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Article

Hierarchical 0D/2D Co₃O₄ hybrids rich in oxygen vacancies as catalysts towards styrene epoxidation reaction

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ABSTRACT

Great efforts have been devoted to the developing of simple, efficient and stable heterogeneous catalysts for the styrene epoxidation reaction (SER). Metal oxides can be of industrial importance by offering an economic and green route for selectively converting styrene into styrene oxide (SO). Herein, by treating the pristine porous 2D Co₃O₄ sheets with NaBH₄ solution, a novel hierarchical structure, *i.e.*, 0D Co₃O₄ nanoparticles decorated on 2D porous Co₃O₄ sheets, was obtained. This simple solution reduction strategy not only realizes the morphology evolution, but also induces the modification of the valence states of metal ions and the simultaneous generation of surface oxygen vacancies. The hierarchical 0D/2D Co₃O₄ hybrids rich in oxygen vacancies (OV-Co₃O₄) exhibit a much better SER performance than the Co₃O₄ sheets (P-Co₃O₄), with the yield of SO more than doubled. The excellent catalytic performance of the OV-Co₃O₄ can be ascribed to the synergistic effects regarding the hierarchical porous structure, the modification of surface chemical composition and the creation of surface oxygen vacancies.

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1. Introduction

The catalytic oxidation of hydrocarbons is a very important reaction in the chemical industry [1–5]. Among the various oxidation reactions, the catalytic epoxidation of alkenes has aroused much attention in recent years both academically and industrially since epoxide products are vital intermediates in pharmaceutical industrials and production of fine chemicals [6–12]. Styrene oxide (SO), as an important epoxide, is widely used in the manufacture of bulk chemicals, surface coatings, cosmetics and epoxy resins, *etc.* [13–15]. The traditional way for synthesis of SO involves the dehydrochlorination of styrene chlorohydrin or the oxidation of styrene with organic peracids [16]. However, both methods suffer from several drawbacks

such as using hazardous chemicals, generating a large amount of chemical wastes and showing poor selectivity for SO [16,17]. From the viewpoint of green and sustainable chemistry, these conventional methods have been replaced by the method involving H₂O₂, O₂ or organic hydroperoxides as sacrificial oxidizing agents.

Among the various homogeneous catalysts for the styrene epoxidation reaction (SER), cobalt ions and their complexes have been identified as more active ones [18–21]. However, the efficient separation and subsequent recycling of these homogeneous catalysts remains a big challenge and gives rise to environmental pollution, which severely limits their further application. Therefore, many heterogeneous catalysts, including cobalt-based catalysts, have been employed in the SER due to

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their mild reaction conditions and ease in catalyst separation and satisfactory recyclability [22–29]. Tang *et al.* [20,30] found that Co^{2+} -containing molecular sieves, mainly faujasite zeolite and MCM-41 exhibited better catalytic performance in the SER as compared with other transition metal (Cr^{3+} , Mn^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+})-containing counterparts. Li *et al.* [22] coated an ultrathin TiO_2 layer onto SBA-15 ($\text{TiO}_2/\text{SBA-15}$), and then introduced CoO_x species on the support by atomic layer deposition. They reported that the $35\text{CoO}_x/5\text{TiO}_2/\text{SBA-15}$ exhibited the best catalytic performance, showing 80.5% conversion with 67.5% selectivity to SO, which can be attributed to the appropriate interaction between the CoO_x species and support. Moreover, Masunga *et al.* [31] prepared mesoporous manganese oxide, cobalt oxide, and hybrid Mn-Co oxide with an inverse surfactant micelle method. The results showed that the catalytic activities of the compared catalysts decreased in the order of $\text{Mn-Co}_{350} > \text{MnO}_{2-350} > \text{Co}_3\text{O}_{4-350}$, while the highest epoxide selectivity was achieved using MnO_{2-350} (53.5%), and the recyclability test indicated that the metal oxides were stable with the structure well retained. Weerakkody *et al.* [32] further synthesized mesoporous Co_3O_4 by an inverse micelle template self-assembly method. They stated that high surface area, mesoporosity, and surface oxygen vacancies could be identified as the major contributors to the catalytic activity. Despite the advantages of these heterogeneous catalysts, however, they generally required complex preparation processes and showed low catalytic activity and/or poor selectivity of SO. Therefore, developing simple but highly active and stable cobalt-based catalysts for the SER is still a challenging and interesting study.

