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ARTICLE

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Investigation of $BiVO_4$ structure variations on the dichlorotoluene ammoxidation performance

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Abstract

In this study, $BiVO_4$ synthesized by hydrothermal and calcination methods were explored as catalysts in the ammoxidation of dichlorotoluenes to shed light on the structure-reactivity correlations. The $BiVO_4$ samples were characterized by X-ray diffraction (XRD), temperature-programmed reduction (TPR), Brunauer–Emmett–Teller (BET), and UV–Vis spectrophotometry. The results showed that the catalytic activity of $BiVO_4$ greatly relied on the structure variations. The hydrothermal prepared $BiVO_4$ exhibited better catalytic activities as a consequence of its greater structure deformation, with maximum yields of 73.1, 72.2, and 70.8% for 3,4-, 2,4- and 2,6- dichlorobenzonitrles, respectively.

KEYWORDS

ammoxidation, $BiVO_4$, structure deformation

1 | INTRODUCTION

Ammoxidations are industrially important reactions due to that the product nitriles are widely used as organic intermediates to prepare lots of industrially important chemicals.[1,2] Statistically, approximately 1,500 papers and more than 1,200 patents have appeared in the literature on various ammoxidation reactions during the last 50 years.[3] Ammoxidation of 3,4-, 2,4- and 2,6-dichlorotoluenes (DCTs) are of high significance, since the target products 3,4-, 2,4- and 2,6-dichlorobenzonitrles (DCBNs) are valuable intermediates for the industrial production of a series of pesticides and many agricultural chemicals such as chlorfluazuron, flufenoxuron, and flucycloxuron.[4–6] In addition, DCBNs are used to prepare a kind of special engineering plastics with high heat-resistant properties.[5] However, it is noted that the direct synthesis of DCBN from DCT in the presence of ammonia and oxygen with high yield is somewhat a difficult process compared to the ammoxidation of other alkyl aromatics and hetero aromatics, because of the steric hindrance caused by the two bulky chlorine atoms.[4,6] This contributes to that only a few papers and patents were dedicated to this route.[7]

In the past few decades, most of the catalysts for the ammoxidation of DCT have been focused on vanadium phosphorus oxides (VPO)-based catalysts.[4,8–11] It was reported that the yields of DCBN obtained over these catalysts were very low; and after they were loaded on supports such as SiO_2, the overall catalytic performance could be improved to some extent, but remained unsatisfactory. On the other hand, Al/V, Ti/V, V/Cr etc. oxides are generally very active, leading to low selective performance. Recently, bismuth vanadate oxides ($BiVO_4$) have been reported to show high catalytic performance among the mental oxide catalysts for the ammoxidation of methyl aromatics or heteroaromatics to nitriles.[12–14] In addition, Bi-based catalysts have been widely synthesized and studied.[15–19] However, studies on analyzing the correlations between structure variations of $BiVO_4$ and catalytic activities have not been reported.

In this contribution, $BiVO_4$ were prepared by hydrothermal and calcination methods. The ammoxidation reactions of DCTs to DCBNs were performed on the $BiVO_4$ catalysts to investigate the structure-reactivity correlations.

2 | RESULTS AND DISCUSSION

The phase structures of as-synthesized $BiVO_4$ catalysts were characterized by XRD, as shown in Figure 1. Inset shows the enlargement of 17°–20° patterns. It can be seen that the diffraction peaks of H-$BiVO_4$ catalyst can be perfectly indexed to the monoclinic scheelite $BiVO_4$ (JCPDS No. 75-1867). In contrast, the peaks attributed to tetragonal scheelite $BiVO_4$ (JCPDS No. 01-078-1535) were detected for sample S-$BiVO_4$, along with the peaks representing monoclinic scheelite $BiVO_4$. It is well known that monoclinic scheelite shows a reversible phase transition to tetrahedral form at 255°C.[20] It indicates that the high-temperature calcinations modified the structure deformation of the H-$BiVO_4$ catalyst, that is, S-$BiVO_4$ was in an intermediate state between monoclinic and tetragonal scheelite, which will be further confirmed below.

To investigate the structure variations, UV–vis absorption spectra were performed in the temperature range of 25–280°C, as shown in Figure 2. As temperature is increasing, the absorption edges of both as-prepared $BiVO_4$ catalysts shift continuously to the longer wavelengths (i.e., red-shift). This is corresponding to the process of monoclinic $BiVO_4$ transforming to the tetragonal phase.[21] And above 250°C, the absorption edge no longer shifts as a consequence of finished phase transition. Comparatively, it is interesting to note that the total red-shift of the H-$BiVO_4$ catalyst is larger than that of S-$BiVO_4$. This clearly reflects that H-$BiVO_4$ has a greater degree of structure deformation compared to S-$BiVO_4$, which is well consistent with the XRD analysis.

