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Mechanochemical synthesis, characterization and catalytic activity of Bi₂WO₆ nanoparticles in CO, n-hexane and methane oxidation reactions

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ABSTRACT

This article represents data on the mechanochemical synthesis, characterization and catalytic properties of Bi_2WO_6 nanoparticles. The synthesis of Bi_2WO_6 nanopowder (10 nm) started after 90 min of milling time interval and it was completely finished after 4 h when using 2.5 g batch of the initial oxides. Longer milling time intervals (8 h) were needed to synthesize the target nanophase (4 nm), when using a 4.0 g batch of precursor oxides. The Bi_2WO_6 powders manifest low absorbance ability in the visible range with a band gap ranging from 2.85 to 2.88 eV. The catalytic activity was investigated in the reactions of CO, n-hexane and methane oxidation, respectively. The oxidation of CO on Bi_2WO_6 proceeds at temperatures higher than 200 °C, while the complete oxidation of n-hexane was found to occur at temperatures higher than 250 °C. A remarkable increase in the catalytic activity was achieved in the case of Bi_2WO_6 supported with 0.14 wt.% Pd. The promotional effect of B ion the catalytic activity of the Pd loaded sample could be explained by the formation of alloy or inter-metallic phases (α -Bi_2Pd and β -BiPd), which is considered as perspective for the development of a catalyst for treatment of methane emissions.

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1. Introduction

Bi₂WO₆ belongs to the Aurivillius family with a general formula $A_{n-1}B_nO_{3n+3}$ (where A = Ca, Sr, Ba, Pb, Na, K; B = Ti, Nb, Ta, Mo, W, Fe), which possess layered structure [1]. This compound exists in three polymorphous forms. At room temperature the Bi₂WO₆ has orthorhombic structure with space group *Pca2*₁, which consists of alternating Bi₂O₂ layers and perovskite-like WO₄ layers, containing corner-linked WO₆ ochatedra [1–6]. This phase was transformed into the same symmetry with space group B2cb at 660 °C. This structural change involves the loss WO₆ tilt mode of perovsike-like WO₄ layer of the structure [5,6]. Above 940–960 °C this phase undergoes phase transition into a high-temperature form having monoclinic symmetry with space group A2/m [3-7]. The orthorhombic Bi₂WO₆ founds application mainly in different fields of catalysis: as photocatalyst for water splitting [8], degradation of organic compounds under visible light irradiation [9-24] and in the CO oxidation reaction [26,27]. Moreover Bi₂WO₆ possesses some piezoelectric, ferroelectric, luminescence and phonon properties [28-32]. Different methods for the synthesis of Bi₂WO₆ have been reported in the current literature: solid state reaction [3,9,26,27], hydrothermal method [10–19], sol-gel method [20,21], solvothermal synthesis [22,23], ultrasound-assisted synthesis [24], low-temperature combustion method [25] and mechanochemical treatment [28-30]. A. Castro et al. [28] used mechanochemical activation for the synthesis of $Bi_2Mo_{1-x}W_xO_6$ solid solution with ferroelectric properties. Maczka et al., applied this method to the synthesis of Bi_2WO_6 and $Eu^{3+}-Bi_2WO_6$ powders [29,30]. The authors showed that these powders possess good photonic and luminescence properties. The mechanochemical technique possesses some advantages to produce nanocrystalline materials with a wide range of properties [33-38]. There are many parameters, which influence the synthesis results such as: milling speed and time, ball to powder mass ratio and the nature of precursors. Changes in the milling parameters appear to be a decisive factor for the preparation and the properties of the final product. Our group performs investigations on mechanochemical synthesis of different inorganic materials using pure oxides as precursors [39–42]. This work is a continuation of the efforts in this direction and accumulation of additional knowledge about the mechanochemical synthesis of Bi₂WO₆.

