This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This Accepted Manuscript will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
Solid state synthesis, characterization, optical properties and cooperative catalytic performance of bismuth vanadate nanocatalyst for Biginelli reactions

Shahin Khademinia, Mahdi Behzad*, Hamideh Samari Jahromi

a: Department of Chemistry, Semnan University, Semnan 35351-19111, Iran
b: Research Institute of Petroleum Industry (RIPI), Environment and Biotechnology Division, West Blvd., Azadi Sports Complex, P.O. Box 14665-1998, Tehran, Iran

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

Abstract

Bi$_2$V$_2$O$_7$ nano powders were synthesized via a solid state reaction at 500 ºC for 8 h using Bi(NO$_3$)$_3$ and VO(acac)$_2$ at stoichiometric 1:1 Bi:V molar ratio as raw materials. The synthesized material was characterized by powder X-ray diffraction (PXRD) technique and Fourier-transform infrared (FTIR) spectroscopy. Structural analysis was performed by the FullProf program employing profile matching with constant scale factors. The results showed that the pattern had a main Bi$_2$V$_2$O$_7$ structure with a space group of Fd$ar{3}$m. Lattice parameters were found as a=b=c=10.259079Å, $\alpha = \gamma = \beta = 90^\circ$. FESEM and TEM images showed that the synthesized Bi$_2$V$_2$O$_7$ particles had mono-shaped sphere morphologies. Ultraviolet–visible spectrum analysis showed that the nanostructured Bi$_2$V$_2$O$_7$ powders possessed strong light absorption properties in the ultraviolet light region. Catalytic performance of the synthesized nanomaterial was also investigated in Biginelli reactions which showed excellent efficiency.

Keywords: Bismuth vanadate; solid state; nanomaterial; catalyst; Biginelli

* Corresponding author email: mbehzad@semnan.ac.ir; mahdibehzad@gmail.com. Tel: +98-233 338 3195
1. Introduction

Among oxides and fluorides with general formula \(A_2B_2X_6\) (where \(A\) is a medium-large cation and \(B\) is an octahedrally coordinated, high-charge cation), there are many compounds widely studied for their great technological properties [1, 2]. Pyrochlore phase is understood as a defect structure of fluoride type with general formula \(A_2B_2O_6\) or \(A_2B_2O_7\). This structure exhibits ccc arrays of cations with anions partially occupying the tetrahedral sites to form a distorted structure containing intrinsic defects. Research on pyrochlore materials have been focused on applications such as catalysis [3, 4], electronics [5], optical [6] and magnetic properties [7] and solid oxide fuel cell (SOFC) electrode materials [8]. Bi-containing perovskites have received a lot of attention as lead-free ferroelectric [9, 10] and multi-ferroic [11, 12] materials. Among them, Bismuth vanadate semiconductors have also received great interest for their photocatalytic application for splitting of water into hydrogen and oxygen [13-16] and organic wastewater treatment [17-19]. Several compounds of Bi-V-O have been previously synthesized via different methods including BiVO\(_4\) [20], BiVO\(_3\), BiVO\(_4\), Bi\(_2\)V\(_2\)O\(_{10.5}\), Bi\(_2\)V\(_2\)O\(_{16}\) [21], different phases of Bi\(_2\)V\(_2\)O\(_5\) [22], Bi\(_2\)V\(_2\)O\(_{11}\) and Bi\(_2\)V\(_2\)O\(_{10}\) [23], Bi\(_2\)V\(_2\)O\(_{11}\) [24], Bi\(_2\)V\(_2\)O\(_5\) and so on [25]. The Biginelli reaction, which was originally reported by Biginelli in 1891 [26], is a methodology for the synthesis of 3,4-dihydropyrimidin-2-(1H)-one derivatives (DHPMs) in a one-step procedure. DHPMs have already shown biological activities [27]. Several metal oxides have been reported as nanocatalysts for the Biginelli reactions including alumina supported Mo catalysts [28], nano ZnO as a structure base catalyst [29], MoO\(_3\) – ZrO\(_2\) nanocomposite [30], MnO\(_2\) – MWCNT nanocomposites [31], TiO\(_2\) nanoparticles [32], Mg–Al–CO\(_3\) and Ca–Al–CO\(_3\) hydroxalcite [33], Bi\(_2\)O\(_3\)/ZrO\(_2\) nanocomposite [34], ZrO\(_2\)–Al\(_2\)O\(_3\)–Fe\(_2\)O\(_3\) [35], imidazole functionalized Fe\(_3\)O\(_4@SiO\(_2\) [36], Alumina supported Mo\(_3\) [37], ZrO\(_2\)-pillared clay [38], ZnO nanoparticle [39], Fe\(_3\)O\(_4@CNT [40], TiO\(_2\)-MWCNT [41], Fe\(_3\)O\(_4@mesoporous SBA-15 [42]. In the present study, a solid state method was explored for the synthesis of nanocrystalline Bi\(_2\)V\(_2\)O\(_7\) powders using Bi(NO\(_3\))\(_3\) and VO(acac)\(_2\) as raw materials. To the best of our knowledge, there is no information available in the literature about the solid state synthesis of nanocrystalline Bi\(_2\)V\(_2\)O\(_7\) crystallites. The band gap energy of the as-prepared Bi\(_2\)V\(_2\)O\(_7\) nanomaterial was initially estimated from ultraviolet - visible spectra. Catalytic application of the synthesized Bi\(_2\)V\(_2\)O\(_7\) was also investigated in Biginelli reactions. It was found that the synthesized Bi\(_2\)V\(_2\)O\(_7\) nanocatalyst had excellent efficiency in the synthesis of DHPMs.

