

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

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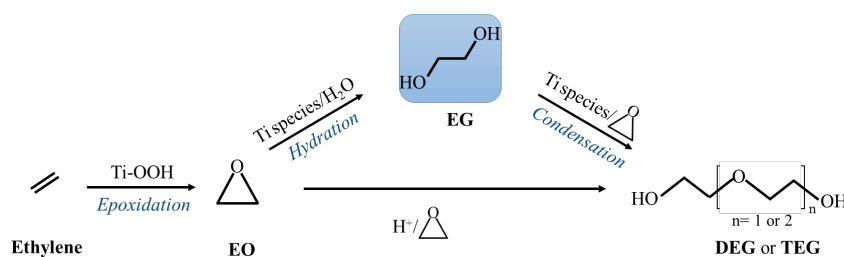
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Abstract: The oxidative hydration of ethylene with hydrogen peroxide was investigated over various titanasilicate catalysts for the purpose of one-pot synthesis of ethylene glycol (EG). The Ti-MWW/H₂O₂/H₂O catalytic system showed the highest EG yield 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: titanasilicate, 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).¹ 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 titanasilicates to the oxidative hydration of ethylene with H₂O₂.²



Scheme 1. Reaction pathways in the oxidative hydration of ethylene.

2. Experimental

Four titanasilicates (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 titanasilicate, 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 of 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.³ The treated product was calcined to obtain Re-Ti-MWW.

3. Results and discussion

Various titanasilicates with different structure topologies and compositions were evaluated in the oxidative hydration of ethylene with H₂O₂ (Table 1). B-free Ti-MWW/H₂O₂/H₂O was considered as the most suitable reaction system with the highest EG yield together with high H₂O₂ 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 H₂O₂ 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 titanasilicates.

Entry	Catalyst	Structure	Si/Ti	Si/B	Si/Al	H ₂ O ₂ (%)		Products distribution (%)			EG yield (%)
						conv.	eff.	EO	EG	others	
1	[Ti, B]-MWW	MWW	49	73	∞	82.7	66.3	56.4	40.1	3.5	22.0
2	Ti-MWW	MWW	50	419	∞	87.9	68.8	60.0	36.7	3.3	22.2
3	Ti-MCM-68	MSE	42	∞	102	13.3	37.6	88.0	12.0	0.0	0.6
4	TS-1	MFI	50	∞	∞	57.1	44.9	27.0	69.2	3.8	17.7
5	Ti-MOR	MOR	51	∞	110	1.9	36.1	100.0	0.0	0.0	0.0

Reaction conditions: cat., 0.1 g; ethylene, 2.5 MPa; H₂O₂, 10 mmol; H₂O, 10 mL; temp., 313 K; time, 2 h.

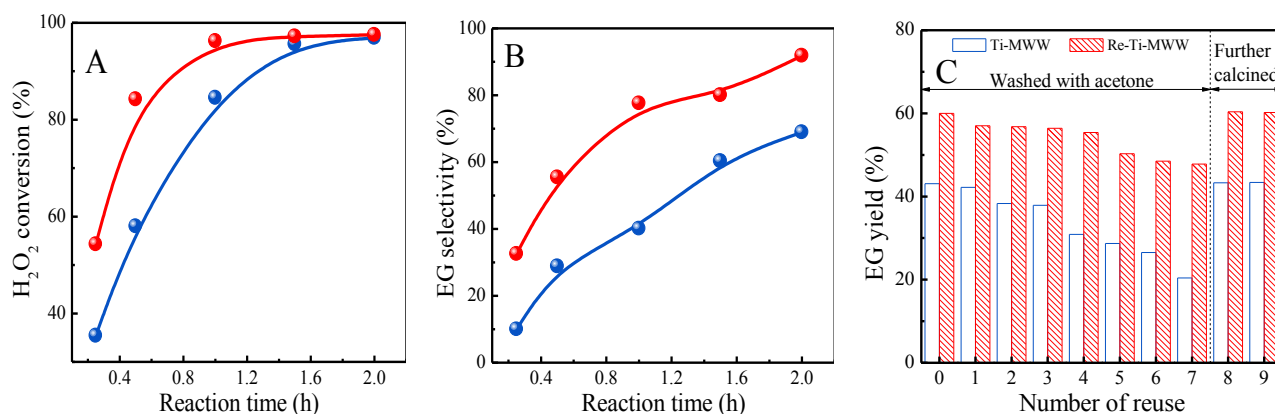


Figure 1. Comparison of H₂O₂ conversion (A) and EG selectivity (B) over Ti-MWW (Si/Ti = 50, Si/B = 419) and Re-Ti-MWW (Si/Ti = 50, Si/B = 417). Reaction conditions: cat., 0.05 g; ethylene, 2.5 MPa; H₂O, 10 mL; H₂O₂, 10 mmol; temp., 333 K. Changes of EG yield with the reaction-regeneration cycles (C) 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; H₂O, 30 mL; H₂O₂, 30 mmol; temp., 333 K; time, 2 h. All the catalytic runs proceeded at a constant ratio of catalyst-oxidant-solvent.

4. Conclusions

Ti-MWW possesses a superior catalytic performance to other titanasilicates in the oxidative hydration of ethylene to EG with H₂O 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

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