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Mechanochemical synthesis of double vanadate in Cu–Fe–V–O system and its physicochemical and catalytic properties

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ABSTRACT

Mechanochemical synthesis has been successfully employed to prepare a $Cu_3Fe_4(VO_4)_6$ powder. The formation of designed compound (in α-polymorphic form) is due to the reactions of copper, iron and vanadium oxide precursors which were activated by high-energy ball milling (*Activator* 2S, Novosibirsk, Russia) for 8 h instead of heat energy required in the conventional multi-stage high-temperature process during 80 h forming β-polymorphic form.

Catalytic properties of $Cu_3Fe_4(VO_4)_6$ compound, which has been prepared by two different mentioned above techniques, tested in the methanol steam reforming reaction are satisfactory and closely the same. However, α-, as well as, β-polymorphic forms of $Cu_3Fe_4(VO_4)_6$ are structural unstable during steam reforming of methanol and form a metallic copper beside V_2O_3 and iron oxides, which probably catalyze simultaneously undesired methanation reaction. The real chemical mechanism is still not clear.

1. Introduction

The main task of our wide research is the creation of new functional materials, which can be used for environmental protection, (e.g. processing of catalyst by mechanical treatment as a method of *green* chemistry). Earlier investigations showed that mechanochemical synthesis of solids by high-energy ball milling can be used to preparing new compounds and this is an alternative method to the conventional high-temperature and ecological hazardous syntheses [1–13].

Recently, special attention is focused on the catalysts' finding for low-temperature conversion of hydrocarbons to hydrogen [14–23]. Hydrogen can be produced from methanol by various processes. The simplest one is its decomposition to CO and H_2 according to reaction (1):

$$CH_3OH_{(g)} = CO_{(g)} + 2H_2 \quad \Delta H^{\ominus}_{298} = +90.6\,\text{kJ mol}^{-1} \tag{1}$$

The formed CO is converted to CO_2 in the water gas shift reaction (reaction 2):

$$CO + H_2O_{(g)} = CO_{2(g)} + H_{2(g)} \quad \Delta H^{\ominus}_{298} = -41.1\,\text{kJ mol}^{-1} \tag{2}$$

However, these two reactions can be performed in one step in the process of catalytic steam reforming of methanol (SRM) (reaction 3):

$$CH_3OH_{(g)} + H_2O_{(g)} \xrightarrow{\text{catalyst}} CO_{2(g)} + 3H_{2(g)} \quad \Delta H^{\ominus}_{298} = +49.5\,\text{kJ mol}^{-1} \tag{3}$$

The known catalysts for SRM are based mostly on copper dispersed in a carrier consisted of pure or mixed oxides e.g. ZnO, Al_2O_3 and Zn–Al_2O_3, Cr_2O_3–Al_2O_3 or ZrO_2–Al_2O_3. They show high activity and high selectivity in low temperature range of 230–300 °C, although they are not stable enough in the process [24–29].

The aim of presented study is the comparison the catalytic properties of $Cu_3Fe_4(VO_4)_6$, as a precursor of Cu-based catalyst in SRM process synthesized by two different ways, i.e. mechanochemically and in high-temperature processing.

2. Experimental

2.1. The synthesis of $Cu_3Fe_4(VO_4)_6$ by mechanochemical activation (MA)

Sample was synthesized by mechanochemical treatment of CuO (p.a., Fluka), Fe_2O_3 (pure, POCh) and V_2O_5 (p.a., POCh) mixture in molar ratio of 3:2:3, respectively. Milling was carried out in a planetary ball mill (*Activator* 2S, Novosibirsk, Russia) using vial and balls made of Cr–Ni steel. The milling conditions were as follows: 1200 rpm, BPR = 20:1, milling time up to 8 h, air atmosphere.

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2.2. The synthesis of $Cu_3Fe_4(VO_4)_6$ by high-temperature treatment (HT)

The method of synthesis double vanadates is described by Kurzawa et al. [30,31]. The following reactants were used for this synthesis: CuO (p.a., Fluka), Fe_2O_3 (p.a., POCh), V_2O_5 (p.a., Riedel-de Haën). A mixture of the composition: 37.5 mol% CuO, 37.5 mol% V_2O_5 and 25 mol% Fe_2O_3 corresponding to the formula $Cu_3Fe_4(VO_4)_6$ was homogenized by grinding and heated in air for following stages: 565 °C (20 h) + 590 °C (20 h) + 610 °C (20 h) + 625 °C (20 h) until the monophase sample was synthesized according to reaction (4).

$$3CuO_{(s)} + 2Fe_2O_3 + 3V_2O_{5(s)} = Cu_3Fe_4(VO_4)_{6(s)} \quad (4)$$

After each heating stage the sample was cooled down in furnace to room temperature, ground and analyzed by XRD method.