On other hand the thermal stability of Bi₂WO₆ could be an advantage for other applications in catalytic reactions, especially







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Fig. 1. (A) X-ray diffraction patterns of the sample **A** (2,5 g batch) mechanochemically activated at: (a) 0 min; (b) 30 min; (c) 60 min; (d) 90 min; (e) 2 h; and (f) 4 h. (B) X-ray diffraction patterns of the sample **B** (4 g batch) mechanochemically activated at: (a) 0 min; (b) 2 h; (c) 4 h; (d) 6 h; and (e) 8 h.

when the practice requires the possibility for stable operation at high temperatures (above 500 °C), for example in catalytic combustion of volatile organic compounds (VOCs), including methane. Therefore it is of interest to investigate the catalytic properties of Bi_2WO_6 in complete catalytic oxidation of CO and n-hexane as a first step in the development of catalytic system, capable of resisting the negative changes due to thermal sintering effects.

The aim of the present work was to study the mechanochemical synthesis of Bi_2WO_6 from pure oxides at constant milling speed varying the amount of the precursors and also to test its catalytic activity in CO, n-hexane and methane oxidation?

2. Experimental

A batch containing stoichiometric mixture of Bi₂O₃ (Merck, purity 99.9%) and WO₃ (Merck, purity 99.9%) in a 1:1 M ratio was subjected to intensive mechanical treatment using a planetary ball mill (Fritsch – Premium line – Pulversette No. 7). Two samples charged as different batch amounts were chosen: sample **A** containing 2.5 g batch of pure oxides and sample **B** containing 4 g batch of pure oxides. The following milling parameters were used:

- ZrO_2 chambers and balls, with ball diameter of 5 mm/
- Air atmosphere and milling speed of 500 rpm/
- Ball to powder mass ratio of 10:1/
- The degree of phase transformation was determined after different time intervals of treatment (30 min, 1, 2, 3, 4, 5, 6, 7 and 8 h)/
- In order to avoid excessive temperature rise within the grinding chamber, 15 min ball milling duration was followed by a pause of 5 min.

Powder XRD patterns were registered on a Bruker D8 Advance diffractometer using Cu K α radiation in the 2 Θ range 10–80°. The average crystallite sizes (*D*) resulting from X-ray diffraction broadening were determined using the Scherrer's formula: $D = K\lambda/\beta \cos \Theta$, where *D* is the mean crystallite size in nm, *K* is Scherrer's constant, conventionally accepted to be 1.0, λ the Cu K α wavelength (1.5406 Å), β the full width at half maximum (FWHM) of the diffraction line, in radians, and Θ is the corresponding diffraction peak. The calculations were carried out using all diffraction peaks and the "PowderCell" program. Infrared spectra were registered in the range 1200–400 cm⁻¹ on a Nicolet-320 FTIR spectrometer using the KBr pellet technique. Differential thermal analysis was performed on DTA, Stanton Redcroft at a heating rate of 5 °C min⁻¹. The specific surface area of the samples was measured using a modified BET method. The particle size and morphology were determined using a TEM JEOL 2100 at an accelerating voltage of 200 kV. The specimens were prepared by grinding the samples in an agate mortar and disintegrating them as ethanol suspension by ultrasonic treatment for 6 min. A droplet of the suspension was coated on standard carbon films on Cu grids. Additional data for crystal structure were obtained by selected area electron diffraction (SAED) method. The optical properties were measured at room temperature using Evolution 300 UV-Vis Spectrophotometer in the range 200-1000 nm wavelength. The catalytic tests were carried out in a continuous-flow type reactor (quartz-glass, inner diameter of 6.0 mm) at atmospheric pressure. The following testing conditions were chosen: catalyst particles sieve fraction: 0.31-0.63 mm; GHSV: 30,000 h⁻¹. For compensation of the adiabatic effect of the reaction, the reaction temperature was kept within the limits of ± 1 °C, measured both at the inlet and at the outlet of the catalyst bed. The inlet concentrations of reactants were fixed as follows: CO: 1500 ppm; n-hexane: 250 ppm; oxygen: 21 vol.%. All feed gas mixtures were balanced to 100% with nitrogen (5.0). The gas analysis was performed by on-line analyzers of CO/CO₂/O₂ (Maihak) and THC (total hydrocarbon content, Horiba, with a flame ionization detector, on-line). After the catalytic test the sample was additionally supported by Pd-nitrate solution (to obtain 0.14 wt.% Pd) and heated at 400 °C for 2 h in air. The presence of the Pd particles on the surface of sample was established by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). The catalytic test of this sample was performed under same above mentioned conditions. The morphology and size distribution of palladium particles on the sample were examined by scanning electron microscopy using a JEOL JSM 6390 electron microscope (Japan), equipped with ultrahigh resolution scanning system (ASID-3D), in regimes of secondary electron image (SEI). The accelerating voltage was 20 kV, $I\!\sim\!65\,\mu\text{A}.$ The pressure was of the order of $10^{-4}\,\text{Pa}.$ The X-ray photoelectron spectroscopy (XPS) measurements were performed in a VG ESCALAB II electron spectrometer using Al K\alpha radiation with energy of 1486.6 eV. The binding energies (BE) were determined with an accuracy of ±0.1 eV utilizing the C1s line at 285.0 eV (from an adventitious carbon) as a reference.

