Glycerol Carbonate Synthesis by Hierarchically Structured Catalysts: Catalytic Activity and Characterization

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SUPPORTING INFORMATION

Table S1. Literature review of synthesis and characterization of Ca-La catalysts for various applications.

Characterization technique and application	Ji et al., [35]	Käßner and Baerns, [45]	Li et al., [36]	Pospieszna-Markiewicz et al., [39]	Ikkour et al., [38]	Luo et al., [41]	Kim et al., [40]	Paryzek et al., [38]	Yan et al., [42]	Taufiq-Yap et al., [43]	Gholami et al., [44]	This Work
	Na/Ca-La	La_2O_3/CaO	Mn/Ca-La hexaaluminate	Ca-La	Ni/Ca-La hexaaluminate	CaO/La_2O_3	CaO–La_2O_3/support	La-Ca	Ca-La	Ca-La oxide	Ca-La/MCM-41	Ca-La
Method of catalyst synthesis	Wet mixing method	Mechanical method	Coprecipitation/supercritical drying	Self-assembly method	Citric acid method	Sol–gel combustion	Impregination	Physical method	Co-precipitation	Co-precipitation	Co-precipitation	Endo- & Exo Templating
XRD	X		X	X	X	X			X	X	X	X
N2-sorpti	X	X	X		X	X	X		X	X	X	X

on												
SEM/EDS			X			X	X		X	X	X	X
FTIR		X		X				X			X	X
Acidity		X					X					X
Basicity		X					X		X	X	X	X
TPR-H_2			X		X							
TEM			X	X							X	X
NMR								X				
TGA	X								X			
CHNS				X				X				
XPS					X							
TPO			X		X							
Application	Oxidative dehydrogenation of ethane	Oxidative coupling of methane	Catalytic combustion of methane	Schiff base con-densation	Dry reforming of Methane	Coal combustion & gasification	Transesterification	Steroid dimer derived from cholic acid	Oil transesterification	Transesterification	Etherification	Glycerol conversion
End Products		Propene and acetone		Salicylaldimines complex	CO, CO_2, H_2	CO_2 capture	Biodiesel	Ethylene bridged	Biodiesel	Biodiesel	Diglycerol	Glycerol Carbonate

*Note-XRD (X-ray Diffraction), SEM/EDS (Scanning electron microscopy/Energy-dispersive X-ray spectroscopy), FTIR (Fourier transform infrared spectroscopy), NMR (Nuclear magnetic resonance), TGA (Thermogravimetric analysis), CHNS elemental analyzer, XPS (X-ray photoelectron spectroscopy), TPO (Temperature programmed oxidation), TEM (Transmission electron microscopy), TPR-H_2 (Temperature-programmed reduction).

Table S2. Elemental analysis of CaLa catalysts.

Catalysts	Nominal value of metals		Actual values of metals from ICP-OES analysis		Actual values of metals from EDX	
	Ca	La	Ca	La	Ca	La
1CaLa	0.5	0.5	0.46	0.54	0.47	0.53
2CaLa	0.666	0.334	0.651	.349	0.63	0.37
3CaLa	75	25	0.741	0.259	0.74	0.26

Table S3. Crystalline size and CO_2-TPD of used (4 times) CaLa catalysts.

Catalysts Properties	1CaLa	2CaLa	3CaLa
Crystallitesize/ nm[a]	14	17	24
CO_2 evolution decomposition mmol g^{-1}[d]	0.270 (771 °C)	0.241 (771 °C)	0.268 (771 °C)
CO_2-TPD / mmol g^{-1}[e]	0.468 (776 °C)	0.632 (764 °C)	0.681 (768 °C)
Total basic site density / mmol g^{-1}	0.198	0.391	0.413
Basic sites per unit surface area / μmolm^{-2})	6.6	8.68	12.51

