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Mechanochemically assisted synthesis of $FeVO_4$ catalysts

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The influence of mechanochemical treatment on the solid state reactions between α-Fe_2O_3 and V_2O_5 was studied. A stoichiometric mixture of both oxides was subjected to an intense milling in air for different time intervals. The mechanochemical treatment for 15 h leads to a drastic decrease of the temperature of synthesis of $FeVO_4$ (from 1073 K to 773 K). The formation of $FeVO_4$ was monitored by X-ray diffraction (XRD), infrared spectroscopy (IR), Mössbauer spectroscopy and scanning electron microscopy (SEM). © *2004 Kluwer Academic Publishers*

1. Introduction

Vanadium oxide compounds are widely used in various catalytic processes [1]. Particularly ferric vanadate ($FeVO_4$) is outlined with its large spectrum of valuable properties. It proved to be a very stable and highly selective catalyst for partial oxidation of primary alcohols and hydrocarbons [2]. The $FeVO_4$ thin films prepared by sol-gel methods, their electrochromic properties and vibration spectra have been studied previously [3, 4]. The transition metal ortovanadates ($M^{3+}VO_4$, $M =$ Fe, Ce, In) have been extensively studied because of their potential for use as cathode materials in lithium rocking chair batteries [5–7]. A mechanical coactivation of V_2O_3 and Fe_2O_3 has been used to prepare a nanoscale vanadium spinel ferrite that has also a promising practical applications [8]. The classical solid state synthesis of the compound studied takes place at temperature close to 1073 K [9]. The high temperature of synthesis leads to aggregation and sintering of the reaction product. A mechanical treatment of the precursors has recently been used in manufacturing of catalysts with a view to their disintegration and activation [10]. Such treatment creates defects in the solids and enhances favorably their reactivity. In addition, a homogenization of the reaction mixture and better contact between the reacting particles are achieved. Another important advantage of the direct mechanochemical synthesis is the possibility to avoid the use of voluminous solutions and manipulations with various residues and effluents.

The aim of the present study was to obtain crystalline $FeVO_4$ by low temperature synthesis at temperatures characteristic for sol-gel synthesis method in order to prevent the sintering and aggregation of the product particles.

2. Experimental

A mixture of vanadium (V) oxide (V_2O_5) (Merck) and iron (III) oxide (Fe_2O_3) (Merck) in a molar ratio 1:1 was subjected to intense mechanical treatment. A planetary ball mill (Fritsch) with stainless (Cr-Ni) steel bowl (80 ml volume) and balls of the same materials (10 mm in diameter) was used for that purpose. After different times of mechanical activation, reagents were subjected to calcination at temperatures below the eutectic point (888 K). The synthesis has been carried out in air atmosphere. The reagent mixture, mechanical activated mixture and thermal treated samples were analyzed by X-ray diffraction (XRD) (Dron-3, diffractometer Co K_α radiation), infrared (IR) spectroscopy using KBr pellet technique (Nicolet-320, FTIR spectrometer), Mössbauer spectroscopy (constant acceleration spectrometer, ^{57}Co/Rh source and α-Fe as a reference sample were used) and scanning electron microscopy (SEM) (Jeol 357).

3. Results and discussion

Fig. 1 presents the XRD patterns of non-activated and activated mixtures calcined at 773 K for 15 h. On the diffraction pattern the non-activated sample (Fig. 1a), along with the peaks characteristic of Fe_2O_3 and V_2O_5, a new weak reflections appear which can be assigned to $FeVO_4$ [9, 11]. The formation of $FeVO_4$ starts under these conditions. Reflections of the $FeVO_4$ become dominant after mechanical treatment of the reagent mixture for 10 h (Fig. 1b). With increasing time of the mechanical activation (15 h) the XRD pattern contains all diffraction peaks of $FeVO_4$. Only an additional weak reflex of the Fe_2O_3 is observed (Fig. 1c).

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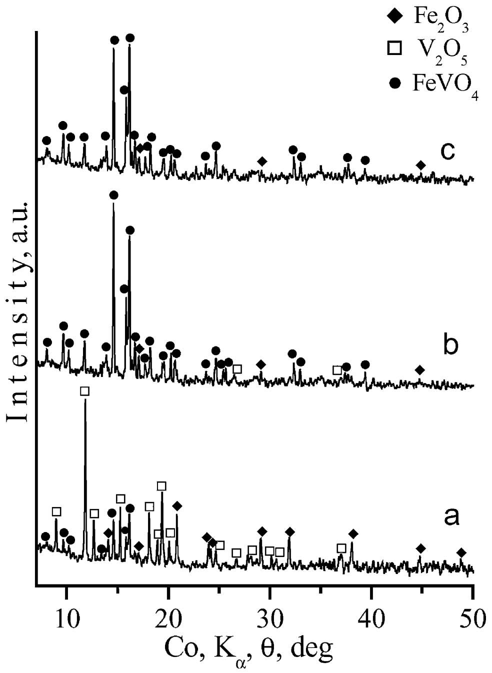

Figure 1 X-ray diffraction patterns of samples heated at 773 K for 15 h: (a) the non-activated mixture of V_2O_5 and Fe_2O_3, (b) the mixture mechanically activated for 10 h, and (c) the mixture mechanically activated for 15 h.