2. Experimental

2.1. General remarks

All chemicals were of analytical grade, obtained from commercial sources, and used without further purification. Phase identifications were performed on a powder X-ray diffractometer D5000 (Siemens AG, Munich, Germany) using CuK\(_\alpha\) radiation.

The morphology of the obtained materials was examined with a field emission scanning electron microscope (Hitachi FE-SEM model S-4160). Bi\(_2\)V\(_2\)O\(_7\) particles were dispersed in water and cast onto a copper grid to study the sizes and morphology of the particles by TEM (Transmission Electron Microscopy) using a Philips – CM300 - 150 KV microscope. From the TEM images the average of particle size distribution was carried out using Image software. FTIR spectra were recorded on a Tensor 27 (Bruker Corporation, Germany). Absorption spectra were recorded on an Analytik Jena Specord 40 (Analytik Jena AG Analytical Instrumentation, Jena, Germany). BET surface areas were acquired on a Beckman Coulter SA3100 Surface Area Analyser. The purity of products was checked by thin layer chromatography (TLC) on glass plates coated with silica gel 60 F254 using n-hexane/ethyl acetate mixture as mobile phase.

2.2. Catalyst preparation

In a typical synthetic experiment, 0.50 g (1.03 mmol) of Bi(NO\(_3\))\(_3\) (Mw = 485.08 g mol\(^{-1}\)) and 0.27 g (1.03 mmol) of VO(acac)\(_2\) (Mw = 262.14 g mol\(^{-1}\)) were mixed in a mortar and ground until a nearly homogeneous powder was obtained. The obtained powder was added into a 25 mL crucible and treated thermally in one step at 500 °C for 8 h. The crucible was then cooled normally in oven to the room temperature. The obtained powder was collected for further analyses. The synthesis yield for Bi\(_2\)V\(_2\)O\(_7\) (Mw=631.88 g mol\(^{-1}\)) was 0.30 g (92%).

2.3. General procedure for the synthesis of DHPMs

In a typical procedure, a mixture of aldehyde (1 mmol), ethyl acetoacetate (1 mmol), urea (1.2 mmol) and 0.02 g (3.1 × 10\(^{-2}\) mmol) of Bi\(_2\)V\(_2\)O\(_7\) as catalyst was placed in a round-bottom flask under solvent free conditions. The suspension was stirred at 90 °C. The reaction was monitored by thin layer chromatography (TLC) [6:4 hexane:ethylacetate]. After completion of the reaction, the solid crude product was washed with deionized water to separate the unreacted raw materials. The precipitated solid was then collected and dissolved in ethanol to separate the solid catalyst. The filtrate was left undisturbed at room temperature to afford the crystals of the pure product.

3. Result and discussion

3.1. Characterizations

The phase composition of the Bi\(_2\)V\(_2\)O\(_7\) nanomaterial was examined by powder X-ray diffraction technique. Figure 1 shows the PXRD pattern of the obtained material in the 20 range 4-70°. The results of structural analysis performed by the FullProf program employing profile matching with constant scale factors are also included in figure 1. Red bars are the observed intensities while the black ones are the calculated data. The blue one is the difference: Yobs-Ycalc. The Bragg reflections positions are
indicated by green bars. The pattern has a well fitted defect pyrochlore structure profile with face centered cubic structure. Lattice parameters were found as $a=b=c=10.259079\text{Å}$ and $\alpha = \gamma = \beta = 90^\circ$ with a space group of $Fd\bar{3}m$ [20]. The results showed that the pattern had a main $\text{Bi}_2\text{V}_2\text{O}_7$ structure. A small fraction of unreacted $\text{V}_2\text{O}_3$ was found in the structure which is identified in figure 1 [43].