In this work, we attempt to achieve high styrene conversion and epoxide selectivity by rationally designing hierarchical 0D/2D Co_3O_4 hybrids rich in oxygen vacancies. As illustrated in Scheme 1, the OV- Co_3O_4 catalyst was prepared by a facile NaBH_4 treatment of the pristine porous Co_3O_4 sheets. Although this solution reductive strategy has just been reported to be effective in the applications of water splitting [33], *p*-nitrophenol reduction [34], and lithium storage and electrocatalytic oxygen evolution [35], to the best of our knowledge, it is the first report regarding this kind of catalyst treatment for the application in the SER. This simple modification of the P- Co_3O_4 can endow the OV- Co_3O_4 several advantages for the SER, such as improved surface area, abundant active sites and numerous surface oxygen vacancies. As expected, the OV- Co_3O_4 exhibits a much better SER performance including higher reac-

tivity and SO selectivity than the P- Co_3O_4 . In addition, a possible reaction pathway for the selective synthesis of SO from the SER with the OV- Co_3O_4 as the catalyst was reasonably proposed.

2. Experimental

2.1. Catalyst preparation

All the chemical reagents were of analytic grade and used without further purification. Deionized (DI) water was utilized throughout the experiments.

The P- Co_3O_4 was prepared according to the method reported in our previous study with some modifications [36]. In a typical procedure, 1.9 g $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was firstly dissolved in 60 mL DI water, and then 1.0 g polyvinylpyrrolidone K30 was added to the solution under vigorous stirring for 1 h. After that, 1.6 g $\text{CO}(\text{NH}_2)_2$ was added into the above mixture and stirred for another 1 h. Subsequently, the resulting mixture was transferred into a 100 mL Teflon-lined stainless steel autoclave and heated at 180 °C for 8 h. Thereafter, the precipitate was filtered, washed with DI water and ethanol several times, and dried at 80 °C for 5 h. The sample was then annealed at 500 °C at a ramping rate of 2 °C/min for 2 h to obtain the P- Co_3O_4 .

For the synthesis of OV- Co_3O_4 , 0.2 g P- Co_3O_4 was added to 0.02 mol/L NaBH_4 solution. After this simple treatment, the sediment was filtered and washed with DI water and ethanol several times. Then, the sample was dried at 80 °C for 5 h, and thus the OV- Co_3O_4 was obtained.

2.2. Catalyst characterization

X-ray diffraction (XRD) analysis was conducted on a D8 Advance diffractometer with $\text{Cu K}\alpha$ radiation. Raman spectra were obtained on a Renishaw inVia laser Raman spectrometer. The morphologies of the samples were analyzed by a field-emission scanning electron microscopy (SEM, Hitachi S-4800). Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were obtained on a JEM-2100 microscope equipped with an energy-dispersive X-ray spectroscopy (EDS) attachment. The N_2 adsorption-desorption isotherms were collected at -196 °C on a Quantachrome Autosorb-iQ3. The X-ray photoelectron spectroscopy (XPS) data were obtained on a Thermo, Fisher Scientific ESCALAB 250Xi spectrometer.

2.3. Catalyst test

The obtained catalysts were applied for the SER in a round bottom flask equipped with a reflux condenser. In a typical process, 15 mmol of styrene and 75 mmol of tert-Butyl hydroperoxide (TBHP) were added to a mixture of 0.1 g of catalyst and 16 mL of acetonitrile in the flask placed in a water bath. During the test, the reaction mixture was sampled once an hour. After centrifugation, the products were analyzed by a gas chromatography equipped with a KB-1 column.

3. Results and discussion

Scheme 1. Schematic illustration of the facile synthesis of hierarchical 0D/2D Co_3O_4 hybrids for the selective oxidation of styrene.

