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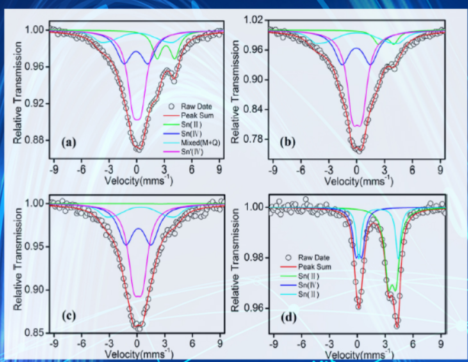
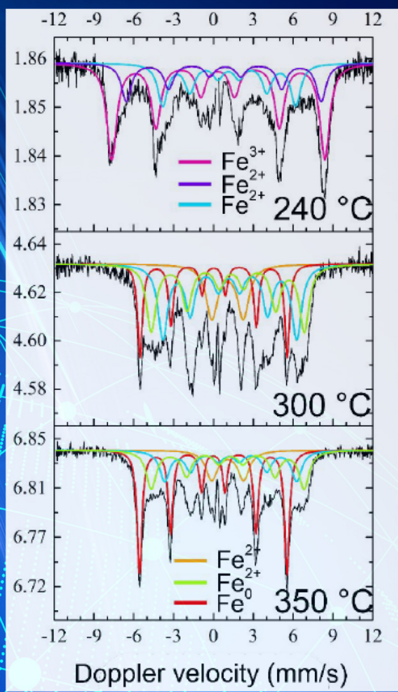
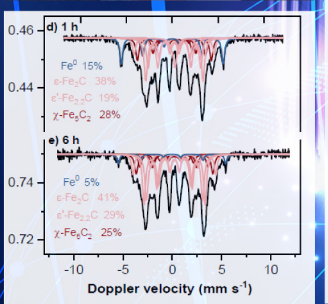
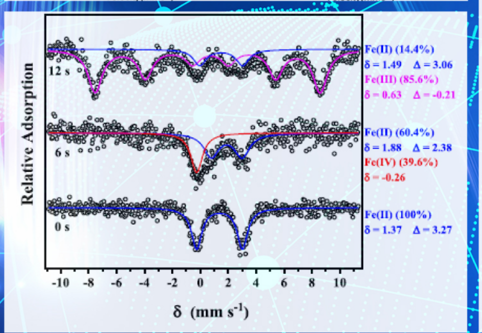
Study of Catalysts with Mössbauer Spectroscopy – Outline of Some Recent Trends

Part C: Bulk Oxides, Fenton and Fisher-Tropsch Catalysts









Mössbauer Effect Reference and Data Journal

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On the cover:
This issue our front cover features photos of Prof. Károly Lázár and his study of catalysts with Mössbauer spectroscopy. This is the third report. (See more in Editor's Comments and in the enclosed Mössbauer Spectroscopy Newsletter.)

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Contents

Guest Editor's Comments

"Study of Catalysts with Mössbauer Spectroscopy–Outline of Some Recent Trends" Part C: Bulk Oxides, Fenton and Fisher-Tropsch Catalysts

An expressed progress is going on in the application of new catalyst materials in the recent years. There are two driving forces behind. On one side promising new materials were developed, and on the other side the environmental aspects and criteria for catalytic processes received strong emphasis. A representative example is the class of the single atomic Fe-N-C catalyst, which are in the focus of several recent studies. On one part they are efficient catalyst in electrochemical processes, e.g. in fuel cell membranes contributing in one stage to the ease of environmental pollution, to decrease the consumption of fossil fuels. On the other aspect the application of them is also advantageous since other expensive catalysts based on precious metals can be replaced by them. Other new classes of materials can also be mentioned, which expect promising applications (e.g. metal-organic-frameworks). Further on the catalytic processes used for restoration of environment gained expressed emphasis (e.g. Fenton catalysts for waste water treatment). Thus it can be noticed that iron containing catalysts gained increasing share among the catalyst materials. Since ^{57}Fe is the most suitable isotope for Mössbauer studies it is obvious that the one of the suitable tools for characterizing iron catalysts is Mösbauer spectroscopy. In correspondence, the coincidence of development of catalyst materials and shift of emphasis in the role of processes with the appropriate advantages of application of Mössbauer method is reflected in the increasing number of related publications.

The Dalian Institute of Chemical Physics is the host institute of the Mössbauer Effect Data Center (MEDC) since 2010. The management of the Center has been maintained by a dedicated team which is also strongly devoted to studying catalysts as is reflected in the great number of publications in prestigious journals. They have also published profound reviews on studying catalysts with the Mössbauer method. On my opinion the recent brief series in the MERDJ suits well to the scope of activity of the MEDC team in Dalian Institute of Chemical Physics.

