In situ Mössbauer investigation of iron oxide catalyst in Water Gas Shift Reaction - Impact of oxyreduction potential and temperature

Z Cherkezova-Zheleva and I Mitov
Institute of Catalysis, Bulgarian Academy of Sciences, Acad. G. Bonchev St., Block 11, 1113 Sofia, Bulgaria
E-mail: zzhel@ic.bas.bg

Abstract. The aim of the study is to obtain the exact state of iron oxide catalyst active phase in reaction conditions, as well as the correlation between the active phase and catalytic properties of iron-containing catalysts. In situ Mössbauer spectroscopy is the major investigation technique. It is established that the change of reaction conditions (temperature and gas reaction mixture) lead to redistribution of the relative weight of spectra components and influence mainly tetrahedrally and octahedrally coordinated cations in Fe₃O₄ phase. It was concluded, that the active sites of the catalyst in studied reaction are probably pairs of Fe³⁺+Fe²⁺-(Fe².⁵⁺) ions, i.e. the mixed valance iron ions. The obtained catalytic activity can be explained with combination of the natural thermo-activated and catalytically induced electron exchange and better synchronizing of oxidation and reduction steps of the catalytic reaction.

1. Introduction
Nowadays, the water gas shift reaction (WGSR) has attracted an increasing interest mainly because of its application in fuel cells [1, 2]. By WGSR, the hydrogen production from steam reforming is increased and, most importantly, the hydrogen stream is purified by the removal of carbon monoxide. Moreover, the WGSR is a key step in automobile exhaust processes, since the hydrogen produced is a very effective reductant for NOₓ removal [3]. The WGSR is one of the basic processes in chemical fertilizer industry, also [4]. Iron based samples are mainly used for catalyzing the WGSR at medium and high temperatures (MHT) (340 - 500 °C). The industrial MHT catalyst is usually hematite (α-Fe₂O₃), which is converted to magnetite (Fe₃O₄) during the activation process, which is the active phase in the MHT reaction [3, 4]. A detail characterization of the target catalyst under operational conditions is then required to succeed in its optimization. The main part of investigations considers the study of structural properties and catalytic performance using different promoters in order to avoid the sintering process. But the morphological/textural properties can be insufficient in explaining the catalytic behavior due to the major impact of the electronic state of the iron ions. On the other hand the active phases form and change their structure and oxidation state depending on in catalytic reaction conditions (temperature and reaction gas mixture oxidation potential). This requires the use of in situ spectroscopies. As one of a handful tools capable of giving chemical and structural information on working catalysts at reaction conditions, Mössbauer spectroscopy is in an elite group of in situ spectroscopies.
characterization methods. The high energy photons “see” inside chemical reactors to reveal catalyst chemistry and structure under in situ conditions [5, 6].

2. Experimental

2.1. Catalyst preparation
The studied catalysts \( \alpha\text{-Fe}_2\text{O}_3 \) were prepared by thermal dissociation of different iron oxy-hydroxide precursors (\( \alpha\text{-FeOOH} \) and \( \text{Fe}_5\text{OH}_{8.4}\text{H}_2\text{O} \)) [7], which allows the investigation of the catalyst optimal precursor. There are presented obtained results with the first precursor, only.

2.2. In situ Mössbauer spectroscopy
The in situ experiments were carried out in a Mössbauer reactor-cell, which permits spectra recording under reaction conditions (high temperature and reaction gas mixture). Sample of 20 mg/cm\(^2\) was placed in a chemically inert holder situated in the cell. The Mössbauer spectrometer used worked in a constant acceleration mode. A \(^{57}\text{Co}\)/Cr source with an activity of about 50 mCi was used. The spectra were collected over 1024 channels in mirror image format. Data analysis was performed using a least squares fitting routine that models the spectra as a combination of quadruple doublets and magnetic sextuplets based on a Lorentzian line shape profile. Identification of the spectral components was based on their isomeric shift (δ), quadruple splitting (\( \Delta \)) and hyperfine magnetic field (B) values. All isomer shift values are reported relative to metallic iron (\( \alpha\text{-Fe} \)). The line widths (Γ) were determined also. The content of the spectral components (G) was determined from the relative area of each component, which was corrected by value of the Debye-Waller factor at this temperature according to literature data [8]. On the basis of different fitting procedures (giving fixed or non-fixed ratio of magnetite line intensities) were obtained firstly the number of different phases (shown on the Figures) and secondly was calculated the non-stoichiometry parameter of magnetite phase in each spectrum (see the Table).