Fig. 1. XRD patterns (a) and Raman spectra (b) of the P-Co₃O₄ and the OV-Co₃O₄.

Fig. 1(a) shows the XRD patterns of the P-Co₃O₄ and OV-Co₃O₄. As observed, in both samples, the representative peaks at 2θ of 19.0°, 31.3°, 36.9°, 44.8°, 59.4° and 65.2° can be well assigned to the (111), (220), (311), (400), (511) and (440) facets of spinel Co₃O₄ [JCPDS 42-1467], suggesting the absence of any other bulk crystalline phases[2]. However, the diffraction peaks for the OV-Co₃O₄ are not as sharp as those of the P-Co₃O₄. The estimated crystallite sizes of Co₃O₄ in the P-Co₃O₄ and OV-Co₃O₄ calculated from the XRD line broadening with the Scherrer equation are 26.8 and 23.1 nm, respectively. These results indicate that the reduction treatment has no effect on the Co₃O₄ crystal structure, while the crystallinity is weakened after treating the P-Co₃O₄ in a NaBH₄ solution. Fig. 1(b) shows the Raman spectra of the P-Co₃O₄ and OV-Co₃O₄. For both samples, five peaks located at ca. 197, 483, 523, 622 and 691 cm⁻¹ can be assigned to the F_{2g}⁽¹⁾, E_g, F_{2g}⁽²⁾, F_{2g}⁽³⁾ and A_{1g} vibrational modes of spinel-type Co₃O₄, respectively, in agreement with the group theory [37]. No other peaks can be distinguished, further indicating no change for the crystal structure after the reduction treatment. However, a tiny blue-shift for A_{1g} can be observed after the reduction treatment, which can be associated with the presence of surface oxygen vacancies in the OV-Co₃O₄ due to the photon-confinement effects [38,39]. The variation of peak intensity in the two samples can be ascribed to the influence of crystallinity and the orientation effect during the Raman test [40].

Fig. 2(a, b) shows the SEM images of the P-Co₃O₄. It can be observed that the P-Co₃O₄ presents a uniform porous sheet-like morphology, and each sheet with a size distribution of 2–4 μm is assembled by interconnected Co₃O₄ nanoparticles. According to the particle size distribution (PSD), the average Co₃O₄ particle size of the P-Co₃O₄ was measured to be 45 nm. After the reduction treatment, the smooth surface of the pristine sheets becomes rough (Fig. 2(c)), indicating the morphology evolution during the reduction process. The magnified image of the OV-Co₃O₄ (Fig. 2(d)) shows that the surface of these sheets is decorated with numerous nanoparticles, exhibiting a hierarchically porous structure (0D/2D hybrids). Noticeably, the PSD analysis shows that the average particle size of these decorated

Co₃O₄ nanoparticles is 125 nm, which is much larger than that of the nanoparticles in the sheets. Representative TEM image (Fig. 3(a)) of the OV-Co₃O₄ further shows its hierarchical nature, with nanoparticles distributing on the sheets. EDS analysis (Fig. 3(b)) indicates that the OV-Co₃O₄ is composed of Co and O (the Cu and C signals come from the carbon-coated TEM grid for supporting the sample). The HRTEM image (Fig. 3(c)) of the OV-Co₃O₄ exhibits clear lattice fringes, indicating the good crystallinity of the OV-Co₃O₄. The interplanar spacing of 0.24 nm corresponds to the (311) plane of Co₃O₄. Additionally, the diffraction rings in the selected area electronic diffraction (SAED) pattern further reveal the spinel Co₃O₄ phase and the polycrystalline feature of the OV-Co₃O₄.

The above discussions show that the simple surface modification strategy is of key importance for the structure evolution from the 2D sheets (P-Co₃O₄) to 0D/2D hybrids (OV-Co₃O₄). This evolution can be attributed to the *in situ* formed hydrogen

Fig. 2. Representative SEM images of the P-Co₃O₄ (a, b) and the OV-Co₃O₄ (c, d) samples.