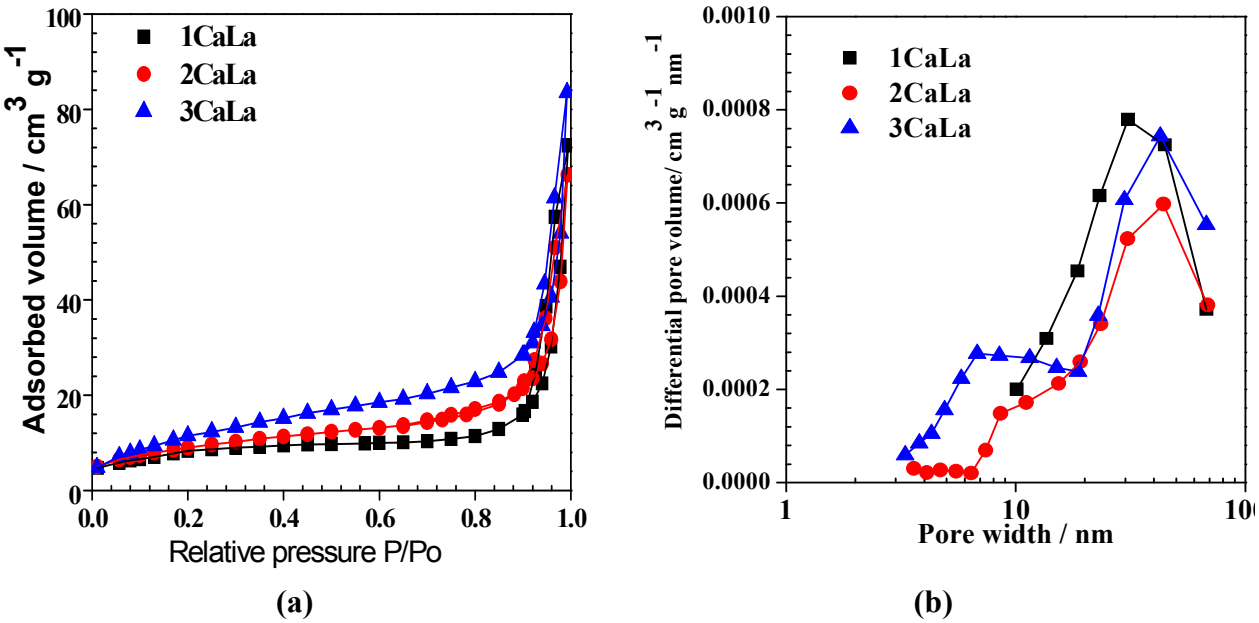
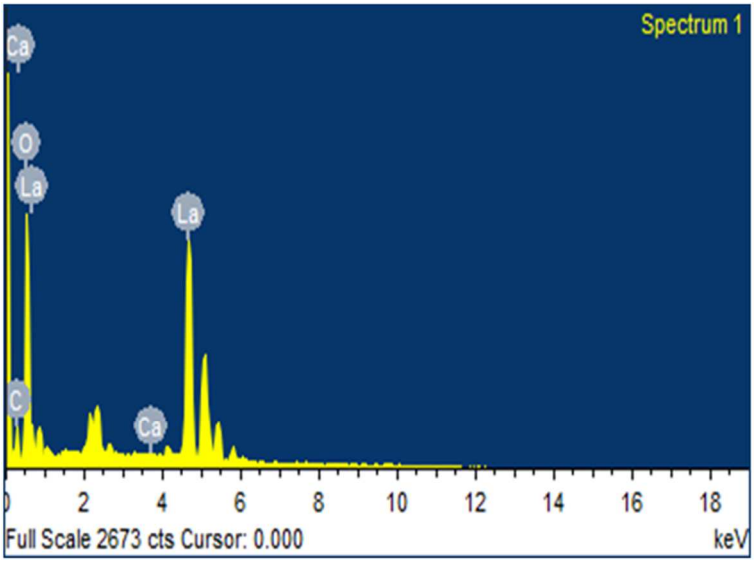
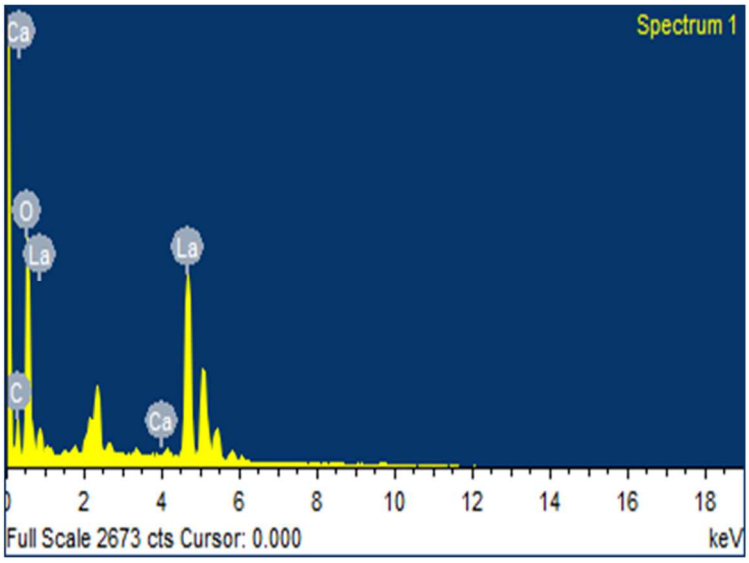


