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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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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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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, $\lambda = 0.154$ 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

Scheme 1. Preparation of DCBN by ammoxidation of DCT using nano-VCrO catalyst.

V₂O₅, CrO₃, and methanol at 180 °C for 24 h was characterized by XRD. There were no diffraction peaks in the XRD patterns, suggesting that no crystal phases were formed at this stage. Replacing methanol with ethanol or isopropanol, extending the reaction time to 48 h, or raising the solvothermal temperature to 200 °C did not alter the amorphousness of the precursors (powder XRD patterns not shown).

3.2. Production of V–Cr–O

The methanol-reduced vanadium-chromium oxide precursor was placed in quartz boats and calcined in a tube furnace under nitrogen atmosphere for 2 h at 200, 300, 400, 500, 600, and 700 °C, and their XRD patterns are shown in Fig. 1. Diffraction peaks began to appear at 400 °C (Fig. 1(3)), indicating the formation of crystal phases. At 500 °C, sharp peaks corresponding to Cr₂V₄O₁₃ (Fig. 1(4), black dot indicated) and tetragonal CrVO₄ (Fig. 1(4), star indicated) could be distinguished. At 600 °C, significant amounts of orthorhombic CrVO₄ (Fig. 1(5), black triangle indicated) were produced, and a small amount of tetragonal CrVO₄ phase was still present. The assignment of these peaks was referred to PDF cards PDF#51-0445, PDF#15-0296, and PDF#38-1376, respectively. At 700 °C, however, only well-resolved orthorhombic CrVO₄ peaks were observed (Fig. 1(6)), suggesting the production of pure-phase crystalline orthorhombic CrVO₄. The diffraction pattern well matches the PDF card (#38-1376) of orthorhombic CrVO₄ and the peaks were indexed accordingly.

Fig. 1. XRD patterns of V–Cr–O samples using methanol as solvothermal medium and calcined at various temperatures. (1) 200 °C, (2) 300 °C, (3) 400 °C, (4) 500 °C, (5) 600 °C, (6) 700 °C.

Precursors using ethanol and isopropanol as solvothermal media were subsequently produced and calcined at 400, 500, 600, and 700 °C. Crystal phases began to appear at 400 °C, and at 700 °C, the major products were still orthorhombic CrVO₄; however, a small amount of another phase, probably CrVO₃, still remained (Fig. 2). In contrast, replacing methanol with mixtures of methanol and distilled water (volume ratio of 1:1) produced pure-phase orthorhombic CrVO₄ (Fig. 2(3)).

3.3. Morphology of the precursor and the calcined powder

The amorphous state of the precursor and the crystalline nature of the orthorhombic CrVO₄ powder were substantiated by TEM measurement. Fig. 3(a), (b), (c) and (d) show the TEM micrographs of the methanol-reduced precursor and calcined powders, respectively. The TEM image of the precursor (Fig. 3(a)) is typical of an amorphous solid, with a particle size of around 20 nm. When calcined at 500 °C, regularly shaped rod-like and cube-like nanocrystals around 100 nm in size were formed (Fig. 3(b)). Raising the calcination temperature to 600 °C and 700 °C led to further growth of the crystallites to about 200 and 500 nm, respectively (Fig. 3(c) and (d)).

The addition of water to methanol produced well-crystalline CrVO₄, and greatly reduced the size of the CrVO₄ nanocrystals. Moreover, the size could be effectively tuned by the methanol/water ratio (Fig. 3(e)–(h)). When a 10:1 ratio was used, well-crystalline particles with ~50-nm diameter were produced (Fig. 3(e)). The particle sizes further decreased to ~30, ~20, and ~10 nm, respectively, when the volume ratios decreased to 5:1, 1:1, and 1:5 (Fig. 3(f), (g), and (h)). The addition of water to the hydrothermal medium is expected to decrease the concentration of methanol as well as its reducing ability; thus, the growth of crystals may be impeded, resulting in the production of finer nanoparticles. Ethanol or mixtures of ethanol/water as a reducing reagent to synthesize transition metal oxides have occasionally been reported, and it was found that the ratio of ethanol/H₂O had significant effects on the mor-

Fig. 2. XRD patterns of V–Cr–O samples using (1) ethanol, (2) isopropanol, and (3) methanol/water (1:1 V/V) as solvothermal media and calcined at 700 °C.