2.3. Methods of catalyst characterization

Powder X-ray diffraction patterns were recorded on a Philips X'Pert diffractometer (CuKα) in the 2Θ range of 10–90°. The samples morphology was observed on SEM images (JEOL JSM 5500 LV). The EDX elemental analyses were carried out on microanalyzer EDX Oxford Instrument equipped with Si(Li) detector at an electron beam voltage of 20 keV.

Specific surface area were estimated by BET method, and pore volume and pore size were performed using BJH method (N_2 adsorption/desorption isotherms at 77 K) using Micromeritics ASAP 2020 V3.04 H apparatus, after sample out-gassing at 250 °C for 4 h.

2.4. Catalytic tests – steam reforming of methanol (SRM)

Catalytic tests were performed in a pulse microreactor connected on-line with the chromatograph SRI 8610C equipped with TCD and FID detectors. Porapak Q and molecular sieves columns were used. Argon as a carrier gas (30 ml min^{-1}), catalyst in amount of 0.1 g (fractions from 0.2 to 0.3 mm), injection of 0.6 μl of CH_3OH–H_2O (1:1) was used. All catalyst samples were stabilized at 300 °C for 1 h. The catalytic reaction temperature was kept 450 °C.

3. Results and discussion

3.1. Characterization of synthesized products used in SRM reaction

Fig. 1a and b illustrate the XRD patterns of synthesized $Cu_3Fe_4(VO_4)_6$ using mechanochemical (MA) and high-temperature (HT) methods, respectively. It is clearly seen that there are two different forms of compound. The product of mechanochemical activation corresponds to the α-form of $Cu_3Fe_4(VO_4)_6$, which is known as a lyonsite (PDF card 84-1393). It crystallizing in the orthorhombic system and belongs to the *Pmcn* space group with parameters of its unit cell as $a = 10.296$ Å, $b = 17.207$ Å, $c = 4.910$ Å, $Z = 2$. This vanadate has been discovered in the summit crater fumaroles of Izalco volcano, El Salvador [32]. α-$Cu_3Fe_4(VO_4)_6$ form exists in nature; until now it has not been obtained under laboratory conditions nor has any information pertaining to the temperature of the polymorphous conversion been established. High-temperature treatment gave β-$Cu_3Fe_4(VO_4)_6$ (PDF card 80-0220). This form crystallizes in the triclinic system, the $P-1$ space group, where the unit cell parameters are: $a = 6.600$ Å, $b = 8.048$ Å, $c = 9.759$ Å, $\alpha = 106.08°$, $\beta = 103.72°$, $\gamma = 102.28°$, $Z = 1$ [33,34].

The additional confirmation of $Cu_3Fe_4(VO_4)_6$ formed during high-energy ball milling is the SEM photomicrograph in Fig. 2 with