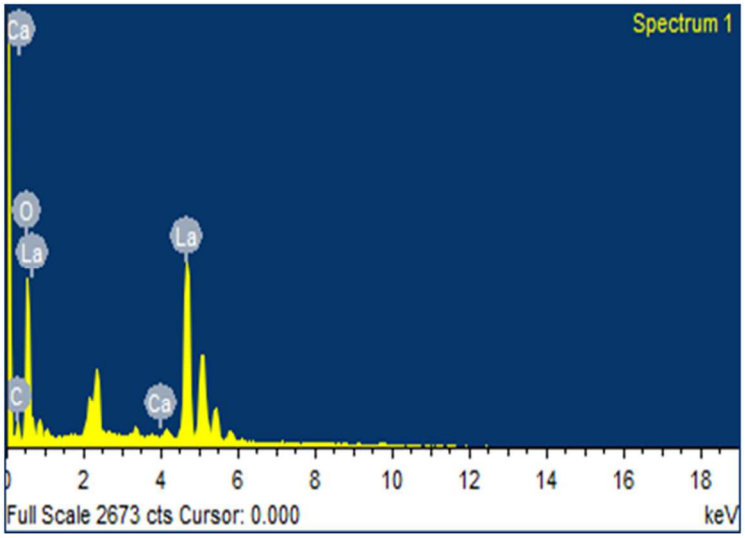
Fig. S1. (a) Nitrogen sorption isotherms, (b) pore size distributions for 1CaLa, 2CaLa and 3CaLa mixed oxide catalysts.



1CaLa



2CaLa



3CaLa

Fig. S2. EDX of CaLa Catalysts.

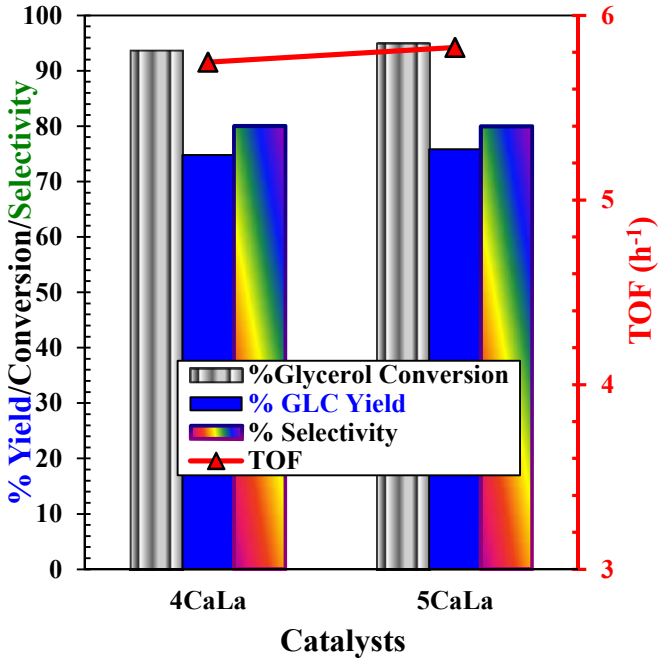


Fig. S3. Glycerol conversion and DMC yield using 4CaLa and 5CaLa. Reaction conditions :($n_{DMC}/n_{glycerol}$ = 5 mol mol^{-1}, $m_{catalyst\ mass}$= 0. 217 g; T = 90 °C, t_r = 90 min).

