

Supplementary Material

Quaternary Ni-Zn-Mg-Al bifunctional nanoclays as catalytic precursors for the production of glycerol carbonate

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Figure S1. Chromatogram of the reaction between dimethyl carbonate and glycerol using the MMO-Ni₁₅Zn₂₀ catalyst.

Figure S2. EDS elemental mapping of MMO-MgAl.

Figure S3. EDS elemental mapping of MMO-Ni₁₅Zn₀.

Figure S4. EDS elemental mapping of MMO-Ni₀Zn₁₅.

Figure S5. EDS elemental mapping of MMO-Ni₁₅Zn₁₅.

Figure S6. EDS elemental mapping of MMO-Ni₁₅Zn₂₀.

Figure S7. EDS elemental mapping of MMO-Ni₁₅Zn₂₅.

Figure S8. Proposed mechanism for transesterification between Gly and DMC, along with the subsequent decarboxylation of CG to GD.

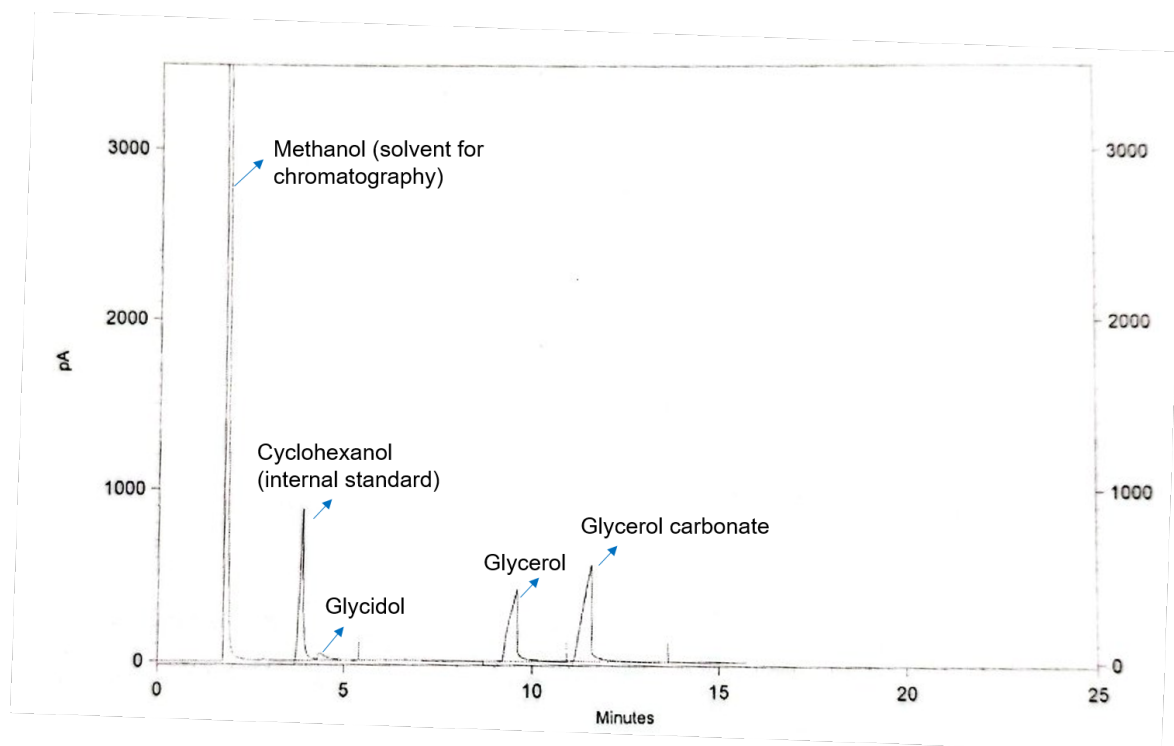


Figure S1. Representative chromatogram of the reaction between dimethyl carbonate and glycerol using the MMO-Ni₁₅Zn₂₀ catalyst.

