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Article

Ordered macroporous boron phosphate crystals as metal-free catalysts for the oxidative dehydrogenation of propane

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ABSTRACT

Ordered macroporous materials with rapid mass transport and enhanced active site accessibility are essential for achieving improved catalytic activity. In this study, boron phosphate crystals with a three-dimensionally interconnected ordered macroporous structure and a robust framework were fabricated and used as stable and selective catalysts in the oxidative dehydrogenation (ODH) of propane. Due to the improved mass diffusion and higher number of exposed active sites in the ordered macroporous structure, the catalyst exhibited a remarkable olefin productivity of $\sim 16 \text{ g}_{\text{olefin}} \text{ g}_{\text{cat}}^{-1} \text{ h}^{-1}$, which is up to 2–100 times higher than that of ODH catalysts reported to date. The selectivity for olefins was 91.5% (propene: 82.5%, ethene: 9.0%) at 515 °C, with a propane conversion of 14.3%. At the same time, the selectivity for the unwanted deep-oxidized CO_2 product remained less than 1.0%. The tri-coordinated surface boron species were identified as the active catalytic sites for the ODH of propane. This study provides a route for preparing a new type of metal-free catalyst with stable structure against oxidation and remarkable catalytic activity, which may represent a potential candidate to promote the industrialization of the ODH process.

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1. Introduction

Ordered macroporous materials have an extremely favorable architecture, which can improve mass transport, reduce diffusion limitations, and expose a large number of active sites [1,2]. Therefore, they have attracted considerable attention for applications in catalysis [3–5]. To date, several types of ordered macroporous materials including silica [6], metals [7], metal oxides [8], polymers [9–11], and carbon [12] have been reported. Nevertheless, being thermodynamically unstable as well as sintering- or surface-inert, these materials are not suit-

able as active catalysts for high-temperature oxidative reactions. Bulk metal-free oxides with thermally stable crystal structures can be potentially used in oxidation reactions, but are commonly associated with a low accessible surface area [13]. An efficient strategy to solve this problem is to create porous structures in metal-free oxides. However, due to the lack of efficient protocols for their synthesis, these materials have rarely been reported. To extend their applications to diffusion-limited reaction processes [14], there is a pressing need to synthesize ordered macroporous materials based on metal-free oxide crystals.

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Metal-free boron phosphate (BPO_4), formed by corner-sharing BO_4 and PO_4 tetrahedra, has superior thermal stability and outstanding oxidation resistance. Based on the established understanding of the oxidative dehydrogenation (ODH) of light alkanes catalyzed by boron-based catalysts [15–24], the B–O (B–OH) sites of edge-functionalized boron nitride and silica-supported B_2O_3 catalysts play a pivotal role in the production of olefins. Recently, B_2O_3 supported on hollow BPO_4 spheres was reported as a liquid-phase catalyst for the oxidative dehydrogenation of propane, and melted B_2O_3 was considered as the active species of the catalyst [25]. Boron-phosphate mixed oxides were reported as active catalysts for the partial oxidation of propane, with high conversion of propane but low selectivity for olefins, as well as a wide spectrum of oxygenated products; however, no clear structural analysis of the oxides was reported [26,27]. On the basis of these results, we can envisage that BPO_4 , a boron-containing metal-free ternary oxide with abundant B–O sites, could be potentially used to catalyze the ODH of propane to propene. In fact, the preparation of BPO_4 commonly requires high-temperature calcination to form the crystals, which often gives rise to the formation of non-porous, bulk solids with low accessible surface areas. Considering the exposure of active sites in reactive processes, there is a pressing need to synthesize porous BPO_4 crystals. Moreover, mass and heat transfer issues are particularly important in the ODH of propane, because the highly exothermic nature of this reaction easily produces hot spots on the catalyst surface, in turn causing secondary reactions of the olefin products. By taking full advantage of the high thermal conductivity [28] of BPO_4 and simultaneously improving the mass transfer to reduce the contact time, we expect to obtain a new type of metal-free boron-based catalyst with excellent catalytic selectivity and productivity in the propane ODH, which would represent key improvements for the industrialization of this process.