Fig. 3. TEM micrographs of the precursor and calcined powders. (a) Precursor, (b) 500 °C, (c) 600 °C, (d)–(i) 700 °C. (a)–(d) were produced using methanol; (e)–(h) were produced using methanol/water: (e) 10:1 (V/V), (f) 5:1 (V/V), (g) 1:1 (V/V), (h) 1:5 (V/V); (i) was produced using $\text{H}_2\text{C}_2\text{O}_4$ solution.

phology and composition of the as-obtained products [35].

In comparison, calcination of the respective oxalates, i.e., using V_2O_5 , CrO_3 , and $\text{H}_2\text{C}_2\text{O}_4$ solutions as the starting materials by a similar hydrothermal approach produced micrometer-sized crystals ($\sim 1 \mu\text{m}$ in diameter, Fig. 3(i)).

3.4. XPS study of CrVO_4 nanocrystals

The chemical states of the elements in the precursor and V–Cr–O complexes calcined at various temperatures were studied by XPS. The spectra were taken on a VG Multilab 2000 XPS spectrometer and calibrated using the C 1s peak (284.6 eV) arising from carbon contamination. As shown in the survey spectrum (Fig. 4), the CrVO_4 nanocrystal showed peaks at about 586, 577, 530, 517, and 285 eV corresponding to Cr $2p_{1/2}$,

Fig. 4. XPS survey spectrum of CrVO_4 nanocrystal (calcined at 700 °C).

Fig. 5. Normalized XPS spectra (Cr $2p$) of the precursor (1) and V–Cr–O complexes calcined at 300 (2), 400 (3), 500 (4), 600 (5), and 700 °C (6).

Cr $2p_{3/2}$, O 1s, V $2p_{3/2}$, and C 1s, respectively.

The high-resolution spectra of the Cr and V + O regions are presented in Figs. 5 and 6, respectively. The data were processed using the XPS Peak41 package as shown in Fig. 7, with the detailed results summarized in Table 1. The fittings of V $2p$ are combined with the O 1s region as G. Silversmit *et al.* [36] suggested because this fit model is significantly better than fitting without the O 1s region included. The binding energies (BE) of Cr $2p_{1/2}$ and Cr $2p_{3/2}$ showed no appreciable differences and appeared at 586.2 and 576.6 eV, respectively, well consistent with the Cr^{3+} oxidation state [37,38]. The V $2p_{1/2}$ and V $2p_{3/2}$ signals were observed at ~ 522 and ~ 516 eV initially and shifted to 526.5 and 516.9 eV, respectively, when the calcination temperature was raised to 700 °C. The results suggested that chromium was reduced to Cr^{3+} after the solvothermal reaction, but vanadium did not fully convert to V^{5+} oxidation state until calcination at 700 °C [36–38].

3.5. Possible reaction mechanism

The possible solvothermal reaction mechanism is shown in

Fig. 6. Normalized XPS spectra (V $2p$ and O 1s) of the precursor (1) and V–Cr–O complexes calcined at 300 (2), 400 (3), 500 (4), 600 (5), and 700 °C (6).

Fig. 7. High-resolution XPS spectra of Cr 2p, O 1s, and V 2p regions.

Scheme 2. Methanol reduced the chromium from hexavalent to trivalent state to form nanocrystalline orthorhombic CrVO_4 with vanadium oxides.

3.6. Ammoxidation of 2,6-dichlorotoluene

DCBN is an important fine chemical and can be prepared by the gas-phase ammoxidation of DCT. However, only a few papers were dedicated to this route and low yields were often obtained due to the low reactivity of the methyl group from the steric hindrance of the two neighboring bulky and electron-withdrawing chlorine atoms. Most of the catalysts for the ammoxidation of DCT were focused on VPO [15,16,18–21]. In this work, nanocrystalline CrVO_4 produced by solvothermal reaction was found to have interesting catalytic performance for the ammoxidation of DCT to DCBN. The findings along with some typical literature results are listed in Table 2.