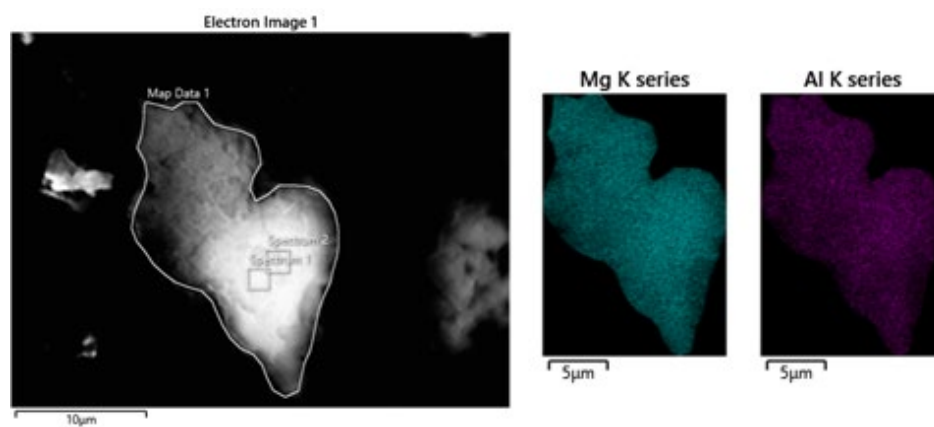


Figure S2. EDS elemental mapping of MMO-MgAl.

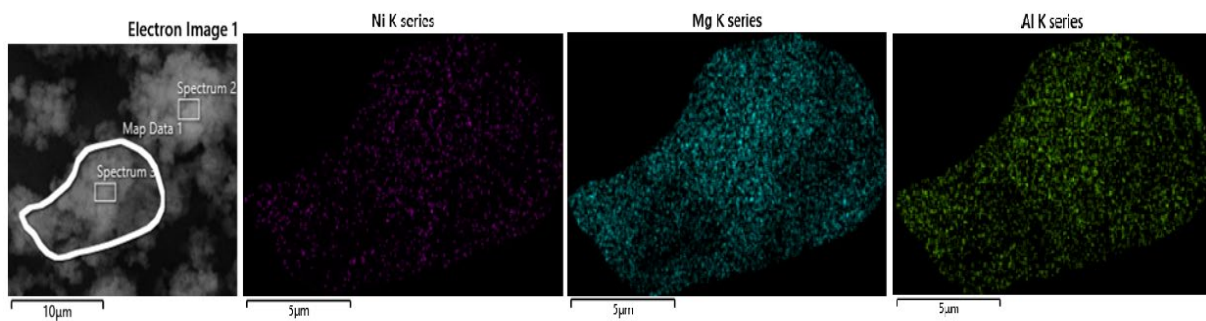


Figure S3. EDS elemental mapping of MMO-Ni₁₅Zn₀.

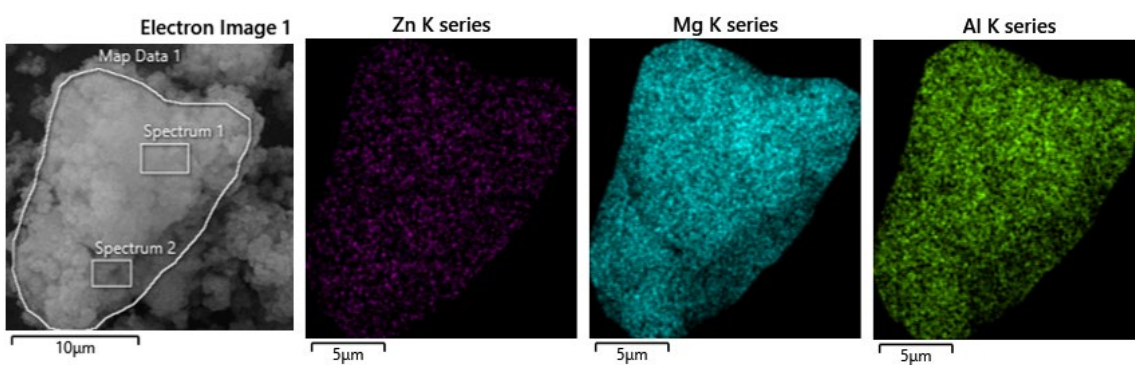


Figure S4. EDS elemental mapping of MMO-Ni₀Zn₁₅.

