Research paper

Accepted Date:

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PII:	\$0020-1693(20)31373-6
DOI:	https://doi.org/10.1016/j.ica.2020.120173
Reference:	ICA 120173
To appear in:	Inorganica Chimica Acta
Received Date:	3 October 2020
Revised Date:	17 November 2020

29 November 2020



Please cite this article as: X. Li, C. Huang, Hydrothermal synthesis of V-doped hexagonal WO₃ microspheres comprising of nanoblocks for catalytic ammoxidation of dichlorotoluene, *Inorganica Chimica Acta* (2020), doi: https://doi.org/10.1016/j.ica.2020.120173

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Hydrothermal synthesis of V-doped hexagonal WO₃ microspheres comprising of nanoblocks for catalytic ammoxidation of dichlorotoluene

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Abstract: V-doped hexagonal WO₃ microspheres comprising of nanoblocks were successfully prepared via a facile hydrothermal approach. Several techniques such as XRD, SEM, TEM, FTIR, EDS, TPR, BET and Raman have been performed and the characterization results reveal that V replaced W atoms into the hexagonal lattice-structure. The microspheres possess diameter of about 4.4 μ m and the nanoblocks have thicknesses of 40-100 nm and widths of about 150 nm. In addition, the catalytic performance of the obtained V-doped WO₃ nanomaterial was investigated in the ammoxidation of dichlorotoluene. The catalytic results indicate that the as-prepared nanostructures show significantly improved selective performance with the selectivities of 3,4-DCBN and 2,6-DCBN reaching up to 89.8% and 86.2%, respectively.

Key words: V-doped WO₃; Microspheres; Dichlorobenzonitrile; Catalytic properties;

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Hydrothermal synthesis

1. Introduction

Recently, metal oxide nanostructures have received increasing attention since their dimensions of nanometer-size magnitude exhibit specific physical and chemical properties, which differ greatly from that of the bulk counterparts [1]. Among the various metal oxides available, the high interest lies in the synthesis and characterization of 3-dimensional (3D) hierarchical tungsten trioxide (WO_3) architectures due mainly to their intriguing physical and chemical properties and wide-ranging technological applications, including sensors, optical devices, catalysts, electrodes, ect [2-5]. For examples, Liu et al.[6] reported that Co-doped WO₃ flower-like nanostructures assembled with nanoplates, were promising for acetone sensors in environmental monitoring; Duan et al.[7] synthesized hexagonal WO3 mesocrystals with biconical morphology, exhibiting an excellent rate capability and cycling performance; Song et al.[8] prepared Fe-doped WO3 ultrathin hollow spheres with enhanced visible-light-driven photocatalytic performance. Despite the formation of various WO₃ nanostructures, the development of V-doped hexagonal WO₃ microspheres comprising of nanoblocks with excellent catalytic performance have not yet been reported.

Ammoxidation of hydrocarbons to produce nitriles is considered to be the most promising techniques considering the advantage of pollution-free. Ammoxidation of dichlorotoluene (DCT) to dichlorobenzonitrle (DCBN) is of high significance due to the increasing demand of DCBN for preparing lots of commercial chemicals [9,10]. However, the reaction is a more difficult process compared to other ammoxidation of alkyl aromatics and heteroaromatics [11]. There is a great deal of research that shows the methyl aromatics with different substituents or same substituents on different positions have different catalytic activities under identical conditions because of the hindered accessibility of methyl group caused by bulky substituent atoms [9,12]. Therefore, the low yield of DCBN were often obtained over previously reported catalysts (<72%) such as $(NH_4)_2[(VO)_3(P_2O_7)_2]$ [13], VPO/SiO₂ [12,14], VPO/Al₂O₃ [9], VPO/TiO₂ [15], etc. Therefore, fabricating highly selective catalysts for ammoxidation of DCT to DCBN remains a worthwhile goal.

Recently, a growing interest has been focused on the development of tungsten-vanadium catalysts [7,16,17]. Tungsten oxides with medium to strong acid strength are well known acidic co-catalysts of vanadium-based catalysts [18]. It is in favor of the formation of surface acid sites which greatly influence the selective performance [19]. On the other hand, the properties of catalysts are closely related to the structure characteristics [20]. Based on these properties, the development of new 3D hierarchical tungsten-vanadium oxide nanostructures to investigate their catalytic ammoxidation properties is fascinating and significant. However, there are quite a few efforts being devoted to the development of W–V binary oxides for the ammoxidation applications [18].

In this communication, V-doped hexagonal WO₃ microspheres comprising of nanoblocks were fabricated via a hydrothermal approach and explored as catalyst for the ammoxidation of DCT to DCBN. The composition and microstructure of the as-prepared nanomaterial were investigated. The catalytic activity was also evaluated in comparison with that of sample prepared by solid-state reaction.

