

Supporting Information for:

**Efficient synthesis of glycerol carbonate over commercially available  
4A molecular sieve via an integrated vacuum reactive distillation  
process**

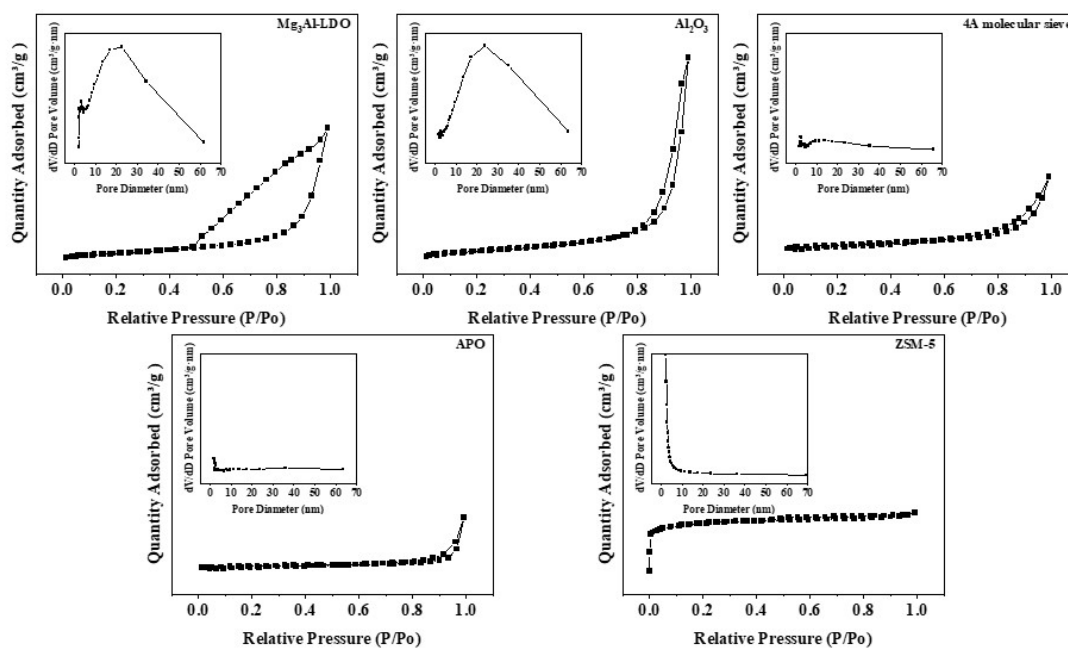
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**Table S1** Comparison with previous reported results.

Catalyst	GL Conv. (%)	GC Sel. (%)	Reference
4A molecular sieve	98	>99	This work
AlCaMO	89	98	[1]
Tri-n-butylamine supported on MCM-41 molecular sieve	94	84	[2]
MMO-M(15)	92	97	[3]
[HPTPA]OH	98	75	[4]