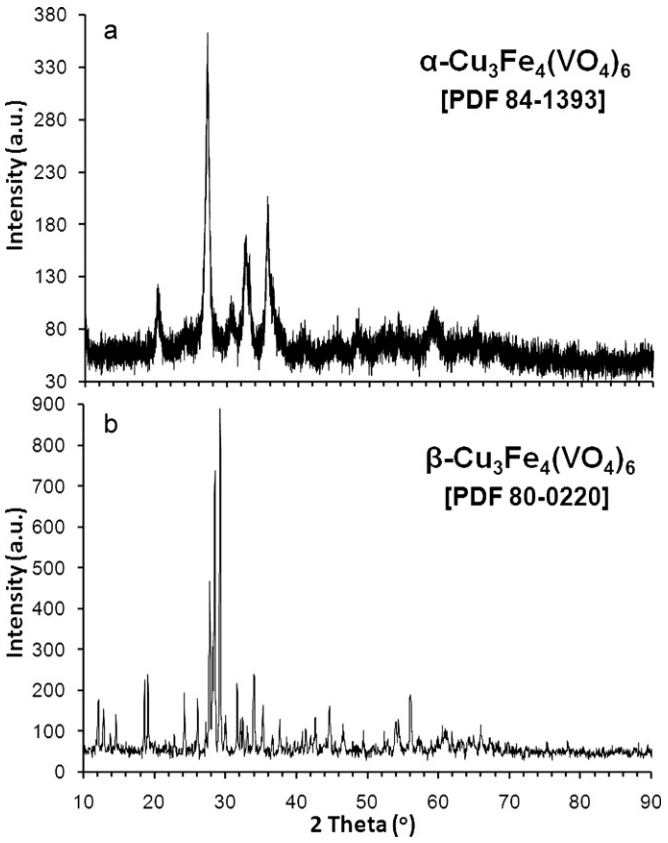

Fig. 1. XRD patterns: (a) α-$Cu_3Fe_4(VO_4)_6$ (lyonsite structure) and (b) β-$Cu_3Fe_4(VO_4)_6$ (howardevansite structure).

elemental analysis by X-ray EDS results given in Table 1. The average elemental ratio of some points corresponds to Cu:Fe:V = 3:4:6, according to $Cu_3Fe_4(VO_4)_6$ formula.

BET surface area and pore characterization of α- and β-forms of $Cu_3Fe_4(VO_4)_6$ are shown in Table 2. In both samples, the BET values are not high.

3.2. Catalytic activities of α- and β-$Cu_3Fe_4(VO_4)_6$ in SRM process

According to reaction (3), molar composition of main products, H_2 and CO_2, as well as by-products, CO and CH_4, and unreacted

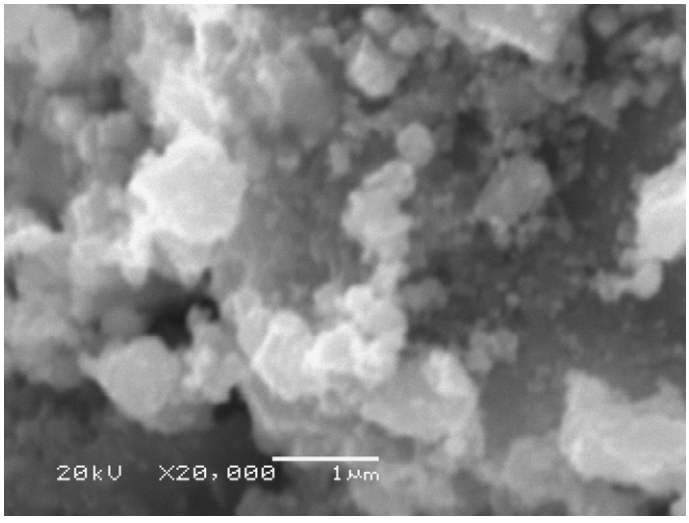

Fig. 2. SEM image of α-$Cu_3Fe_4(VO_4)_6$.

Table 1
Elemental analysis of $Cu_3Fe_4(VO_4)_6$ prepared by MA.

Element	Weight (%)	Atomic (%)
O	40.75	70.42
V	25.25	13.70
Fe	18.09	8.95
Cu	15.91	6.93

Table 2
BET surface area, pore volume and pore size of $Cu_3Fe_4(VO_4)_6$ samples.

Sample	S_{BET} ($m^2\ g^{-1}$)	V_{BJH} ($cm^3\ g^{-1}$)	S_{BJH} (Å)
α-Form	8.4	0.027	137.6
β-Form	2.2	0.005	142.4

methanol were registered as a function of injection numbers of reactant mixture shown in Fig. 3a and b for α- and β-$Cu_3Fe_4(VO_4)_6$, respectively. The total conversion of methanol together with molar ratio of H_2/CO_2 using the above mentioned samples is shown in Fig. 4. Catalytic behavior of α- and β-form is similar. The conversion degrees of CH_3OH are close to 100%, however, the selectivity to CO_2 (as a H_2/CO_2) is lower (<3) than could be expected. The course of hydrogen yield (Fig. 3) indicates on two different stages. At the beginning (up to 10 injections) H_2 increases rapidly and then slightly decreases. It can be stated that Cu^0 is formed by CuO reduction with first portions of hydrogen (reaction 4). Further, metallic copper on oxides carrier catalyzes, the main SRM process.