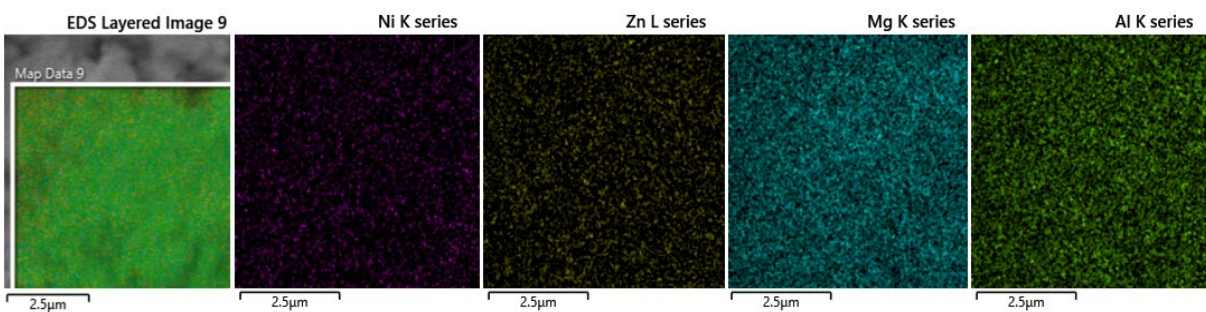


Figure S5. EDS elemental mapping of MMO-Ni₁₅Zn₁₅.

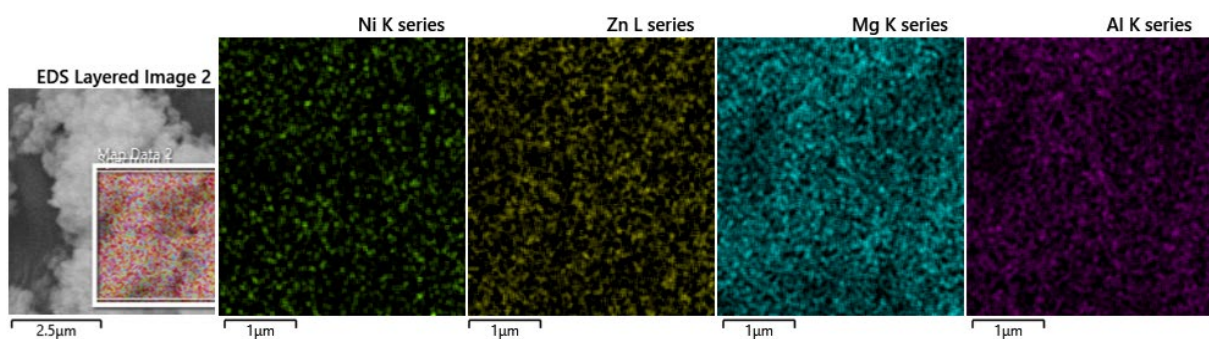


Figure S6. EDS elemental mapping of MMO-Ni₁₅Zn₂₀.

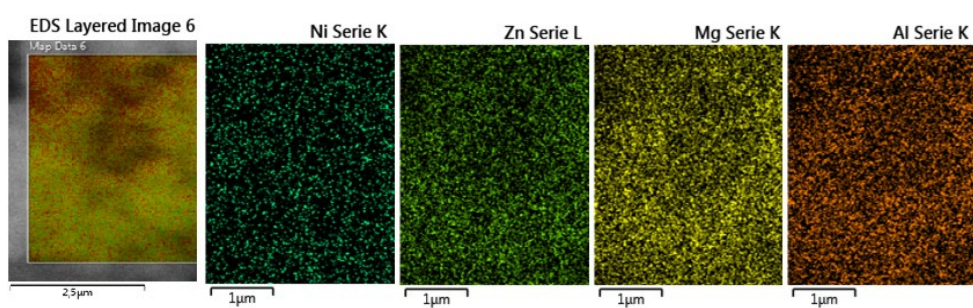


Figure S7. EDS elemental mapping of MMO-Ni₁₅Zn₂₅.

