

Supporting information

Highly Selective Cross Ketonization of Renewable Acids by Magnesium Oxide

Tejas Goculdas^{1,2}, Siddharth Deshpande¹, Weiqing Zheng¹, Raymond J. Gorte^{1,3}, Sunitha Sadula*¹, Dionisios G. Vlachos*^{1,2}

¹Catalysis Center for Energy Innovation, 221 Academy St., Newark, DE 19716

²Department of Chemical and Biomolecular Engineering, University of Delaware, 150 Academy Street, Newark, DE, 19716 USA

³Department of Chemical and Biomolecular Engineering, University of Pennsylvania, Philadelphia, PA 19104, USA

* Corresponding author: vlachos@udel.edu and sunithak@udel.edu

S.1 Supporting Characterization Results

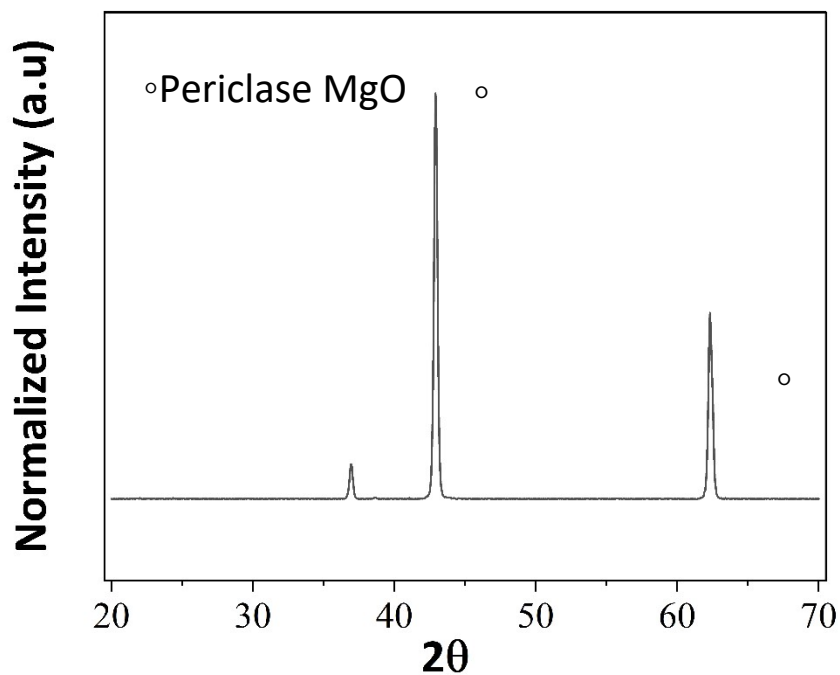


Figure S1 XRD Spectra of fresh MgO, identified as periclase MgO and displaying no impurities.

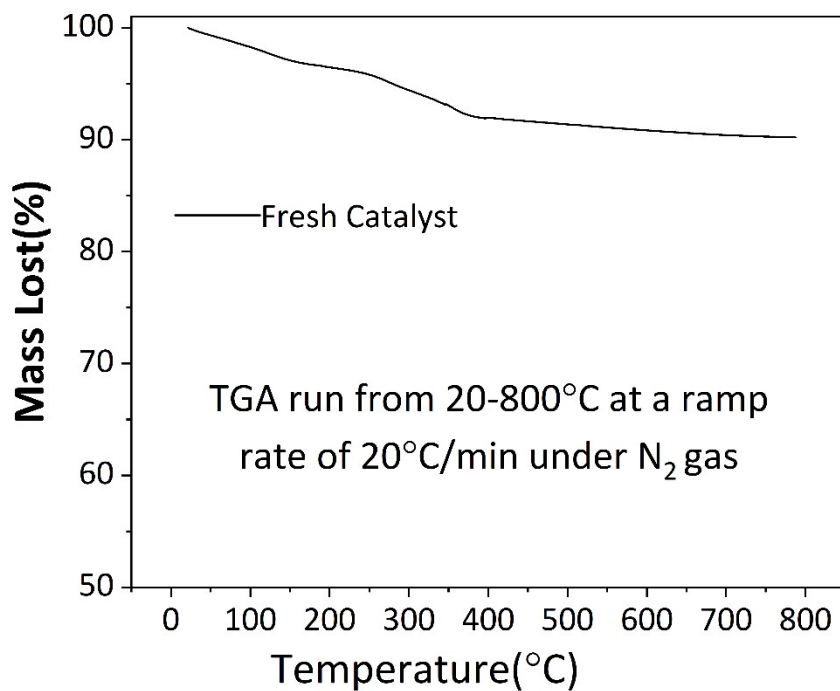


Figure S2 TGA spectra of the catalyst, showing negligible weight loss across the selected temperature range indicating that the catalyst is thermally stable at reaction temperature (350 °C).

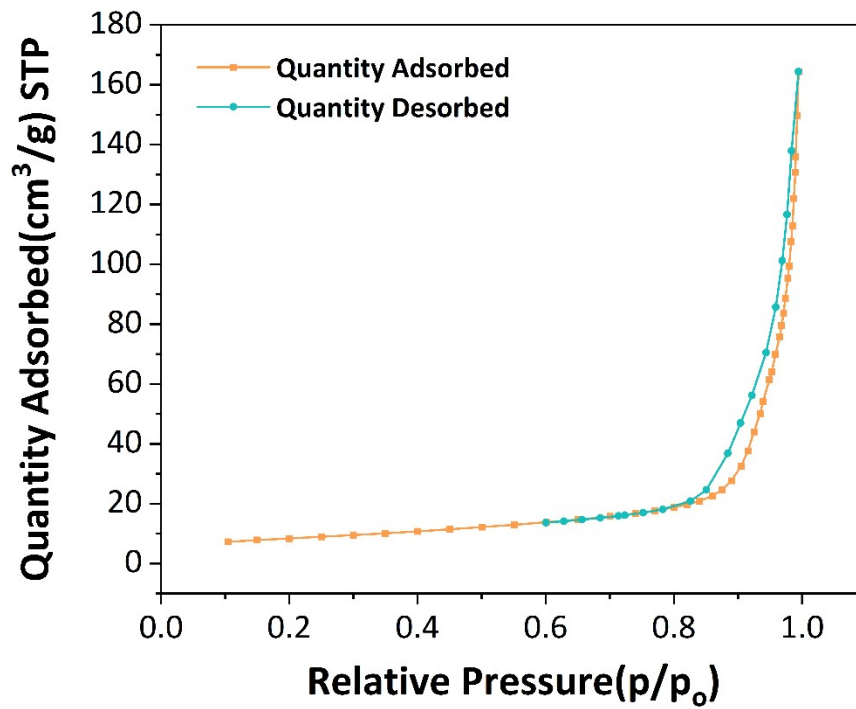


Figure S3 BET adsorption and desorption curves for MgO, the catalyst has a surface area of 29 m²/g.