2.3. Catalytic measurements
The investigation was performed with two different gas mixtures: CO/Ar (14% CO+86% Ar) – Reaction media 1 and CO/H\(_2\) (15% CO+10% CO\(_2\)+63% H\(_2\)+12% N\(_2\)) – Reaction media 2. Purity of all used gases was 99.995%. The gas mixtures were saturated with water vapour up to the chosen pressure: \( P_{\text{H}_2\text{O}} = 0, 5.6, 15.7 \) or 31.2 kPa. The reaction products were determined with gas analyzer “Infralit-2000”. The catalytic activity was expressed by the CO moles converted over a 1 m\(^2\) of the catalyst for 1 h (W, mol/m\(^2\)h). The experiments were performed according to the following procedure: blowing through Ar at a temperature \( T = 472 \) K for an one hour. The catalyst was reduced for 7 h with the gas mixture CO/H\(_2\) under \( P_{\text{H}_2\text{O}} = 5.6 \) kPa, a flow rate \( V = 4 \) ml/min and a temperature was increased from \( T = 470 \) K to \( T = 620 \) K. A steady state of catalyst was attained at the given \( T \) and \( P_{\text{H}_2\text{O}} \) with a flow \( V = 2 \) ml/min. Recording of the spectrum and determination of the reaction mixture concentration at the outlet and the inlet of the reactor-cell under the steady state conditions was attained.

3. Results and discussion
The samples were studied using Mössbauer spectroscopy before and after catalytic test (ex situ) and in catalytic reaction conditions (in situ), also. The registered change of catalyst steady state depends on the temperature (293-673K) and oxyreduction potential of reaction gases (\( P_{\text{CO}}/P_{\text{H}_2\text{O}} \)), studying two catalytic reaction medias, which can be seen on Figures 1 and 2. The calculated parameters are listed in Table 1. It is well known, that studied WGSR is catalytic reaction of oxyreduction type, having both oxidation and reduction steps. Thus, the catalyst must be characterized by the facile change of the oxidation state of its cations. The catalytic cycle involves two adsorbed redox couples: oxidation of molecule in which the first injects electrons into the oxide catalyst and reduction step, in which the second molecule extracts them from the oxide. In order to study the impact of oxidation potential of
reaction media on the steady state of catalyst, two different gas mixtures were investigated, having predominantly oxidation (Reaction media 1) or predominantly reduction potential (Reaction media 2), respectively. The main attention was paid to the Fe$^{+2}$/Fe$^{+3}$ ratio in magnetite phase, as it has been suggested that it is responsible for the catalytic activity in HT WGSR [9, 10].

The obtained in situ Mössbauer spectra with the increase of temperature in reaction conditions of Reaction media 1, i.e. in predominantly oxidation media are shown on Figure 1. It can be seen the steady state of iron oxide catalyst, i.e. phase and dispersity transformations performing with the catalyst during catalytic reaction. Formation of (Fe$^{+3}$)$_{tetra}$[Fe$^{+2}$(1-3x)Fe$^{+3}$(1+2x)]$_{octa}$O$_4$; [x - vacancies; (x=0.012 –0.023), i.e. nonstoichiometric magnetite, as catalyst active phase was registered. The value of nonstoichiometry parameter ($x$) (Fe$_{3-x}$O$_4$) was obtained according to relative arias of the octahedrally and tetrahedrally coordinated iron ions (S$_B$/S$_A$). Depending on T and $P_{H_2O}$ the amount of vacancies passes through a maximum (0.023) at $T$ = 623 K, when the catalytic activity have maximal value (24.4 mol/m$^2$h). It was obtained a small amount of $\alpha$-Fe$_2$O$_3$, which grow up, when the $P_{H_2O}$ increases. High dispersed (HDM) and superparamagnetic (SPM) components were registered also.

The change of reaction conditions (temperature and gas mixture) lead to formation of different catalyst steady state during the Reaction media 2 (Figure 2). The predominantly reduction gas mixture lead to a presence of other type catalyst active phase - non-stoichiometric magnetite (Fe$_{3-x}$O$_4$) - (Fe$^{+2}$_$\bullet$Fe$^{+3}$_$\bullet$)$_{tetra}$[Fe$^{+2}$(1+2x)Fe$^{+3}$(1-x)]$_{octa}$O$_4$; x=0.004 – 0.005. An effect of change of catalyst dispersity was registered as a result of catalyst performance. It was obtained SPM component in the spectra. Its partial weight increases with an increasing of number of consecutive oxidation/reduction cycles of catalytic process (i.e. with an increasing of residence time in reaction conditions) and it is higher for the Reaction media 2, then for the Reaction media 1.

The absence of catalytic reaction, i.e. the in situ Mössbauer spectra obtained in Ar media didn’t show neither phase composition of catalyst (which is stoichiometric Fe$_3$O$_4$), nor catalyst dispersity.

Comparison between the change of vacation quantity ($x$) and catalyst performance with the temperature increase gives a correlation between the catalysts steady state and structure, and the catalytic activity (Table 1). It was obtained a parallel behavior. On the other hand study of the change of all spectra components showed that the line width of octahedrally coordinated Fe$^{+3}$ ions in this...
non-stoichiometric Fe$_{3-x}$O$_4$ phase have the same change with temperature increase as catalytic activity (Table 1).