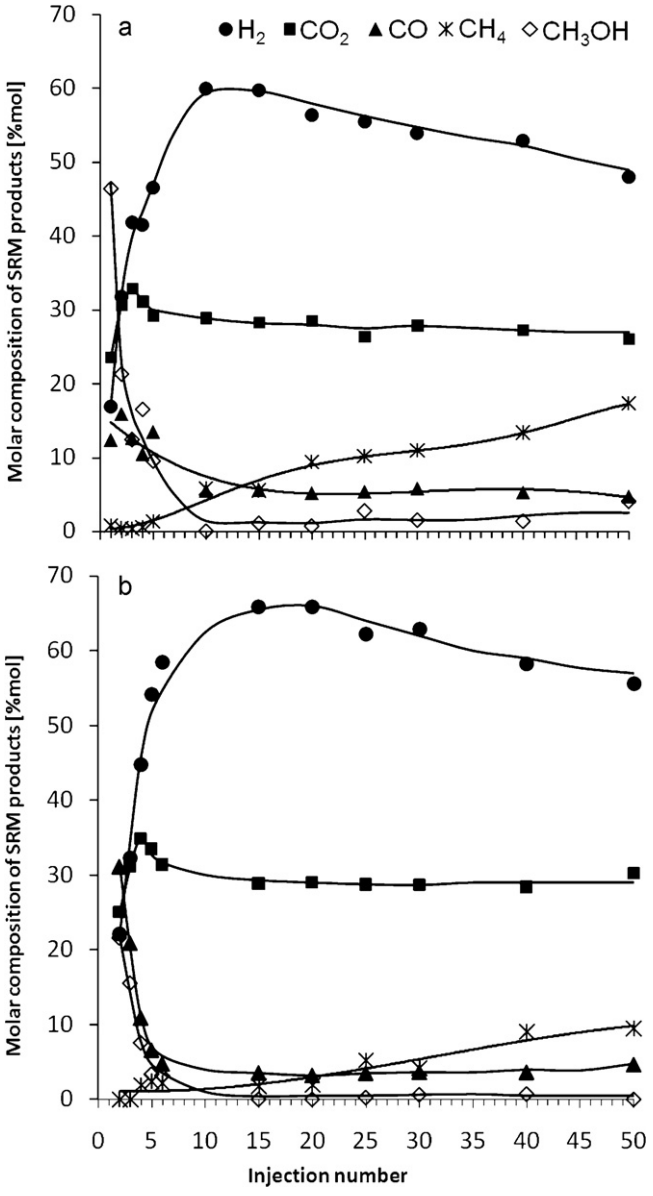

Fig. 3. Molar composition of SRM reaction products tested on samples: (a) α-$Cu_3Fe_4(VO_4)_6$ and (b) β-$Cu_3Fe_4(VO_4)_6$.

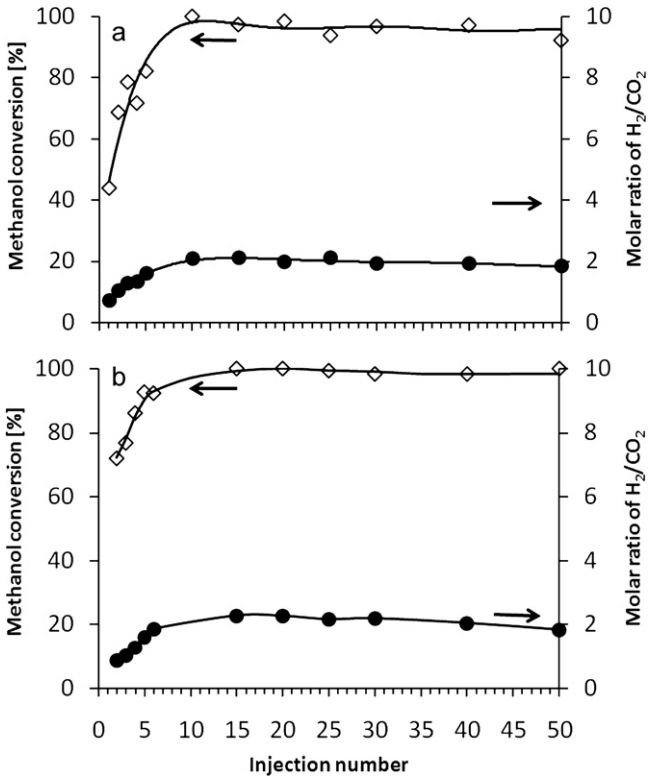

Fig. 4. Total methanol conversion and molar ratio of H_2/CO_2 during SRM reaction on samples: (a) α-$Cu_3Fe_4(VO_4)_6$ and (b) β-$Cu_3Fe_4(VO_4)_6$.