To achieve this goal, in this paper we report the synthesis of a three-dimensional (3D)-ordered macroporous BPO_4 material with a robust framework, which exhibits excellent activity and selectivity for the ODH of propane to propene, with a remarkably high weight hourly space velocity (WHSV).

2. Experimental

2.1. Chemicals

Resorcinol (99.5%) was purchased from Tianjin Kermel Chemical Reagent Co., Ltd. Formaldehyde (37 wt%), 1,6-diaminohexane (DAH, 99.0%), boric acid, and phosphoric acid were supplied by Sinopharm Chemical Reagent Co., Ltd. All chemicals used in this work were of analytical grade.

2.2. Synthesis of polybenzoxazine polymer spheres

Polybenzoxazine polymer spheres with a uniform particle size of ca. 350 nm were prepared according to a modified method [29]. Typically, resorcinol (8.8 g) was first dissolved in deionized water (8 L) with vigorous stirring at 30 °C, and then formaldehyde (37 wt%, 11.8 mL) was added to form a clear

solution. After addition of DAH (1.16 g), the clear solution turned into a white colloid within 1 min, followed by the addition of dilute ammonia solution (20 mL, 1.5 M). The resulting solution was heated to 80 °C under vigorous stirring for 4 h. The polymer products were rinsed three times with deionized water, and water was removed by centrifugation. Finally, the purified products were dispersed in water.

2.3. Synthesis of ordered macroporous BPO_4 [$\text{BPO}_4(\text{OM})$]

Ordered macroporous boron phosphate crystals were prepared according to a modified method [3,30,31], based on *in situ* nanocasting. First, monodisperse polybenzoxazine polymer spheres were assembled into highly ordered 3D monoliths by centrifugation. Then, 1.08 g boric acid and 1.2 mL phosphoric acid were dissolved into 48 mL ethanol and 2 mL water. The 3D monoliths were soaked in the mixed ethanol-water solutions and then hydrothermally treated at 140 °C for nucleation and growth of BPO_4 over 6 days. After removing the excess solvent and drying at 50 °C, the materials were collected and pyrolyzed at 550 °C for 2 h in Ar atmosphere. The final macroporous BPO_4 product, denoted as $\text{BPO}_4(\text{OM})$, was obtained by calcination at 550 °C for 5 h in air to remove the template.

2.4. Synthesis of bulk BPO_4 [$\text{BPO}_4(\text{bulk})$]

After dissolving H_3BO_3 (1.75 mmol) and H_3PO_4 (120 μL) into 3 mL deionized water with stirring for 15 min, the solution was placed in a rotary evaporator. After reacting and drying at 70 °C for 20 h, the collected powders were calcined at 550 °C for 5 h in air to obtain the nonporous BPO_4 product, denoted as $\text{BPO}_4(\text{bulk})$. The structural characterizations are shown in Fig. S8.

2.5. Catalytic tests

The catalytic oxidative dehydrogenation of propane was performed in a packed-bed quartz microreactor (i.d. = 6 mm) with 100 mg of catalyst under atmospheric pressure. A $\text{C}_3\text{H}_8/\text{O}_2/\text{N}_2$ reaction mixture with a molar ratio of 1:1.5:3.5 was employed in the experiments. The flow rate was fixed at 48 mL/min (the WHSV was 9.4 $\text{g}_{\text{C}_3\text{H}_8} \text{g}_{\text{cat}}^{-1} \text{h}^{-1}$), and the reaction temperature was varied in the range of 470–550 °C. Before the reaction, each catalyst was pretreated under reaction conditions until the conversion was stabilized. The productivity experiments were performed in the temperature range of 500–550 °C. The catalyst mass and flow rate were varied in the ranges of 25–100 mg and 48–120 mL/min, respectively (the WHSV was 9.4–94 $\text{g}_{\text{C}_3\text{H}_8} \text{g}_{\text{cat}}^{-1} \text{h}^{-1}$). Reactants and products were analyzed by an online gas chromatograph (Techcomp, GC 7980). GDX-102 and 5A molecular sieve columns connected to a thermal conductivity detector (TCD) were used to analyze the O_2 , N_2 , C_3H_8 , C_3H_6 , C_2H_4 , CO, and CO_2 products.