From Table 2, it was found that the composition and structure of the catalysts could exert great influence on the catalytic behavior. For example, unsupported VPO catalysts showed weak catalytic activity toward ammoxidation of DCT even at very high temperatures (Entry 1 and 3, Table 2), while the activity could be considerably improved as the VPO catalysts were loaded on supports such as SiO_2 , Al_2O_3 , or TiO_2 (Entry 2, 4, and 5, Table 2), probably owing to the larger specific surface areas and more exposed active centers. Furthermore, some micro- or nano-sized composite oxides may exist on the supports.

Table 1

BE of V 2p, Cr 2p, and O 1s and the fitting parameters.

Core line	Precursor	Calcined V–Cr–O Powders				
		300 °C	400 °C	500 °C	600 °C	700 °C
V 2p _{3/2}	516.2	516.8	516.4	515.9	516.3	516.9
V 2p _{1/2}	522.6	524.2	523.7	523.1	523.3	526.5
O 1s	530.6	530.1	530.0	529.9	529.6	529.9
Cr 2p _{3/2}	576.5	576.8	576.4	576.5	576.5	576.6
Cr 2p _{1/2}	586.2	586.6	586.1	586.2	586.3	586.3

Scheme 2. Possible solvothermal reaction mechanism.

The nano- CrVO_4 exhibited excellent catalytic activity for the ammoxidation of DCT even at relatively low temperatures. At 335 °C, the conversion of DCT is 84%, and the yield and selectivity of DCBN were 75% and 89%, respectively (Entry 7, Table 2). The nano- CrVO_4 catalyst exhibited (5–6)% higher conversion and yield with similar selectivity compared with those of the micro-sized V–Cr–O catalysts reported by Huang's group (Entry 6, Table 2). When the temperature was raised to 390 °C, the conversion of DCT and the yield of DCBN increased to 99% and 81%, respectively (Entry 8, Table 2), which was almost the highest activity for ammoxidizing DCT to DCBN among the reported bi-component composite oxides. In contrast, the micro- CrVO_4 that we prepared by solvothermal reaction using $\text{H}_2\text{C}_2\text{O}_4$ solution as a reducing agent showed a similar catalytic activity compared to the micrometer-sized V–Cr–O reported by Huang's group (Entry 9 vs. 6, Table 2). The excellent catalytic performances of the nanostructured VCrO were thus attributable to the very small particle sizes, which led to high surface

Table 2

Catalytic performances of different catalysts for ammoxidation of DCT^a.

Entry	Catalyst	T (°C)	Conversion (%)	Yield (%)	Selectivity (%)	Ref.
1	$(\text{NH}_4)_2[(\text{VO})_3(\text{P}_2\text{O}_7)_2]$	420	50	18	36	[39]
2	VPO/ $\gamma\text{-Al}_2\text{O}_3$	400	99	71	72	[18]
3	Bulk VPO	440	92	55	60	[18]
4	VPO/ SiO_2	380	87	57	66	[15]
5	VPO/ SiO_2	400	90	57	63	[16]
6	V–Cr–O	335	78	70	90	[6]
7	Nano- CrVO_4	335	84	75	89	This work ^b
8	Nano- CrVO_4	390	99	81	82	This work ^b
9	Micro- CrVO_4	335	77	68	88	This work ^c
10	Micro- CrVO_4	390	92	73	79	This work ^c

^a The catalytic performance as characterized by conversion, yield, and selectivity. The conditions of the ammoxidation reactions were as follows: 300 space velocity (SV, the volume of a gas reactant passed through a unit volume of catalyst in unit time, h^{-1}), $n(\text{Air})/n(\text{DCT}) = 30$, $n(\text{NH}_3)/n(\text{DCT}) = 9$.

^b Nano- CrVO_4 was produced using 1:1 methanol/water mixture and then calcined at 700 °C.

^c Micro- CrVO_4 was prepared using $\text{H}_2\text{C}_2\text{O}_4$ as a reducing agent and then calcined at 700 °C.

areas and exposed a large amount of active centers.

