



# The continuous conversion of ethanol and water mixtures into hydrogen over Fe<sub>x</sub>O<sub>y</sub>/MoO<sub>3</sub> catalytic system—XPS and Mössbauer studies



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## ARTICLE INFO

### Article history:

Received 11 February 2016

Received in revised form 18 May 2016

Accepted 1 June 2016

Available online 2 June 2016

### Keywords:

Iron oxides

Hydrogen production

Ethanol

XPS spectroscopy

Mössbauer spectroscopy

## ABSTRACT

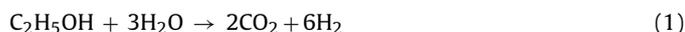
A preparation of the new catalytic systems consisting of ultrafine nanoparticles of Fe<sub>x</sub>O<sub>y</sub> (below 10 nm) supported on MoO<sub>3</sub>, active in the generation of hydrogen from ethanol and water mixtures, is described. The catalysts were obtained as a result of thermal decomposition of iron dodecamolybdophosphates FeHPMo<sub>12</sub>O<sub>40</sub> and FePMo<sub>12</sub>O<sub>40</sub>. Detailed characterization of catalysts was performed by several methods, especially by the Mössbauer and XPS spectroscopies. It was shown that studied catalysts can convert both components forming the ethanol-water mixture to hydrogen with the total yield of ca. 74% at 773 K. The mechanism of this continuous process on Fe<sub>x</sub>O<sub>y</sub>/MoO<sub>3</sub> catalytic system is also proposed. The ethanol plays a role of reducing agent of MoO<sub>3</sub> because the latter is stable under hydrogen atmosphere up to 823 K. The reduced molybdenum can be re-oxidized by an electron transfer to iron oxides and then iron can be re-oxidized by water producing hydrogen. The water may origin from the used mixture as well as from the dehydration of ethanol. Small amount of oxygen strongly decreases the activity of the catalysts when high-concentrated ethanol is applied. In the presence of low-concentrated ethanol the oxygen does not affect the activity of the catalyst up to 723 K.

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## 1. Introduction

Currently, the hydrogen is mainly used in the chemical industry, but becomes more significant as fuel for power generation. Hydrogen fuel cells are highly efficient electrochemical systems converting the chemical energy into electricity. It is expected that the use of hydrogen in fuel cell vehicles and in stationary fuel cell as well as the demand for it will grow rapidly in near future.

The hydrogen is mostly extracted from natural gas, coal and liquid hydrocarbons but production using the catalytic steam reforming of ethanol (1) is being intensively investigated [1–9]. Steam reforming does not require oxygen, has lower operating temperature and therefore it is preferred in the industry [10]. However, a thermal decomposition of ethanol (2) has been also proposed [11].



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Moreover, the low cost of hydrogen's production is very important. From an economical point of view, steam reforming or thermal decomposition of bio-ethanol seems to be the optimal choice because of its low-toxicity, easy and low-cost production from renewable resources, and relatively high content of hydrogen. Due to the potential of both processes, (1) and (2), a wide range of the catalysts including solid oxides, transition and noble metals, and mixed metal-oxide systems have been studied recently [3–14]. Depending on the nature of the catalyst many reactions can occur simultaneously, other than those mentioned above: ethanol dehydrogenolysis, dehydration, dehydrogenation or acetone formation. Moreover, the reactions between the products originating from mentioned processes may be possible [6,8]. As was described previously [9,15], among the catalytic systems used for the production of hydrogen from ethanol, the redox cycle involving iron oxides and metallic iron has a high potential. In the first step, ethanol reduces iron oxide (e.g. Fe<sub>2</sub>O<sub>3</sub>) to a pure metal and in the second step the hydrogen is produced, as a result of iron oxidation by water. According to the best of our knowledge, the application of iron oxides in the continuous process of hydrogen generation from ethanol was not described so far.