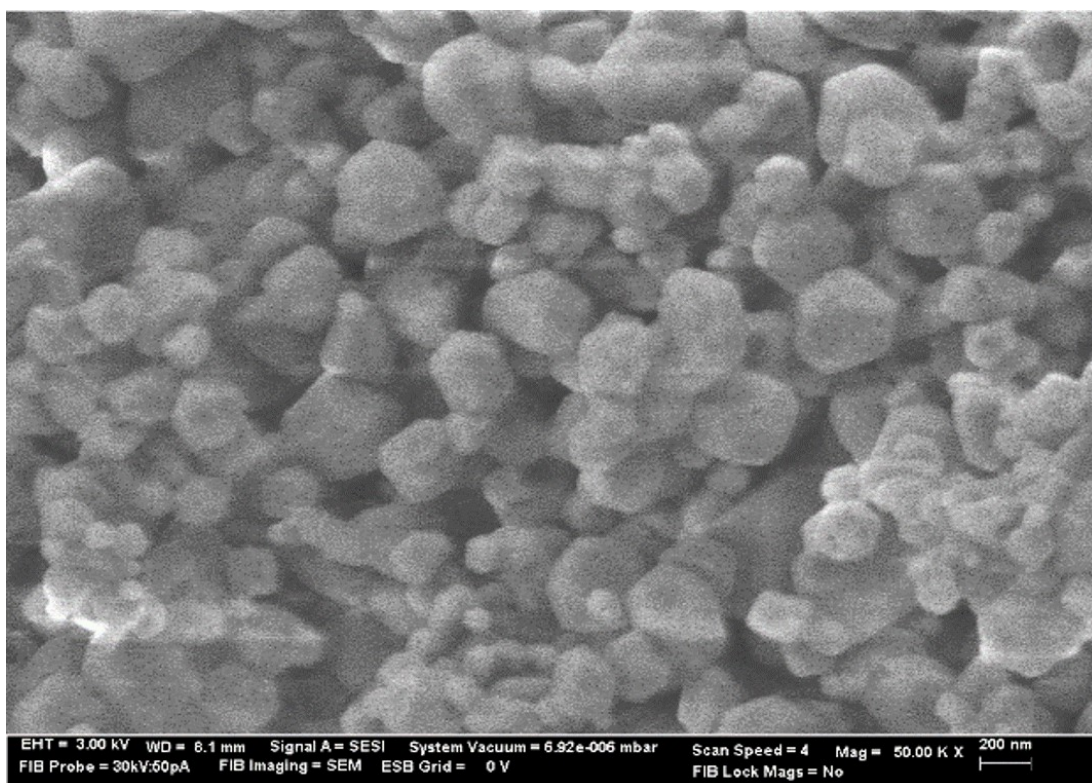


Figure S4 SEM image of MgO taken at 50kx Mag,EHT 3.00Kv.

S.2 Calibration curves for quantification of reactants and products

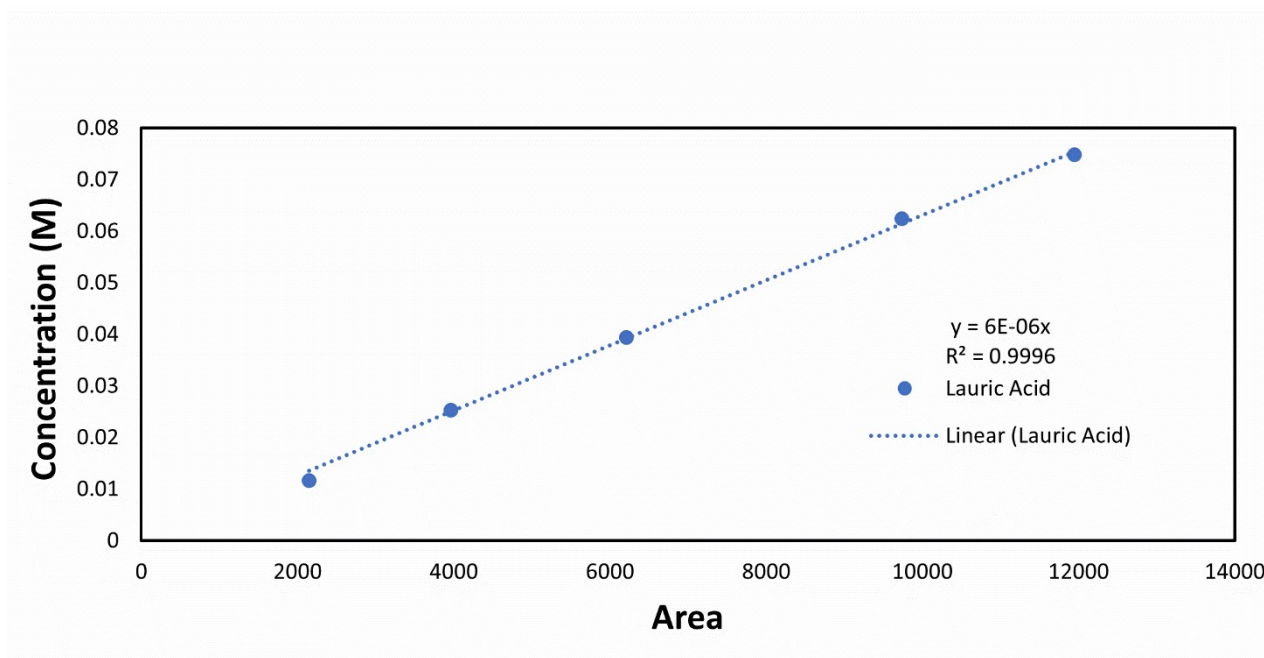


Figure S5 GC calibration curve used for quantification of the reactant lauric acid.

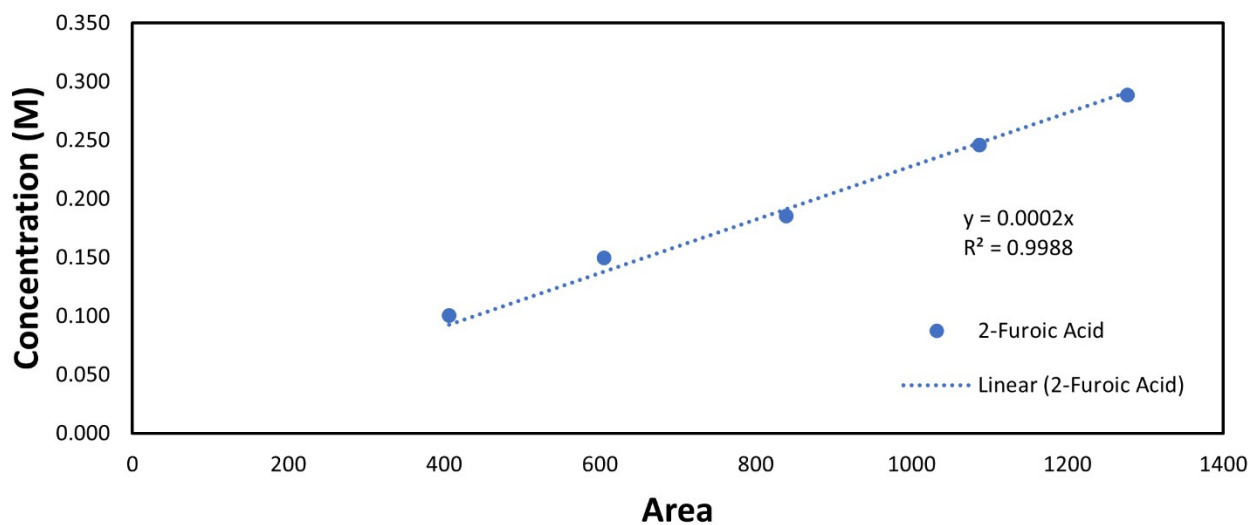


Figure S6 GC calibration curve used for quantification of the reactant 2-furoic acid.