Fig. 3. TEM image (a), EDS analysis (b), HRTEM image (c) and SAED pattern (d) of the OV-Co₃O₄.

bubbles in the freshly prepared aqueous NaBH₄ solution [35]. The formation and collapse of the hydrogen bubbles acting on the pristine Co₃O₄ sheets can induce the generation of nanoparticles on the porous sheets. These initial small nanoparticles continue to interact with each other to form large ones due to the Ostwald ripening effect, which finally facilitates the formation of uniform nanoparticles on the porous sheets. As expected, this morphology transformation results in an increase in the Brunauer-Emmett-Teller (BET) surface area from 20.9

Fig. 4. N₂ adsorption-desorption isotherms of the P-Co₃O₄ and the OV-Co₃O₄.

m²/g (P-Co₃O₄) to 37.0 m²/g (OV-Co₃O₄) calculated from the N₂ adsorption-desorption isotherm (Fig. 4).

XPS measurement was carried out to analyze the elemental composition and state of the sample surface [41,42]. As expected, the XPS survey (Fig. 5(a, b)) shows that only three elements of Co, O and C can be detected, and the presence of C can be due to the hydrocarbon contaminants that inherently exist in the detection. Both the high-resolution XPS Co 2p spectra of the OV-Co₃O₄ (Fig. 5(c)) and P-Co₃O₄ (Fig. 5(d)) can be fitted into two peaks corresponding to Co²⁺, two corresponding to Co³⁺, and the other two corresponding to shakeup satellites [43]. By estimating the area that the fitted curve covers, the relative molar ratio of Co²⁺/Co³⁺ on the surface of the P-Co₃O₄ is calculated to be 0.43, which is close to the theoretical value (0.5). Noticeably, the OV-Co₃O₄ presents a much larger

Fig. 5. XPS survey (a, b), high-resolution Co 2p spectra (c, d) and O 1s spectra (e, f) of the OV-Co₃O₄ (a, c, e), and P-Co₃O₄ (b, d, f).

$\text{Co}^{2+}/\text{Co}^{3+}$ ratio of 0.97, which is more than twice of what it is in the $\text{P-Co}_3\text{O}_4$, indicating that more Co^{2+} presents due to the surface reduction modification. It should be noted that the oxygen vacancies are produced with the reduction of higher valent metal ions to lower valent metal ions in the metal oxides since two electrons are left behind and then transfer to the neighbor metal ions when an oxygen vacancy is formed [39,44,45]. This indicates that the oxygen vacancies were successfully generated by the simple NaBH_4 solution treatment, which can also be confirmed by the high-resolution O 1s spectrum of the $\text{OV-Co}_3\text{O}_4$ (Fig. 5(e)). As observed, the peak can be deconvoluted into three peaks, with O1 (529.8 eV), O2 (531.1 eV) and O3 (531.9 eV), assigned to surface lattice oxygen, surface adsorbed hydroxyl groups and surface adsorbed water molecules, respectively [32,35]. Among them, the O2 peak is directly associated with the oxygen vacancies or defects [33,46]. As observed, the O2 peak area is greatly increased for the $\text{OV-Co}_3\text{O}_4$ as compared with its counterpart (Fig. 5(f)), further confirming the efficient creation of oxygen vacancies by treating the $\text{P-Co}_3\text{O}_4$ with NaBH_4 solution. Such a hierarchical 0D/2D architecture with large surface area, abundant pore channels and numerous oxygen vacancies is expected to endow the $\text{OV-Co}_3\text{O}_4$ a good catalytic performance for the SER.

The SER using TBHP as the oxidant was carried out to assess the catalytic properties of the $\text{OV-Co}_3\text{O}_4$. For comparison, the $\text{P-Co}_3\text{O}_4$ was tested as well under the same reaction condi-