The conversion was defined as the number of moles of carbon converted to the products divided by the number of moles present in the feed. The selectivity was defined as the number of moles of carbon in the product divided by the number of

moles that reacted. Under our typical testing conditions, the carbon balance was normally in the range of 95%–100%.

The effect of internal and external mass transfer on the conversion was determined using the experimental procedure reported in the literature.[32] Internal diffusion effects were investigated by monitoring the propane rate with catalyst particle sizes between 20 and 100 mesh, at constant WHSV ($9.4 \text{ g}_{\text{C}_3\text{H}_8} \text{ g}_{\text{cat}}^{-1} \text{ h}^{-1}$). A diagnostic test was performed to check for external diffusion. In the packed-bed reactor, two series of tests with different catalyst masses (25 and 50 mg) were performed for each catalyst. The W/F ratio in each series was varied from 1.5 to 13 $\text{min g}_{\text{cat}} \text{ g}_{\text{C}_3\text{H}_8}^{-1}$, and two conversion vs. W/F plots were generated.

2.6. Characterization

The morphology of the samples was characterized by field-emission scanning electron microscopy (SEM), using a Hitachi SU8220 instrument. Transmission electron microscopy (TEM) images were obtained by a FEI Tecnai F30 high-resolution microscope operating at an accelerating voltage of 300 kV, by dispersing ground powders in ethanol and then onto holey carbon films supported on copper grids. X-ray powder diffraction (XRD) patterns were obtained with a PANalytical X'Pert3 powder diffractometer, using $\text{Cu } K_\alpha$ radiation (40 kV, 40 mA, $\lambda = 0.15406 \text{ nm}$). Infrared (IR) spectra were collected on a Nicolet 6700 Fourier-transform IR (FT-IR) spectrometer using a mercury cadmium telluride (MCT) detector. Hg intrusion isotherms and pore size distributions (PSDs) of pores larger than 50 nm were measured using a Micromeritics AutoPore IV 9500 analyzer. Thermogravimetric (TG) profiles were measured from 40 to 900 °C with a heating rate of 10 °C min^{-1} under air flow, using a STA449 F3 Jupiter TG analyzer (Netzsch). X-ray photoelectron spectroscopy (XPS) analysis was performed with an Escalab 250 electron energy analyzer equipped with an *in situ* reaction cell. A monochromatic Al K_α X-ray source (1486.6 eV, anode operating at 15 kV and 300 W) was used as incident radiation. Solid-state ^{11}B and ^{31}P magic-angle spinning nuclear magnetic resonance (MAS-NMR) measurements were performed on a Bruker Avance III 600 MHz spectrometer with a 14.1 T magnet. The spectra were acquired using 4-mm MAS-NMR probes with a spinning rate of 10 kHz. One-dimensional (1D) ^{11}B MAS-NMR spectra acquired at 14.1 T were obtained with a $\pi/12$ pulse width of 0.66 μs . The chemical shifts were referenced to a 1 M H_3BO_3 aqueous solution at 19.6 ppm for ^{11}B NMR and 85% H_3PO_4 for ^{31}P NMR.

3. Results and discussion

3.1. Structural characterization of ordered macroporous BPO_4 catalyst

The synthesis of ordered macroporous BPO_4 was conducted via hydrothermal-assisted synthesis and calcination, as illustrated in Fig. 1(a). Boric acid and phosphoric acid were employed as sources of boron and phosphorus, respectively, and monodisperse polybenzoxazine polymer spheres were used as

the hard template. $\text{BPO}_4(\text{OM})$ materials with ordered macropores were obtained after removing the template. First, the monodisperse polybenzoxazine polymer spheres were assembled into highly ordered 3D monoliths. The monoliths were then immersed in the mixed ethanol-water solutions of boric acid and phosphoric acid, and further sealed in an autoclave for the nucleation and growth of BPO_4 . After the hydrothermal-assisted synthesis, the dried materials were collected and thermally treated under argon atmosphere (yielding the $\text{BPO}_4@ \text{carbon}$ product), then calcined in air to remove the hard template. As a result, the precursors smoothly turned into the $\text{BPO}_4(\text{OM})$ product. As a control experiment, BPO_4 was directly prepared by mixing aqueous solutions of boric acid and phosphoric acid, followed by drying. The dried materials were subjected to the same calcination treatment as that applied for $\text{BPO}_4(\text{OM})$, yielding the $\text{BPO}_4(\text{bulk})$ sample.

