Efficient Mechanochemical Synthesis of Polyoxometalate⊂ZIF Complexes as Reusable Catalysts for Highly Selective Oxidation

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ABSTRACT: One-pot mechanochemical synthesis was demonstrated to be an efficient strategy to synthesize host–guest POM⊂rho-ZIF complexes (POM = polyoxometalate; rho-ZIF = zeolitic imidazolate framework with rho topology) with high crystallinity. In this work, the metastable rho-ZIF with large interior cavities and windows was used as host matrix for encapsulating and immobilizing bulky guest molecules with high loading efficiency and chemical stability. As novel catalysts, POM⊂rho-ZIF complexes were found effective for the selective oxidation of a series of sulﬁdes to sulfoxides. Moreover, the heterogeneity of these composite catalysts was conﬁrmed by leaching tests, and they can be recycled at least four times without signiﬁcant loss of activity.

INTRODUCTION

The development of selective and recyclable heterogeneous catalysts is highly desirable yet remains an important challenge. Polyoxometalates (POMs) that possess unique metal–oxygen framework and excellent acid/oxidation catalytic properties have great application prospects in industry.1,4 Nevertheless, the application of pure POMs is limited by low surface areas as solid catalysts5 and poor reusability as homogeneous catalysts. To overcome these drawbacks, POMs have been dispersed and immobilized to various supports with high surface areas such as zeolites,4 silica,5 activated carbon,6 mesoporous molecular sieves,7 and even metal–organic macrocycles.8 Recently, one of the most attractive strategies for heterogenizing POMs is using metal–organic frameworks (MOFs) as host matrices.9,10 For instance, Liu10 and Hill11 et al. have reported a series of highly crystalline Cu-BTC MOFs (BTC = 1,3,5-benzenetricarboxylic acid) incorporating the protonated POMs in hydrothermal synthesis and used them as effective solid catalysts for the hydrolysis and oxidation reactions. However, the solvothermal synthesis to encapsulate POMs into the cages of an MOF in a “ship-in-a-bottle” manner usually suffered from high temperature, long reaction time, a large excess of active POMs centers, bulky organic solvents, and low loading efficiency. In addition, the relatively closed structure and confined opening of Cu-BTC MOFs hindered the diffusion of bulky substrates to the active sites, limiting the scope of substrate molecules.

Mechanochemical synthesis12 is emerging as an alternative method for energy-efficiently constructing MOFs, and it avoids bulk solvents, excess reagents, and harsh conditions. Recently, Frisˇčič et al. presented improved approaches including liquid-assisted grinding (LAG) and ion- and liquid-assisted grinding (ILAG) to successfully prepare a number of MOFs.13,14 Among these MOFs, zeolitic imidazolate frameworks (ZIFs) are extremely attractive host matrices for synthesizing guest-CMOF materials because of the large interior cages and relatively small windows, which are beneﬁcial for encapsulating and immobilizing bulky guest molecules such as POMs. In 2014, Wang et al. has reported that the hydrophilic unsubstituted Keggin-type POM⊂ZIF material has not been studied, which is probably due to relatively small windows (3.2 Å) and low POM loading (maximal occupancy is ca. 11% of POM in each cavity).
Compared with sod-type ZIFs, ZIFs with rho topology have larger cavities (18.1 Å vs 12.5 Å) and windows (7.6 vs 3.2 Å), which can greatly favor the porosity accessibility by bulky substrate molecules and accelerate their diffusion rate. In addition, large interior cavities of rho-type ZIFs can increase the POM loading ratio and thus enhance the density of active centers. Consequently, exploiting rho-type ZIFs as host matrix for encapsulating POMs to prepare POM−rho-ZIF materials as heterogeneous catalysts by the one-pot mechanochemical method is very attractive, not only owing to efficient and environmentally friendly synthesis but also because of the abundant porosity and high chemical stability of the host−guest hybrid materials.