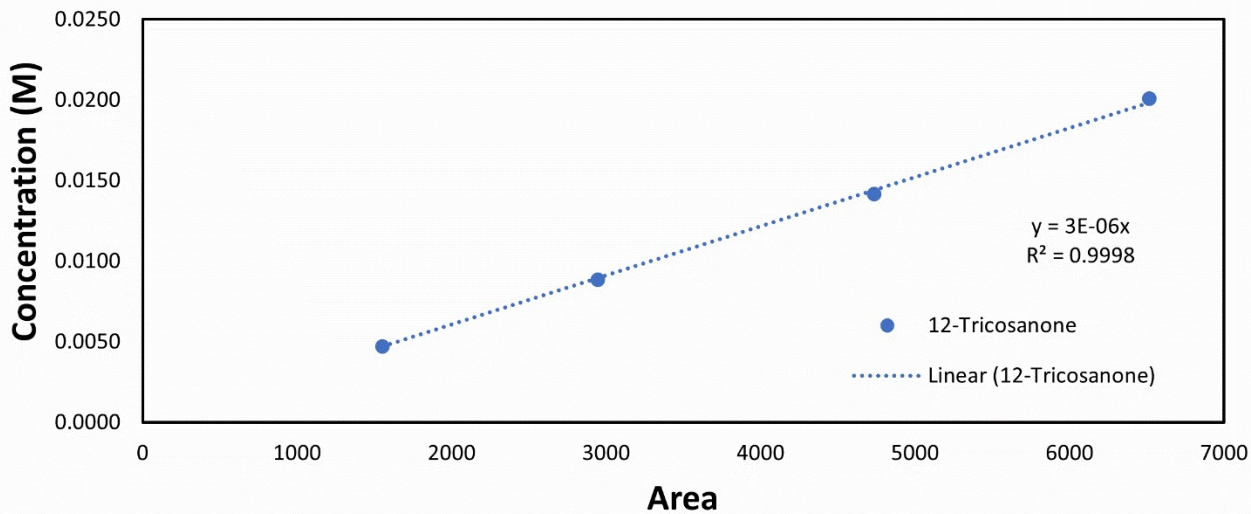


Figure S7 GC calibration curve used for quantification of the product 12-tricosanone.

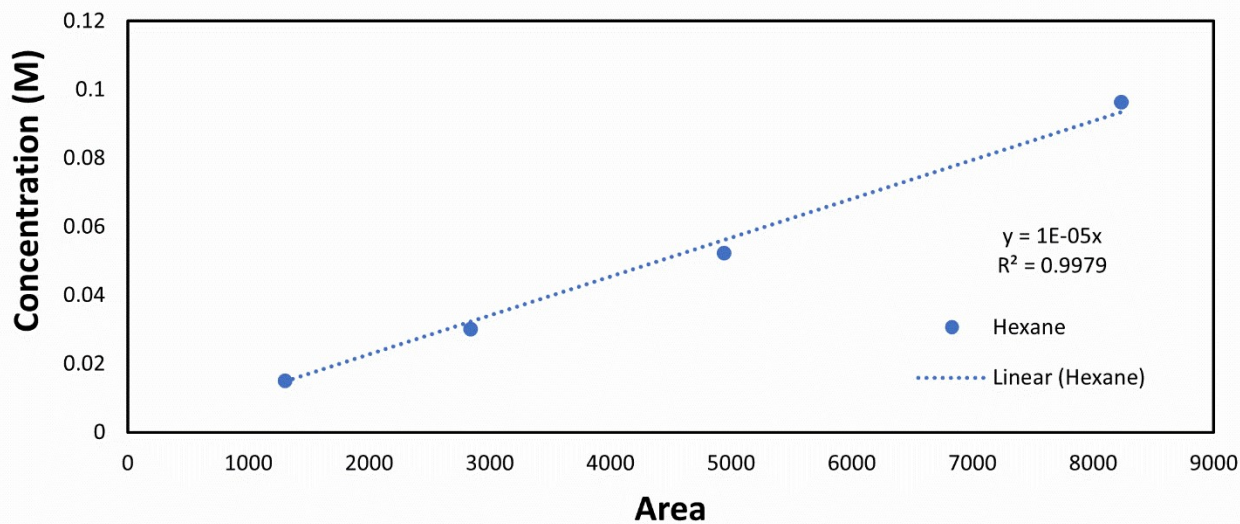


Figure S8 GC calibration curve used for quantification of the product 2-dodecanoyl furan derived from a calibration of hexane using the effective carbon number method.

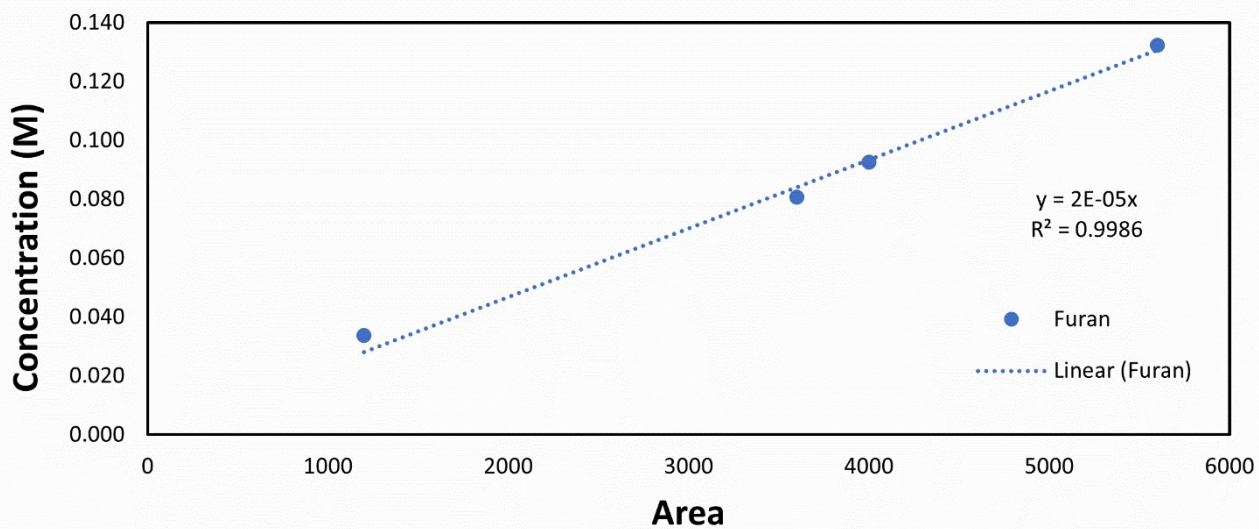


Figure S9 GC calibration curve used for quantification of the product furan.