3. Results and discussion

Fig. 1A and B shows the XRD patterns of mechanochemically synthesized Bi_2WO_6 using different batch amounts (sample **A** contains 2.5 g and **B** contains 4 g batch) depending on milling time interval. There is no interaction between oxides after 1 h mechanical treatment of sample **A** (Fig. 1A-c). The observed broadening and lower intensity of the diffraction lines is an indication of the formation of defects and decrease in the crystallites size. New peaks characteristic of orthorhombic Bi_2WO_6 (JCPDS-79-2381)



Fig. 2. DTA analysis of the mechanochemically synthesized ${\rm Bi}_2{\rm WO}_6$ (samples A) and amorphous phases (sample B).

were detected after 90 min of milling time (Fig. 1A-d). But still some small amount of WO₃ (JCPDS-83-0951) remained after 2 h milling time intervals (Fig. 1A-e). The reaction was completed after 4 h of milling time and broad diffraction lines characteristic only of orthorhombic Bi₂WO₆ were registered (Fig. 1A-f). The calculated average crystallite size of the Bi₂WO₆ is 10 nm. Upon using higher batch amount (4 g) there is no interaction between oxides after 2 h mechanical treatment of the sample **B** (Fig. 1B-b). An intermediate stage of amorphization was observed after 4 h of milling time (Fig. 1B-c). The amorphous phase is transformed into single orthorhombic Bi₂WO₆ after 8 h of milling time (Fig. 1B-e). The calculated average crystallite size of Bi₂WO₆ under these experimental conditions is 4 nm. This fact is probably due to the formation of the amorphous phase, which is a favorable prerequisite for the formation of the particles of very small size. Maczka et al. [29] realized a solid state metathesis reaction between Bi(NO₃)₃·5H₂O, Na₂WO₄·2H₂O and NaOH by mechanochemical activation at 350 rpm for 1 h, forming BiWO precursor, which was washed, milled and treated thermally. We achieved a faster synthesis technique of the Bi_2WO_6 (after 4 h activation) using small amount (2.5 g) of pure oxides. Activation of higher amount (4 g) of pure oxides led to longer time interval of the synthesis (8 h).