One can be noted that methane appears along with H_2 decreasing in the system. This may be caused by iron oxides presence, which catalyze the methanation reaction according to reaction (5) [35].

$$CO_{(g)} + 3H_{2(g)} \xrightarrow{Fe_xO_y} CH_{4(g)} + H_2O_{(g)} \quad (5)$$

3.3. Characterization of catalysts after SRM reaction

Fig. 5 shows the XRD spectra for catalyst samples after catalytic tests. The decomposition of α- and β-$Cu_3Fe_4(VO_4)_6$ structures, as well as, the forming the metallic copper, V_2O_3 and Fe_3O_4 are evident (compare also: Fig. 1a and b). Exemplary, the results EDS analysis shown in Table 3 confirm the composition of sample after catalytic test. The atomic ratio of Cu:Fe:V = 4.6: 4.0: 6.0 indicates the excess of Cu^0 in the sample after catalytic process.

Table 3
Elemental analysis of MA sample after SRM process.

Element	Weight (%)	Atomic (%)
O	19.20	45.51
V	29.73	22.14
Fe	22.83	15.50
Cu	28.24	16.85

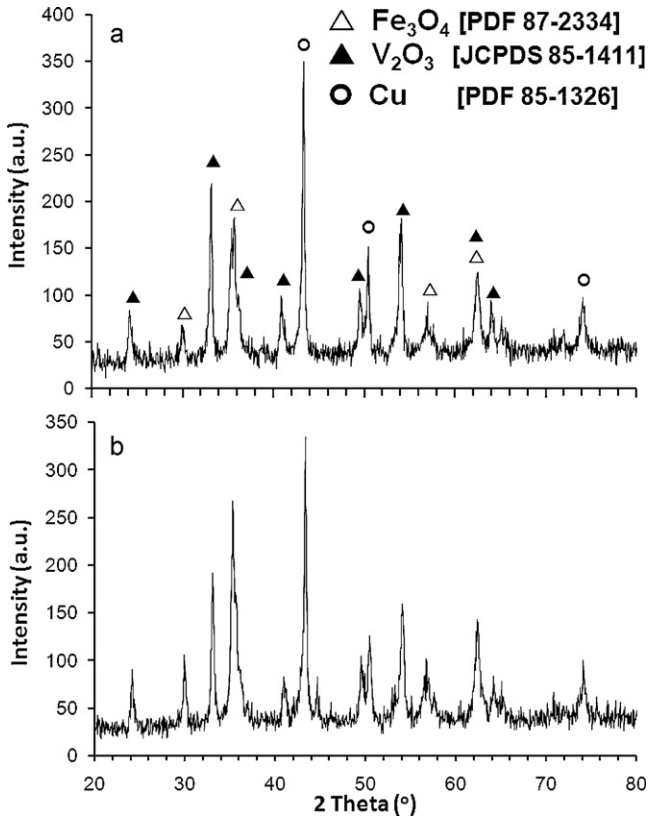

Fig. 5. XRD patterns of samples after SRM processes: (a) α-$Cu_3Fe_4(VO_4)_6$ and (b) β-$Cu_3Fe_4(VO_4)_6$.

4. Final remarks

Mechanochemical synthesis *in situ* in Cu–Fe–V–O system brings about the formation of $Cu_3Fe_4(VO_4)_6$ compound. This vanadate is α-polymorphic form that was not prepared until now by laboratory way. Both forms of $Cu_3Fe_4(VO_4)_6$ compound exhibit catalytic activity in steam reforming of methanol, although their stability during the process is not satisfactory providing to formation of by-products (CH_4, CO). The reason of it is probably an "aggressive" medium (steam), not a SRM temperature (450 °C).

The results demonstrate the case, when the values of the specific surface area do not influence on the catalytic properties, but formed active centers.

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