2. Experimental section

Synthesis of V-doped WO₃ nanostructures

In a typical procedure, 0.03 mol of commercial V_2O_5 powder, 0.005 mol of $(NH_4)_{10}W_{12}O_{41}$ and 0.270 mol of $H_2C_2O_4 \cdot 2H_2O$ were dispersed into 400 mL of redistilled water with magnetic stirring. The mixture was heated to 80 °C for about 2 h to get a homogeneous solution. Then, the above solution was transferred into a 500 mL stainless steel autoclave, which was sealed and maintained at 180 °C for 48 h and then cooled to room temperature naturally. The products were filtered off, washed with distilled water and absolute ethanol several times, and dried in the oven at 70 °C for 12 h. In addition, another of the above mixed solution was slowly evaporated at 80 °C to dryness on a hot plate with stirring. The obtained solid was further dried at 110 °C for 8 h in an oven and calcined in air at 400 °C for 24 h (denoted as SSR-V-W-O).

Characterization

Scanning electron microscopy (SEM, Quanta 200) and transmission electron microscopy (TEM, JEM-2100) were used to study the morphologies of the samples. The phase and crystal structure of the obtained samples were tested by X-ray powder diffraction (XRD) using D8 X-ray diffractometer equipment with Cu Ka radiation, λ =1.54060 Å. The chemical composition of the samples was confirmed by means of the energy dispersive X-ray spectrometer (EDS) attached to the scanning electron

microscope (SEM). FT-IR spectra were recorded on a Nicolet 60-SXB spectrometer using KBr pellet technique from 4000 to 400 cm⁻¹ with a resolution of 4 cm⁻¹. Raman spectra were carried out by a Renishaw RM-1000 spectrometer (Confocal Raman Microspectroscopy) equipped with an excitation laser wavelength of 514.5 nm. The specific surface area was examined by Brunauer-Emmett-Teller (BET) N₂ gas adsorption method at 77 K and carried out on JW-BK equipment. Pore size distributions were calculated by Barrett-Joyner-Halenda (BJH) formula from the adsorption branch. The redox properties of catalysts were studied by temperature programmed reduction (TPR) on a TP-5080 adsorption instrument (TianJin XianQuan Co., gas composition: H₂ (3 mL/min) and N₂ (27 mL/min), heating rate: 10 °C/min).

Catalytic activity evaluation

Ammoxidation runs were conducted in a fixed-bed micro reactor equipped with a 30 mm inside diameter quartz tube, loaded with 5g of catalyst. DCT was injected to the vaporizer by a micro-pump, and mixed with NH₃ and air measured by gas flow meter. Test runs were carried out at different conditions by varying the temperature, space velocity of the reactant (*GHSV*), and the molar ratios of ammonia and air to DCT. The product stream was cooled and collected every 1/2 h after attaining steady state conditions and then analyzed off-line by a gas chromatograph (Lunanruihong, China; column: SE-30) equipped with FID module. Every test was repeated by three times and then taken the average with a margin of error of 0.5%. The reaction equations of the ammoxidation of 3,4-DCT, and 2,6-DCT to the corresponding DCBN could be expressed in Scheme 1.



Scheme 1 The ammoxidation of 3,4-DCT and 2,6-DCT to the corresponding DCBN

over V-W-O catalysts.

3. Results and discussion



Fig. 1 XRD patterns of the prepared V-doped WO₃ nanomaterial.

The phase and composition of the prepared V-doped WO₃ products were investigated by XRD, as depicted in Fig. 1. It can be seen that all the reflection peaks can be readily indexed to the hexagonal tungsten bronze (JCPDS: 33-1387) with the main reflections at $2\theta = 13.97$, 22.75, 24.35, 26.86, 28.19, 33.61, 36.61, 49.99, 55.55, 58.33 and 63.55° [19,21]. No characteristic peaks related to the impurities of vanadium or other tungsten oxides were detected. Furthermore, the peaks shift slightly to larger reflection angles in comparison to standard JCPDS: 33-1387, indicating the reduced adjacent interplanar distance $d_{(h k l)}$. These results reveal that the smaller V ions substituted W doped into hexagonal structure of WO₃ by the present hydrothermal synthetic route.



Fig. 2 FT-IR spectra of (a) prepared V-doped WO₃, (b) pure V₂O₅ and (c) pure WO₃.