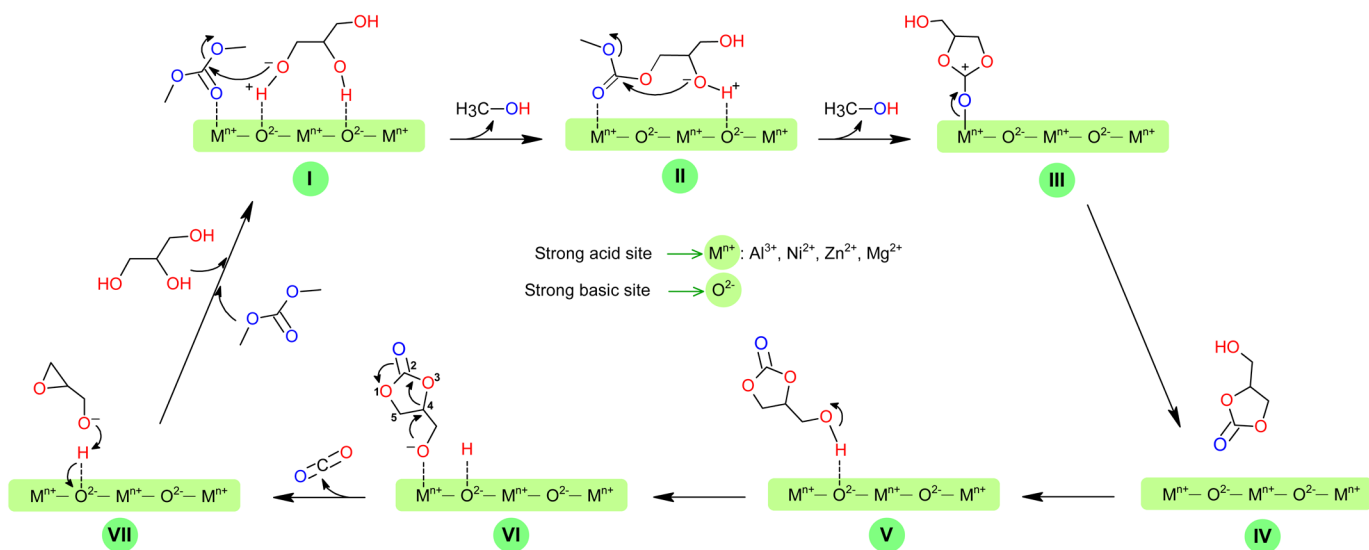


Figure S8. Proposed mechanism for transesterification between Gly and DMC, along with the subsequent decarboxylation of CG to GD.

The reaction is promoted through two cooperative activation modes, as previously reported in the literature [1–6]. Initially, glycerol activation takes place, where its hydroxyl groups are adsorbed onto basic sites through hydrogen bonding interactions (I). Considering the low acidity of the hydroxyl groups, a strong basic site is required to abstract the acidic proton from one of the two primary hydroxyl groups of glycerol, leading to the formation of a glyceroxide anion.

Simultaneously, activation of dimethyl carbonate occurs via coordination of its carbonyl carbon to a strong acid site (M^{n+} , where M represents a metal cation). The glyceroxide anion then nucleophilically attacks the activated carbonyl carbon of DMC, forming the methyl glycerol carbonate intermediate and a methoxide anion (II). The methoxide anion subsequently combines with the proton abstracted by the basic site to produce methanol, thereby regenerating the basic site.

In the following step, the basic site abstracts another proton from the secondary hydroxyl group of the methyl glycerol carbonate intermediate. As a result, the oxygen atom of this

hydroxyl group undergoes a second intramolecular nucleophilic substitution at the carbonyl carbon, leading to a cyclization reaction that yields glycerol carbonate (GC), an additional methanol molecule, and complete regeneration of the catalytic sites (III and IV).

The formation of glycidol (GD) as a side-product proceeds through the decarboxylation of GC. This pathway involves the abstraction of the proton from the primary hydroxyl group of GC by very strong basic sites present on the catalyst surface (V). The resulting oxygen species attacks the C4 carbon atom, inducing cleavage of the C–O bonds at the 3–4 and 1–2 positions of the carbonate ring and leading to the formation of a three-membered cyclic GD structure (VI and VII). Strong basic sites, as well as strong acid sites, are known to more effectively promote this decarboxylation step.

References

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