### N<sub>2</sub> adsorption/desorption isotherms and pore size distributions



**Fig. S1.** N<sub>2</sub> adsorption/desorption isotherms and pore size distributions.

XRD for catalyst

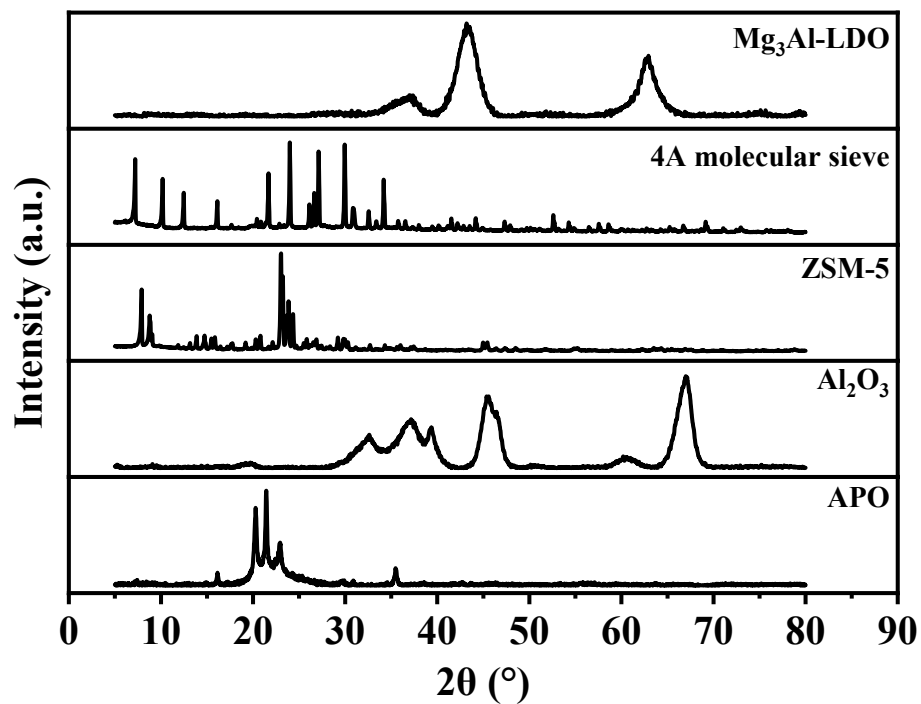


Fig. S2. XRD for Mg<sub>3</sub>Al-LDO, 4A molecular sieve, ZSM-5, Al<sub>2</sub>O<sub>3</sub> and APO.

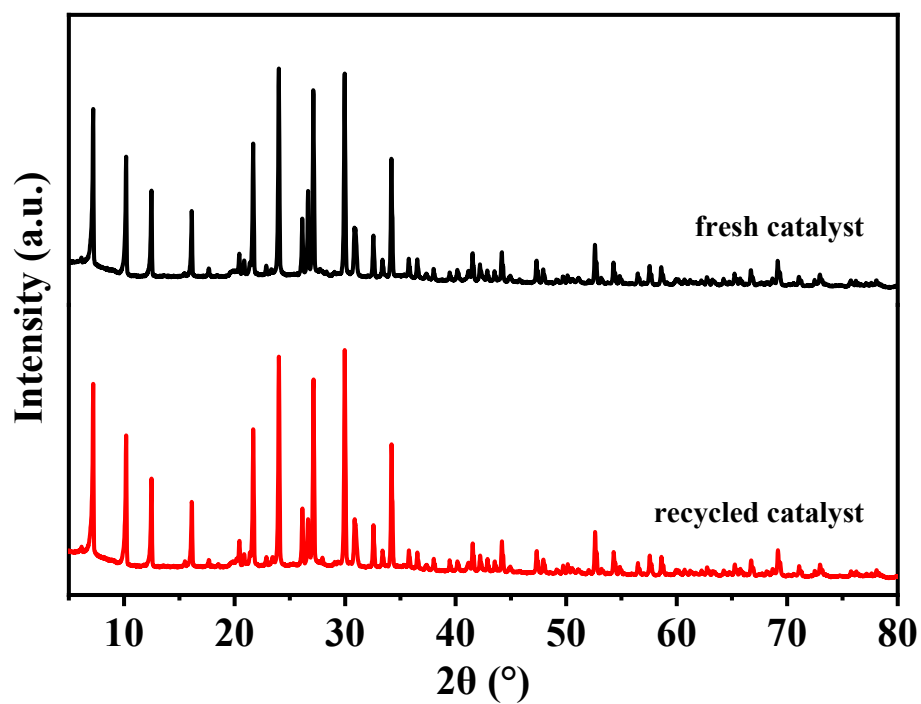
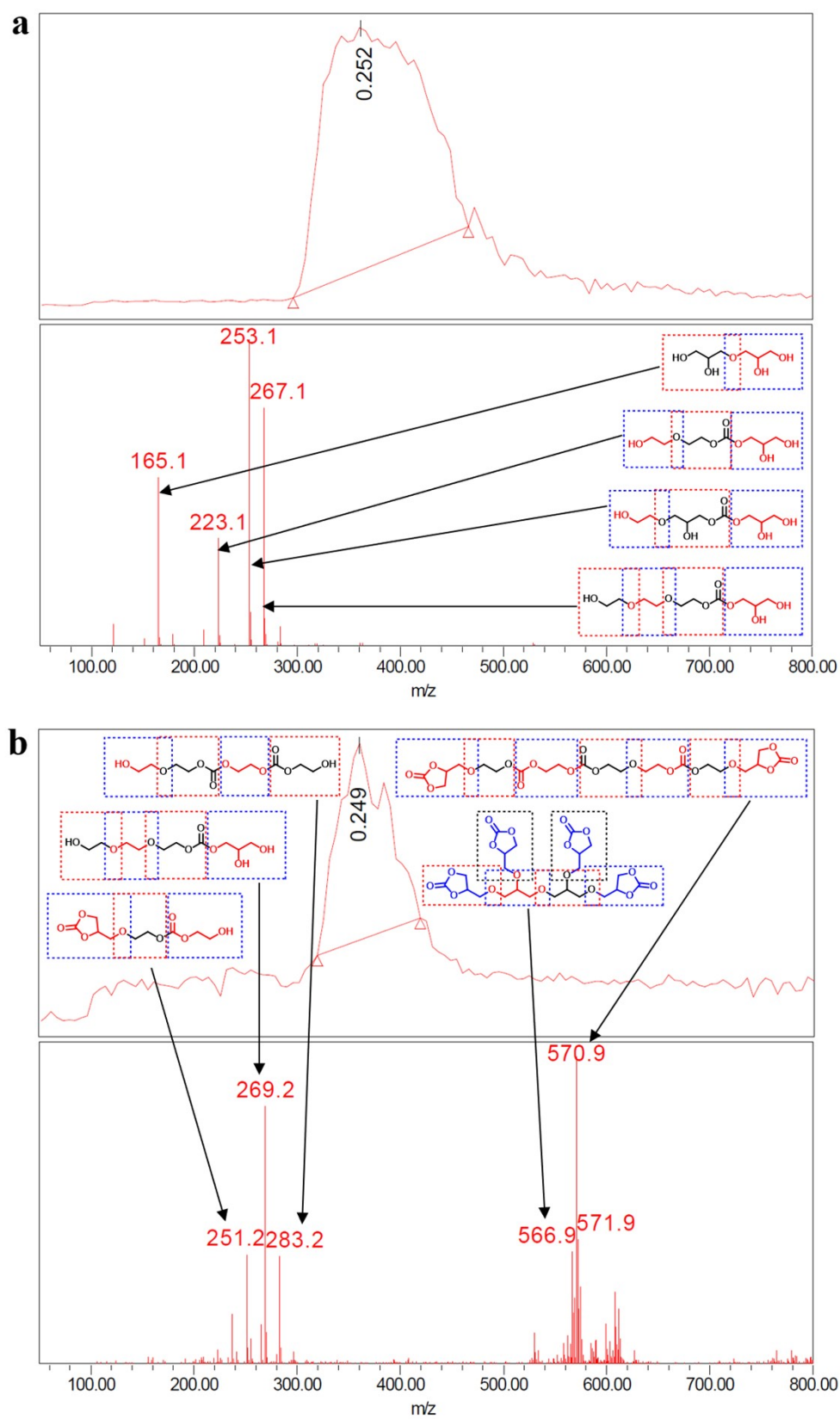