Fig. 2 represents DTA curves of the mechanochemically synthesized Bi_2WO_6 (sample **A**) and amorphous phase (sample **B**), respectively. Two exothermal peaks of low and high intensity were observed in the DTA curves. The peaks at 440 °C and 470 °C can be attributed to the process of crystallization (Fig. 1A and B). Comparing with the DTA data, reported by Maczka et al. [29], the crystallization temperature of amorphous phase in our case is higher by 60 °C. This is probably because of the different nature of the precursors and different synthesis stage. The first low intensive exothermal peaks at 400 °C (sample **A**) and 440 °C (sample **B**) can be attributed to the formation of an intermediate fluorite-like phase before the crystallization of the Bi₂WO₆ having Aurivillius type of structure [28]. The endothermal peaks within the range 870-920 °C are due to phase transformation of Bi₂WO₆ from orthorhombic into monoclinic form [3-7]. Taking into account the above given DTA data we performed thermal treatment of these samples (Fig. 3A and B). After the thermal treatment of mechanochemically synthesized Bi_2WO_6 (sample **A**) the diffraction lines become sharper with higher intensity, which indicates that an additional crystallization process was occurring (average crystallite size was 11 nm). The heat treatment at 470 °C of the amorphous phase

(sample **B**) led to crystallization of orthorhombic Bi_2WO_6 (average crystallite size was 4 nm). The thermal treatment of both phases did not lead to increase in the crystallites size. With Fig. 4 we present evidence for polycrystalline nature of the particles, but some of them are amorphous also. The main purpose of our TEM investigation was to confirm the phase composition of the sample A obtained by mechanochemical synthesis. The poorly crystalline sample makes the investigation by TEM (SAED) very difficult because the particles are thicker and non-transparent in electron microscope. From XRD we receive information for crystallite size, but in bright field micrographs, obtained by TEM we have probably the particles which consist of small grains size. These particles can be considered like agglomerates. With Fig. 4 we present only variations in particles size (20-100 nm) in the sample. The selected area electron diffraction (SAED) pattern showed that only one crystal phase of orthorhombic Bi₂WO₆ has been obtained. The observed strongest peak at (131) as well as the peaks at (141) and (152)planes are in good agreement with the XRD data (Fig. 1A-f). The specific surface area of this sample is $5 \text{ m}^2/\text{g}$. A similar value range for the surface area was reported for this compound, prepared by solid state reaction, as well as for some other inorganic compounds, obtained by us applying this technique [26,27,39–42].



Fig. 3. (A) XRD patterns of the mechanochemically synthesized Bi_2WO_6 and heat-treated at 440 °C (sample **A**). (B) XRD patterns of the amorphous phase and heat-treated at 470 °C (sample **B**).



Fig. 4. TEM micrograph and SAED pattern (inset) of the mechanochemically synthesized Bi_2WO_6 (sample A).

We monitored by IR spectroscopy (Fig. 5A and B) the phase formation of Bi_2WO_6 using different batch amounts (sample **A** and **B**) depending on the milling time interval. The intensity and the number of absorption bands of Bi_2O_3 [43] and WO_3 [44] decrease after mechanical treatment due to destruction of the long range order and partial amorphization of these oxides (Fig. 5A-b, c and B-b). The appearance of new absorption bands at 880, 740, 710 and 540 cm⁻¹ is the result of formation of new bonds between the initial oxides during mechanochemical activation. According to the IR and Raman studies of Bi_2WO_6 made by Maczka et al. [29,30] these bands are characteristic of vibration of the WO₆ octahedra building up the orthorhombic crystalline Bi_2WO_6 structure. The band at 540 cm⁻¹ is superposition between bending vibration of WO₆ and stretching and bending vibrations of the Bi–O polyhedra [12,19,20,29,30,45]. The IR spectrum of amorphous phase, obtained by us, is similar to that obtained by Maczka et al. [29,30] although they used different precursors. The IR spectra of Bi_2WO_6 as a function of batch amount showed that the spectra exhibit significant changes upon decreasing the particle size. Broadening of the absorption band, centered at 740 cm⁻¹ with lower intensity, is observed in the spectra of Bi_2WO_6 containing smaller particles size (4 nm).

