ( $x = 0, 0.25, 0.5, 0.75$  and  $1$ ) at 573, 598, and 623 K. The most active and selective catalyst was the Cu:Co = 1:1 catalyst. The comparison of the corresponding Mössbauer spectra revealed that the CuFe<sub>2</sub>O<sub>4</sub> decomposes to Cu, Cu<sub>2</sub>O and Fe<sub>3</sub>O<sub>4</sub> after 3 h reaction at 623 K. Presence of iron

carbide was detected in the  $x = 0.25$  catalyst in a significant portion (with 19 % spectral area). In the spectrum of the most active  $x = 0.5$  catalyst the contribution of iron carbide was less, amounting only 12 % in spectral area. In the  $x = 0.75$  and 1.0 catalysts only a minor part of iron was reduced to ferrous state, otherwise the spectra of the fresh and spent catalysts were similar.

Thus, participation of the catalyst in the reaction process depending on its composition was revealed in different extents. The interaction with  $\text{CuFe}_2\text{O}_4$  resulted in phase separation to different oxides, and loss of activity. In the most active catalyst at 1:1 Cu:Co ratio the structure was primarily retained and a limited interaction with the reactants was also proven at the same time (cf. formation of carbide). Dominance of cobalt depressed the interactions, thereby the catalytic effect has also been lost [39].

## 5 Zeolites, micro- and mesoporous materials

Principally zeolites are also oxides. But an essential difference is in comparison with the bulk oxides that the portion of the active transition metal ions is small in the solid oxide host matrix and they are highly dispersed mostly located in separate sites, embedded into the silicium (and aluminium) oxide host. Furthermore, the permeable channel structure may be connected in geometric constraints for the reaction partners thus shape selectivity can also be observed in the microporous zeolite catalysts.

Iron may occupy two types of sites in zeolites, that is framework (FW) and extra-framework (EFW) ones. In FW siting the coordination is usually tetrahedral, ferric ions are coordinated by four oxygens in forming negatively charged  $[\text{FeO}_{4/2}]^-$  structural units. In the simplest case the charge compensation is provided by protons, and in correspondence Bronsted acidic centres are formed. Ferrous ions have larger ionic radii, usually they do not fit to the FW tetrahedral site in siliceous frameworks. Iron may also occupy EFW sites in the channels and pores of zeolites. In these positions both ferric and ferrous ions may occur, thus  $\text{Fe}^{3+} \leftrightarrow \text{Fe}^{2+}$  reversible redox changes may proceed. In correspondence, EFW iron ions form Lewis catalytic centres. Contributions of FW and EFW ions can usually be distinguished in the Mössbauer spectra as well. Bronsted acidic FW ferric ions exhibit large quadrupole splitting, whereas EFW ions are prone to reversible  $\text{Fe}^{3+} \leftrightarrow \text{Fe}^{2+}$  changes. Based upon these differences the contributions of FW and EFW ions to the catalytic activity in various reactions can be distinguished (e.g. in alkylation with Fe-MFI see [40]).

In less rigid microporous structures, like MCM-22, removal of iron from FW to EFW positions in a limited extent during moderate reduction/oxidation treatments can also be observed [41]. Formation of dinuclear  $\text{Fe}_{\text{FW}}\text{-O-Fe}_{\text{EFW}}$  pairs can also be suggested in instances when iron may occur both in FW and EFW siting. This substances may catalyse processes with direct oxidation (e.g. oxidation of n-hexane to hexan-3-one or phenol to mixture of hydroquinone and catechol can be performed with hydrogen peroxide by using Fe-FER [42]).

Microporous iron zeolites attracted particular attention in relation with the activation and storage of the so-called “alpha-oxygen” which is a very reactive atomic oxygen species attached to iron in zeolites and is able to oxidise methane to methanol or benzene to phenol at low temperatures [43]. Several studies were performed on

these type of zeolites in order to characterise their structures. In situ Mössbauer observations were also carried out among them, it can be suggested that the active species is linked to presence of ferrous FW iron [44–46].

Iron can also be incorporated into mesoporous ferrisilicates (MCM-41, SBA-15, etc.). The extent of ordering and crystallinity is less strict in these substances, the pore walls are amorphous in a certain degree. In correspondence, the distinction of the FW and EFW types of iron is not obvious and reversible  $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$  transformations may proceed in the pore walls of these substances [47]. Due to the flexibility of their structure even hematite particles can be embedded into an Fe-SBA-15 structure, and this composite catalyst can be applied for e.g. total oxidation of phenol with hydrogen peroxide in aqueous media [48].

Microporous zeolite analog substances are the AIPO-s, the alterations of Al and phosphorous in the framework provides the charge neutrality. Iron can also be introduced to these structures. The geometrical constraints are more loose in these structures, the  $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$  reversible redox changes may easily proceed in these substances, with iron ions without being removed from the framework (see e.g. on Fe-AIPO-5 and Fe-AIPO-11 [49]).

Finally, it can be mentioned that stannic tin can also be introduced to the framework of siliceous micro- and mesoporous substances. Stannous tin is less stable thermodynamically, but in porous frameworks it can be stabilized. Thus,  $\text{Sn}^{4+} \leftrightarrow \text{Sn}^{2+}$  may easily proceed providing a mean to promote transfer of oxygen. In correspondence, microporous Sn-MFI, Sn-MEL and Sn-MTW can be used to catalyse oxidation of aromatic compounds (phenol, toluene, cresol, xylene) with hydrogen peroxide. Corresponding in situ Mössbauer spectra prove the existence and reversibility of  $\text{Sn}^{4+} \leftrightarrow \text{Sn}^{2+}$  process in these catalysts [50]. For catalysing the reactions of larger molecules the mesoporous Sn analogues can be used, e.g. hydroxylation of 1-naphthol with hydrogen peroxide or epoxidation of norbornene with tertiary butyl hydroperoxide can be performed. Corresponding Mössbauer spectra performed on the catalysts attest the  $\text{Sn}^{4+} \leftrightarrow \text{Sn}^{2+}$  reversible change [51]. In analogy, the mesoporous Sn-SBA-15 is also suitable catalyst for processes with spacious reactants, eg. transesterification of dimethyl malonate with different alcohols, or for synthesis of Nopol carried out by the Prins condensation of  $\beta$ -pinene with para formaldehyde. Sn-SBA-15 performs also better in the epoxidation of norbornene as the previously mentioned Sn-MCM-41. The corresponding Mössbauer spectra reveal the temporary stabilisation of  $\text{Sn}^{2+}$  in the framework and the reversibility of the  $\text{Sn}^{4+} \leftrightarrow \text{Sn}^{2+}$  process [52].

## 6 Summary

In situ Mössbauer spectroscopy can advantageously be used in studying supported heterogeneous catalysts. In certain cases the method may provide unique and specific informations which are hardly attainable for other methods. For the appropriate interpretation, the results of Mössbauer studies should be evaluated with regard to the catalytic performance.

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