**Table 1.** Calculated in situ Mössbauer parameters in Reaction media 1 (RM-1) and 2 (RM-2). Experimental errors were ±0.01 mm/s for IS, QS and G; ±0.1 T for B, respectively.

| Conditions | Spectra components | $\delta$, T | $\Delta$, T | B, T | $\Gamma$, mm/s | G, % | $S_B/S_A$ | Parameter of non-stoichiometry ($x$) | Catalytic activity, W, mol/m$^2$h |
|------------|--------------------|-------------|-------------|-----|---------------|------|-----------|---------------------------------|-------------------------------|
| 573K, RM-1 | $\alpha$-Fe$_2$O$_3$ | 0.15        | -0.11       | 42.5 | 0.28          | 2  | -         | 1.817                           | 20.0                          |
|            | Fe$_3$O$_4$ - Fe$_{2.5+}$ tetra | 0.07        | 0           | 41.8 | 0.36          | 98 | 0.012     | 1.817                           | 20.0                          |
|            | Fe$_{2.5+}$ octa | 0.44        | 0           | 37.3 | 0.42          | 0.012 | 1.817 | 20.0                          |
| 623K, RM-1 | $\alpha$-Fe$_2$O$_3$ | 0.12        | -0.11       | 41.7 | 0.28          | 3  | -         | 1.667                           | 24.4                          |
|            | Fe$_3$O$_4$ - Fe$_{2.5+}$ tetra | 0.05        | 0           | 39.1 | 0.50          | 97 | 0.023     | 1.667                           | 24.4                          |
|            | Fe$_{2.5+}$ octa | 0.41        | 0           | 34.6 | 0.52          | 0.023 | 1.667 | 24.4                          |
| 673K, RM-1 | $\alpha$-Fe$_2$O$_3$ | 0.12        | -0.11       | 39.4 | 0.28          | 7  | -         | 1.717                           | 21.2                          |
|            | Fe$_3$O$_4$ - Fe$_{2.5+}$ tetra | 0.02        | 0           | 36.0 | 0.49          | 93 | 0.017     | 1.717                           | 21.2                          |
|            | Fe$_{2.5+}$ octa | 0.37        | 0           | 31.5 | 0.52          | 0.017 | 1.717 | 21.2                          |
| 573K, RM-2 | Fe$_3$O$_4$ - Fe$_{2.5+}$ tetra | 0.07        | 0           | 40.8 | 0.33          | 100 | 2.085     | 18.9                           |
|            | Fe$_{2.5+}$ octa | 0.43        | 0           | 36.6 | 0.39          | 100 | 2.085     | 18.9                           |
| 623K, RM-2 | Fe$_3$O$_4$ - Fe$_{2.5+}$ tetra | 0.03        | 0           | 38.2 | 0.36          | 100 | 2.075     | 19.5                           |
|            | Fe$_{2.5+}$ octa | 0.39        | 0           | 33.6 | 0.41          | 100 | 2.075     | 19.5                           |
| 673K, RM-2 | Fe$_3$O$_4$ - Fe$_{2.5+}$ tetra | 0.01        | 0           | 35.4 | 0.40          | 100 | 2.085     | 18.4                           |
|            | Fe$_{2.5+}$ octa | 0.36        | 0           | 30.9 | 0.44          | 100 | 2.085     | 18.4                           |

Then it can be concluded, that under the catalytic reaction conditions the natural electron exchange, which is an intrinsic property of solid state magnetite catalyst is probably combined with electron exchange between reactants in the course of redox catalytic reaction, i.e. with catalytically induced electron exchange. This leads to the observed redistribution of electron density and valence state of the iron ions. Therefore the active sites of this catalyst might be related with pairs of Fe$^{3+}$+Fe$^{2+}$-(Fe$^{2.5+}$) ions. These mixed valence pairs have an improved possibilities of exchange interactions. The formation of such active complex allow synchronizing of electron exchange leading to simultaneous participation of these ions in the oxidation and reduction steps of the catalytic reaction. Its activation energy decreases due to the more appropriate initial mobility of the catalyst electrons.

**Acknowledgments:** The authors are grateful for the financial support to the Bulgarian National Science Fund at the Ministry of Education and Science - Project DO 02-295/2008.

**4. References**

[1] Pereira A L, Berrocal G J, Marchetti S, Albornoz A, de Souza A and Rangel M C 2008 *J. Mol. Catal. A: Chemical* **281** 66–72

[2] Scariot M, Francisco M S, Jordao M, Zanchet D, Logli M and Vicentini V 2008 *Catal. Today* **133–135** 174–80

[3] Kappen P, Grunwaltd J D, Hammersho B, Tröger L and Clausen B 2001 *J. Catal.* **198** 56–65

[4] Byun I S, Choi O L, Choi J G and Lee S H 2002 *Bull. Korean Chem. Soc.* **23/11** 1513-8

[5] Niemantsverdriet J W 2007 *Spectroscopy in catalysis: an introduction* Third revised edition, (Weinheim: Wiley-VCH) pp 121-46

[6] Niemantsverdriet J W and Delgass W N 1999 *Topics Catal* **8** 133–40

[7] Mitov I, Paneva D and Kuniev B 2002 *Thermochim. Acta* **386** 179-88

[8] Sawatzky G, Van der Woude F and Morish A 1986 *Phys. Rev.* **183** 383-6

[9] Cherkezova-Zheleva Z, Tsoncheva T, Tuyliev G and Mitov I 2006 *Appl. Catal. A* **298** 24-31

[10] Haber J and Witko M 2003 *J. Catalysis* **216** 416–24