The SEM images of the polybenzoxazine polymer template and $\text{BPO}_4@ \text{carbon}$ composite (Fig. 1(b) and (c)) reveal that the porous spaces derived from the tight packing of polybenzoxazine polymer spheres were fully filled with BPO_4 . After pyrolysis and calcination of the composite, the tightly packed ordered polybenzoxazine polymer spheres were imprinted into the BPO_4 crystals. The structure of $\text{BPO}_4(\text{OM})$ (Fig. 1(d)) shows large domains of ordered macroporous 3D networks, along with the interconnected pore structure of BPO_4 . The XRD patterns of the $\text{BPO}_4(\text{OM})$ sample (Fig. 3(e)) show four main characteristic diffraction peaks at $2\theta = 24.5^\circ$, 40.0° , 48.9° , and 63.8° corresponding to the (101), (112), (121), and (213) facets of the known BPO_4 crystal structure, respectively, indicating the existence of the crystalline BPO_4 phase.

The ordered macroporous structure was an inverse replica of the template, with an average diameter of $\sim 200 \text{ nm}$ for the interconnected macropores (Fig. 1(d)); this diameter was

Fig. 1. Schematic of the fabrication of ordered macroporous BPO_4 (a); SEM images of polymer template (b), $\text{BPO}_4@ \text{carbon}$ (c), and ordered macroporous BPO_4 (d); TEM image (e), HRTEM image (f), and STEM-EDX mapping (g) of ordered macroporous BPO_4 .

slightly smaller than that of the polybenzoxazine polymer spheres, due to the thermal shrinkage of the spheres during the pyrolysis process. The presence of macroporosity in BPO₄ was further confirmed by mercury intrusion analysis (Fig. S1); the cumulative pore volume vs. pore diameter curve showed a continuous increase in mercury uptake with decreasing pore diameter (i.e., increasing Hg intrusion pressure). The interconnected macropores of the BPO₄(OM) sample were formed through the inverse templating effect of the polybenzoxazine polymer spheres, consisting of a matrix of macropores bridged by ink-bottle neck-like channels of ~80 nm in diameter. This indicated that BPO₄(OM) possessed abundant and fully interconnected macropores with a large volume. Based on the mercury intrusion analysis (Fig. S1), the specific surface areas of BPO₄(OM) and BPO₄(bulk) were estimated to be ~75 and 22 m² g⁻¹, respectively.

The TG analysis (Fig. S2) of the BPO₄(OM) and BPO₄(bulk) precursors before calcination shows that the first stage for all BPO₄ precursors was the removal of physically adsorbed water at ~100 °C. The marked weight loss (approximately 80 wt%) above 450 °C for the BPO₄(OM) precursors was assigned to the decomposition processes of the polybenzoxazine-based carbon template. For comparison, the slight weight loss with increas-

ing temperature observed for BPO₄(bulk) was caused by the loss of water due to the dehydration reaction.

TEM images provided direct insight into the effects of the monodisperse polybenzoxazine polymer spheres, serving as templates, on the morphological features of BPO₄ crystals. Figure 1(e) shows that the interstitial spaces between ordered and packed polybenzoxazine polymer spheres were filled with BPO₄ crystals. The high-resolution TEM (HRTEM, Fig. 1(f)) image shows an interplanar distance of 3.62 Å corresponding to the (101) plane of BPO₄, revealing that BPO₄ was present as intergrown crystals. The elemental mapping images (Fig. 1(g)) show a homogeneous distribution of the B, O, and P elements in the whole BPO₄ crystals.