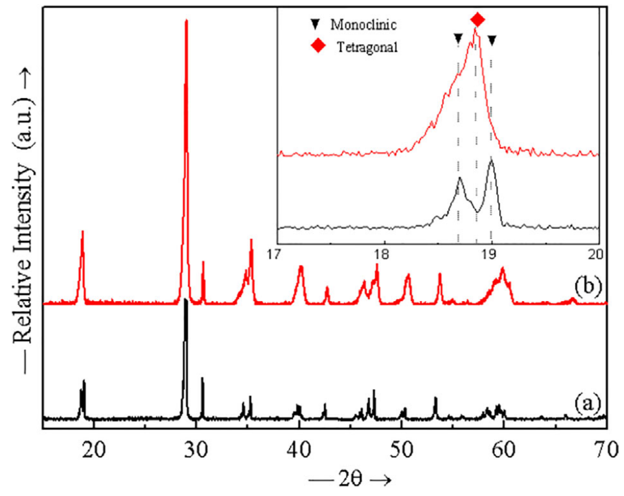


FIGURE 1 XRD patterns of as-prepared catalysts: (a) H-$BiVO_4$, (b) S-$BiVO_4$. Inset shows the enlargement of 17°–20° patterns

The BET surface area and pore parameters of $BiVO_4$ catalysts are shown in Table 1. It can be seen that the

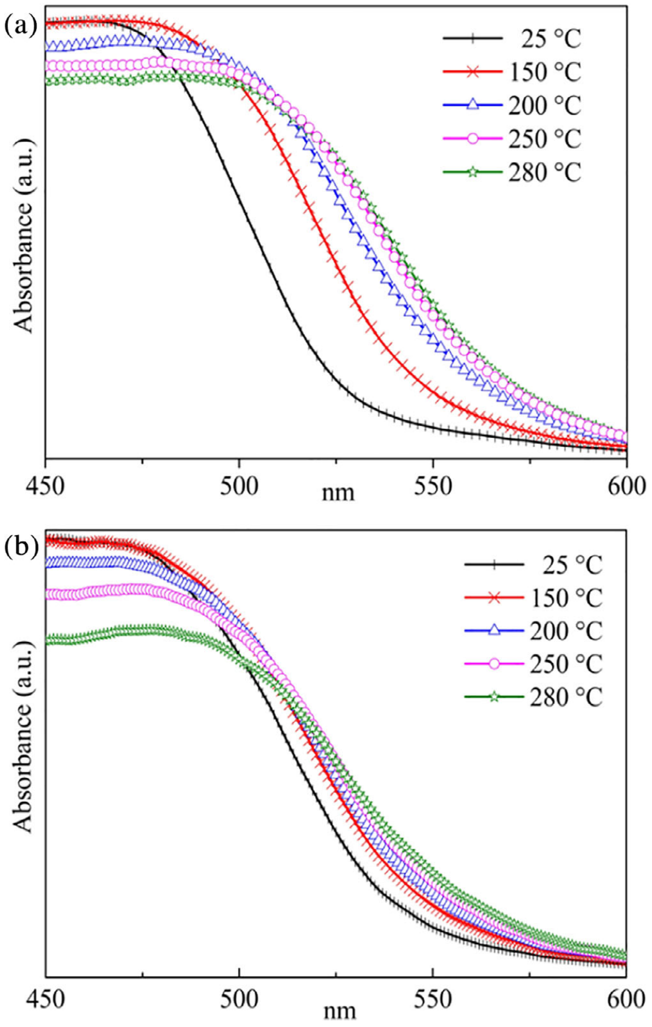


FIGURE 2 Temperature-dependent UV–vis diffuse reflectance spectra of as-obtained catalysts: (a) H-$BiVO_4$, (b) S-$BiVO_4$

TABLE 1 BET surface area and pore parameters of as-prepared $BiVO_4$ catalysts

Sample	Surface area (m^2/g)	Average pore size (nm)
H-$BiVO_4$	3.6	10.56
S-$BiVO_4$	1.8	8.89

samples appear similar in surface area and average pore size, which cause no difference in catalytic performance.