![Figure 1. PXRD pattern of the synthesized $\text{Bi}_2\text{V}_2\text{O}_7$ nanomaterial and the Rietveld analysis. ∟ is due to $\text{V}_2\text{O}_3$ impurity.](image)

Figure 2 shows the FESEM images of the synthesized $\text{Bi}_2\text{V}_2\text{O}_7$ nanomaterial. Figure 3 also shows the TEM images as well as the particle size distribution profile. As could be seen from figures 2 and 3, the materials are consisted of nearly homogeneous narrow size distributed spherical particles. Figure 3 also indicates that the maximum particle size distribution were in the range of 40 – 60 nm.

![Figure 2. FESEM images of the synthesized $\text{Bi}_2\text{V}_2\text{O}_7$ nanomaterial.](image)
Figure 3. TEM images of the synthesized Bi$_2$V$_2$O$_7$ nanomaterial. (e) particle size distribution.

UV–Vis absorption spectrum of the Bi$_2$V$_2$O$_7$ nanomaterial is shown in figure 4a. The optical band gap is also shown in figure 4b. The pure Bi$_2$V$_2$O$_7$ nanomaterial displays a typical visible absorption edge at about 720 nm. According to the results of Pascual et al. [44], the relation between the absorption coefficient and incident photon energy can be written as $(\alpha h\nu)^2 = A(h\nu - E_g)$, where $A$ and $E_g$ are constant and direct band gap energy, respectively. Band gap energy was evaluated by extrapolating the linear part of the curve to the energy axis. It was found that the band gap was 2.0 eV [45, 46].

Figure 4 shows the UV–Vis spectrum and $\alpha h\nu$ versus $h\nu$ for Bi$_2$V$_2$O$_7$ nanomaterial.

Figure 5 shows the FTIR spectrum of the obtained material. There are some peaks at around 420, 472, 516, 611, 655, 794, 1020, 1097 and 1151 cm$^{-1}$ that are the characteristic bands for Bi$_2$V$_2$O$_7$. The band at 420 cm$^{-1}$ is attributed to BiRO vibration [47, 48]; the bands at 516 – 611 and 655 [24] cm$^{-1}$ are attributed to the O-V=O deformation mode vibration. The broad band at about 794 – 950 cm$^{-1}$ is assigned to the V=O asymmetric stretching vibration [25, 47 - 49]. The signal at around 1020 cm$^{-1}$ is also assigned to the V=O stretching vibration. This band is usually observed in vanadium oxide compounds with intermediate oxidation state between $V^{5+}$ and $V^{4+}$ ions [50]. The peak at around 601 cm$^{-1}$ is assigned to the Bi–O stretching vibration and the peak at around 1090 cm$^{-1}$ is assigned to the Bi–O vibrations caused by the interaction between the Bi–O bonds and their surroundings [51, 52]. The surface area, average pore size and average pore volume of the synthesized material was analyzed by BET and BJH textural analyses. The sample was degassed at 150 °C for 120 min in the nitrogen atmosphere prior to N$_2$-physical adsorption measurements. The specific surface area ($S_{BET}$) of the obtained materials was determined with adsorption-desorption isotherms of N$_2$ at 77 K. The surface area, pore volumes and average pore diameters of the synthesized materials are summarized in table 1 [53].

<table>
<thead>
<tr>
<th>$S_{BET}$ (m$^2$/g)</th>
<th>Pore size (Å)</th>
<th>Pore volume (cm$^3$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0</td>
<td>139.6</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Table 1. BET data for Bi$_2$V$_2$O$_7$ showing the textural properties of the obtained materials.

3.2. Catalytic studies

3.2.1. Biginelli reaction for the synthesis of DHPMs

The direct synthesis involves the condensation between ketoesters, aldehydes and ureas in the presence of either Lewis or mineral acids. DHPMs were prepared by the reaction of aromatic aldehyde, ethyl/methyl acetoacetate and urea with $3.1 \times 10^{-2}$ mmol of Bi$_2$V$_2$O$_7$ at 90 °C for 60 min under solvent-free conditions (Scheme 1). Several parameters affecting the catalytic reactions were analysed and optimized.
3.2.2. Effect of different parameters on the catalytic reaction