On the other hand, the use of bio-ethanol is always connected with the presence of water and, in fact, the mixture of water and ethanol (high or low-concentrated) can be taken into account. Hence, primarily the steam reforming of ethanol should be considered. Our research is focused on the finding a catalyst active in the reaction, when low or high-concentrated ethanol is applied. In present paper the new catalysts obtained by thermal decomposition of iron dodecamolybdophosphates, composed of ultrafine nanoparticles of  $\text{Fe}_x\text{O}_y$  on  $\text{MoO}_3$ , were investigated. Their catalytic activity was tested in the continuous process of hydrogen generation from the mixtures containing various amounts of ethanol and water. The role of water content and the influence of oxygen on the hydrogen yield is considered. The mechanism of reaction carried out on  $\text{Fe}_x\text{O}_y/\text{MoO}_3$  catalytic systems is also proposed.

## 2. Experimental

### 2.1. Catalysts preparation

Iron dodecamolybdophosphates  $\text{FeHPMo}_{12}\text{O}_{40}$  and  $\text{FePMo}_{12}\text{O}_{40}$  were obtained by the addition of stoichiometric quantities of  $\text{FeCl}_2$  and  $\text{Fe}_2(\text{SO}_4)_3$ , respectively, to an aqueous solution of  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$  acid (Sigma-Aldrich, all reagents). The syntheses were carried out at ambient temperature without stirring and the resulting precipitates were dried in air at 363 K. The Keggin structure of prepared heteropolysalts was verified by FT-IR method (Supplementary material, Fig. S1), while the oxidation state of iron was determined by Mössbauer spectroscopy. Then, both heteropolysalts were annealed at 773 K in air atmosphere for 50 h. These decomposed materials (denoted as FeHMo-cal and FePMo-cal, respectively) have been characterized by number of techniques and afterwards used in the catalytic experiments.

### 2.2. Catalysts characterization

#### 2.2.1. FT-IR spectroscopy

The infrared spectra were registered with a Nicolet 380 FTIR spectrometer in the mid-infrared (MIR) region  $4000\text{--}400\text{ cm}^{-1}$ . The samples (1 mg) were mixed with 200 mg of spectroscopically pure KBr and pressed into disks before the spectra were recorded. Spectra were obtained by co-addition of 64 scans at a resolution of  $4\text{ cm}^{-1}$  and next were normalized to  $870\text{ cm}^{-1}$  band using the Thermo Scientific OMNIC<sup>TM</sup> software package.

#### 2.2.2. Mössbauer spectroscopy

The local properties of  $\text{FePMo}_{12}\text{O}_{40}$  and  $\text{FeHPMo}_{12}\text{O}_{40}$  precursors were investigated by means of Mössbauer spectroscopy employing the  $^{57}\text{Fe}$  gamma resonance transition. A Mössbauer system that consists of the Janis top loaded liquid helium cryostat (Janis Research Company, Wilmington, MA 01887, USA) integrated with a conventional constant-acceleration spectrometer (Science Engineering & Education Co., USA) of the Kankleit type in transmission geometry was used. During measurements, 100 mCi Mössbauer  $^{57}\text{Co}(\text{Rh})$   $\gamma$ -ray source and the absorbers were kept at room temperature. The absorbers were made of the fine powdered materials placed in a thin-walled ( $\sim 0.1$  mm) cylindrical plastic containers. The used absorber thicknesses of about  $40\text{ mg/cm}^2$  were calculated from the optimisation procedure [16]. The resonance of 14.4 keV gamma rays (for a given measurement and the energy scale calibration) was detected simultaneously by means of two independent LND Kr/ $\text{CO}_2$  proportional gas counters attached at opposite sides of the driving system. The drive velocity calibration was performed with a second  $^{57}\text{Co}(\text{Rh})$  source against a standard metallic iron foil at ambient temperature.