The UV-Vis absorption spectra of the mechanochemically synthesized Bi_2WO_6 (samples **A** and **B**) and amorphous phase (sample **B**) are represented in Fig. 6A. The samples show strong absorption in the UV to visible light range at wavelength shorter than 450 nm. which was in good agreement with other reports [10–14. 18-25,29,30]. The amorphous phase possesses slightly higher absorption compared to the two crystalline phases. This fact could be related to the distortion structure of the amorphous phase. For crystallite semiconductors, the optical absorption band follows the equation $\alpha hv = A(hv - E_g)^n$, where α is the absorption coefficient, A is a constant, h is Plank's constant, v the photon frequency, E_{σ} the optical band gap and $n^{1/2}$ in case of direct semiconductor. An extrapolation of the linear region of a plot of $(\alpha hv)^{1/2}$ on the y-axis versus photon energy (hv) on the x-axis gives the value of the optical band gap E_g (Fig. 6B) [46]. The calculated band gaps of mechanochemically synthesized Bi_2WO_6 (sample A with crystallites size of 10 nm), amorphous and crystalline phase (sample **B** with crystallites size of 4 nm) were 2.85, 2.81 and 2.88 eV. The band gap energies decrease with the increase in the crystallites size. A similar result was reported in Refs. [12,16,29,30].

The above described properties of mechanochemically synthesized Bi_2WO_6 enable the option to develop a thermally stable material with potential application in the environmental catalysis. In order to investigate this possibility, tests on catalytic



Fig. 5. (A) IR spectra of the sample A (2.5 g batch) mechanochemically activated at: (a) 0 min; (b) 30 min; (c) 60 min; (d) 90 min; (e) 2 h; and (f) 4 h. (B) IR spectra of the sample B (4 g batch) mechanochemically activated at: (a) 0 min; (b) 2 h; (c) 4 h; (d) 6 h; (e) 8 h.

oxidation of CO and n-hexane were performed. Fig. 7 shows the results from catalytic activity tests obtained with the mechanochemically synthesized Bi_2WO_6 (sample **A**). It can be seen that the CO oxidation reaction is proceeding at temperatures higher than 200 °C and it reaches 98% conversion degree at 395 °C, while the complete oxidation of n-hexane was found to occur at temperatures higher than 250 °C, a significant conversion degree (of the order of 70%) was measured only at about 500 °C. It should be pointed out that the obtained results are in good agreement



Fig. 6. (**A**) UV–Vis absorption spectra of the mechanochemically synthesized Bi_2WO_6 (samples **A** and **B**) and amorphous phase (sample **B**). (B) Plot of the $(\alpha h v)^{1/2}$ versus photon energy (hv) for the mechanochemically synthesized Bi_2WO_6 (samples **A** and **B**) and amorphous phase (sample **B**).

with the catalytic activity in CO oxidation reaction on Bi_2WO_6 , prepared by solid state reaction [26,27]. It should be noted that there are no data in the literature on the complete oxidation of n-hexane over Bi_2WO_6 . The catalytic performance of pure Bi_2WO_6 cannot be characterized as very satisfactory, comparing with the sample having 0.14 wt.% of palladium supported additionally. Although the palladium content is very small the effect on the catalytic activity is remarkable – the decrease in reaction temperature is with about 150 °C in the case of CO oxidation and 130 °C



Fig. 7. Dependencies of the conversion on the temperature during the catalytic oxidation of CO, n-hexane and methane on the mechanochemically synthesized Bi_2WO_6 (sample **A**) and same sample contains 0.14 wt.% Pd.



Fig. 8. SEM image of the mechanochemically synthesized Bi_2WO_6 (samples A) contains 0.14 wt.% Pd.

Surface composition (at.%) estimated from the XPS intensities.