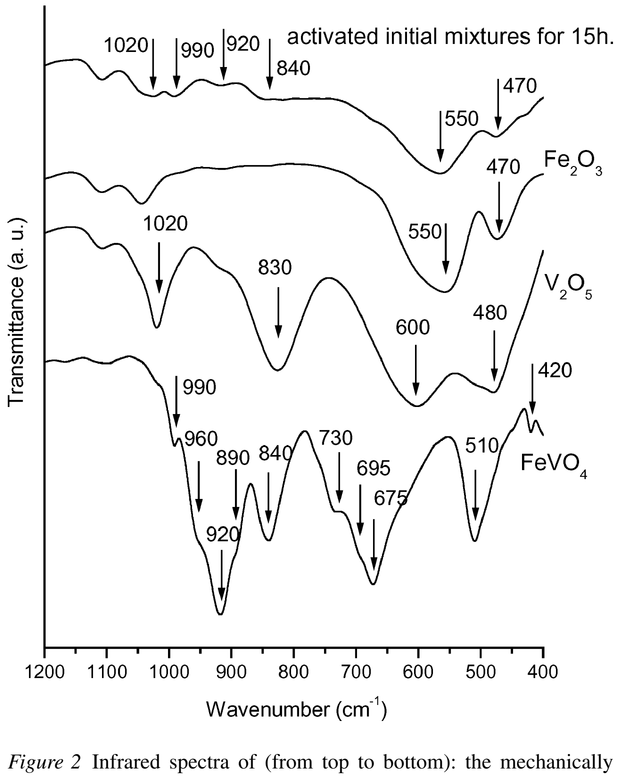

Figure 2 Infrared spectra of (from top to bottom): the mechanically activated mixture of V_2O_5 and Fe_2O_3; Fe_2O_3; V_2O_5; the synthesized $FeVO_4$.

The infrared spectra of the initial oxides (V_2O_5, Fe_2O_3), mechanically activated mixtures and of synthesized $FeVO_4$ are shown in Fig. 2. In the infrared spectrum of activated mixture (Fig. 2, top), the intensity of absorption band at 1020 cm^{-1} corresponding to stretching vibration of double vanadyl bonds $\nu(V=O)$ in V_2O_5 decreases. New bands appear at 990 and 920 cm^{-1}, which could be assigned, according to previously obtained data of the same amorphous sample [12, 13] to the elongation of some vanadyl bonds and to the change in coordination number of V from 5 to 4. This is a result of incorporation of ferric ions into the vanadate network. These spectroscopic data indicate that structural transformations in the initial mixture of solid reagents occur during mechanical activation. The IR spectrum of crystalline $FeVO_4$ phase obtained by mechanically assisted synthesis (Fig. 2, bottom) shows absorption bands typical for $FeVO_4$ compound [14].