tion. GC analysis showed that the catalytic oxidation of styrene produced two major products, *i.e.*, SO and benzaldehyde. Plots of styrene conversion and SO selectivity *versus* reaction time are presented in Fig. 6(a). As observed, for the $\text{OV-Co}_3\text{O}_4$, the styrene conversion increases continuously within the reaction duration of 8 h despite the sluggish increase after 6 h. The selectivity of SO, however, decreases quickly after 6 h, which can be attributed to the over-oxidation of SO and the hydrolysis of SO into 1-phenyl-1,2-ethanediol[47]. As a result, the yield of SO *versus* reaction time shows a volcano shape (Fig. 6(b)), with the highest value obtained at 6 h. Therefore, we chose 6 h as the optimal reaction time. As shown in Fig. 6(c), the $\text{P-Co}_3\text{O}_4$ shows a styrene conversion of 53.4% with 62.2% selectivity to SO at 6 h, and gives a total yield of 33.2%. In sharp contrast, the $\text{OV-Co}_3\text{O}_4$ exhibits a much better catalytic performance. Its styrene conversion, SO selectivity and yield at 6 h reach up to 99.3%, 71.4% and 70.9%, respectively. This indicates that the simple solution reduction strategy can significantly enhance the SER performance, with the yield of SO more than doubled.

To optimize the reaction conditions of the $\text{OV-Co}_3\text{O}_4$ catalyst, the effects of the two key reaction parameters, *i.e.*, styrene/TBHP molar ratio and reaction temperature, on the SER performance were investigated in detail. Fig. 7(a) shows the effect of styrene/TBHP molar ratio (1:3, 1:4, 1:5 and 1:6) on the catalytic activity and SO selectivity. As observed, both the styrene conversion and SO selectivity present a volcano-type de-

Fig. 6. (a, b) The effect of reaction time on the SER performance over the $\text{OV-Co}_3\text{O}_4$ catalyst. Reaction conditions: 0.1 g catalyst, 15 mmol styrene, 75 mmol TBHP, 16 mL acetonitrile, 80 °C. (c, d) The reaction performances of the $\text{P-Co}_3\text{O}_4$ and the $\text{OV-Co}_3\text{O}_4$ catalysts. Reaction conditions: 0.1 g catalyst, 15 mmol styrene, 75 mmol TBHP, 16 mL acetonitrile, 80 °C, 6 h.

Fig. 7. (a) The effect of molar ratios of styrene to TBHP on the reaction performance of the OV-Co₃O₄ catalyst. Reaction conditions: 0.1 g catalyst, 15 mmol styrene, 16 mL acetonitrile, 80 °C, 6 h. (b) The effect of reaction temperature on the catalytic results over the OV-Co₃O₄ catalyst. Reaction conditions: 0.1 g catalyst, 15 mmol styrene, 75 mmol TBHP, 16 mL acetonitrile, 6 h.

pendence on the styrene/TBHP molar ratio, suggesting the existence of an optimal value of this ratio. With the styrene/TBHP molar ratio decreasing from 1:3 to 1:5, the styrene conversion increases continuously from 82.2% to 99.3%, revealing that sufficient TBHP as the oxidant is a powerfully driving force for the SER reaction. However, further lowering the styrene/TBHP molar ratio to 1:6, the styrene conversion decreases to 93.4%, which can be attributed to the influence of competing adsorption of styrene and TBHP on the catalyst surface. Superfluous TBHP may reduce the opportunity for the interaction of the styrene molecules with the active sites, and therefore results in the decrease of the reaction rate. Moreover, too much TBHP can over-oxidize SO into several byproducts such as phenylacetaldehyde, 1-phenylethane-1,2-diol and benzoic acid [4]. Therefore, the styrene/TBHP molar ratio of 1:5 was selected as the optimal one for the further experiments. To investigate the effect of reaction temperature on the catalytic performance, the SERs were carried out within the temperature range of 60–90 °C, and the results were shown in Fig. 7(b). It can be found that the variation trend of styrene conversion and SO selectivity *versus* reaction temperature is similar with that of Fig. 7(a). With the reaction temperature increasing from 60 to 80 °C, the styrene conversion increases from 75.5% to 99.3%, and the SO selectivity increases from 55.4% to 71.4%. It seems that the higher the reaction temperature, the better the catalytic performance. However, this is not true since further increasing the reaction temperature to 90 °C results in the decrease of the styrene conversion although the SO selectivity remains almost unchanged. This can be attributed to the undesired high temperature-induced decomposition of TBHP. Among the tested temperatures, the SER at 80 °C gives the highest yield of SO. Therefore, the styrene/TBHP molar ratio of 1:5 and reaction temperature of 80 °C were selected as the optimized reaction parameters. Under this condition, the SO yield can achieve 70.9% with 99.3% styrene conversion and 71.4% SO selectivity. This yield value of 70.9% is better or comparable to those of the reported heterogeneous co-