In order to investigate the redox properties of as-prepared $BiVO_4$ catalysts, H_2-TPR experiments were performed, as shown in Figure 3. It can be seen that both $BiVO_4$ catalysts show a maximum reduction peak in the range 450–650°C attributed to the simultaneous reduction of Bi^{3+} and V^{5+} to Bi^0 and V^{3+}. Compared to the S-$BiVO_4$ catalyst, H-$BiVO_4$ shows a lower reduction temperature, indicating enhanced capabilities of oxygen anions free from metal cations due to a greater degree of structure deformation.[14,22]

The catalytic results obtained over as-prepared $BiVO_4$ catalysts in the ammoxidation of 2,6-DCT to 2,6-DCBN are shown in Figure 4. It can be seen that H-BiVO4 shows higher catalytic activities than S-$BiVO_4$ under identical conditions. These results reveal that the activity of $BiVO_4$ catalyst strongly depends on the reduction performance which is greatly related to the structure variations. Earlier, we have deeply studied the structure deformation of $BiVO_4$, it has been found that greater structure distortion leads to better thermochromic performance.[21] In addition, Yu et al.[23] reported the degree of structure distortion of BiVO4 providing a significant effect on the photocatalytic performance. Based on these, the better catalytic performance of H-$BiVO_4$ catalyst is attributed to the greater structure deformation. Under optimum conditions, the H-$BiVO_4$ catalyst exhibits a maximum 2,6-DCBN yield of 70.8% with a conversion of 83.3%, as a result of a larger distortion of structure.

Furthermore, the catalytic performance of the $BiVO_4$ catalysts was also investigated in the ammoxidation of 3,4- and 2,4-DCT, as shown in Figure 5 and Figure 6, respectively. It can be seen that the catalytic activities of H-BiVO4 catalyst are higher than those of S-BiVO4 under identical conditions. The best yields of 3,4- and 2,4-DCBN obtained over H-$BiVO_4$ are higher than that over the S-$BiVO_4$ catalyst, reaching up to 73.1 and 72.2% with corresponding conversions of 89.1 and 85.6%, respectively.

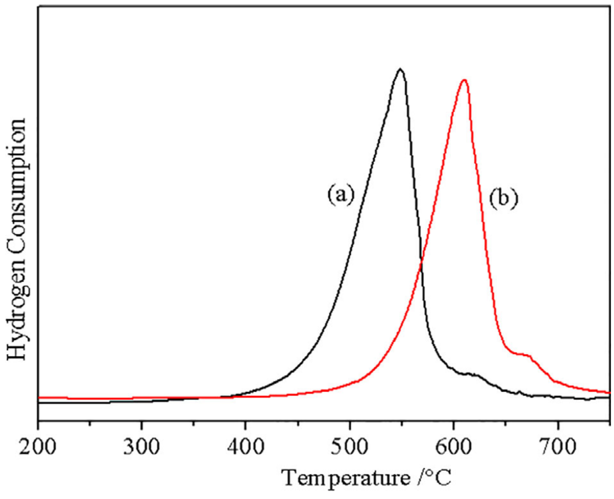


FIGURE 3 H_2-TPR profiles of as-obtained (a) H-$BiVO_4$ and (b) S-$BiVO_4$ catalysts

3 | EXPERIMENTAL

3.1 | Preparation of $BiVO_4$

In a typical process, 4.850 g of $Bi(NO_3)_3 \cdot 5H_2O$ and a certain amount of concentrated HNO_3 were dissolved in 200 ml of distilled water to obtain Bi-solution; meanwhile, V-solution was prepared by stirring 0.91 g of V_2O_5 and 12 ml of H_2O_2 in deionized water for 6 hr. Then, the Bi-solution was added dropwise into the V-solution, with PH settled at 11 by adding ammonia solution. The mixture was sealed in a 500 ml stainless steel autoclave and heated at 180°C for 16 hr. The products were filtered, washed, and dried at 75°C for 12 hr. The obtained samples were denoted as H-$BiVO_4$. Additionally, some of the H-$BiVO_4$ products were calcined at 650°C for 10 hr, denoted as S-$BiVO_4$.

3.2 | Characterization

X-ray diffraction (XRD) patterns of samples were recorded on a D8 X-ray diffractometer with a Cu Kα radiation source, λ = 1.54060 Å. The redox property of the catalysts were studied by temperature-programmed reduction (TPR) on a TP-5080 adsorption instrument (TianJin XianQuan Co., gas composition: H_2 (3 ml/min) and N_2 (27 ml/min), heating rate: 10°C/min). Temperature-dependent UV–vis absorption spectra were collected by adding a heater at the sample holder on a Shimadzu UV-3600 spectrophotometer using $BaSO_4$ as reference. The specific surface area was examined by Brunauer–Emmett–Teller (BET) N_2 gas adsorption method at 77 K and carried out on JW-BK equipment.