Fig. S3. Comparison of XRD after five repetitions with that at the beginning.

The LC-MS chromatograms of the distillation residue at temperatures above 125 °C



**Fig. S4.** The LC-MS chromatograms (a. negative ion mode; b. positive ion mode) of the distillation residue with a reaction temperature of 125 °C.

### NH<sub>3</sub>-TPD and CO<sub>2</sub>-TPD analysis of catalysts.

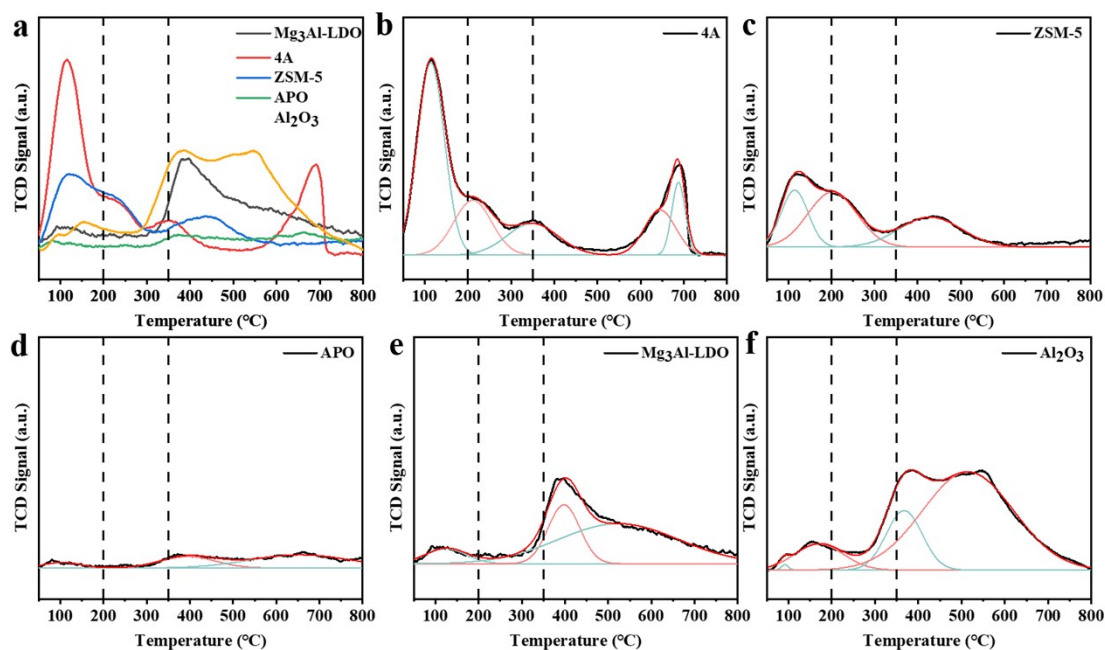


Fig. S5 NH<sub>3</sub>-TPD analysis of catalysts

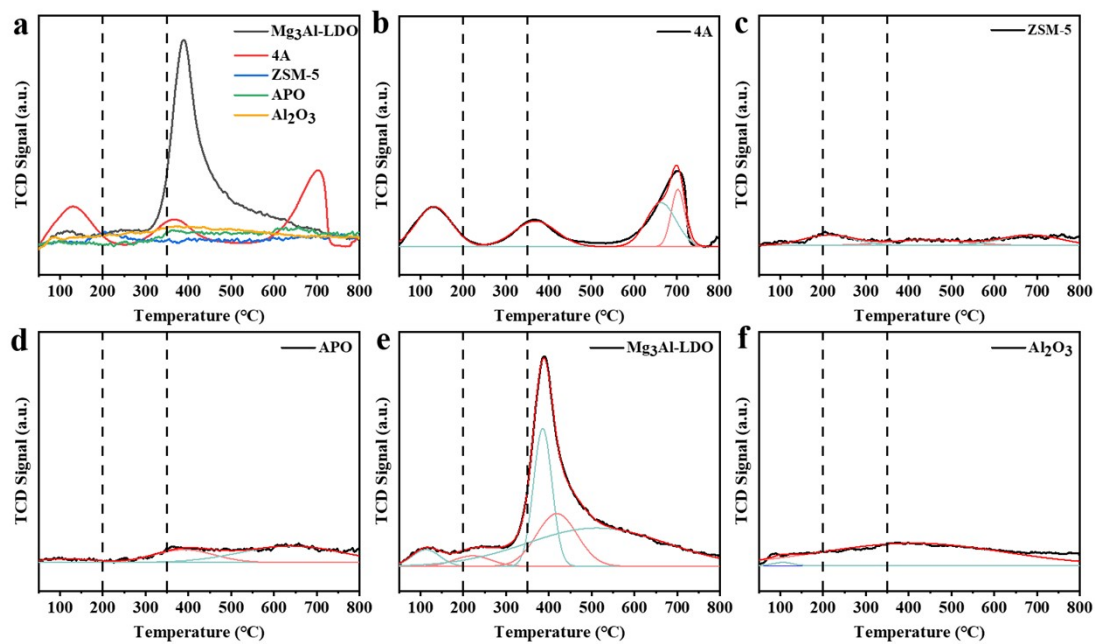
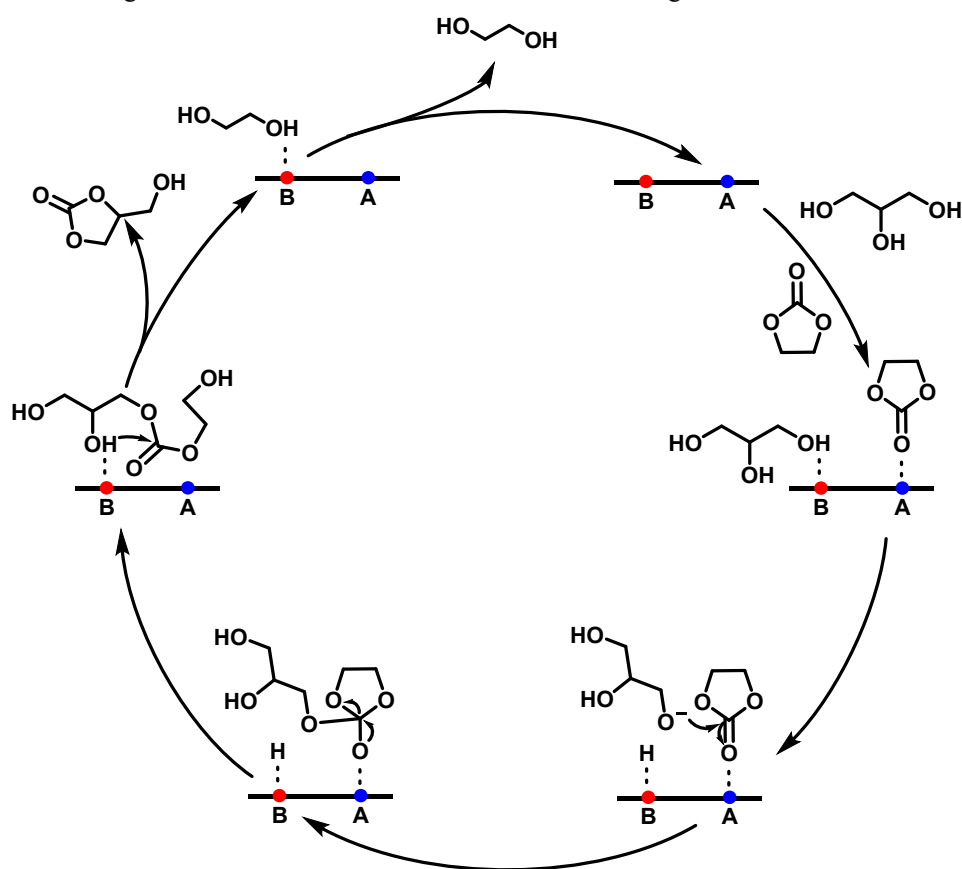