In this work, by one-pot mechanochemical synthesis, metastable rho-ZIF was used as host matrix for the first time to efficiently synthesize host−guest complexes PMoV−rho-ZIF (PMoV = H₄PMo₁₁VO₄₀; H₂PMo₉V₃O₄₀; H₄PMo₈V₇O₄₀; H₆PMo₇V₉O₄₀; H₈PMo₆V₁₁O₄₀) with high crystallinity and chemical stability. In these complexes, POMs were demonstrated to be immobilized within interior cavities of ZIFs with high loading efficiency by physical imprisonment and cannot be released without destroying the host matrix. As novel catalysts, PMoV−rho-ZIFs 1−3 were found effective for selective oxidation of a series of sulfoxides or sulfones, including bulky diphenyl sulfoxides or sulfones, and that all of the complexes kept stable crystallinity and chemical stability of the host−guest hybrid materials.

**RESULTS AND DISCUSSION**

**Preparation of PMoV−rho-ZIF.** Because PMoV belongs to the substituted Keggin-type polyoxometalate, the diameter of PMoV is ~10 Å according to the literature, which can be readily accommodated in the cavities of rho-ZIF (18.1 Å). As shown by Scheme 1, PMoV−rho-ZIF complexes were synthesized by an improved ILAG method, which needs only small amounts of salts and liquid to obviously accelerate the formation of MOFs. After a series of comparative experiments, the optimized amounts of 1 mmol of ZnO, 1.5 mmol of 2-ethylimidazole, 1.5 mmol of 4,5-dichloroimidazole, 10 mg of (NH₄)₂SO₄, 200 μL of N,N-dimethylformamide, and 0.05 mmol of corresponding PMoV were put into the zirconia milling pot and then ball-milled using zirconia balls for 2 × 30 min.

Notably, the formation of rho-ZIF is subtle, and long grinding time will lead to appearance of impurity with other topologies. After it was washed with a large mount of deionized water and alcohol, the green solids were dried under vacuum and collected to afford complexes 1−3. The PMoV/Zn ratios can be adjusted by altering the initial relative amount of PMoV and ZnO. Nevertheless, the targeted products will not form if the ratio exceeds 1:10. In all cases, almost quantitative samples of 1−3 were obtained.

**Characterization of PMoV−rho-ZIF.** Powder X-ray diffraction (XRD) patterns of complexes 1−3 have typical diffraction peaks that match well with the simulated rho-ZIF from the single-crystal XRD data, as shown in Figure 1. It is noteworthy that the powder XRD patterns of 1−3 are superior to the original ones of rho-ZIF reported by Frisčič et al. and close to the samples through solution synthesis by Chen et al. No diffraction peaks of PMoV were observed in these complexes, which indicated that aggregated PMoV particles were not formed during the mechanochemical synthesis. Therefore, the original ordered structure of rho-type ZIF remained intact after encapsulation of PMoV. When the dried samples 1−3 were immersed in various solvents such as water, methanol, ethanol, acetonitrile, and chloroform for 12 h, UV−vis spectra suggested that there were no PMoV leaching out from 1−3 and that all of the complexes kept stable crystallinity in these solvents (Figure S1). Compared with the impurity and easy structural transform of pristine rho-ZIF by ILAG method, the high chemical stability of PMoV−rho-ZIF
materials is probably due to strong POM-ZIF interaction from the complementary shape. Besides, the microscopic architecture morphology and granularity of 1 were studied by scanning electron microscopy (SEM) images, which demonstrated that all composites are exactly nanoparticles from 50 to 400 nm (Figure S2).

The Fourier transform infrared (FT-IR) spectra of 1–3 exhibited that the typical characteristic peaks of PMoV (1060, 960, 871, and 784 cm$^{-1}$, respectively, corresponding to the P–O, Mo = O, Mo–O=Mo, and Mo–O−Mo band vibrations$^{18}$) and rho-ZIF (2971, 1631, 1452, and 1279 cm$^{-1}$) all existed in PMoVrho-ZIF and proved successful hybridization of PMoV and rho-ZIF (Figure S2).