S.3 Decomposition products observed on GC-MS

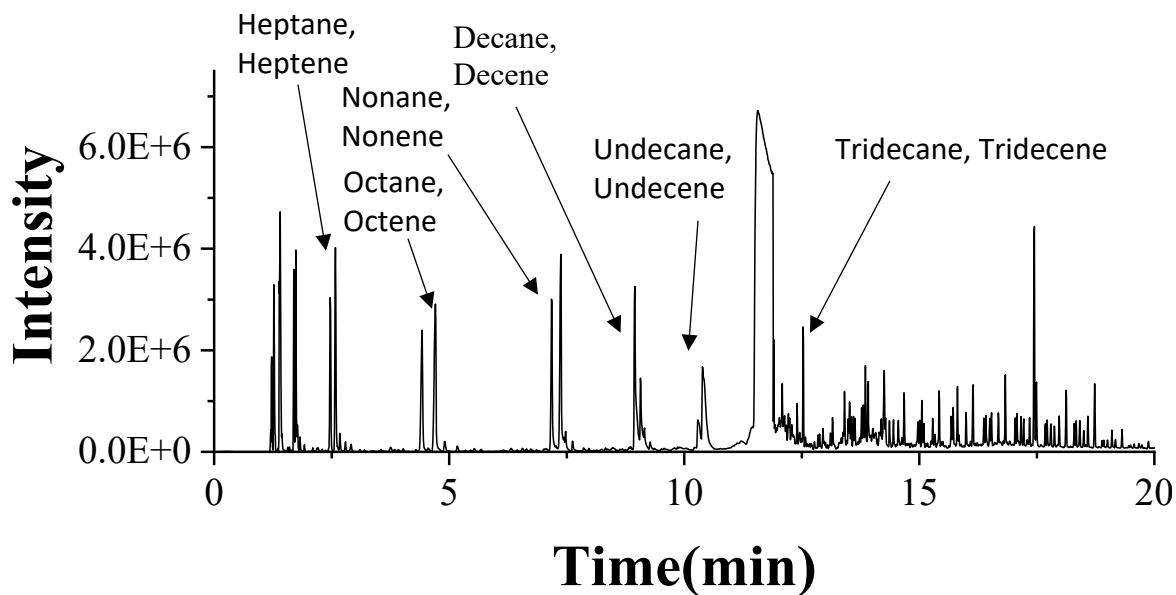


Figure S10. GC-MS Chromatogram for the decomposition products observed in the product effluent at 400°C.

S.4 ICP-MS Results to test for catalyst leaching

Table S1. ICP-MS Results from a post-reaction solution.

Run	MgO Content in Effluent(ppm)_
1	62
2	61
3	65

S.5 Testing the activity of leached Mg²⁺ ions

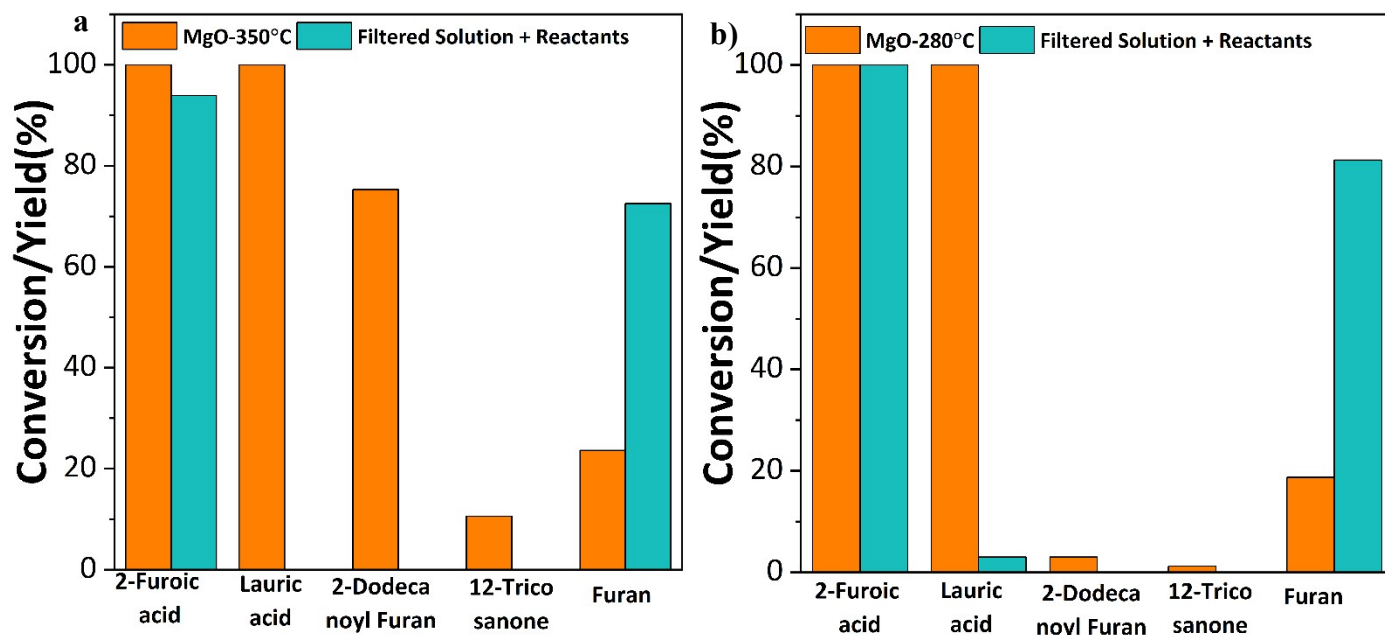


Figure S11. Reactivity of the magnesium species in the filtered solution collected after ketonization reaction. (a) 350 °C and (b) 280 °C. Reaction conditions for the filtered solution: 0.25 M 2-furoic acid, 0.15 M lauric acid, 30 ml dodecane 350 °C, 90 min, 20 bar N₂, 800 rpm.

Table S2. Moles of the products formed per moles of MgO catalyst used at different loadings, one turnover= 1 mole of ketone product/1 mol of catalyst.

MgO Wt(g)	Total Reactant Moles	TON (Turnover number)
0.25	0.012	0.67
0.20	0.012	0.80
0.15	0.012	1.00
0.10	0.012	1.19
0.06	0.012	1.74
0.02	0.012	4.78

S.6 Mass balance correction from TGA

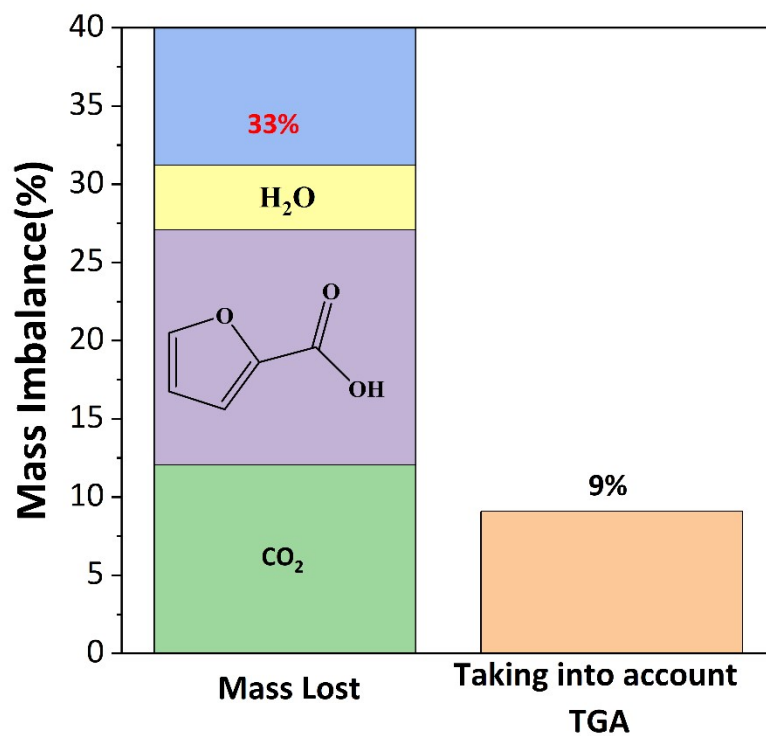


Figure S12. Mass balance corrections considering the mass loss of the spent catalyst in TGA analysis. TGA run at a ramp rate of 20°C/min under N₂ gas from 20-800°C.