3.3 | Catalytic activity evaluation

The ammoxidation of DCTs were carried out in a quartz tube fixed-bed with 30 mm inside diameter at atmospheric pressure.[24,25] In a typical experiment, 5 g of $BiVO_4$ catalyst was loaded. The tests were carried out at different conditions by varying the temperature, space velocity (GHSV) of the reactant, and the molar ratios of air and ammonia to DCT. The flow rates of ammonia and

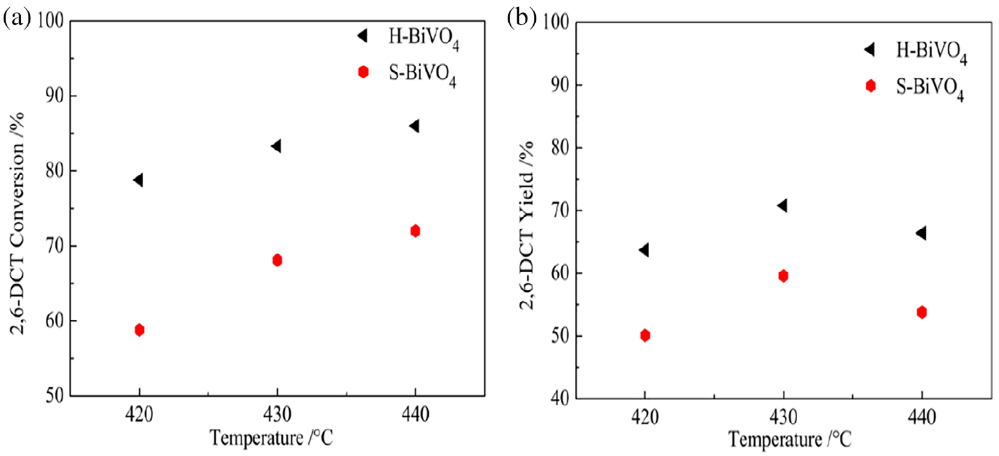


FIGURE 4 Conversion (a) and yield (b) performance of the $BiVO_4$ catalysts in the ammoxidation of 2,6-DCT; molar ratio of 2,6-DCT: air: $NH_3 = 1:25:7$, GHSV = 126 h^{-1}

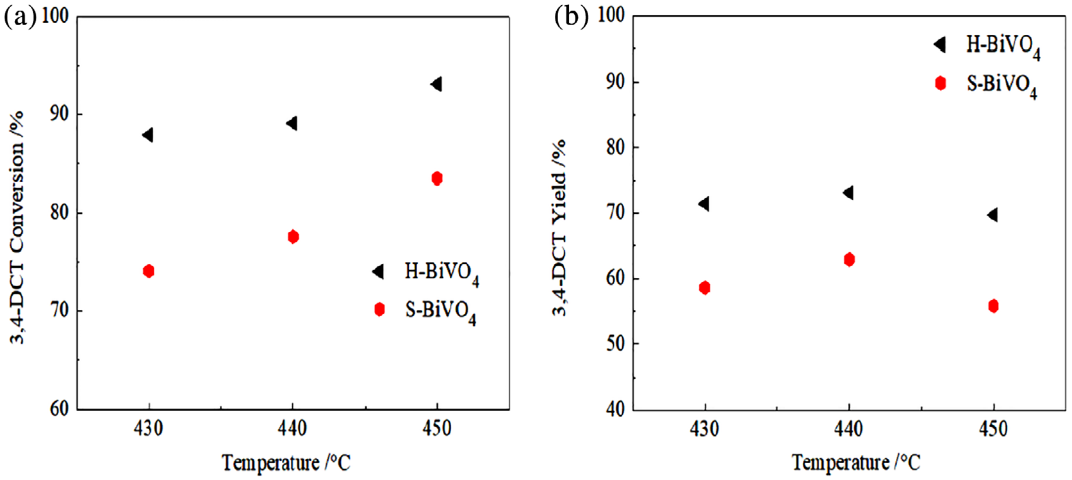


FIGURE 5 Conversion (a) and yield (b) performance of the $BiVO_4$ catalysts in the ammoxidation of 3,4-DCT; molar ratio of 3,4-DCT: air: $NH_3 = 1:25:9$, GHSV = 220 h^{-1}