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Mössbauer Effect Data Center

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Mössbauer Effect Reference and Data Journal

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The Mössbauer Effect Data Center developed and administers two separate Web sites for the Mössbauer community (<www.mossbauer.info> and <www.medc.dicp.ac.cn>). These sites provide Mössbauer researchers with pertinent and timely information, free of charge. Included on the sites are general information pertinent to the Mössbauer community, news items, regional lab information, position postings, information on upcoming conferences, the most recent *Mössbauer Spectroscopy Newsletter*, IBAME information, an E-Mail and Fax Directory of Mössbauer Authors, links to Mössbauer instrument and source suppliers, and further information regarding the Center's products and services. Access to the MEDC Web-Access Database is also provided through the MEDC site. Researchers may now access and search the MEDC database *from their computers* via the MEDC Web site.

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MÖSSBAUER SPECTROSCOPY
NEWSLETTER

March 2022

Study of Catalysts with Mössbauer Spectroscopy – Outline of Some Recent Trends
Part C: Bulk Oxides, Fenton and Fisher-Tropsch Catalysts

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Abstract/Introduction

The present three-part series provides a brief outline on recent developments of the catalysts studies applying the method of Mössbauer spectroscopy. There is a significant progress in the development and introduction of new catalyst substances in recent years, thus it is worth overviewing them shortly from the aspect of related Mössbauer studies. The brief account is primarily based on a selection of reports published in the last couple of years. Catalyst substances are discussed from the aspect of materials science, the classification of discussed reports is based primarily on the composition of materials. In the first part of the series the principles of the Mössbauer method were shortly discussed and some particular conditions which may play role in studying catalysts were considered. In addition, the rapidly developing Fe-C-N catalysts were also discussed in [1]. Further, a short overview was given on other types of single atomic catalysts, namely complex molecules, quickly frozen reaction intermediates, enzymes were discussed in Part B [2]. In the present, last part of the series oxides, oxyhydroxides, Fenton- and Fischer-Tropsch catalysts are considered, and summarizing conclusions for all the three parts are drawn. Serial numbers for marking the sections are continuously used throughout the three parts, thus the next section is straight C.3.3.

C.3.3 Bulk oxides and (oxy)hydroxides

In this section examples are shown for various applications of oxides in heterogeneous catalytic reactions, including stabilized catalysts for Fenton processes and an example for chemical looping is also included.

Influence of the support on the stabilization of oxide nanoparticles is an important issue in catalytic processes. Stabilization of Fe_xO_y nanoparticles with 7 nm mean size were compared on silica and titania supports in Fischer-Tropsch to olefin reaction. Deactivation of titania supported catalyst was observed, explained with growth of oxide particles to c.a. 48 nm size, with formation of $FeTiO_3$. The silica supported particles maintained their activity and original particle size. Formation and stabilization of various phases containing iron were studied with Mössbauer spectroscopy as well Figure 1 [3].

Oxidation of methane is a large scale

industrial process. Direct oxidation without catalysts proceeds at high temperature resulting in formation of harmful nitrogen oxides. The reaction temperature can significantly be decreased by using a porous perovskite ($SrTi_{0.65}Fe_{0.35}O_{3-\delta}$). The bulk phase participates in the process by releasing lattice oxygen. Presence of Fe^{4+} component is detected in the corresponding Mössbauer spectra [4].

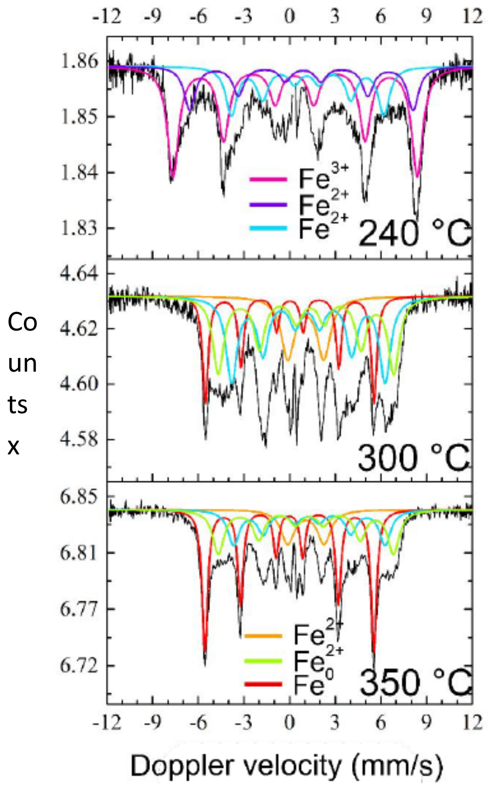

Figure 1. 120 K *in situ* spectra illustrating the conversion of silica supported 7 nm Fe_xO_y oxides after reduction at the marked temperatures in hydrogen (Adapted from [3] under Creative Commons (CC-BY-NC-ND) Attribution License).