S.7 Total Carbon Recovery

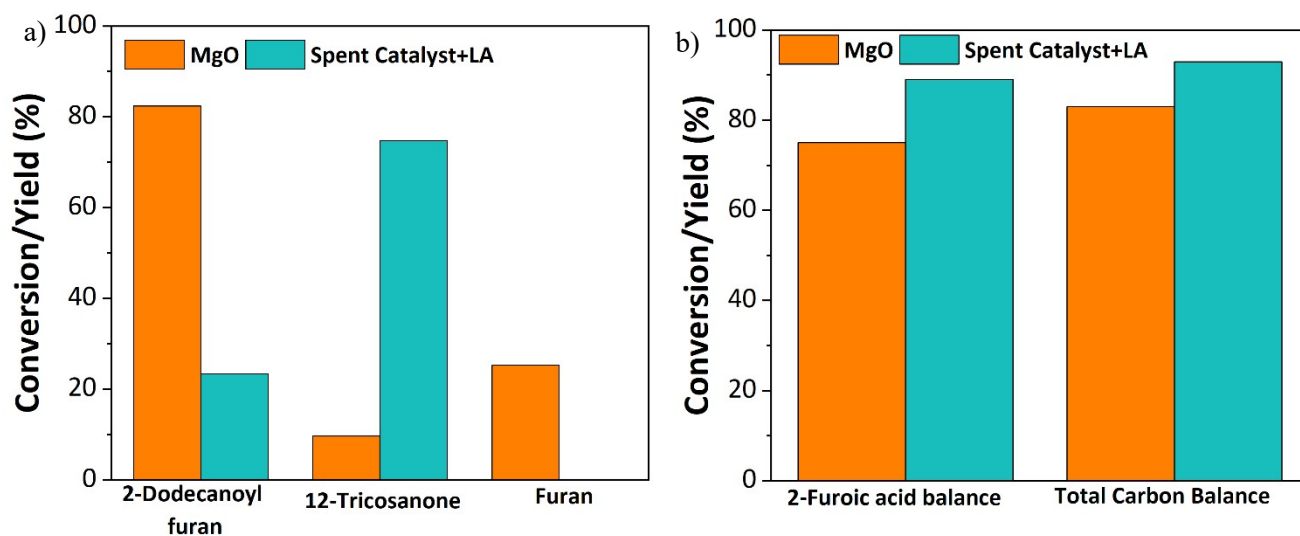


Figure S13. Demonstrating carbon recovery for 2-furoic acid through semi-batch addition of lauric acid. Reaction conditions for run 1: 0.25 M 2-furoic acid, 0.15 M lauric acid, 30 ml dodecane, 350 °C, 90 min, 20 bar N₂, 800 rpm, 0.2 g catalyst. Reaction conditions for second run: Filtered material, 0.15 M lauric acid, 30 ml dodecane, 350 °C, 90 min, 20 bar N₂, 800 rpm (a) Product yields at the optimum reaction conditions and the activity of the spent material after the second addition of lauric acid. (b) Carbon balance of 2-furoic acid and of the entire system before and after the second addition of lauric acid.

S.8 Determining the cause of complexation with the MgO catalyst

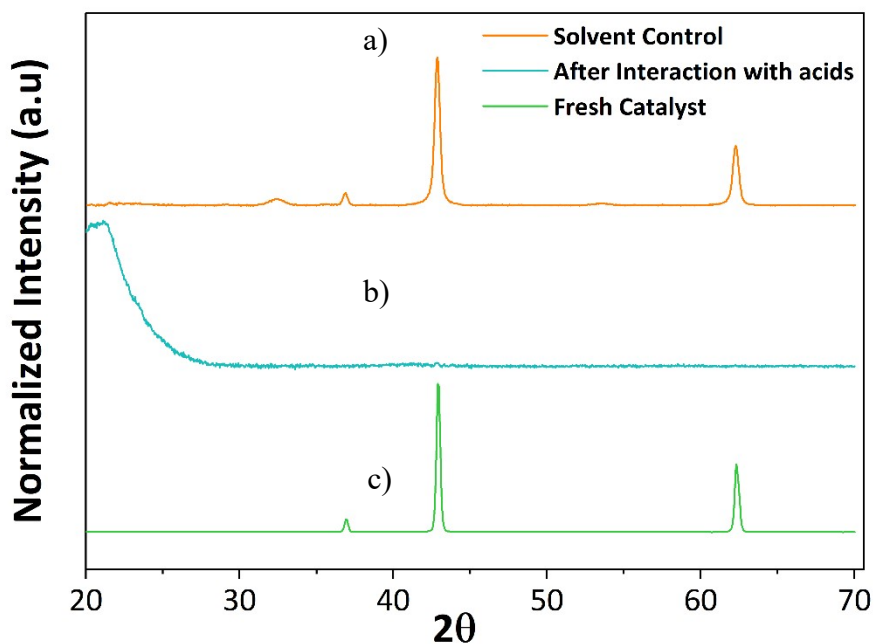


Figure S14 XRD Spectra of the catalyst a) the control, b) after interaction with the acid reactants and c) fresh Catalyst.