Different parameters such as reaction time, temperature and the amount of the nanocatalyst were optimized on the catalytic reaction using benzaldehyde as the aldehyde derivative. Table 2 shows the effect of the different parameters on the reaction efficiency. It was found that the efficiency was increased with increasing the amount of the nanocatalyst; however, by changing its amount over 0.02 g, the efficiency was nearly constant. So we found that the optimal amount of the nanocatalyst was 0.02 g. The effect of temperature on the reaction was also investigated using the optimized amount of the catalyst. According to the table, it was found that the reaction efficiency was increased with increasing the temperature from 60 to 90 °C but over 90 °C the efficiency maintained almost constant. Hence, the optimal temperature for the reaction was found to be 90 °C. Table 2 also shows that the efficiency of the synthesis procedure was increased with increasing the reaction time from 15 to 60 min and the efficiency maintained constant with increasing the reaction time. So, 0.02 g of the catalyst, 90 °C reaction temperature, and 60 min reaction time were used for the other Biginelli reactions in this work.

Table 2. Optimization of the different conditions for the synthesis of DHPMs.

<table>
<thead>
<tr>
<th>Amount of catalyst (g)</th>
<th>Time (min)</th>
<th>Temperature (°C)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>60</td>
<td>90</td>
<td>43</td>
</tr>
<tr>
<td>0.02</td>
<td>60</td>
<td>90</td>
<td>89</td>
</tr>
<tr>
<td>0.03</td>
<td>60</td>
<td>90</td>
<td>89</td>
</tr>
<tr>
<td>0.04</td>
<td>60</td>
<td>90</td>
<td>89</td>
</tr>
<tr>
<td>0.05</td>
<td>60</td>
<td>90</td>
<td>89</td>
</tr>
<tr>
<td>0.02</td>
<td>60</td>
<td>60</td>
<td>58</td>
</tr>
<tr>
<td>0.02</td>
<td>60</td>
<td>70</td>
<td>77</td>
</tr>
<tr>
<td>0.02</td>
<td>60</td>
<td>80</td>
<td>81</td>
</tr>
<tr>
<td>0.02</td>
<td>60</td>
<td>90</td>
<td>89</td>
</tr>
<tr>
<td>0.02</td>
<td>60</td>
<td>100</td>
<td>89</td>
</tr>
<tr>
<td>0.02</td>
<td>15</td>
<td>90</td>
<td>50</td>
</tr>
<tr>
<td>0.02</td>
<td>30</td>
<td>90</td>
<td>66</td>
</tr>
<tr>
<td>0.02</td>
<td>45</td>
<td>90</td>
<td>81</td>
</tr>
<tr>
<td>0.02</td>
<td>60</td>
<td>90</td>
<td>89</td>
</tr>
<tr>
<td>0.02</td>
<td>90</td>
<td>90</td>
<td>89</td>
</tr>
</tbody>
</table>

* Benzaldehyde:Ethylacetoacet:Urea molar ratios is as follows: 1:1:1.2

The optimized parameters from the previous section were used for the synthesis of other derivatives and the results are collected in table 3. Scheme 1 shows a summary of the reaction pathway.

Scheme 1. Schematic representation of the reaction pathway for the synthesis of DHPMs.

Table 3. Biginelli reactions using ethyl/methyl acetoacetate and urea with different benzaldehyde derivatives.

<table>
<thead>
<tr>
<th>( R_1 )</th>
<th>( R_2 )</th>
<th>mmol of product</th>
<th>Turnover number (TON)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>OEt</td>
<td>0.89</td>
<td>29</td>
</tr>
<tr>
<td>4-Cl</td>
<td>OEt</td>
<td>0.92</td>
<td>30</td>
</tr>
<tr>
<td>2-Cl</td>
<td>OEt</td>
<td>0.98</td>
<td>32</td>
</tr>
<tr>
<td>4-Br</td>
<td>OEt</td>
<td>0.62</td>
<td>20</td>
</tr>
<tr>
<td>4- F</td>
<td>OEt</td>
<td>0.69</td>
<td>22</td>
</tr>
<tr>
<td>2-OMe</td>
<td>OEt</td>
<td>0.98</td>
<td>32</td>
</tr>
<tr>
<td>4-OMe</td>
<td>OEt</td>
<td>0.72</td>
<td>23</td>
</tr>
<tr>
<td>4- Cl</td>
<td>OMe</td>
<td>0.98</td>
<td>32</td>
</tr>
<tr>
<td>2-Cl</td>
<td>OMe</td>
<td>0.90</td>
<td>29</td>
</tr>
<tr>
<td>4-Br</td>
<td>OMe</td>
<td>0.93</td>
<td>30</td>
</tr>
<tr>
<td>4- F</td>
<td>OMe</td>
<td>0.98</td>
<td>32</td>
</tr>
<tr>
<td>2- OMe</td>
<td>OMe</td>
<td>0.92</td>
<td>30</td>
</tr>
<tr>
<td>4- OMe</td>
<td>OMe</td>
<td>0.62</td>
<td>20</td>
</tr>
</tbody>
</table>
The turnover numbers (TON, mol of product per mol of catalyst) for the synthesis of DHPMs were calculated by the following equation [54].