FT-IR spectra of the prepared V-doped WO₃ sample, pure V_2O_5 and WO₃ are shown in Fig. 2. The peaks at 1620 cm⁻¹ and 1401 cm⁻¹ are the characteristics of absorbed H₂O and residual impurities of C–H, respectively [22]. The signals at 795 cm⁻¹ for prepared V-doped WO₃ catalyst is assigned to W–O vibrations in hexagonal tungsten bronze; in addition, the broad band at approximately 621 cm⁻¹ is related to the overlaps of W–O–W and W–O–V rocking vibrations [19].



Fig. 3 Raman spectrum of (a) as-obtained V-doped WO₃ sample and (b) pure WO₃.

Further information about the composition of the obtained V-doped WO₃ sample was studied by Raman spectroscopy, as shown in Fig. 3. The band at 966 cm⁻¹ indicates the higher presence of W-O bonds generated by a structural defect as a result of vanadium incorporation and/ or V-O bonds associated to polymeric V–O–W chains [19,23], while the bands at around 807 cm⁻¹ and 684 cm⁻¹ are related to two different

types of bridging oxygen of O–W–O vibrations in tungsten bronzes [24,25]. These results particularly sheds light on the vanadium doped into hexagonal tungsten bronzes [23], which are in agreement well with the XRD and FT-IR results.



Fig. 4 (a) SEM, (b) TEM and (c) HRTEM images of prepared V-doped WO₃ sample. The inset of (b) gives the SAED pattern.

The morphology and particle size of V-doped WO₃ sample were investigated by SEM, TEM and SAED technologies, as shown in Fig. 4. The SEM image (Fig. 4a) exhibits an individual microsphere with a diameter of about 4.4 µm, composed of numerous zero-dimensional nanoblocks. The TEM image (Fig. 4b) shows that the typical nanoblocks possess thicknesses of approximately 40–100 nm and widths of about 150 nm. Distinctly visual lattice fringes of 0.315 nm, matching well with the [200] crystal planes of hexagonal WO₃, is observed in the HRTEM image (Fig. 4c) revealing that the nanoblocks are of monocrystalline nature. In addition, The SAED pattern (top right corner in Fig. 4b) gives partial garbled light spots, further confirming that the obtained V-doped WO₃ catalyst is monocrystalline and the V was doped into hexagonal WO₃ bronzes.

The typical EDS spectrum (Fig. 5) corroborates that the nanoblocks composed of only C, O, V and W elements, where the C peak is owing to residual impurities absorbed on the surface of sample [26]. The molar ratio of V:W atom for V-doped

 WO_3 catalyst is 0.25. In addition, Fig. 6 clearly shows V, W and O elements are uniformly distributed.



Fig. 5 EDS spectrum of prepared V-doped WO₃ sample.



Fig.6 EDS elemental maps of obtained V-doped WO₃ products.



Fig. 7 SEM images of the products prepared at 180 °C for different reaction times: (a)

12 h, (b) 24 h.

A series of time-dependent experiments were performed to reveal the formation mechanism of nanoblock-built microspheres, as shown in Fig. 7. The SEM

observation (Fig. 7a) of the precursor, which were collected after reacting for 12 h, exhibits that lots of solid nanoblocks were formed and aggregated into irregular spheres to reduce the surface energy. As the reaction time prolonging to 24 h, the later formed nanoblocks grew preferentially at the surface defect sites of the spheres and thereby inhibited the accumulation (Fig. 7b). Finally, the nanoblock-built microspheres were formed (Fig. 4a) [27].



Fig. 8 H₂-TPR profiles of (a) prepared V-doped WO₃, (b) WO₃ and (c) V₂O₅.

The redox properties of the V-doped WO₃ sample were investigated by H₂-TPR, as shown in Fig. 8. In contrast to the TPR profiles of pure WO₃ and V₂O₅, the profile of prepared nanostructures shows three reduction peaks at 525, 630-700, and 734 °C, which could be attributed to reduction of V⁵⁺ \rightarrow V⁴⁺ \rightarrow V³⁺ in hexagonal structure, and W⁶⁺ \rightarrow W⁵⁺, respectively. Similar reduction peaks were observed by Chieregato et al. when tungsten-vanadium oxide catalysts were treated in 10% H₂/Ar mixture up to 800 °C [23]. These further prove that vanadium is successfully incorporated into hexagonal WO₃ framework.

The N_2 adsorption-desorption isotherms of the V-doped hexagonal WO₃ architecture are depicted in Fig. 9. It exhibits a typical hysteresis loop, inferring the nanostructures having mesoporous characteristics [28,29]. The pore size distribution



(inset in Fig. 9) shows a peak centered at around 3.4 nm. The BET surface area of the nanomaterial is $4.3 \text{ m}^2 \text{ g}^{-1}$.