balt-containing catalysts under similar reaction conditions, such as mesoporous Co₃O₄ (8.3%) [31], Co-NH₂-KIT-6 (33.0%) [48], CoO (34.6%) [49], CoO_x/TiO₂/SBA-15 (54.3%) [22] and CuO/CoAl-HT (71.6%) [50].

Catalytic stability is one of the key parameters for the actual application of the catalysts [51,52]. The stability of the OV-Co₃O₄ was investigated for six repeated reactions under similar reaction conditions. As shown in Fig. 8, the recycled catalyst presents only a slight decrease in the catalytic activity and SO selectivity within the six runs, suggesting the excellent stability of the OV-Co₃O₄. Additionally, the analysis of the liquid phase separated from the reaction mixture after the catalytic reaction did not show the presence of cobalt, indicating no leaching of cobalt element from the catalyst.

Previous studies have demonstrated that the formation of M-peroxo species should be responsible for the SER [16,30,50,53]. Based on this understanding and the above dis-

Fig. 8. Reusability of the OV-Co₃O₄ catalyst for the selective oxidation of styrene. Reaction conditions: 0.1 g catalyst, 15 mmol styrene, 75 mmol TBHP, 16 mL acetonitrile, 80 °C, 6 h.

Scheme 2. Possible reaction pathway for the epoxidation of styrene over the OV- Co_3O_4 catalyst.

cussions, the possible reaction pathways for the SER over the Co_3O_4 -based catalysts were reasonably proposed. As presented in Scheme 2, the oxygen radicals obtained by the activation of the TBHP adsorbed on the Co_3O_4 surface will coordinate with Co^{II} to form a complex composed of a higher valence transition metal-oxo compound ($\text{Co}^{\text{III}}\text{-oxo}$), which further interacts with TBHP to generate $\text{Co}^{\text{III}}\text{-peroxo}$ species. And then these active $\text{Co}^{\text{III}}\text{-peroxo}$ will attack the $\text{C}=\text{C}$ bond of styrene to generate the peroxo metalocycle, which then decomposes into SO with the simultaneous regeneration of the Co^{II} species. The generation of the undesired byproducts, such as benzaldehyde, benzoic acid and 1-phenyl-1,2-ethanediol, can be caused by several side reactions, such as the cleavage of the $\text{C}=\text{C}$ bond of styrene and

the deep oxidation or hydrolysis of SO. The reaction result that the OV- Co_3O_4 greatly surpasses its counterpart (P- Co_3O_4) in the SER performance, especially in the reactivity, can be attributed to several possible reasons. Firstly, the porous 0D/2D hybrid structure of the OV- Co_3O_4 owns large surface area, which can offer adequate active sites and facilitate the mass transfer of reactants and products. Secondly, the solution reduction strategy significantly increases the number of surface reactive Co^{II} species required for the SER, which can effectively promote the activation of styrene. Thirdly, previous studies show that the oxygen vacancies can create new defect states located in the band gap and the two electrons on the defect sites can be easily excited, assisting to improve the conductivity of Co_3O_4 [44,45,54]. Therefore, the large amount of oxygen vacancies on the surface of the OV- Co_3O_4 are beneficial for the electron transfer process and thus enhance the SER performance since structural distortion can usually improve the catalytic activity [54–56]. In addition, the introduction of oxygen vacancies in the OV- Co_3O_4 can be advantageous for the activation of the TBHP and binding of reactants onto the surface, inducing an increase in the SER efficiency [40,57,58].

