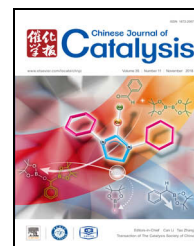


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Article

Solvothermal synthesis and characterization of nanocrystalline vanadium-chromium composite oxides and catalytic ammoxidation of 2,6-dichlorotoluene

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ARTICLE INFO

Article history:

Received 12 April 2018

Accepted 1 June 2018

Published 5 November 2018

Keywords:

CrVO₄

Nanocrystalline material

Composite oxide

Solvothermal synthesis

Ammoxidation

ABSTRACT

Vanadium-chromium oxides (VCrO) were usually prepared by high-temperature solid-state reactions; however, mixed phases were frequently produced and the morphology of the products was not well controlled. In this work, we prepared amorphous VCrO precursors by using V₂O₅ and CrO₃ and alcohols or mixtures of alcohol and water via solvothermal reaction at 180 °C. The precursors were then calcined under nitrogen at various temperatures. The products were characterized by powder X-ray diffraction, transmission electron microscopy, and X-ray photoelectron spectroscopy. It was revealed that pure-phase nanocrystalline orthorhombic CrVO₄ was obtained when methanol or methanol/water was used as the solvothermal medium and the precursor was calcined at 700 °C. The size of the CrVO₄ crystals was around 500 nm when methanol was used, whereas it reduced significantly to less than 50 nm when a mixture of methanol and water was used. The sizes could be effectively tuned from 10 to 50 nm by varying the methanol/water volume ratio. To the best of our knowledge, this is the first report on the synthesis of pure-phase CrVO₄ nanocrystals. The nano-CrVO₄ showed almost the highest catalytic activity for the ammoxidation of 2,6-dichlorotoluene to 2,6-dichlorobenzonitrile among the reported bi-component composite oxides, owing to its smaller particle size, larger specific surface area, and more exposed active centers.

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1. Introduction

Ammoxidation of alkyl aromatics and heteroaromatics to their corresponding aromatic nitriles has been considered another significant breakthrough in the chemical industry after

the ammoxidation of propylene to acrylonitrile, and has attracted a great deal of attention [1–21] because the nitriles are very useful organic intermediates for the preparation of a good number of industrially important chemicals such as aromatic acids, amides, amines and so on, which provide raw materials

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This work was supported by the National Natural Science Foundation of China (21172269), Innovation Group of Hubei Natural Science Foundation (2018CFA023) and Opening Project of Key Laboratory of Optoelectronic Chemical Materials and Devices, Ministry of Education, Jiangnan University (JGDG-201809).

DOI: 10.1016/S1872-2067(18)63119-5 | <http://www.sciencedirect.com/science/journal/18722067> | Chin. J. Catal., Vol. 39, No. 11, November 2018

for further production of pharmaceuticals, pesticides, pigments, dyes, rubbers, and optoelectronic materials. Gas-phase ammoxidation of 2,6-dichlorotoluene (DCT) to 2,6-dichlorobenzonitrile (DCBN) is of particular importance owing to the high industrial significance of DCBN for manufacturing many effective herbicides, fungicides, and various special kinds of engineering plastics [15–21]. Nevertheless, the realization of this reaction with high conversion and yield remains a challenging task and is much more difficult compared to the ammoxidation of various other alkyl aromatics and heteroaromatics due to steric hindrance of the reacting methyl group by two neighboring bulky chlorine atoms.

Martin *et al.* [18–21] have used vanadium phosphates (VPO) as catalysts to successfully ammoxidize DCT to DCBN with almost 99% conversion and *ca.* 70% yield at 400–420 °C. Our group has been committed to developing highly active and selective catalysts and effective strategies for the ammoxidation of methyl aromatics to the corresponding aromatic nitriles [1–5,15–17], and has studied the catalytic performances of silica-supported vanadium-phosphorus oxides (VPO/SiO₂) [15,16] and vanadium-chromium oxides (VCrO/SiO₂) [17] for the ammoxidation of DCT to DCBN.