3.2. Catalytic performance

First, preliminary experiments were conducted in order to rule out internal and external mass diffusion effects (Fig. S3). The temperature dependence of the propane conversion and the distribution of products over the catalysts (Fig. 2(a) and (b)) clearly show that BPO₄(OM) was more active than BPO₄(bulk) in the ODH of propane. For example, to reach the same conversion of 14.3%, the BPO₄(OM) catalyst required a

Fig. 2. (a) Influence of temperature on the ODH conversion of propane over BPO₄(OM) and BPO₄(bulk) catalysts; (b) Propane conversion and product distribution over BPO₄(OM) catalyst at 515 °C; (c) Long-term stability test. Reaction conditions: temperature, 515 °C; catalyst weight, 100 mg; gas feed C₃H₈/O₂/N₂ with 1:1.5:3.5 molar ratio; flow rate, 48 mL min⁻¹. (d) Comparison of olefin (C₃H₆ + C₂H₄) selectivity and productivity of propane ODH as a function of C₃H₈ conversion for BPO₄ and several representative catalysts (Table S1).

reaction temperature of 515 °C, while BPO₄(bulk) required a temperature of 550 °C. Increasing the temperature from 475 to 528 °C caused the propane conversion to increase from 3.1% to 29.8% when using BPO₄(OM). The conversion remained below 10% for BPO₄(bulk) at 528 °C. The stronger response to the temperature for the propane conversion on the BPO₄(OM) than the BPO₄(bulk) catalyst indicates that the presence of ordered macropores facilitated the exposure of a higher number of active sites, participating in the catalysis and achieving an equivalent conversion at lower reaction temperatures (at least by 40 °C). This represents a significant improvement, attributed to the well-developed macropores of the catalyst. Nevertheless, both BPO₄(OM) and BPO₄(bulk) exhibited identical trends of the olefin selectivity at the same conversion (Fig. 2(d)), demonstrating that the ordered macropores did not affect the active region. Furthermore, after normalizing the reaction rates of propane to the surface area of the BPO₄(OM) and BPO₄(bulk) catalysts, the rates at the same reaction temperature became quite similar, indicating that the two catalysts had identical active sites (Table S2). The products consisted of C₃H₆, C₂H₄, CO, and CO₂, and the selectivity for the desired propene product slightly decreased with increasing temperature (Fig. S4). When taking into account the equally important ethene product, the selectivity of the BPO₄(OM) catalyst for light olefins (C₂₋₃=) remained mostly above 90%, e.g., the C₂₋₃= selectivity reached 94.1% at 500 °C (propene: 85.6%, ethene: 8.5%), 91.5% at 515 °C (propene: 82.5%, ethene: 9.0%), and 90.7% at 520 °C (propene: 79.9%, ethene: 10.8%). It is noteworthy that the selectivity for the unwanted deep-oxidized CO₂ product remained below 1.0% for the BPO₄ catalyst (Fig. 2(b)). The catalytic performance of the BPO₄(OM) catalyst was tested for 20 h at a constant reaction temperature of 515 °C (Fig. 2(c)), and the catalyst remained stable, owing to the superior thermal stability and outstanding oxidation resistance of BPO₄.