The Mössbauer spectra were analyzed numerically by fitting a hyperfine parameter distribution (HPD) using the Voigt-line-based

method of Rancourt and Ping [17]. In this method, the HPD for a given crystal site corresponding to similar structural, chemical and magnetic properties is constructed by a sum of Gaussian components for the quadrupole splitting (QS) distributions and, if necessary, the magnetic hyperfine field  $B_{\text{hf}}$  distributions. The isomer shift (IS) can be linearly coupled to the primary hyperfine parameters (QS,  $B_{\text{hf}}$ ).

#### 2.2.3. DSC/TG method

The DSC/TG measurements of  $\text{FeHPMo}_{12}\text{O}_{40}$  and  $\text{FePMo}_{12}\text{O}_{40}$  heteropolysalts were performed in the air flow using Netzsch STA 409 PC Luxx apparatus (Supplementary section, Fig. S2). The samples of about 40 mg were heated in air at the temperature range of 293–1000 K with the heating rate of 10 K/min.

#### 2.2.4. X-ray diffraction

The X-ray diffraction patterns for FeHMo-cal and FePMo-cal catalysts were recorded at ambient temperature within the range of  $2\theta = 5\text{--}90^\circ$ , step size  $0.02^\circ$  and 12 s/step using the Siemens D5005 diffractometer (CuK $\alpha$  radiation, 40 kV, 40 mA) equipped with the secondary beam graphite monochromator. Before measurements the catalysts were annealed at 363 K for 2 h to remove physically adsorbed water. The crystallite sizes of studied samples as well as the  $\text{MoO}_3$  and  $\text{Fe}_2\text{O}_3$  standards were calculated by 'Full-Pattern Decomposition' method, which was completed by TOPAS R2.1 software [18]. The fundamental parameters approach was also applied [19].

#### 2.2.5. $\text{H}_2$ TPR method

The reducibility profiles of FeHMo-cal and FePMo-cal catalysts were obtained using the quartz gas flow-through microreactor at the temperature range of 293–1100 K. A gas mixture of 5%  $\text{H}_2$  in Ar as a reducing agent was passed through the catalyst of ca. 0.025 g. Before the  $\text{H}_2$ TPR experiments both catalysts were kept in a stream of helium at 373 K for 1.5 h to remove physically adsorbed water. Subsequently, each catalyst was cooled down to ambient temperature and the  $\text{H}_2$ TPR measurement was performed with the heating rate of 10 K/min and the flow rate of reducing mixture of  $30\text{ cm}^3/\text{min}$ . The  $\text{H}_2$ TPR profiles of FeHMo-cal and FePMo-cal catalysts recorded using a TCD detector were compared with those obtained for spectrographically standardized  $\text{MoO}_3$  and  $\text{Fe}_2\text{O}_3$  (Johnson Matthey Chemicals Ltd., both).

#### 2.2.6. XPS spectroscopy

The X-ray Photoelectron Spectroscopy (XPS) measurements were carried out with a hemispherical analyzer (SES R4000, GammaData Scienta, pass energy 100 eV). The unmonochromatized AlK $\alpha$  X-ray source (1486.6 eV, 12 kV, 15 mA), with no charge neutralizer, was applied to generate core excitation. The system was calibrated according to ISO 15472:2001. The energy resolution of the system, measured as a full width at half maximum (FWHM) for Ag 3d $_{5/2}$  excitation line, was 0.9 eV. The powder samples were pressed into indium foil and mounted on a dedicated holder then UHV evacuated. During the measurements, the base pressure in the analysis chamber was about  $10^{-9}$  mbar. The area of the sample analysis was approximately  $3\text{ mm}^2$ . Because of insulating character of  $\text{FeHPMo}_{12}\text{O}_{40}$  and  $\text{FePMo}_{12}\text{O}_{40}$  salts, their binding energy (BE) values were charge-corrected to the carbon C 1s excitation set at 285.0 eV. The Shirley-type background subtraction was used to the spectra prior to fitting procedure where Voigt line shape i.e. Gaussian/Lorentzian functional (70:30) was applied. The Fe 2p core excitations were deconvoluted with relative intensity ratio of 2p $_{3/2}$  and 2p $_{1/2}$  lines fixed to 2:1.

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