Furthermore, the components of PMoVrho-ZIF were confirmed by inductively coupled plasma atomic emission spectrometry (ICP-AES). Taking 1 as an example, according to the molar ratio of Zn/Mo = 2.75, it represented that ~79.4% cavities of rho-ZIFs are occupied by H$_4$PMo$_{11}$VO$_{40}$. The ICP-AES results of 2 (Zn/Mo = 2.67) and 3 (Zn/Mo = 2.81) revealed that the occupancy of PMoV in each cavity is 89.9% and 94.9%, respectively.

The N$_2$ adsorption isotherms of 1–3 were measured at 77 K to evaluate the effects of PMoV encapsulation into the large cages of the rho-ZIF (Figure 2). The Brunauer–Emmett–Teller (BET) surface areas of pristine rho-ZIF, 1, 2, and 3 are 1113, 379, 269, and 318 m$^2$ g$^{-1}$, respectively, which suggest obvious reduction after introducing PMoV into the reaction systems. These results indicated that the cages in rho-ZIF are indeed occupied by PMoV.

**Catalytic Oxidation.** By virtue of the excellent stability in common solvents and highly ordered porosity, PMoVrho-ZIF 1–3 are extraordinarily attractive candidates as heterogeneous catalysts. As we know, vanadium-substituted Keggin-type PMo$_{12}$V$_2$O$_{40}$ ($n = 1$–3, PMoV) have been investigated for effectively catalyzing oxidation reactions;$^{19}$ thus, sulfetation oxidation with hydrogen peroxide was selected as the model reaction for PMoVrho-ZIF catalysts. In comparison with the homogeneous PMoV, the catalytic selectivity for sulfoxides of all PMoVrho-ZIF systems for oxidizing thioanisoles were significantly enhanced from 51%–85% to 93%–96% (Table 1). Besides, controlled experiments were also performed for pristine rho-ZIF and a blank under the same conditions, and only ~22%–23% of thioanisoles were oxidized, which suggested that PMoV played a key role in the catalytic performance of PMoVrho-ZIF.

![Figure 2. N$_2$ adsorption–desorption isotherms of pristine rho-ZIF, 1, 2, and 3.](image)

**Table 1. Performance of Various Catalysts**

<table>
<thead>
<tr>
<th>catalyst$^{a}$</th>
<th>conversion (%)</th>
<th>select for sulfoxides (%)</th>
<th>system</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$<em>4$PMo$</em>{11}$VO$_{40}$</td>
<td>97</td>
<td>85</td>
<td>homo</td>
</tr>
<tr>
<td>H$<em>4$PMo$</em>{11}$V$<em>2$O$</em>{40}$</td>
<td>97</td>
<td>59</td>
<td>homo</td>
</tr>
<tr>
<td>H$<em>4$PMo$</em>{11}$V$<em>3$O$</em>{40}$</td>
<td>96</td>
<td>51</td>
<td>homo</td>
</tr>
<tr>
<td>H$<em>4$PMo$</em>{11}$V$<em>{10}$O$</em>{40}$Crho-ZIF (1)</td>
<td>97</td>
<td>96</td>
<td>hetero</td>
</tr>
<tr>
<td>H$<em>4$PMo$</em>{11}$V$<em>{10}$O$</em>{40}$Crho-ZIF (2)</td>
<td>98</td>
<td>97</td>
<td>hetero</td>
</tr>
<tr>
<td>H$<em>4$PMo$</em>{11}$V$<em>{10}$O$</em>{40}$Crho-ZIF (3)</td>
<td>98</td>
<td>93</td>
<td>hetero</td>
</tr>
<tr>
<td>blank</td>
<td>22</td>
<td>95</td>
<td></td>
</tr>
<tr>
<td>rho-ZIF</td>
<td>22</td>
<td>96</td>
<td>hetero</td>
</tr>
</tbody>
</table>

$^{a}$Reaction conditions: 0.25 mmol thioanisole, 0.000 45 mmol catalysis, 0.3 mmol H$_2$O$_2$, 25 °C, 2 mL of methanol.