4. Conclusions

In conclusion, the hierarchical 0D/2D Co_3O_4 hybrids rich in oxygen vacancies were developed by a facile NaBH_4 treatment of the pristine porous Co_3O_4 sheets. The solution reduction strategy not only induces a morphology evolution, but also facilitating the modification of the surface composition and the generation of oxygen vacancies. The obtained OV- Co_3O_4 cata-

Graphical Abstract

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Hierarchical 0D/2D Co_3O_4 hybrids rich in oxygen vacancies as catalysts towards styrene epoxidation reaction

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The hierarchical 0D/2D Co_3O_4 hybrids rich in oxygen vacancies exhibit a much better catalytic performance than the Co_3O_4 sheets in the styrene epoxidation reaction, with the yield of styrene oxide more than doubled.

lyst can be employed as an efficient and robust catalyst for the SER. Under the optimum reaction condition, the yield of SO can reach 70.9% with a styrene conversion of 99.3% and a SO selectivity of 71.4%. The excellent catalytic performance of the OV-Co₃O₄ can be attributed to the synergistic effects of hierarchical porous structure, the alteration of surface metal valence states and the presence of oxygen vacancies. In addition with the good catalytic performance, the easy modification process and cost-effectiveness also endow the OV-Co₃O₄ catalyst a great potential in the SER and beyond.

Acknowledgments

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富含氧空位的多级0D/2D Co₃O₄催化剂在苯乙烯环氧化反应中的应用

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摘要: 碳氢化合物的催化氧化是化学工业中一个非常重要的反应。在各种氧化反应中, 由于环氧化物是制药工业和精细化学品生产中的重要中间体, 而使得烯烃的催化环氧化反应近年来得到了广泛关注。环氧苯乙烷(SO)作为一种重要的环氧化物, 广泛用于精细化学品、表面涂料、化妆品和环氧树脂等的生产过程中。合成SO的传统方法均需使用危险化学品, 产生大量有害物质, 且SO选择性差。因此, 从绿色化学和可持续化学的观点来看, 以苯乙烯为底物, 研究使用H₂O₂, O₂或有机氢过氧化物作为氧化剂来制取SO的方法具有非常重要的意义。

在苯乙烯环氧化反应所使用的各种均相催化剂中, 钴离子及其配合物具有较高的活性。然而, 这些均相催化剂的分离和随后的再循环过程仍然是一个巨大的挑战, 严重限制了它们的进一步应用。因此, 多相催化剂, 包括钴基催化剂, 由于易于分离和回收, 且反应条件较为温和, 已被应用于苯乙烯的环氧化反应中。然而, 它们通常需要复杂的制备方法, 并且催化活性和SO选择性待提高。因此, 开发简单但具有高活性和稳定性的钴基多相催化剂并将其用于苯乙烯的环氧化反应仍然是一个有趣而富有挑战性的研究。

本文通过一种简易的液相NaBH₄还原策略制备了一种富含氧空位的多级0D/2D Co₃O₄催化剂, 采用XRD, Raman, SEM, TEM, EDS, XPS和N₂吸附-脱附等手段对材料的理化性质进行了系统表征。结果显示, 还原处理使得初始的二维多孔的Co₃O₄片演变为具有多级结构的0D/2D Co₃O₄材料, 比表面积由20.9 提升至37.0 m²/g, 且表面出现了丰富的氧空位, 具有更多的Co²⁺物种。将所制催化剂用于苯乙烯的环氧化反应, 结果显示, 在优化的反应条件下, 富含氧空位的0D/2D Co₃O₄催化剂的苯乙烯转化率和SO选择性分别可达到99.3%和71.4%, 且具有较好的循环使用性能, 其SO收率(70.9%)较初始的2D Co₃O₄催化剂(33.2%)提高了一倍多。结果表明, 0D/2D Co₃O₄催化剂在苯乙烯环氧化反应中的优异性能得益于其多级的形貌结构、表面元素价态的改变和氧空位的生成所产生的协同效应。这种简易的液相还原策略是一种非常有效的催化剂处理方法, 可改变催化剂形貌结构、表面元素价态和产生缺陷位, 有望应用于更多的催化反应过程中。

关键词: Co₃O₄; 还原; 氧空位; 苯乙烯; 环氧化

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