4. Conclusions

Pure-phase nanocrystalline orthorhombic CrVO_4 was obtained through calcination of an amorphous precursor, which was produced from the solvothermal reaction using V_2O_5 and CrO_3 as raw materials and either methanol or mixtures of methanol and water as the reducing agent. When using mixtures of methanol and water, CrVO_4 crystals with much smaller size were produced and the size could be effectively tuned from 10 to 50 nm by changing the methanol/water volume ratio. The nano- CrVO_4 could catalyze the ammoxidation of DCT to produce DCBN with high catalytic activity at relatively low temperatures owing to its very small particle sizes and large specific surface areas.

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Graphical Abstract

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- Pure phase CrVO_4 nanocrystals were synthesized for the first time.
- The size of the CrVO_4 could be effectively tuned from 10 to 50 nm.
- The nano- CrVO_4 showed the highest activity among the bi-component composite oxides.

Nano- CrVO_4 was obtained for the first time through solvothermal reaction of V_2O_5 and CrO_3 in either methanol or methanol/water mixtures at 180 °C to prepare the precursor followed by calcination at 700 °C, which showed almost the highest catalytic activity among the bi-component composite oxides reported for the ammoxidation of 2,6-dichlorotoluene to 2,6-dichlorobenzonitrile.

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纳米钒铬复合氧化物的溶剂热合成、表征及催化2,6-二氯甲苯氨氧化反应

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摘要: 甲基芳烃气相氨氧化反应制备对应的芳香腈被认为是丙烯氨氧化制备丙烯腈之后化工领域又一重大进展, 芳香腈是重要的精细化学品, 广泛应用于医药、农药、颜料、染料、橡胶、光电材料等领域。其中2,6-二氯甲苯氨氧化反应制备2,6-二氯苯腈是特别重要的反应, 2,6-二氯苯腈工业上可用于制备高效除草剂、杀菌剂及各种特种工程塑料; 然而相较于其它的甲基芳烃, 2,6-二氯甲苯由于甲基邻位有两个较大位阻且较强吸电子的氯原子影响, 甲基活性较低, 较难发生氨氧化反应, 原料转化率和产品收率均较低。本课题组一直致力于发展高活性和选择性的氨氧化催化剂以及有效的策略实现甲基芳烃高效转化为芳香腈, 我们曾以硅胶负载的钒磷氧化物(VPO/SiO₂)和钒铬氧化物(VCrO/SiO₂)为催化剂, 成功实现了2,6-二氯甲苯氨氧化反应制备2,6-二氯苯腈。

钒铬复合氧化物(VCrO)具有广泛的应用, 可用于多相催化、气体传感、能量储存等领域。VCrO通常通过高温固相反应制备, 然而一般得到的是混合相, 产品形态和颗粒大小也不能很好控制; 当用于氧化或氨氧化反应时, 需要较高的反应温度, 原料也容易发生过度氧化, 导致积碳及活性降低。

我们以V₂O₅和CrO₃为原料, 在醇或者醇水溶液中于180 °C进行溶剂热反应制备了无定形的VCrO前驱体, 然后将前驱体在不同温度下氮气气氛中煅烧, 产品通过粉末X射线衍射、透射电镜和X射线光电子能谱等进行表征。当以甲醇或甲醇水溶液为溶剂热反应介质, 并且前驱体700 °C进行煅烧后, 产品为纯的正交晶系CrVO₄纳米晶相; 当以甲醇为溶剂时, CrVO₄晶相的尺寸大约为500 nm; 而改为甲醇水溶液为溶剂时, 产品尺寸急剧减小到50 nm以下, 而且通过改变甲醇和水的体积比分别为10:1, 5:1, 1:1和1:5时, CrVO₄纳米晶相的尺寸从50 nm逐渐减小到30, 20和10 nm, 能够进行有效调控。据我们所知, 这是首次合成纯的CrVO₄纳米晶相。我们以该纳米CrVO₄为催化剂催化2,6-二氯甲苯氨氧化反应制备2,6-二氯苯腈, 在335 °C的相对较低温度下反应, 原料转化率为84%, 产品收率为75%; 进一步升高温度到390 °C, 原料转化率为99%, 产品收率可达81%。在所有已报道的二元复合氧化物催化剂中, 纳米CrVO₄显示了最高的催化活性, 主要归功于它较小的粒子尺寸、较大的表面积和更多暴露的活性中心。

关键词: CrVO₄; 纳米晶相材料; 复合氧化物; 溶剂热合成; 氨氧化

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