To investigate the heterogeneity of PMoVrho-ZIF catalysts, the reaction activity of the supernatant solution after filtration of the catalyst was studied when the reaction was performed for 30 min. The reaction does not proceed after the removal of 1, implying no leaching of PMoV in the reaction process (Figure 3). More importantly, ICP-AES analysis of the filtrate demonstrated that there are only traces of Mo (16 ppm), and no other metals were detected in the supernatant solution. Consistent with ICP-AES results, the UV–vis spectroscopy further confirmed that no PMoV were existing in the filtrate (Figure S6).

Because of the exceptional catalytic activity in the oxidation of thioanisoles, 1 was chosen as the model catalyst to optimize the reaction conditions, and the selected examples are summarized in Table 2. Several reaction variables such as the solvent, oxidant amount, reaction time, and catalyst amount were modulated to afford optimized conditions, which representatively involved 0.25 mmol of thioanisole, 0.3 mmol of H$_2$O$_2$, 0.00045 mmol of catalyst, and 2 mL of methanol at 25 °C for 12 h.

To evaluate the recyclability of catalyst 1, the catalyst was isolated by sedimentation after each experiment and then washed with EtOH and H$_2$O and dried under vacuum for using
in the subsequent run. As shown by Figure 4, the catalyst can be reusable with no evident loss of activity in oxidation for at least four times, and FT-IR spectra and powder XRD of catalysts showed no obvious alteration after five cycles (Figures S7 and S8). The excellent activity and selectivity for the transformation of thioanisoles to sulfoxides of the catalyst encouraged us to explore the selective oxidation of other sulfer compounds. With optimized conditions in hand, we explored the scope of substrates with a series of valuable sulfer compounds. As shown in Table 3, it is reasonable to conclude that as the size of the substrates increase, the conversion and selectivity of substrates decrease slightly owing to the larger steric hindrance. However, the activity and selective oxidation of various sulfoxides retained high catalytic level.

### CONCLUSION

In summary, one-pot mechanochemical synthesis has been demonstrated to be an efficient and environmentally friendly method to prepare host–guest POMCMOF complexes with high crystallinity, and vanadium-substituted Keggin-type POMs can be accommodated within the cavities of rho-type ZIF with high loading efficiency and chemical stability by physical imprisonment and cannot be released without destroying the host matrice. To our knowledge, this is the first example that metastable rho-ZIF with large interior cavities and windows is used as host matrice for encapsulating and immobilizing bulky guest molecules. More importantly, the mechanochemically prepared POMCMOF materials were used as effective heterogeneous catalyst for selective oxidation of a series of sulfoxides to sulfoxides and can be recycled at least four times without significant loss of activity. This work provides a versatile and efficient strategy for design and synthesis of novel catalysis systems that realize excellent dispersion and immobilization of the catalytically active centers. Further developments of this methodology are warranted.

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**Table 2. Effect of Reaction Conditions**

<table>
<thead>
<tr>
<th>entry</th>
<th>solvent</th>
<th>oxygenant (mmol)</th>
<th>time (h)</th>
<th>conversion (%)</th>
<th>select for sulfoxides (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MeCN</td>
<td>0.55</td>
<td>18</td>
<td>99</td>
<td>4</td>
</tr>
<tr>
<td>2</td>
<td>EtOH</td>
<td>0.55</td>
<td>18</td>
<td>99</td>
<td>73</td>
</tr>
<tr>
<td>3</td>
<td>BDO</td>
<td>0.55</td>
<td>18</td>
<td>99</td>
<td>19</td>
</tr>
<tr>
<td>4</td>
<td>CHCl₃</td>
<td>0.55</td>
<td>18</td>
<td>99</td>
<td>42</td>
</tr>
<tr>
<td>5</td>
<td>MeOH</td>
<td>0.55</td>
<td>18</td>
<td>99</td>
<td>39</td>
</tr>
<tr>
<td>6</td>
<td>MeCN</td>
<td>0.55</td>
<td>&gt;99</td>
<td>&lt;1</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>MeCN</td>
<td>0.3</td>
<td>18</td>
<td>90</td>
<td>70</td>
</tr>
<tr>
<td>8</td>
<td>MeOH</td>
<td>0.3</td>
<td>&gt;99</td>
<td>&gt;99</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>MeOH</td>
<td>0.3</td>
<td>8</td>
<td>88</td>
<td>&gt;99</td>
</tr>
<tr>
<td>10</td>
<td>MeOH</td>
<td>0.3</td>
<td>12</td>
<td>99</td>
<td>&gt;99</td>
</tr>
</tbody>
</table>