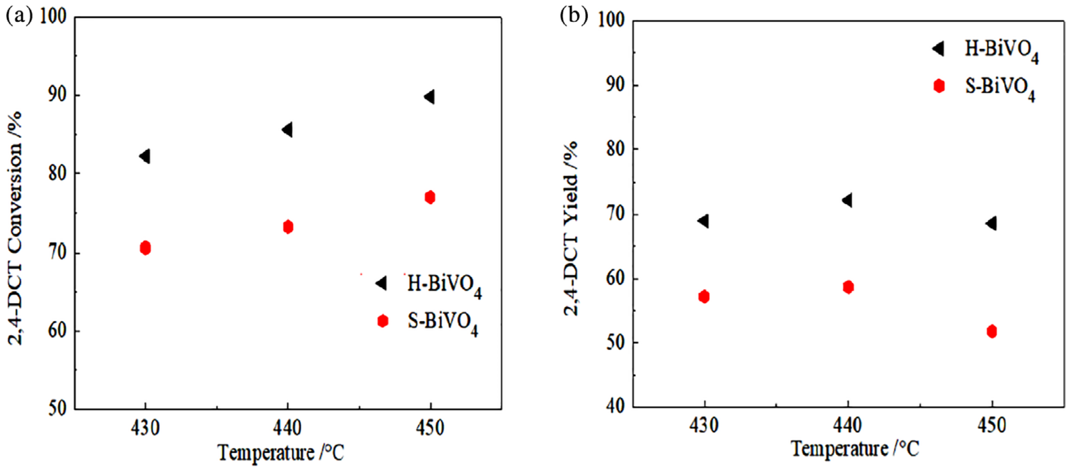
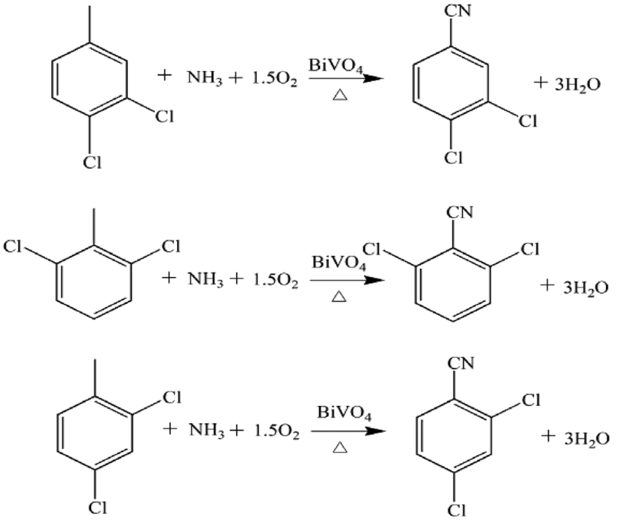


FIGURE 6 Conversion (a) and yield (b) performance of the $BiVO_4$ catalysts in the ammoxidation of 2,4-DCT; molar ratio of 2,4-DCT: air: $NH_3 = 1:20:7$, GHSV = 176 h^{-1}

air were adjusted by gas flowmeters, and the liquid DCTs were introduced by a micropump, vaporized, and mixed in a preheated vessel with ammonia and air. The reaction was performed at 430–450°C, depending on the $BiVO_4$



SCHEME 1 Ammoxidation of 3,4-, 2,4- and 2,6- DCTs to DCBNs over $BiVO_4$ catalysts

catalysts. The outlet stream was cooled and collected every 1 hr after attaining steady-state conditions and then analyzed off-line by a gas chromatograph (Lunanruihong, China; column: SE-30) equipped with FID module. The reaction equations of the synthesis of DCBNs by the ammoxidation of DCTs could be expressed in Scheme 1.

4 | CONCLUSIONS

In conclusion, the catalytic properties of $BiVO_4$ catalysts prepared by hydrothermal and calcination methods were investigated in the ammoxidation of dichlorotoluenes. It was found that the activity of $BiVO_4$ catalyst is greatly related to the structure variations. Hydrothermal synthesized $BiVO_4$ catalyst displayed better ammoxidation activities, attributed to the greater structure deformation leading to better redox properties. The maximum yields of 3,4-, 2,4- and 2,6-DCBN obtained over hydrothermal prepared $BiVO_4$ reached up to 73.1, 72.2 and 70.8%, respectively.

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