Vanadium-chromium composite oxides (VCrO) have been the subject of extensive research because of their use in a wide range of applications such as heterogeneous catalysis [1–9,22,23], gas sensing [24], and energy storage [25,26]. They were traditionally prepared by high-temperature solid-state reactions between pure oxide components. Depending on the reaction conditions, various phases such as CrVO₄ [27], Cr(VO₃)₃ [28], Cr₄(V₂O₇)₃ [29], and Cr₂V₄O₁₃ [30] may occur. Among these, CrVO₄ has been widely used as an oxidation catalyst in some important industrial reactions, including oxidation of benzene to maleic anhydride or methanol to formaldehyde and the ammoxidation of aromatic compounds [1–9,14,31]. CrVO₄ has three different crystal structures, namely orthorhombic, monoclinic, and tetragonal [32]. Orthorhombic CrVO₄ has been obtained by heating an amorphous precursor, CrVO₄·3H₂O, at 450 °C, whose precursor was synthesized by the reaction of solutions of ammonium vanadate (NH₄VO₃) and chromium nitrate [Cr(NO₃)₃·9H₂O] [33]. It could also be prepared by grinding a mixture of hydrous amorphous chromium oxide and vanadium oxide [34]. However, mixed phases of VCrO complexes were produced in these cases and the particle sizes were not well controlled. When used in an oxidation or ammoxidation reaction, a high temperature was required and resulted in the over-oxidation of the raw material as well as the deposition of carbon and loss of activity over time [27].

Recently, Huang *et al.* [6] reported the synthesis of sphere-like amorphous VCrO particles several micrometers in size and studied their catalytic performance for the ammoxidation of dichlorotoluenes. It was found that the size and morphology of the solid catalysts could influence the catalytic behaviors significantly. However, to the best of our knowledge, no literature about nano-sized crystalline CrVO₄ has been reported. Here, we present a facile solvothermal route to synthesize pure-phase nanocrystalline orthorhombic CrVO₄ for the first

time, which exhibited excellent catalytic performance for the ammoxidation of DCT with high conversion and yield at a relatively low temperature.

2. Experimental

2.1. Materials and procedure

All reagents used in the experiments were of analytical grade and purchased locally. In a typical synthesis, (1) 0.01 mol (1.82 g) of V₂O₅ powder, 0.02 mol (2.0 g) of CrO₃ powder, and 80 mL methanol were successively added to a 100-mL Teflon-lined autoclave, stirred and mixed thoroughly, and then heated at 180 °C for 24 h. After cooling to room temperature, the dark-green mixture was separated by filtration and washed with distilled water and absolute ethanol several times. The residue was vacuum dried at 60 °C for 5 h to afford a precursor. Appropriate amounts of the precursors were then placed in quartz boats and calcined in a tube furnace under nitrogen atmosphere (more than 99% pure nitrogen was introduced) for 2 h at 200, 300, 400, 500, 600, and 700 °C, respectively. (2) Methanol was replaced with ethanol, isopropanol, or methanol/water (1:1 V/V) and the above procedure was repeated and the precursor was calcined at 400, 500, 600, and 700 °C, respectively.

2.2. Characterization

X-ray powder diffraction (XRD) was performed on a Bruker D8 X-ray diffractometer with Cu K_α radiation, λ = 0.154 nm. X-ray photoelectron spectroscopy (XPS) was conducted on a VG Multilab 2000 X XPS spectrometer. The morphology of the powder particles was examined using a TECNAI G2 20 S-TWIN transmission electron microscope (TEM).

2.3. Ammoxidation of 2,6-dichlorotoluene

The catalytic reactions were conducted in a fixed-bed micro-reactor equipped with a 30-mm inner diameter glass tube loaded with 10 g of nanocrystalline CrVO₄. DCT was injected into the vaporizer by a micro-injection pump, and the vaporized reactant was then mixed with ammonia and air and fed into the reactor. The outlet stream was cooled and the products were condensed to solid in a condensing apparatus. Test runs were carried out at different conditions by varying the temperature, space velocity of the reactant, and the molar ratios of ammonia and air to DCT. The product steam was collected every 30 min after attaining steady state conditions and then analyzed off-line by gas chromatograph. The chemical reaction of DCBN synthesis by the ammoxidation of DCT is shown in Scheme 1.

3. Results and discussion

3.1. Synthesis of the V–Cr–O precursor

The precursor prepared by the solvothermal reaction of

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