Table 1

Surface composition (at.%)			
0	Pd	W	Bi
71.8	12.5	3.4	12.3



Fig. 9. X-ray photoelectron spectra of the mechanochemically synthesized Bi₂WO₆ (sample A) contains 0.14 wt.% Pd: on the Bi4f and Pd3d levels.

for the complete oxidation of n-hexane (at conversion degree of 50%). Additionally, the presence of palladium on the catalytic surface leads to about fourfold decrease in the selectivity of the catalyst towards undesirable products of incomplete oxidation (in the case of CO it declined from 6% in the absence of palladium to less than 1.5% of the totally converted n-hexane, when 0.14 wt.% palladium was applied). The reaction of complete oxidation of methane on Pd/Bi₂WO₆ was also investigated at temperatures up to 505 °C. The maximum conversion degree of methane was 7.1% and this result shows the need of remarkable improvement of the catalyst in order to apply it in the process of preventing the global warming by elimination of methane emissions into the atmosphere. The SEM analysis was performed to study the distribution and morphology of the palladium particles on the mechanochemically synthesized Bi_2WO_6 (sample A). Two areas with a smooth and rough surface were observed (Fig. 8). The high magnification image shown in the inset of Fig. 8 clearly proves that Pd particles are in the range of nanometer size. The SEM image shows that the Pd nanoparticles are not uniformly distributed on the surface. The surface state of mechanochemically synthesized Bi₂WO₆ loaded with 0.14 wt.% Pd was analyzed by X-ray photoelectron spectroscopy. Table 1 represents the surface composition of the Pd/Bi₂WO₆ sample. The observed atomic intensity ratio Bi/W is much higher than the theoretical value. This means that the surface layers of tungstate are enriched in bismuth. Further, the XPS analysis of Pd/Bi₂WO₆ sample revealed that a considerable fraction of Pd was in a close contact with Bi as indicated by both Pd 3d and Bi 4f photoelectron spectra in Fig. 9. The Bi 4f core level spectra can be fitted by two doublets, assigned to Bi⁰ (158.9 eV) and Bi³⁺ (160.1 eV), respectively. The Pd 3d core level spectra also display two doublets, which correspond to Pd⁰ (336.2 eV) and Pd²⁺ (337.4 eV). The zerovalent Bi is probably stabilized in association with Pd⁰ in the form of Bi-Pd alloy during the pretreatment of Pd/Bi₂WO₆ at 400 °C. According to the Bi–Pd phase diagram [47] both the α -Bi₂Pd and β -BiPd phases could be formed at temperatures below 380 °C. Thus the formation of alloy or inter-metallic phase could explain the promotional effect of Bi on the catalytic activity of the Pd loaded sample [48].

4. Conclusion

This study shows the opportunity to synthesize nanostructured Bi₂WO₆ by mechanochemical activation of pure oxides. It was established that the amount of the batch is a decisive factor for the synthesis time interval. Single Bi₂WO₆ phase was obtained after 4 h of milling time at room temperature using a small batch amount (2.5 g). The increase in the batch amount (4 g) preserving the other milling parameters constant is a prerequisite for the formation of amorphous phase and it led to prolongation of the synthesis time interval (8 h of milling time). The amorphous phase favors the obtaining of particles of smaller size (4 nm). The mechanochemically synthesized Bi₂WO₆ was successfully investigated in the reaction of complete oxidation of CO, n-hexane, which was observed at relatively high temperatures (above 200 °C for CO and above 250 °C for n-hexane). The catalytic activity was increased remarkably when the sample is modified by 0.14 wt.% Pd, supported on the surface of Bi₂WO₆. The promotional effect of Bi on the catalytic activity of the Pd loaded sample could be explained by the formation of alloy or inter-metallic phases (α -Bi₂Pd and β -BiPd), which is a basis for the development of a stabile catalyst for treatment of methane emissions. The reported results should be considered as a beginning of the process of catalyst development and many new tasks related to the optimization of the composition appear now, which will be the aim of further investigations.

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