\[
\text{Turnover Number (TON)} = \frac{\text{mol of product}}{\text{mol of catalyst}}
\]

Table 4 shows the catalytic efficiency of the synthesized Bi\(_2\)V\(_2\)O\(_7\) nanomaterial compared to the starting materials Bi(NO\(_3\))\(_3\) and VO(acac)\(_2\). The optimized conditions from the previous section were used. As could be seen from table 4, Bi\(_2\)V\(_2\)O\(_7\) was much more efficient catalyst compared to the two starting materials which mean that the presence of the both metal ions was important and the two ions have acted cooperatively.

Table 4. Comparison study of the catalytic ability of the synthesized Bi\(_2\)V\(_2\)O\(_7\) with raw materials.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reagents</th>
<th>Time (min)</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi(_2)V(_2)O(_7)</td>
<td>Benzaldehyde</td>
<td>60</td>
<td>89</td>
</tr>
<tr>
<td>VO(acac)(_2)</td>
<td>Benzaldehyde</td>
<td>60</td>
<td>38</td>
</tr>
<tr>
<td>Bi(NO(_3))(_3)</td>
<td>Benzaldehyde</td>
<td>60</td>
<td>35</td>
</tr>
</tbody>
</table>

To show the merit of the present work, we have compared Bi\(_2\)V\(_2\)O\(_7\) nanocatalyst results with some of the previously reported catalysts in the synthesis of DHPMs (Table 5). It is clear that Bi\(_2\)V\(_2\)O\(_7\) showed greater activity than some other heterogeneous catalysts.

Table 5. Comparison study of the catalytic ability of the synthesized Bi\(_2\)V\(_2\)O\(_7\) with other catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>R(_x)</th>
<th>Catalyst amount</th>
<th>Condition</th>
<th>Yield %</th>
<th>Time (min)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi(_2)V(_2)O(_7)</td>
<td>H</td>
<td>3.1 × 10(^{-2}) mmol</td>
<td>solvent-free, 90°C</td>
<td>89</td>
<td>60</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>4-Cl</td>
<td></td>
<td></td>
<td>92</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2-Cl</td>
<td></td>
<td></td>
<td>98</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bi(_2)O(_3)/ZrO(_2)</td>
<td>H</td>
<td>20 mol%</td>
<td>solvent-free, 80-85°C</td>
<td>85</td>
<td>120</td>
<td>[34]</td>
</tr>
<tr>
<td></td>
<td>4-Cl</td>
<td></td>
<td></td>
<td>85</td>
<td>120</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2-Cl</td>
<td></td>
<td></td>
<td>82</td>
<td>165</td>
<td></td>
</tr>
<tr>
<td>ZrO(_2)-Al(_2)O(_3)-Fe(_2)O(_4)</td>
<td>H</td>
<td>0.05 g</td>
<td>Ethanol, reflux, 140°C</td>
<td>82</td>
<td>300</td>
<td>[35]</td>
</tr>
<tr>
<td></td>
<td>4-Cl</td>
<td></td>
<td></td>
<td>66</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2-Cl</td>
<td></td>
<td></td>
<td>40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo(_x)/Al(_2)O(_3)</td>
<td>H</td>
<td>0.3 g</td>
<td>solvent-free conditions at 100°C</td>
<td>80</td>
<td>60</td>
<td>[37]</td>
</tr>
<tr>
<td>ZnO</td>
<td></td>
<td>25 mol%</td>
<td>solvent-free conditions at 90°C</td>
<td>92</td>
<td>50</td>
<td>[39]</td>
</tr>
<tr>
<td></td>
<td>4-Cl</td>
<td></td>
<td></td>
<td>95</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

4. Conclusion
In this work, Bi\(_2\)V\(_2\)O\(_7\) nanomaterial was synthesized via solid state method. PXRD patterns and structural analysis done by the FullProf program employing profile matching showed that the synthesis was successfull. FESEM and TEM images showed the sphere-like structure in the as-synthesized materials. The catalytic application of the synthesized nanomaterial was investigated in Biginelli reaction in solvent free conditions. It was found that Bi\(_2\)V\(_2\)O\(_7\) nanomaterial had excellent efficiency in the synthesis of DHPMs. Besides, the two metal ions have performed the catalytic reactions cooperatively.

Reference