S.9 FT-IR Characterizations of metal-acid complexes

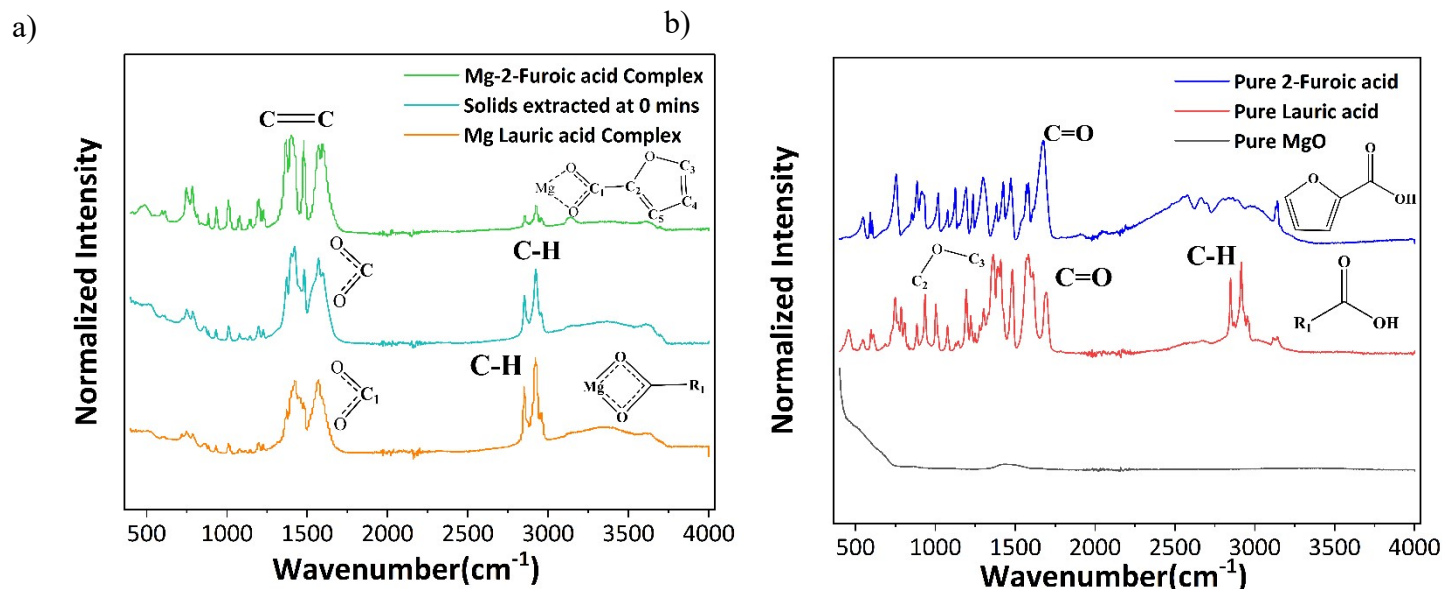


Figure S15. Comparison of FTIR Spectra of the magnesium acid complexes and the pure acid. The complex formation is confirmed by the disappearance of the OH stretch, shifting of the C=O Carbonyl group and the symmetrical, asymmetrical vibrations observed on the complexes between $1350\text{-}1550\text{cm}^{-1}$.

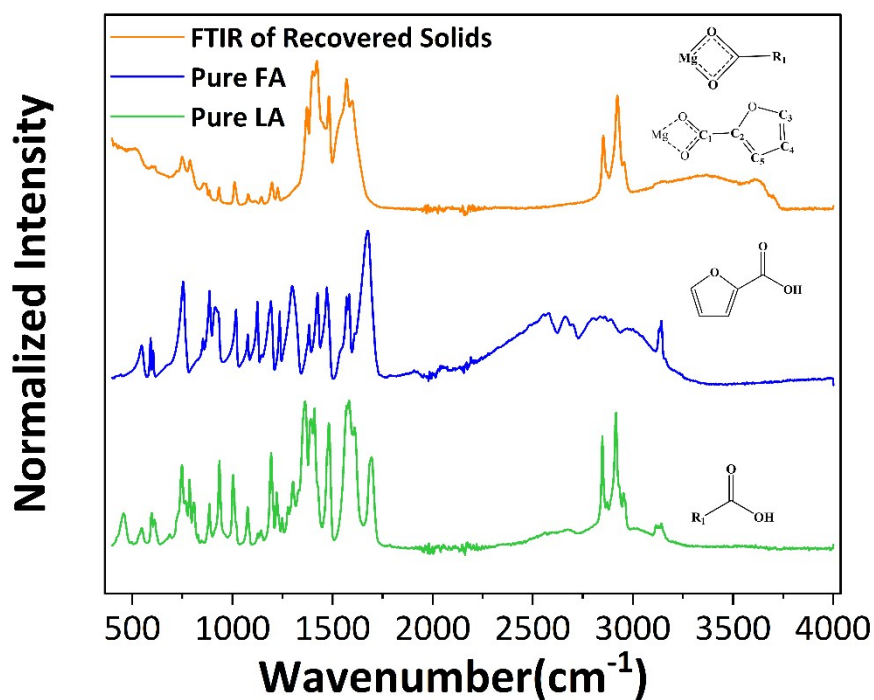


Figure S16. FTIR analysis of the intermediate solids compared with pure lauric and 2-furoic acid, the intermediate solid show complete disappearance of the C=O group and OH stretches, indicating complex formation.

S.10 Impact of Reaction time

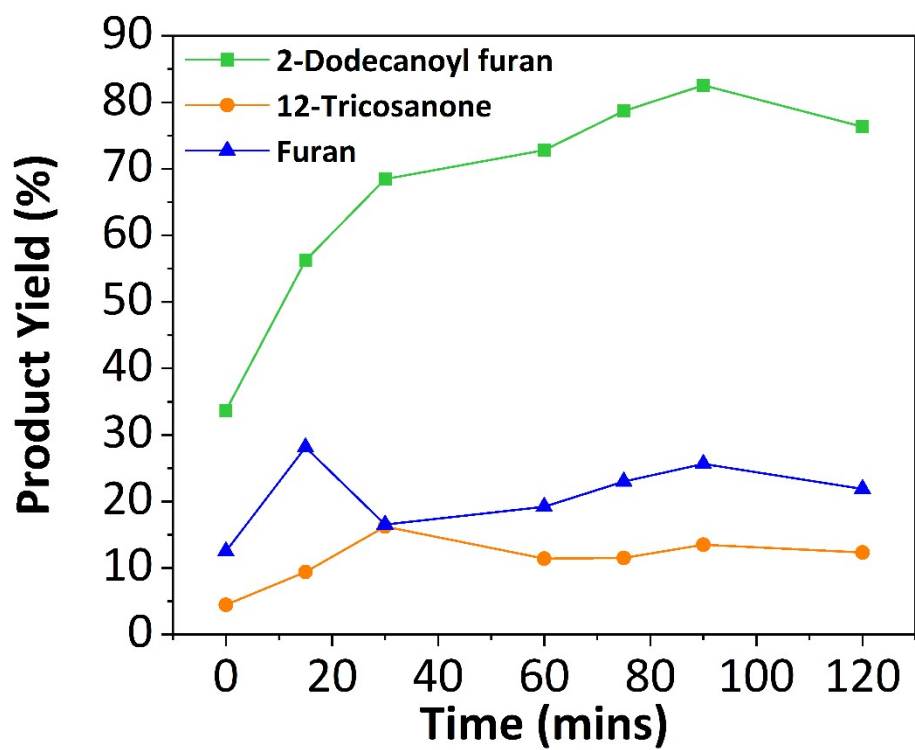
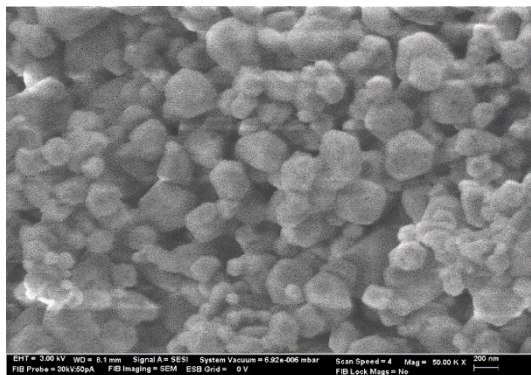


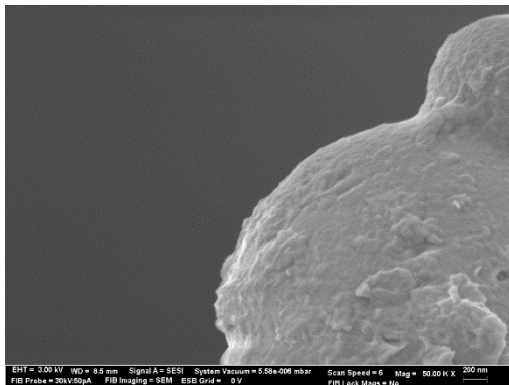
Figure S17. Impact of reaction time on product distribution. Reaction conditions: 0.25 M 2-furoic acid, 0.15 M lauric acid, 30 ml dodecane 350 °C, 20 bar N₂, 800 rpm, 0.2 g MgO.