Fig. S6 CO<sub>2</sub>-TPD analysis of catalysts

### An acid-base bifunctional model-based feasible mechanism

An acid-base bifunctional model-based feasible mechanism for the transesterification between glycerol and ethylene carbonate can be proposed based on the analysis of published literature on similar reactions that dimethyl carbonate ester interchange with glycerol (Scheme S1). In the initial step, the acidic sites on the catalyst's surface facilitate the adsorption of ethylene carbonate by forming a connection with its carbonyl oxygen. Meanwhile, a proton-capturing alkaline site on the catalysts' surface activates the primary O-H bond of GL. In the second step, the intermediate, which swiftly generate a ring-opening intermediate through an intramolecular reaction, is formed by the reaction between the activated GL and the activated carbonyl carbon of the EC. In the final step of the reaction, the ring-opened intermediate is decarboxylated by an intramolecular nucleophilic substitution reaction, converting into glycerol carbonate and ethylene glycol. The catalyst is also regenerated in the interim. Thus, it is meaningful to consider the effect of Acids and bases during the reaction.



**Scheme S1.** An acid-base bifunctional model-based feasible mechanism [1, 5-6].

## References

- [1] M. J. Climent, A. Corma, P. De Frutos, S. Iborra, M. Noy, A. Velty, P. Concepción, *J. Catal.* 269 (1) (2010) 140-149. <https://doi.org/10.1016/j.jcat.2009.11.001>
- [2] H.-J. Cho, H.-M. Kwon, J. Tharun, D.-W. Park, *J. Ind. Eng. Chem.* 16 (2010) 679–683. <https://doi.org/10.1016/j.jiec.2010.07.019>
- [3] A. Dalma, B. Nancy, E. Griselda, C. Mónica, *Front. Chem. Sci. Eng.* 4 (2022) 1027152. <https://doi.org/10.3389/fceng.2022.1027152>
- [4] E. Elhaj, H. Wang, Y. Gu, *Mol. Catal.* 468 (2019) 19-28. <https://doi.org/10.1016/j.mcat.2019.02.005>
- [5] C.-W. Chang, Z.-J. Gong, N.-C. Huang, C.-Y. Wang, W.-Y. Yu, *Catal. Today* 351 (2020) 21-29. <https://doi.org/10.1016/j.cattod.2019.03.007>
- [6] G. M. De Paula, J. G. Eid, D. Cardoso, *React. Kinet. Mech. Cat.* 136 (1) (2023) 107-124. <https://doi.org/10.1007/s11144-023-02349-4>