One of the most important requirements for commercially attractive ODH catalysts is their ability to achieve a high productivity ($\text{g}_{\text{olefin}} \text{g}_{\text{cat}}^{-1} \text{h}^{-1}$) of olefins (Fig. 2(d)). BPO₄(OM) exhibited a productivity of $\sim 16 \text{ g}_{\text{olefin}} \text{g}_{\text{cat}}^{-1} \text{h}^{-1}$. This value was remarkably higher than that of the BPO₄(bulk) ($1.2 \text{ g}_{\text{olefin}} \text{g}_{\text{cat}}^{-1} \text{h}^{-1}$) and of the reported catalysts (Table S1) used in the ODH process, including hydroxylated boron nitride ($6.7 \text{ g}_{\text{olefin}} \text{g}_{\text{cat}}^{-1} \text{h}^{-1}$) and metal oxide catalysts ($0.17\text{--}8.5 \text{ g}_{\text{olefin}} \text{g}_{\text{cat}}^{-1} \text{h}^{-1}$). The catalytic performances of ordered macroporous BPO₄(OM) and nonporous BPO₄(bulk) under different WHSV conditions are shown in Table S1. BPO₄(OM) showed a productivity of $\sim 16 \text{ g}_{\text{olefin}} \text{g}_{\text{cat}}^{-1} \text{h}^{-1}$ at a WHSV of $94 \text{ g}_{\text{C}_3\text{H}_8} \text{g}_{\text{cat}}^{-1} \text{h}^{-1}$, with a propane conversion of 20.8%. This productivity is 2–100 times higher than that of previously reported ODH catalysts (Table S1). In contrast, BPO₄(bulk) showed a productivity of $0.31 \text{ g}_{\text{olefin}} \text{g}_{\text{cat}}^{-1} \text{h}^{-1}$ at a lower WHSV of $37.6 \text{ g}_{\text{C}_3\text{H}_8} \text{g}_{\text{cat}}^{-1} \text{h}^{-1}$, and its propane conversion was already as low as 0.9% at same reaction temperature of 535 °C. This comparison reveals that the interconnected and open macropores of BPO₄ are beneficial to the mass transfer to allow the active sites easily accessible and lead to better catalytic efficiency under high space velocity conditions [33], which cannot be promoted or achieved using bulk and nonporous BPO₄. The improved kinetic diffusion to the reactive

sites results in a greatly improved yield.

3.3. Structural stability and active sites of ordered macroporous BPO₄ catalyst

The structural stability of the BPO₄(OM) catalyst was characterized using various techniques including SEM, TEM, XRD, FTIR, and NMR (Figs. 3 and 4). The SEM and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images (Fig. 3(a)–(d)) show that the spent catalyst BPO₄(OM) after react 20 h was characterized by an ordered macroporous framework. The macropore sizes and the intergrown nanocrystals were essentially unchanged. Furthermore, the XRD pattern of the spent BPO₄(OM) after the catalytic reaction (Fig. 3(e)) was identical to that of the fresh catalyst. These results strongly indicate that the crystallized

Fig. 3. SEM (a,b) and HAADF-STEM (c,d) images of fresh and spent BPO₄(OM) catalyst; XRD patterns (e) and surfaces of four crystal planes (f) identified in XRD experiments (O: orange, B: red, P: yellow).

Fig. 4. Structural characterizations of fresh and spent BPO₄(OM) catalysts. (a) FTIR; (b) ³¹P MAS-NMR; (c) ¹¹B MAS-NMR spectra.

macroporous BPO₄ framework exhibited excellent structural stability during the ODH of propane. The examination of the crystal plane surfaces in Fig. 3(f) reveals that they crossed the channels formed by alternating BO₄ and PO₄ units, leading to a high exposure of B–O groups, especially for the (101) surface. The FTIR spectra of the fresh and spent BPO₄(OM) catalysts are displayed in Fig. 4(a). The peaks located at 1100 and 1620 cm^{−1} were assigned to PO₄ groups and P–O bonds [34,35]. The transmittance peaks at 935 cm^{−1} were attributed to the asymmetric stretching vibration of BO₄ tetrahedra, and the peaks at ~1350 cm^{−1} were tentatively assigned to tri-coordinated boron (BO₃) species. These results suggest that both fresh and spent BPO₄(OM) catalysts mainly consisted of BO₄ and PO₄ groups.

¹¹B and ³¹P NMR measurements of the fresh and spent BPO₄(OM) catalysts were then carried out (Fig. 4(b), (c)). The B and P species, with chemical shifts of *ca.* −5.3 and −31 ppm, respectively, were essentially retained after the reaction. This result clearly demonstrates that the BPO₄(OM) catalyst was structurally stable after the ODH of propane, and boron predominantly existed as tetra-coordinated species. Compared to the catalyst enriched in tri-coordinated boron species [18], BPO₄(OM) showed a slightly lower selectivity for ethene at the same propane conversion. The presence of abundant tetra-coordinated boron species in the catalysts had two consequences: on one hand, the boron sites were too crowded to be accessible to nucleophilic species; on the other hand, the electron density in the vicinity of the boron sites was enhanced (the

calculated natural population atomic charges at B3LYP/6-31(d) level changed from −3.02*e* to −4.12*e* on O atoms bound to B, and from 1.37*e* to 1.32*e* on B). Both hindered the approach of electron-rich species, e.g., propene, and inhibited the breakage of surface C–C bonds, which led to reduced formation of ethene and deep oxidation products (Fig. 2(b) and (d)).

