One-pot synthesis of ethylene glycol by oxidative hydration of ethylene with hydrogen peroxide over titanosilicate catalysts

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Abstract: The oxidative hydration of ethylene with hydrogen peroxide was investigated over various titanosilicate catalysts for the purpose of one-pot synthesis of ethylene glycol (EG). The Ti-MWW/H₂O₂/H₂O catalytic system showed the highest EG yield together with high H₂O₂ conversion and utilization efficiency for the EG formation. Amine-assisted structural rearrangement of Ti-MWW not only enhanced the catalytic activity but also improved its stability in the one-pot synthesis of EG.

Keywords: titanosilicate, oxidative hydration, ethylene glycol.

1. Introduction
Ethylene glycol (EG) as the simplest diol is widely used as engine coolants, antifreezes as well as raw material for the manufacture of polyesters, cosmetics, and other down-stream products. The non-catalytic hydration of ethylene oxide (EO) to EG at elevated temperatures (423 - 493 K) still accounts for the major market share, since it was developed in 1937 by Union Carbide Corporation (UCC). Tandem catalysis, that enables multistep reactions to take place in one-pot, holds great potential for increasing the efficiency of chemical synthesis. Direct synthesis of EG through oxidative hydration of ethylene by H₂O₂, which formally combines together ethylene epoxidation and subsequent EO hydration, could be a more economically viable process because it operates with the low-cost and easily available feedstock of alkenes, and requires no separation of epoxide after the first step (Scheme 1). In this present study, with the aim of producing EG efficiently and selectively, we applied titanosilicates to the oxidative hydration of ethylene with H₂O₂.

2. Experimental
Four titanosilicates (Ti-MWW, TS-1, Ti-MCM-68 and Ti-MOR) have been employed in the one-pot synthesis of ethylene glycol by oxidative hydration of ethylene. The oxidative hydration of ethylene to EG with hydrogen peroxide was carried out under vigorous stirring in an autoclave reactor equipped with a teflon-inner. In a typical run, 0.1 g titanosilicate, 10 g H₂O, and 10 mmol H₂O₂ (30 wt%) were added into the reactor, and then ethylene was charged into the autoclave to replace the air inside three times, reaching a constant reaction pressure at 2.5 MPa at 313 K. After specified reaction time, the reactor was cooled down with ice water to stop the reaction and depressurized slowly before opening. The structural rearrangement treatment for Ti-MWW was performed in aqueous solution of piperidine. The treated product was calcined to obtain Re-Ti-MWW.
3. Results and discussion

Various titanosilicates with different structure topologies and compositions were evaluated in the oxidative hydration of ethylene with H$_2$O$_2$ (Table 1). B-free Ti-MWW/H$_2$O$_2$/H$_2$O was considered as the most suitable reaction system with the highest EG yield together with high H$_2$O$_2$ conversion and utilization efficiency for the oxidative hydration of ethylene. The positive effect of structural rearrangement over Ti-MWW catalysts was found in the oxidative hydration of ethylene, as the H$_2$O$_2$ conversion, the EG selectivity and the EG yield over Re-Ti-MWW were increased in comparison to Ti-MWW (Fig. 1). Moreover, Re-Ti-MWW is more resistance to deactivation in comparison to Ti-MWW. In addition, further calcination at 823 K for 6 h can restore the activity (Fig. 1C, the eighth and ninth reuses), suggesting the deactivation, mainly due to the deposition of heavy molecules within pores, was reversible and reproducible.

### Table 1. A comparison of the oxidative hydration of ethylene over various titanosilicates.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Structure</th>
<th>Si/Ti</th>
<th>Si/B</th>
<th>Si/Al</th>
<th>H$_2$O$_2$ (%)</th>
<th>Products distribution (%)</th>
<th>EG yield (%)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>[Ti, B]-MWW</td>
<td>MWW</td>
<td>49</td>
<td>73</td>
<td>∞</td>
<td>82.7</td>
<td>66.3</td>
<td>56.4</td>
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<tr>
<td>2</td>
<td>Ti-MWW</td>
<td>MWW</td>
<td>50</td>
<td>419</td>
<td>∞</td>
<td>87.9</td>
<td>68.8</td>
<td>60.0</td>
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<tr>
<td>3</td>
<td>Ti-MCM-68</td>
<td>MSE</td>
<td>42</td>
<td></td>
<td>102</td>
<td>13.3</td>
<td>37.6</td>
<td>88.0</td>
</tr>
<tr>
<td>4</td>
<td>TS-1</td>
<td>MFI</td>
<td>50</td>
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<td>∞</td>
<td>57.1</td>
<td>44.9</td>
<td>27.0</td>
</tr>
<tr>
<td>5</td>
<td>Ti-MOR</td>
<td>MOR</td>
<td>51</td>
<td></td>
<td>110</td>
<td>1.9</td>
<td>36.1</td>
<td>100.0</td>
</tr>
</tbody>
</table>

Reaction conditions: cat., 0.1 g; ethylene, 2.5 MPa; H$_2$O$_2$, 10 mmol; H$_2$O, 10 mL; temp., 313 K; time, 2 h.

Figure 1. Comparison of H$_2$O$_2$ conversion (A) and EG selectivity (B) over Ti-MWW (Si/Ti = 50, Si/B = 419) and Re-Ti-MWW (Si/Ti = 50, Si/B = 417). Reaction conditions: cat., 0.05 g; ethylene, 2.5 MPa; H$_2$O$_2$, 10 mL; H$_2$O, 10 mmol; temp., 333 K. Changes of EG yield with the reaction-regeneration cycles (C) on Ti-MWW (Si/Ti = 50, Si/B = 419) and Re-Ti-MWW (Si/Ti = 50, Si/B = 417). Reaction conditions for the first run: cat., 0.15 g; ethylene, 2.5 MPa; H$_2$O$_2$, 30 mL; H$_2$O, 30 mmol; temp., 333 K; time, 2 h. All the catalytic runs proceed at a constant ratio of catalyst-oxidant-solvent.

4. Conclusions

Ti-MWW possesses a superior catalytic performance to other titanosilicates in the oxidative hydration of ethylene to EG with H$_2$O as the solvent. The structural rearrangement proves to be an effective way to increase the catalytic activity and the resistance of Ti-MWW to the deactivation in the oxidative hydration of ethylene.

References