Fig. 9 The N₂ adsorption-desorption isotherms of V-doped WO₃ nanostructures.

Inset is pore size distribution curve.

Table 1 shows the catalytic performances of the prepared V-doped WO₃ nanostructures and SSR-V-W-O sample in the ammoxidation of 3,4-DCT and 2,6-DCT to the corresponding DCBN. In comparison to SSR-V-W-O, although V-doped hexagonal WO₃ catalyst shows lower catalytic activities, it exhibits much higher selective performance and yields of DCBN under identical conditions. In the ammoxidation reaction, V of as active component undergoes process oxidation-reduction reaction; $V=O^{5+}$ catalyzes -CH₃ to aldehyde intermediates; then the acid sites of W with medium to strong acid strength in close proximity to the redox sites (V) adsorb NH₃ and insert nitrogen into the intermediates. On the other hand, WO₃ as support promotes the dispersion of vanadium beneficial to the formation active sites. For SSR-W-V-O catalyst, V is in bulk with stronger oxidizing properties [30,31,32], and shows improper distances to the acid sites of W, thus leading to decreasing efficiency of nitrogen insertion into oxidized aldehyde intermediates. In contrast, the vanadyl species of prepared V-doped WO₃

nanostructures are highly dispersed and incorporated into the framework of hexagonal tungsten bronze; this makes that the acid sites of W are in close proximity to the redox sites of V, facilitating nitrogen insertion [33]. Therefore, the prepared V-doped WO₃ exhibited remarkable improvement of selectivity. The yield and selectivity of 2,6-DCBN obtained over the nanostructural catalyst reach up to 67.6% and 86.2%, respectively. As for 3,4-DCT, it exhibits 72.5% yield with selectivity of 89.9%.

Substrate	Catalyst	<i>T</i> (°C)	Conversion (%)	Yield (%)	Selectivity (%)
3,4-DCT	V-doped WO ₃	380	80.7	72.5	89.8
	SSR-W-V-O	380	89.8	68.4	76.2
2,6-DCT	V-doped WO ₃	390	78.4	67.6	86.2
	SSR-W-V-O	390	83.2	63.1	75.8

Table 1 Catalytic results in the ammoxidation of 3,4-DCT^{*a*} and 2,6-DCT^{*b*}.

^aConditions: 3,4-DCT: air:NH₃ molar ratio 1:25:7, T = 380 °C, GHSV = 363 h⁻¹;

^{*b*}Conditions: 2,6-DCT:air:NH₃ molar ratio 1:20:9, T = 390 °C, GHSV = 315 h⁻¹.

4. Conclusion

In conclusion, V-doped WO₃ microspheres comprising of numerous zero-dimensional nanoblocks were fabricated via a hydrothermal method. SEM and TEM observations suggest the typical nanoblocks have thicknesses of 40-100 nm and widths of about 150 nm. XRD, Raman and SAED confirms the hexagonal lattice structure of WO₃ with vanadium species incorporated inside the framework. The yields of 3,4-DCBN and 2,6-DCBN obtained over the prepared V-doped WO₃ microspheres are 72.5% and 67.6%, corresponding to the selectivities of 89.8% and 86.2%, respectively.

Acknowledgments

This work was partially supported by the National Natural Science Foundation of China (Grant 51572201).

Reference

Author statement

I have made substantial contributions to the conception or design of the work; or the acquisition, analysis, or interpretation of data for the work; And I have drafted the work or revised it critically for important intellectual content; And I have approved the final version to be published; And I agree to be accountable for all aspects of the work in ensuring that questions related to the accuracy or integrity of any part of the work are appropriately investigated and resolved.

All persons who have made substantial contributions to the work reported in the manuscript, including those who provided editing and writing assistance but who are not authors, are named in the Acknowledgments section of the manuscript and have given their written permission to be named. If the manuscript does not include Acknowledgments, it is because the authors have not received substantial contributions from nonauthors.

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No conflict of interest exits in the submission of this manuscript, and manuscript is approved by all authors for publication. I would like to declare on behalf of my co-authors that the work described was original research that has not been published previously, and not under consideration for publication elsewhere, in whole or in part. All the authors listed have approved the manuscript that is enclosed.

Graphical Abstract



This paper investigated the formation of V-doped hexagonal WO_3 microspheres comprising of nanoblocks and the nanomaterial showed significantly improved selective performance in the ammoxidation of dichlorotoluene.

Highlights

- 1. V-doped hexagonal WO₃ microspheres comprising of nanoblocks were prepared.
- 2. The prepared microspheres showed significantly improved selective

performance.

- The selectivities of 3,4-DCBN and 2,6-DCBN reached up to 89.8% and 86.2%, respectively.
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