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Parallel migration of potassium and oxygen ions in hexagonal tungsten bronze – Bulk diffusion, surface segregation and desorption

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ABSTRACT

The hexagonal potassium tungsten bronzes ($K_{0.3}WO_3$) were synthesized via solid state reaction method. The materials were characterized in terms of their chemical composition (XRF), structure (XRD, RS) and morphology (SEM). The migration of oxygen and potassium in the synthesized materials were investigated by means of ionic conductivity (bulk diffusion), work function and soot oxidation (surface segregation) and potassium thermal desorption studies. The energetic barrier for potassium bulk diffusion (1.2 eV) and desorption (4.4 eV), as well as the corresponding characteristic temperature of their onsets ~450 °C and ~500 °C were determined. The results are discussed in terms of a simple proposed model of potassium and oxygen migration in $K_{0.3}WO_3$ coupled with changes of the tungsten oxidation state. It was revealed that the structure of potassium tungsten bronze is preserved in an inert atmosphere in a wide temperature range of 400–700 °C, regardless the migration processes. This specific feature of the $K_{0.3}WO_3$ phase predisposes its possible application as an alkali reservoir in composite catalysts for processes where the coking appears.

1. Introduction

Majority of transition metal oxides are environmentally friendly, relatively cheap and exhibit valuable properties for various applications. One of the most common ways of improving their performance is doping with alkali due to their properties (high mobility, high reactivity, low ionization potential). Alkali cations are usually located on the surface of the transition metal oxide influencing its electrodonor properties [1–3] or interacting with substrates, but they can also be incorporated into the structure of the material [4–7]. If the process leads to forming tunnels or layers (nanostructurisation) such material exhibit very high alkali ions mobility: diffusion, segregation, and desorption [6]. Overall it can result in the storage and release of alkali in and from the transition metal oxide matrix.

Tungsten bronzes and other WO_3 – based materials are being intensively studied in the field of infrared shielding, gas sensing, electrocatalysis and heterogeneous catalysis [8–17]. Bronzes are non-stoichiometric compounds with the general formula of A_xWO_3, where A stands for alkali cation which is located inside the tunnels formed with WO_6 octahedral units. Structure and properties of bronze differ depending both on the size and the amount (the x value) of an alkali cation. For the material investigated in the paper, potassium tungsten bronze (K_xWO_3) with $x \le 0.33$, the symmetry is hexagonal and potassium cations are located in the tunnels formed of six octahedral WO_6 units. If the amount of potassium is larger, the tetragonal structure with three - four - and five-membered tunnels is being formed. Potassium tungsten bronzes have been intensively investigated mostly in terms of their optical and electrical conductivity properties, but these materials are also considered as a potential catalyst support or even as an active phase [14–17].

Alkali-containing materials are often used as a decoking agent [18–20]. Coking of catalysts is a relevant and actual issue in many carbohydrate processing technologies (for example steam reforming [16,21–23], dehydrogenation [24,25]). The process involves formation of carbon deposits on the surface of catalysts resulting in blocking active sites. In consequence, it leads to a significant lowering of the catalytic activity and enforces replacing or regenerating of the catalytic bed. One of the most effective ways of preventing carbon deposit to form is to add a certain amount of an alkali into the system, as it is proven to possess the anti-coking properties. However, high temperature required for most of the processes (>500 °C) results in alkali migration (diffusion inside the bulk, agglomeration on the surface and thermal desorption) leading to lowering the promotional effect. To solve this problem, some composite catalysts has been proposed [16,26] where one of the components plays a role of an alkali reservoir. Due to the high alkali mobility and thermal stability tungsten bronzes can work as an alkali source and storage

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what could be especially efficient in systems where carbon deposit is being formed.

The aim of this work is to investigate the potassium and oxygen migration processes

in hexagonal tungsten bronze at the temperature range characteristic for the coking process (400–700 °C) with a focus on diffusion of ions inside the oxide lattice, segregation on the surface and thermal desorption.

2. Experimental

2.1. Materials

Potassium tungstate (K_2WO_4) has been prepared via ceramic method by grinding K_2CO_3 (POCh), WO_3 (Dor-chem) and KNO_3 (Merck) (23 mmol, 46 mmol, and 46 mmol respectively) in a mortar and calcining at 550 °C for 2 h. Potassium tungsten bronzes were synthesized by the following reaction:

$$\frac{x}{2}K_2WO_4+\frac{3-2x}{3}WO_3+\frac{x}{6}W\overset{950^{\circ}C}{\rightarrow}K_xWO_3$$

Stoichiometric amounts of K_2WO_4, $WO_{3,}$ and W (Aldrich) were grinded for 30 min, pelletized under the pressure of 8 MPa, and thermally treated at 500 °C for 2 h in Ar flow. Afterwards substrates were grinded and pelletized under similar conditions again. Then the pellet was heated up to 950°°C for 4 h in the quartz tube that was constantly purged with Ar in order to keep inert reaction atmosphere. After the synthesis the samples were washed with water to remove the residual potassium from the surface and dried at 120 °C for 4 h.

