Supporting information

Epoxides hydrolysis and alcoholysis reactions over crystalline Mo–V–O oxide

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Materials
All chemicals were of analytical grade and used as purchased without further purification. Most materials were purchased from Tianjin Kermel Chemical Reagent Co. Ltd. VOSO$_4$·nH$_2$O (64.83 wt%) was obtained from Shanghai Huating Chemicals Factory Co. Ltd.

Mo-V-O materials synthesis
The Mo-V-O materials were synthesized by hydrothermal method. An amount of aqueous solution of VOSO$_4$·nH$_2$O was dropped into the aqueous solution of (NH$_4$)$_6$Mo$_7$O$_{24}$ with stirring for ten minutes at ambient temperature. The mixture was transferred into an autoclave with a Teflon inner tube and Teflon thin sheet, and bubbled with N$_2$ to remove the oxygen. The pH for preparation of the orthorhombic material is about 3.2. Then hydrothermal synthesis is continued for 48 h at 175 °C. The obtained gray solid was separated by filtration, washing and drying. The obtained solid (1 g) was purified with 50 mL oxalic acid of 0.4 mol L$^{-1}$ and washed to neutral and dried. The preparation of trigonal material followed the same procedures as the above, except that the pH was adjusted to 2.2 using H$_2$SO$_4$ (9 vol %). The tetragonal material was prepared by heat-treatment of the orthorhombic material in air for 2 h at 400 °C and then in nitrogen for 2 h at 575 °C with a heating rate of 10 °C min$^{-1}$.

Characterization
The morphology of the materials was characterized by scanning electron microscopy on JSM-7800F (Japan). The powder XRD patterns were measured on X-pert Pro-1 X-ray diffractometer (Netherlands) with Cu Ka (tube voltage: 40 kV, tube current: 30 mA, Scan rate 10 °C min$^{-1}$). The infrared (FT-IR) spectra were measured as KBr disks on a Bruker Tensor 27 FT-IR spectrometer (Germany) with 16 scan at a resolution of 4 cm$^{-1}$. The $^1$H NMR and $^{13}$C NMR spectra of products were characterized with liquid nuclear magnetic resonance spectrometer (AVANCE III HD 700MHz).

The acidity was measured by NH$_3$-TPD with ThermoStar$^\text{TM}$ (Germany), gas flow 50 mL min$^{-1}$. Before measurements, the samples were treated at the N$_2$ flow at 100 °C to remove the adsorbed surfaced species. Then NH$_3$ was introduced and pass through the sample. The adsorption of NH$_3$ was maintained until the adsorption peak intensity of NH$_3$ was not increased. Finally, the NH$_3$ adsorbed by the sample was desorbed with temperature rising (10 °C min$^{-1}$) till the desorption line equilibrium.

Catalytic test
Catalytic reactions were carried out in a 15-mL pressure bottle under stirring. The catalyst (0.01 g) was added to the distilled water (1 mL) containing 3 mmol of epoxide. The reaction was continued at a desired temperature. After reaction, the residue was extracted and filtered out using membrane filter. The filtrate was analyzed in GC-MS and GC (7890). The conversion of epoxide and yield of ring-opening products were quantified using internal standard (1,3,5-trimethyl-benzen).
### Table S1 Alcoholysis of propylene oxide with different alcohols in different conditions

<table>
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<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Product</th>
<th>Conv./%</th>
<th>Sel./%</th>
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<td>MeOH</td>
<td>![Product Structure]</td>
<td>79</td>
<td>44/54</td>
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<tr>
<td>2 c</td>
<td>MeOH</td>
<td>![Product Structure]</td>
<td>90</td>
<td>47/53</td>
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<tr>
<td>3 d</td>
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<td>![Product Structure]</td>
<td>&gt;99</td>
<td>39/54</td>
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<td>4</td>
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<td>79</td>
<td>39/53</td>
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<tr>
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<td>n-BuOH</td>
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<td>64</td>
<td>32/61</td>
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<td>56</td>
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<td>10</td>
<td>benzyl alcohol</td>
<td>![Product Structure]</td>
<td>36</td>
<td>35/52</td>
</tr>
</tbody>
</table>

**Reaction conditions:** 3 mmol propylene oxide, 1 mL alcohol, 0.01 g trigonal Mo-V-O, 100 °C, 8 h.

![XRD Patterns](image)

**Fig. S1** XRD patterns of fresh and used crystalline trigonal Mo-V-O.
The catalysts after reaction show similar structure with the fresh catalyst measured by the XRD.

Fig. S2 The SEM images of used trigonal Mo-V-O (milling time-10 min).
The catalyst material after the reaction still keep the morphology of rod crystal, and there is no obvious change in the average particle size.

Fig. S3 The scheme with the structure of the trigonal Mo-V-O.
In the hydrolysis and alcoholysis catalysis, we identified the final products by matching the GC-MS spectrum of the products with the standard spectrum. Some GC-MS spectrum of the products selected are showed as follows (Fig. S4- Fig. S17):
In the hydrolysis and alcoholysis catalysis, the products were separated from the reaction system and characterized with $^1$H NMR and $^{13}$C NMR. The spectrum of some products are showed as follows (Fig. S18- Fig. S22):

$^1$H NMR (400 MHz, CD$_3$OD) 3.87 (d, J=5.2 Hz, 1H), 3.84-3.23 (m, 24H), 1.11 (t, J=6.4 Hz, 13H).

$^{13}$C NMR (101 MHz, CD$_3$OD) δ=77.91, 77.62, 65.80, 64.87, 57.94, 55.45, 18.38, 14.79.
$^1$H NMR (400 MHz, D$_2$O) $\delta$=3.92-3.84 (m, 1H), 3.69-3.59 (m, 2H), 3.56 (ddd, $J$=11.7, 6.0, 2.8 Hz, 2H).

$^{13}$C NMR (101 MHz, D$_2$O) $\delta$=71.14, 62.54, 45.92.
$^1$H NMR (400 MHz, D$_2$O) $\delta$=3.78-3.68 (m, 1H), 3.35 (ddd, $J$=18.2, 11.5, 5.5 Hz, 2H), 1.01 (d, $J$=6.5 Hz, 3H).

$^{13}$C NMR (101 MHz, D$_2$O) $\delta$=67.85, 66.58, 18.09.

Fig. S19

Fig. S20
$^1$H NMR (400 MHz, D$_2$O) $\delta$=3.48-3.17 (m, 2H), 1.95-1.76 (m, 2H), 1.66-1.48 (m, 2H), 1.16 (d, J=4.5 Hz, 4H).

$^{13}$C NMR (101 MHz, D$_2$O) $\delta$=74.81, 32.55, 23.80.
$^1$H NMR (400 MHz, D$_2$O) $\delta=7.36$-7.21 (m, 5H), 4.67 (t, $J=6.0$, 1H), 3.60 (d, $J=6.0$ Hz, 2H).

$^{13}$C NMR (101 MHz, D$_2$O) $\delta=140.54$, 128.65, 128.09, 126.39, 74.06, 66.31.

Fig. S22