S.11 SEM Images of MgO taken at different reaction times

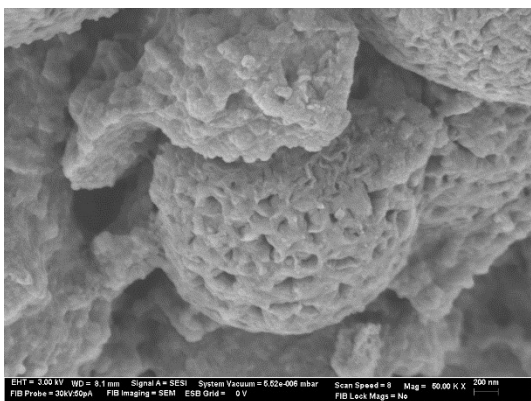
MgO Fresh



MgO 0mins



MgO 30mins



MgO 75 mins

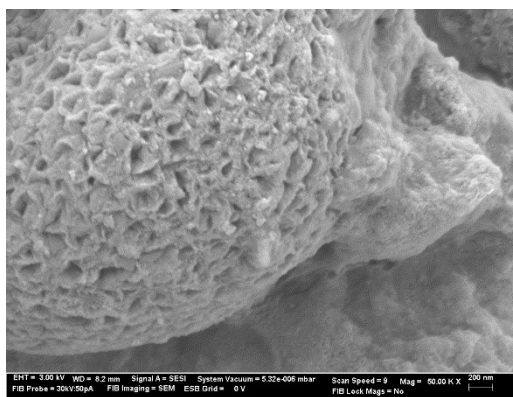


Figure S18. SEM Images of the recovered solid material from the experiments conducted at 0 min, 30 min and 75 min zoomed in at 50kx.

S.12 Complex formation preventing decarboxylation

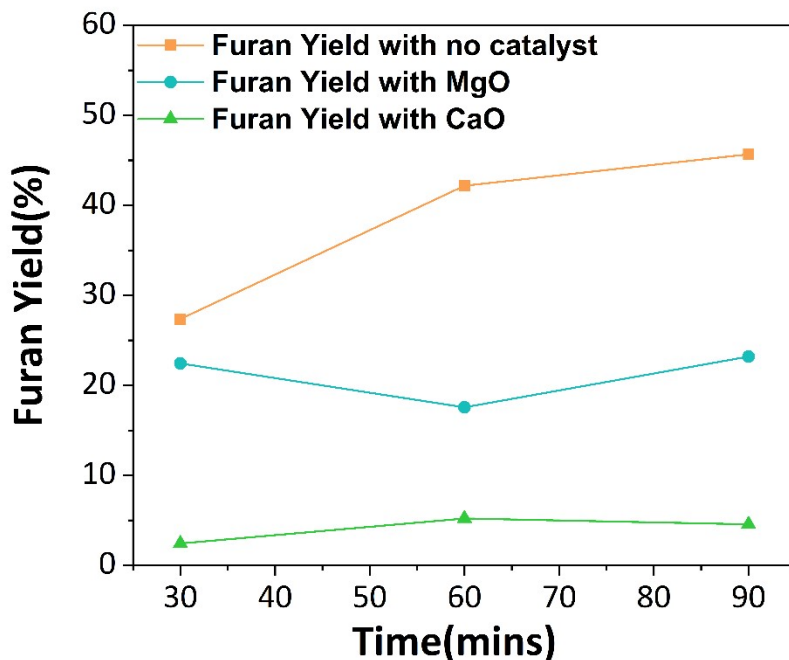


Figure S19. Blank reaction of 2-furoic acid with MgO and CaO demonstrating that complex formation is key in reducing decarboxylation of 2-furoic acid. a) Reaction conditions: 0.25 M 2-furoic acid, 30 ml dodecane 316 °C, 20 bar N₂, 800 rpm 7.5 mmol cat.

S.1

3 Temperature of complex formation over alkaline earth metals

Table S3. Lauric acid Concentration from complexation studies. Conditions: 0.15M Lauric acid, 10ml dodecane, 120mins 1.5mmol catalyst: 0.3g of Lauric acid was added to 10ml of dodecane in a 20ml glass vial along with an equimolar amount of metal oxide. The vial was placed in an oil bath for temperature control (stir speed 400rpm) for 2hrs. The heated vials were quenched in an

Temperature (°C)	Lauric acid conversion (mol%)
ice bath.	

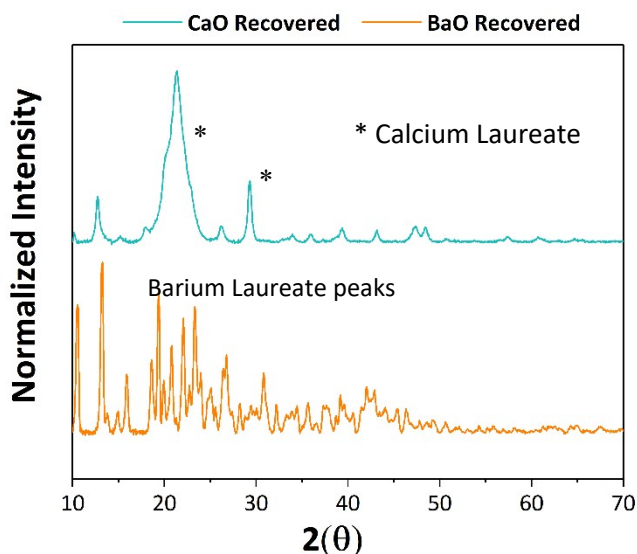


Figure S20 XRD spectra of the solid material recovered from complexation experiments at 25 °C. The MgO crystal structure remained constant until 150 °C.

	MgO	CaO	BaO
25	12	100	100

75

15

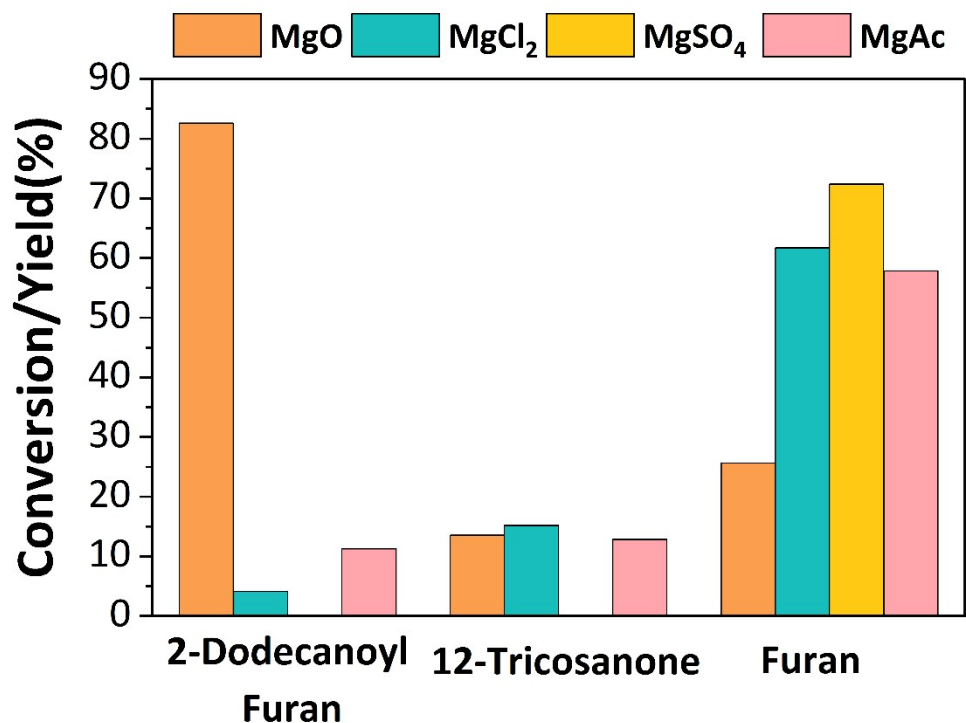


Figure S21 Activity of different MgO salts compared with the oxide at the optimum reaction conditions. Reaction conditions: 0.25 M 2-furoic acid, 0.15 M lauric acid 30ml dodecane 350 °C, 20 bar N₂, 800 rpm 5 mmol cat.