XPS measurements were conducted to determine the surface chemical properties of the fresh and spent BPO₄(OM) catalysts. The XPS results (Fig. 5) show that the atomic percentages of P (estimated from the P 2*p* XPS profile) in the fresh and spent BPO₄(OM) catalysts were 12.2% and 12.5%, respectively. Since the BPO₄(OM) catalyst was active under the reaction conditions (Fig. S5), we deduced that the catalytic activity was not directly related to the phosphorus concentration on the catalyst surfaces. On the other hand, the atomic percentages of B in the fresh and spent BPO₄(OM) catalysts were estimated to be *ca.* 33.1% and 33.7%, respectively. The B 1*s* spectra could be deconvoluted into three peaks at 193.6, 191.8, and 189.3 eV. These peaks were attributed to BO₃ (tri-coordinated boron), BO₄ (tetra-coordinated boron), and boron suboxides (B_xO_y, 1.5 < *x/y* < 3), respectively [36,37]. The tri-coordinated B site has less electron density in its vicinity than the tetra-coordinated B site since in these species B always remained with a former oxidation state of +3, which was neutralized when being tri-coordinated while felt excess negative charge when tetra-coordinated. The presence of the excess electron density in its vicinity is expected to perturb the binding strength of 1s

Fig. 5. XPS measurements of the fresh and spent BPO₄(OM) catalysts. (a) B 1*s*; (b) P 2*p*.

electron and shift the bind energy to a lower value. The tetra-coordinated boron species represented the transition region to extend the bulk structure to the surface. The content of tri-coordinated surface boron species increased from *ca.* 41% in fresh BPO₄(OM) to 51% in the spent catalyst (Table S3). These results likely indicate that the tri-coordinated boron species were responsible for the ODH of propane. In short, the presence of BO₃ is related to the catalytic activity of the BPO₄(OM) catalyst. This is consistent with our recent study of the ODH of light alkanes catalyzed by supported B₂O₃ [18]. It should be noted that the solid-state MAS-NMR technique is used to analyze the bulk structure, rather than the surface structure. XPS is a surface analysis technique, which can commonly probe regions located approximately 5–10 nm beneath the surface. For the fresh and spent catalysts, no NMR signal (600 MHz spectrometer with a 14.1 T magnet) corresponding to BO₃ could be detected under such strong magnetic field, in turn indicating that the BO₃ content on the catalyst surface was low. Even though there were signals, they may have already been overspread by the bulky signals of BO₄.

In an earlier work [26], a calcined H₃BO₃/P₂O₅ mixture was found to be active in the partial oxidation of light alkanes, and its role was proposed to involve the activation of gaseous oxygen; however, the understanding of the corresponding active sites and mechanism remained limited. In this study, we carefully designed a BPO₄(OM) catalyst with an interconnected macroporous structure and compared its performance in the ODH of propane with that of crystalline BPO₄(bulk). In this way, we identified BO₃ as the active sites, which, under the reaction conditions, activated gaseous oxygen and participated in the dehydrogenation of alkanes.

In addition, kinetic ODH experiments were performed for the BPO₄ catalysts (Figs. S6 and S7). The activation energies (*E_a*) for propane dehydrogenation on BPO₄(OM) (*ca.* 200 kJ/mol) and BPO₄(bulk) (*ca.* 207 kJ/mol) were quite similar,

indicating that the active sites of the ordered macroporous BPO₄ and bulk materials were identical. In the current study, oxygen remained present even at high propane conversions, and the *E_a* for oxygen conversion was estimated to be 231 kJ/mol, higher than that of propane; this shows that the reaction mechanism was controlled by molecular oxygen activation on the catalyst surface. These results indicate that the cleavage of C–H bonds could readily happen after oxygen activation on the BPO₄(OM) catalyst. Based on the effect of the oxygen concentration on the reaction rate of propane, the oxygen reaction order was estimated to be 0.5.