As a reference material, tungsten(VI) oxide sample with potassium deposited on the surface was prepared by wet impregnation of WO_3 with K_2CO_3 solution followed by calcination in 400 °C for 4 h in air.

2.2. Methods

The XRD patterns were recorded by a Rigaku MiniFlex powder diffractometer with Cu Kα radiation at 10 mA and 10 kV, 2θ step scans of 0.02° and a counting time of 2 s per step.

The elemental analysis was performed with an Energy-Dispersive XRF spectrometer (Thermo Scientific, ARL QUANT'X). The X-rays of 4–50 kV (1 kV step) with the beam size of 1 mm were generated with the Rh anode. The detector used was a 3.5 mm Si(Li) drifted crystal with a Peltier cooling (~185 K). For quantitative analysis, the calibration with a series of metallic standards and an UniQuant software were used.

The morphology of the samples was examined with a HITACHI S-4700 scanning electron microscope (SEM) at magnifications of ×2000.

The TG/DTA experiments were conducted by placing the samples of typical mass of 40–70 mg in an alumina crucible and heated in the gas flow (air 40 ml/min + purge Ar 20 ml/min or 40 ml/min Ar) at temperature increase 10 °C/min in the range from room temperature to 820 °C.

The temperature programmed oxidation of soot method (TPO) was used to determine the temperature of the process of oxygen migration to the surface. A quartz fixed-bed reactor was heated (10 °C/min) from room temperature to 900 °C in He (60 ml/min). The reaction mixture, weighing 50 mg, was prepared by grinding a bronze sample with soot (Degussa—Printex80) in an 8:1 ratio. The mixture was ground for 10 min in the *tight contact* regime in an agate mortar. The soot combustion was monitored by a quadrupole mass spectrometer (SRS RGA200) following the line for $m/z = 44$ (CO_2).

Ionic conductivity measurements were performed by means of a standard four-probe method using a Metex Digital Multimeters MXD 4660-A and TeleVox control and acquisition system. Before the experiments the samples were calcined at 1100 °C for 1 h in Ar with the heating rate of 10 °C/min and pelletized under 6 MPa. Conductivity was measured at a frequency of 33 kHz every 50 °C in the 200–700 °C range.

Potassium thermal desorption was investigated by measuring the potassium atom flux from sample pellet (200 mg, 13 mm diameter) heated in the vacuum chamber ($p \approx 10^{-6}$ mbar). Due to the low ionization potential of potassium ($I = 4.3$ eV) from solid surfaces potassium is thermally emitted in the form of atoms and ions. The samples were biased with a positive potential of +5 V to prevent the thermal emission of electrons. During the measurements the samples were heated rapidly up to 300 °C and then up to ~520 °C in the stepwise mode at the rate of ~0.5 °C/min, waiting after a temperature ramp for the steady-state signal. For each temperature the resultant positive current was averaged over four independent data points and measure with the use of Keithley 6512 digital electrometer.

Work function (contact potential difference), measurements were performed with a Kelvin Probe (McAllister KP6500). For each measurement, the 150 mg of the sample was pelletized (d = 10 mm) under the 8 MPa pressure. The measurements were performed in a vacuum of 10^{-7} mbar at 150 °C after annealing the sample at 400 °C in order to standardize the surface. The stainless steel electrode (d = 3 mm, ϕ = 4.1 eV) was used as a reference.

3. Results and discussion

3.1. Characterization

After the synthesis, the samples were evaluated in terms of elemental composition and phase homogeneity. The X-ray fluorescence spectroscopy measurements were performed in order to evaluate the potassium amount in the synthesized samples. The $K_{0.3}WO_3$ stoichiometry was confirmed. The typical XRD patterns and Raman spectra for tungsten(VI) oxide substrate and obtained potassium tungsten bronze are presented on Fig. 1. The diffractograms were indexed in $P2_1/n$ (ICSD entry 80056, [27]) and $P6_3/mcm$ (ICSD entry 100484, [28])

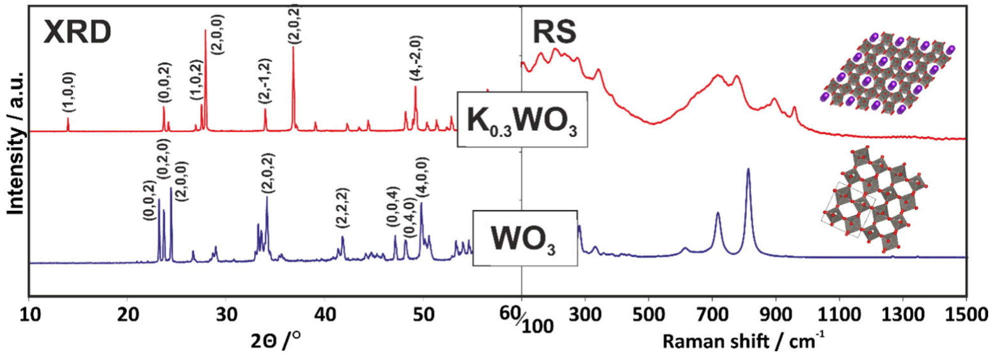

Fig. 1. XRD patterns and Raman spectra obtained for tungsten(VI) oxide and potassium tungsten bronze.