*aReaction conditions: 0.25 mmol of thioanisole, 0.00045 mmol of catalysis, H₂O₂ (30%), 25 °C, 2 mL of solvent. BDO is 1,4-butylene glycol.*

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**Table 3. Substrate Expansion for Catalytic Oxidation**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Conversion (%)</th>
<th>Selection for sulfoxides (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image.png" alt="Substrate" /></td>
<td>97.0</td>
<td>95.5</td>
</tr>
<tr>
<td>2</td>
<td><img src="image.png" alt="Substrate" /></td>
<td>92.8</td>
<td>84.2</td>
</tr>
<tr>
<td>3</td>
<td><img src="image.png" alt="Substrate" /></td>
<td>90.4</td>
<td>89.5</td>
</tr>
<tr>
<td>4</td>
<td><img src="image.png" alt="Substrate" /></td>
<td>94.4</td>
<td>91.3</td>
</tr>
<tr>
<td>5</td>
<td><img src="image.png" alt="Substrate" /></td>
<td>82.7</td>
<td>89.0</td>
</tr>
<tr>
<td>6</td>
<td><img src="image.png" alt="Substrate" /></td>
<td>97.1</td>
<td>92.0</td>
</tr>
<tr>
<td>7</td>
<td><img src="image.png" alt="Substrate" /></td>
<td>&gt;99</td>
<td>91.3</td>
</tr>
</tbody>
</table>

*aReaction conditions: 0.25 mmol of substrates, 0.00045 mmol of catalyst, 0.3 mmol of H₂O₂, 25 °C, 2 mL of MeOH.*

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**Figure 4.** Recyclability of catalyst in the selective oxidation of thioanisole.
attempts to encapsulate various guest molecules for extending the functionality of MOFs are being undertaken.

**Experimental Section**

**Materials and Methods.** All materials used in this work were purchased from commercial sources and used without further purification. PMoV (PMo$_{12}$V$_{n}$, $n = 1$–3) were produced according to a procedure described in the literature. Powder XRD was performed on a Bruker D8 diffractometer with a Cu Kα X-ray radiation source ($λ = 0.154056$ nm). FT-IR spectra were recorded from KBr pellets in the range of 4000–500 cm$^{-1}$ on a Nicolet 170 FT-IR spectrometer. Gas chromatography (GC) analyses were performed on a Shimadzu GC-2014C with a flame ionization detector (FID) equipped with an HP-5 capillary column in flowing $N_{2}$ with a heating rate of 5 °C min$^{-1}$. GC mass spectra were recorded on an Agilent 7890A-5975C at an ionization voltage of 1200 V. C, H, and N elemental analyses were conducted on a PerkinElmer 240 °C elemental analyzer, and Mo, W, and V elemental analyses were performed on an axial view ICP-AES. The one-pot mechanochemical synthesis was performed in a ball mill (QM-3C, Nanjing University, China).

PMoVCr$^{3+}$-ZIF. Synthetic reactions were performed in an 80 mL zirconia milling pot with 10 mm diameter zirconia balls. One millimole synthesis was performed in a ball mill (QM-3C, Nanjing University performed on an axial view ICP-AES. The one-pot mechanochemical reaction mixtures were analyzed by GC-MS and GC.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b02163.

X-ray powder diffraction patterns, SEM pictures, infrared and UV–vis spectra. (PDF)

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**Author Contributions**

All authors have given approval to the final version of the manuscript.

**Notes**

The authors declare no competing financial interest.

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