4. Conclusions

In summary, an ordered macroporous and metal-free BPO₄ material with an interconnected crystal framework has been prepared by hydrothermal-assisted synthesis. The material showed excellent catalytic performance in the ODH of propane to propene, as evidenced by high propane conversion, high propene selectivity, and low CO₂ emission. The olefin productivity of BPO₄ was much higher than that of reported boron-containing catalysts [15–20]. Structural characterizations revealed that the ordered macroporous BPO₄ framework exhibited a remarkable structural stability, and the tri-coordinated B–O surface species incorporated in the framework were responsible for catalyzing the ODH reaction of propane. This study provides a new strategy for improving the catalytic activity of metal-free oxides and offers a platform for investigating the composition and fracture of boron-based catalysts.

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Graphical Abstract

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Ordered macroporous boron phosphate crystals as metal-free catalysts for the oxidative dehydrogenation of propane

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Ordered, macroporous, and metal-free BPO₄ materials with an interconnected robust framework have been prepared by hydrothermal-assisted synthesis. This material can be used as a stable and selective catalyst for the ODH of propane to propene with high productivity.

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非金属有序大孔磷酸硼晶体合成及催化丙烷氧化脱氢反应性能

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摘要: 有序大孔材料具有大的比表面积和有序开放的立体孔道结构, 有利于暴露更多的活性位点, 促进传质扩散, 从而提高催化活性. 目前, 已有报道的有序大孔材料包括金属及氧化物、氧化硅、炭、聚合物等. 非金属含氧化合物具有耐氧化的结构特点, 适合应用于高温氧化反应, 但是体相非金属含氧化合物的比表面积低, 并且孔道极不发达, 因此亟需合成有利于传质的有序大孔非金属含氧化合物晶体材料.

最近研究者发现, 硼基催化剂在催化低碳烷烃氧化脱氢制烯烃反应中呈现出高的反应活性、选择性和稳定性, 且我们发现B–O (B–OH)位点在硼基催化材料中起着至关重要的作用. 三元非金属磷酸硼晶体由BO₄和PO₄四面体组成, 具有优异的热稳定性和抗氧化性能, 有可能适合于催化丙烷氧化脱氢制丙烯的反应. 但制备磷酸硼晶体过程通常需要经过高温焙烧, 从而导致产物结构密实、无孔、外表面积低. 此外, 丙烷氧化脱氢反应具有强放热特性, 易在催化剂表面形成热点, 引起烯烃产物的二次反应, 降低目标产物选择性, 因此解决传质传热问题尤为重要. 如果能充分利用磷酸硼的高导热性, 同时调控孔结构以改善传质, 减少接触时间, 则有望设计一种具有良好催化选择性和产率的非金属催化剂, 助力丙烷氧化脱氢制丙烯研究领域的发展.

本文设计合成了结构稳定的三维有序大孔磷酸硼晶体材料, 在丙烷氧化脱氢反应中表现出优异的催化活性及选择性. 在515 °C反应丙烷转化率达14.3%, 丙烯选择性达82.5%, 烯烃选择性达91.5%, 同时, 深度氧化的产物CO₂选择性不超过1%. 由于有序大孔的结构改善了传质, 并暴露出更多的活性位点, 该催化剂可在高空速下展现出较高的烯烃产率 (~16 g_{olefin} g_{cat}⁻¹ h⁻¹), 是目前报道的大部分丙烷氧化脱氢催化剂所能得到的烯烃产率的2–100倍. 本文采用电镜、X射线衍射、红外、

固体核磁及X射线光电子能谱等手段探究了有序大孔磷酸硼催化剂在丙烷氧化脱氢反应中的结构稳定性及活性位点。结果表明,有序大孔磷酸硼骨架在反应过程中稳定性好,反应后作为活性位的磷酸硼催化剂表面的三配位硼物种有所增加。本文为制备结构稳定、抗氧化性强且催化活性优异的新型非金属催化剂提供了新的途径,为促进氧化脱氢制烯烃研究领域的发展提供了材料支撑平台。

关键词: 有序大孔材料; 非金属催化剂; 磷酸硼; 氧化脱氢; 丙烷

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