The possibility to oxidize CO at ambient temperature is an important issue e.g. in air purification in confined spaces. Catalysts used with this purpose are expected to maintain their activity during occasional long term storage as well. Robust Pt catalysts were developed on $LaFeO_3$ perovskite support with the inclusion of a stabilizing FeO_x interphase between the metal and support phases. Presence of high dispersion FeO_x phase embedded to the support can be revealed from corresponding Mössbauer spectra [5].

Another important process is the preferential oxidation of CO in hydrogen (PROX) to provide sufficiently pure hydrogen for polymer electrolyte fuel cells to avoid poisoning of the platinum in the anode. Water gas shift reaction can be used for production of hydrogen in large scale, the process results usually 1 % CO residual. As alternative to the high cost precious metal containing PROX catalyst a set of Cu-Fe/Al_2O_3, $CuFe_2O_4$, Cu/$CuFe_2O_4$ and Fe/$CuFe_2O_4$ catalysts were assessed, with the best conversion from the latter one (100 % at 200 °C). Influence and presence of oxide phases in various extents were evaluated from Mössbauer spectra [6].

Oxides and hydroxides are suitable ***for electrocatalytic (OER, HER)*** reactions as well. Detailed structural characterization was performed on the influence of Co^{3+} substitution into hematite nanorods. Several effects are discussed, and improvement of the OER activity (decrease of overpotential) was reported [7].

Presence of Fe^{4+} was clearly evidenced in electrodes in $NiFe_{0.2}$ (oxy)hydroxide, developed from topotactic transformation of Prussian blue analogue. ^{57}Fe Mössbauer studies revealed the *in-situ* production of high-valent iron species under OER conditions [8].

Performance of Ni,Fe,Zn ternary metal hydroxides were also assessed in OER process. Morphology transformation and *in-situ* self-reconstruction was observed in the uppermost hydroxide layer resulting in the improvement of the electrochemical efficiency [9].

Perovskites are also efficient electrocatalysts. A $La_{0.6}Ca_{0.4}Fe_{0.7}Ni_{0.3}O_{2.9}$ catalyst exhibits good performance and stability in OER process with a stabilized Ni-Fe (oxy)hydroxide layer on the top of the oxide. The non-stoichiometry in the oxide was revealed by presence of Fe^{4+} signal in the corresponding Mössbauer spectra [10].

^{119m}Sn is also a suitable Mössbauer isotope beside ^{57}Fe, however its application for catalyst studies is rather scarce. In a recent study preparation of defect-rich tin oxides with modulated Sn^{2+}/Sn^{4+} ratios was followed by the method (Figure 2) [11]. These catalysts exhibit good performance in photocatalytic water splitting.

Removal of harmful contaminants from waste water is of high importance to avoid further damage of environment. The ***Fenton process*** is an important tool for these treatments. In principle, $HO^{\bullet}$ radicals are procuded from H_2O_2 in aqueous phase with the help of Fe^{2+} ions. A crucial point is the stabilization of Fe^{2+} ions to avoid their leaching from the solid phase. A comprehensive review on details of the Fenton

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May 18 - 19, 2022
Spectrométrie Mössbauer et Interdisciplinarité, Magnétisme et Sciences Environnementales (GFSM2022)
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https://gfsm2022.sciencesconf.org

September 4 - 9, 2022
IXVI International Conference on Mössbauer Spectroscopy and its Applications 2022 (XVI ICMSA)
Ekaterinburg, Russia
http://icmsa.ru/

September 11 - 16, 2022
International Symposium on the Industrial Applications of the Mössbauer Effect (ISIAME 2022)
Olomouc, Czech Republic
https://isiame.upol.cz

November 6 - 11, 2022
The XVII Latin American Conference on the Applications of the Mössbauer Effect (LACAME 2022)
Vitória, Brazil
http://www.lacame20-vitoria.org

September 3 - 8, 2023
International Conference on the Applications of the Mössbauer Effect (ICAME 2023)
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