S.14 Activity of different Mg-Salts for ketonization

S.15 Testing for Mass transfer limitations

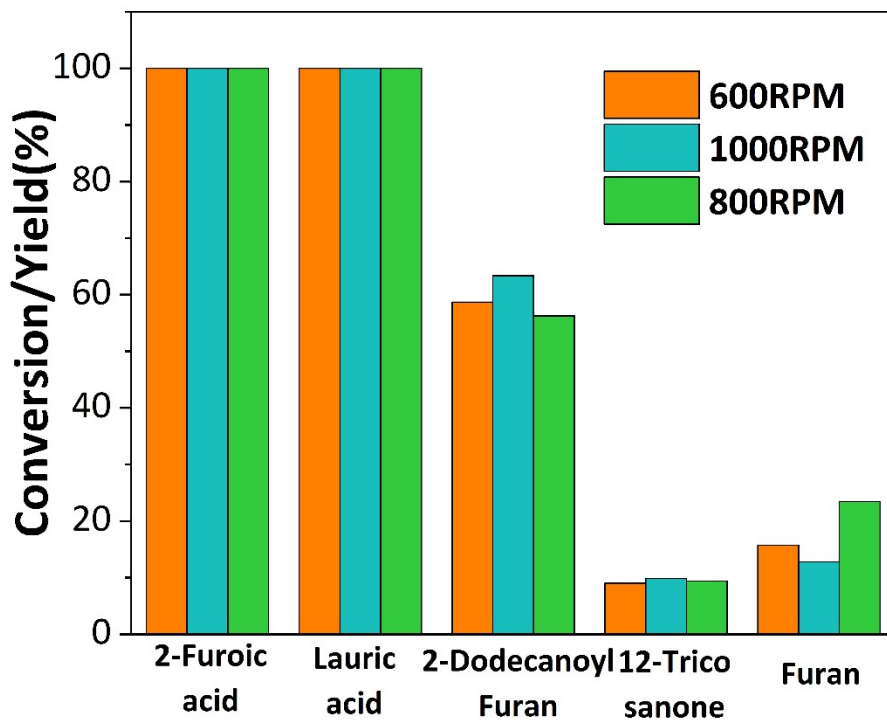
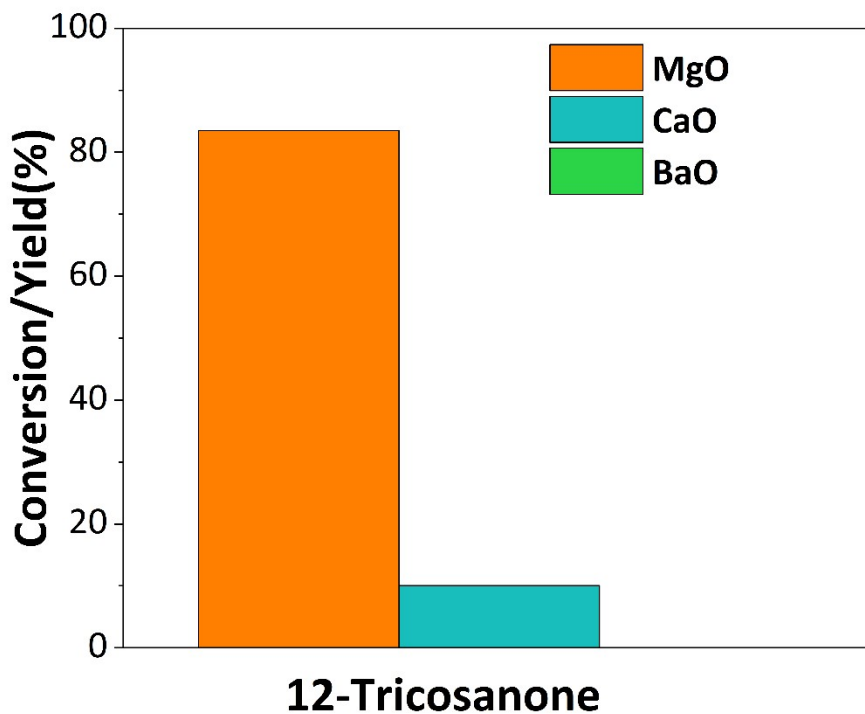
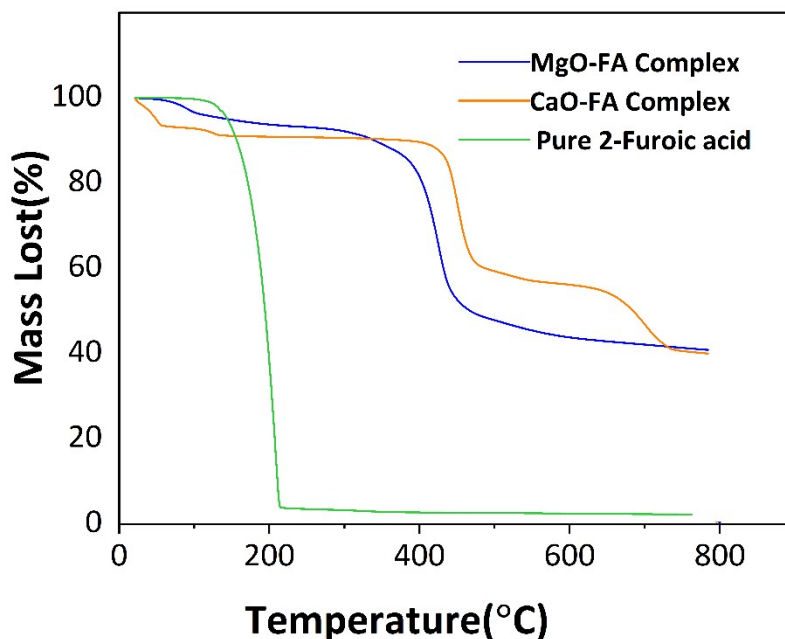


Figure S22. Yields at different stir rates of products in the cross-ketonization reaction system. No trends are evident between yields and stir rates, indicating the reaction system does not experience mass transport limitations in this stir rate regime. Reaction conditions for the filtered solution: 0.25 M 2-furoic acid, 0.15 M lauric acid, 350 °C, 90 min, 20 bar N₂, 800 rpm.



the MgO, CaO and BaO

S.17 Determining the thermal stability metal-2-furoic acid complexes



17

Figure S23 Demonstrating that the stability of the metal-lauric acid complex is the key factor differentiating the activity of MgO, CaO, BaO. a) Activity of the LA complex of the metals at the optimum temperature and time. Reaction conditions: 0.15 M metal-lauric acid complex, 30ml dodecane 350 °C, 20 bar N₂, 800 rpm.

Figure S24 Thermal analysis of 2-furoic acid complexes with MgO, CaO with 2-furoic acid as a reference. TGA run at a ramp rate of 20°C/min under N₂ gas from 20-800°C.