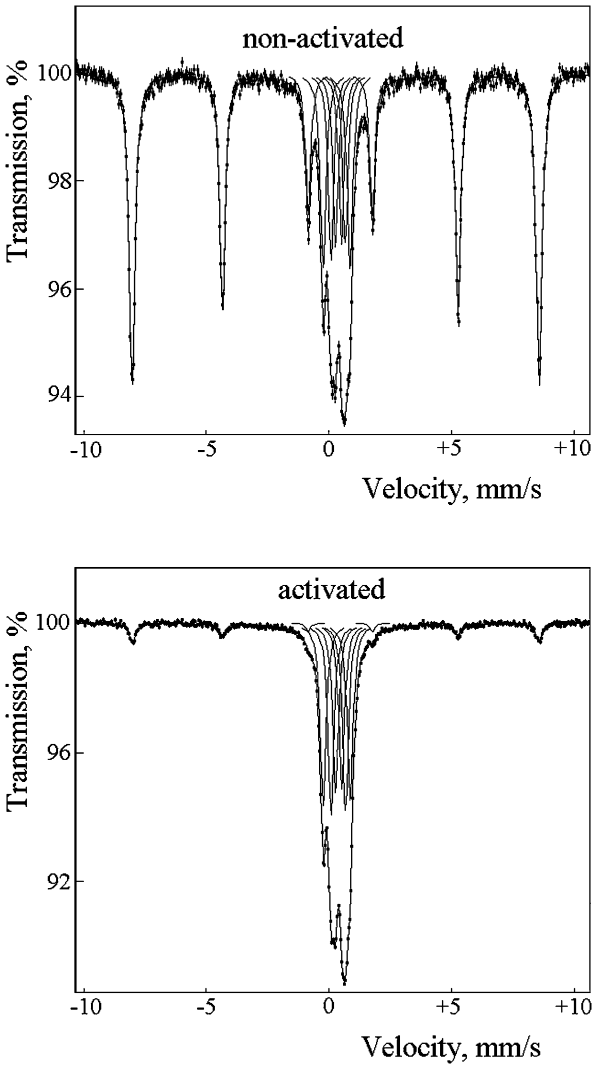

Figure 3 The room-temperature ^{57}Fe Mössbauer spectra of samples heated at 773 K for 15 h: (top) the non-activated mixture of V_2O_5 and Fe_2O_3; (bottom) the mixture of V_2O_5 and Fe_2O_3 mechanically activated for 15 h.

The Mössbauer spectroscopy was used to provide information on the complete evolution of the synthesis reaction product. The room-temperature ^{57}Fe Mössbauer transmission spectra of both non-activated and mechanically activated (15 h) mixtures heated at 773 K for 15 h are plotted in Fig. 3. The spectra involve a magnetic phase, represented by Zeeman hyperfine sextet, and a broadened central paramagnetic phase. The sextet is due to the magnetic hyperfine splitting of a hematite (α-Fe_2O_3). The observed values for the isomer shift (IS = 0.37 mm/s), the quadrupole splitting (QS = −0.19 mm/s) and the hyperfine magnetic field (Bhf = 51.7 T) of the sextet are completely identical

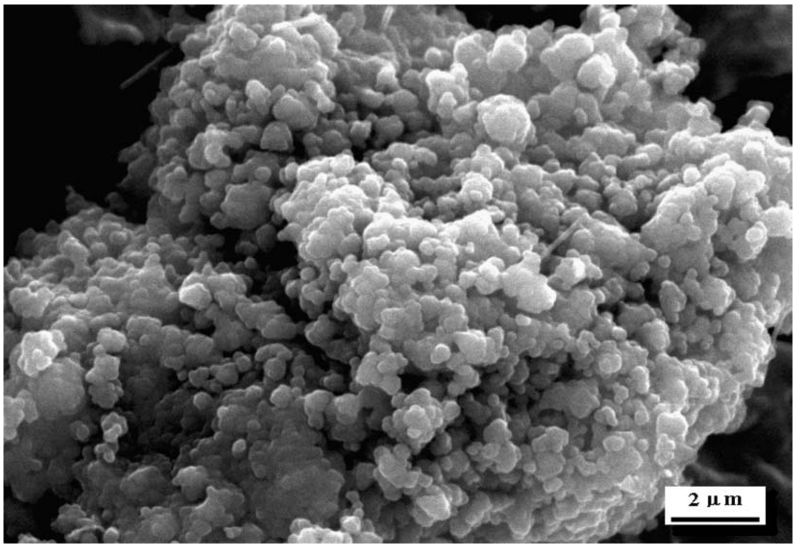

Figure 4 Scanning electron micrograph of the synthesized $FeVO_4$.

with the parameters of the initial reagent α-Fe_2O_3. The central part of the spectra exhibits a specific characteristic overall shape and is fitted to three Lorentzian quadrupole—split doublets (six lines) assuming three different iron site populations. The value of the parameters of the doublets as estimated from the spectra are: IS = 0.395; 0.378; 0.317 mm/s and QS = 0.246; 0.587; 1.099 mm/s, respectively. These values are typical of the $FeVO_4$ compound [2, 9] and the paramagnetic phase is identified as $FeVO_4$. The relative content of α-Fe_2O_3 and of $FeVO_4$ in the samples is calculated directly from the absorption area of the hematite (α-Fe_2O_3) sextet and the $FeVO_4$ doublets, assuming the same recoil-free fraction. The α-Fe_2O_3 phase fraction considerably decreases: from 56.71% for the non-activated sample to 7.38% for the activated samples.

SEM image of the $FeVO_4$ synthesized at 773 K reveals particles with mean size of 400 nm (Fig. 4). The product obtained in this way has improved uniformity of the particles and a high dispersion.

4. Conclusions

This study demonstrates a favorable effect of the mechanochemical treatment on the synthesis of $FeVO_4$. It is shown that mechanochemical treatment of the initial mixture for 15 h leads to a drastic decrease of the synthesis temperature of $FeVO_4$ from 1073 to 773 K.

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