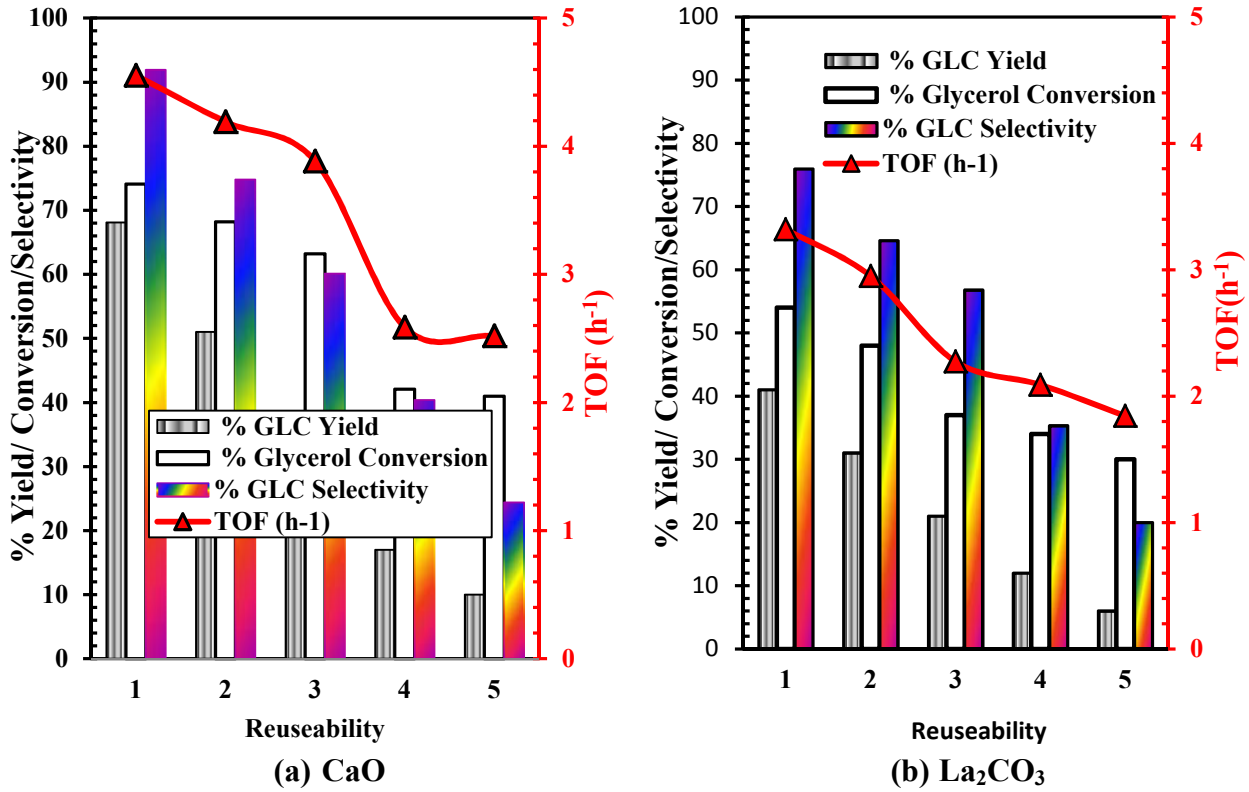


Fig. S4. (a) Reuseability of CaO, (b) Reuseability of La_2O_3 catalyst, in the transesterification of glycerol with DMC ($n_{DMC}/n_{glycerol}$ = 5, $m_{catalyst\ mass}$ = 0. 217 g; T = 90 °C, t_r = 90 min).

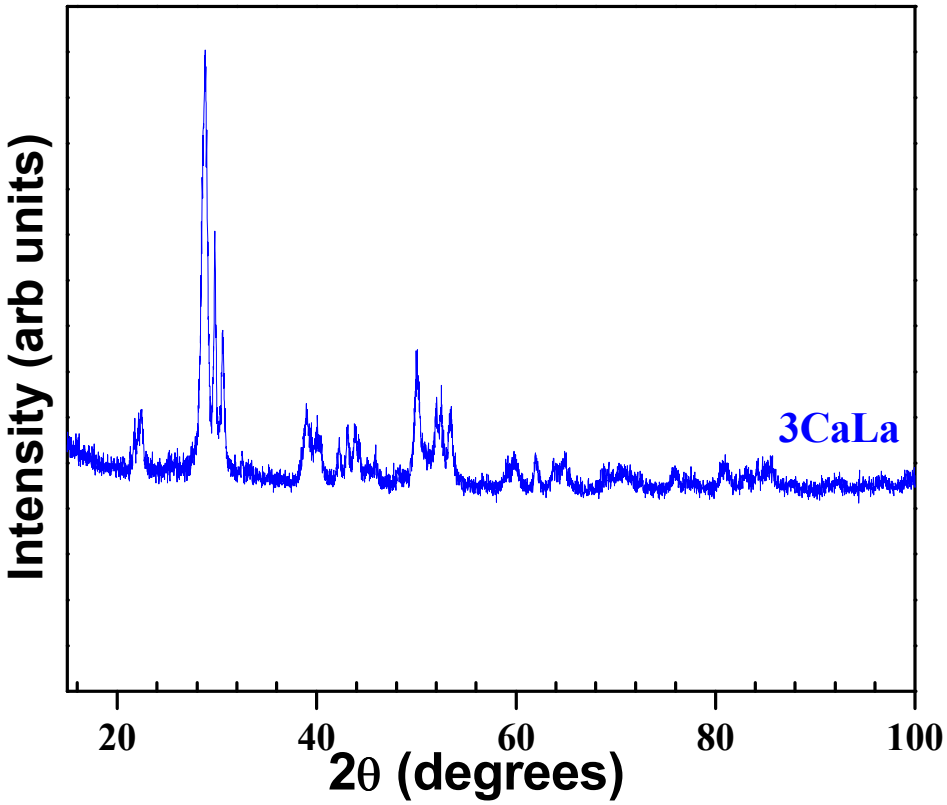


Fig. S5. XRD patterns of reused 3CaLa catalysts.

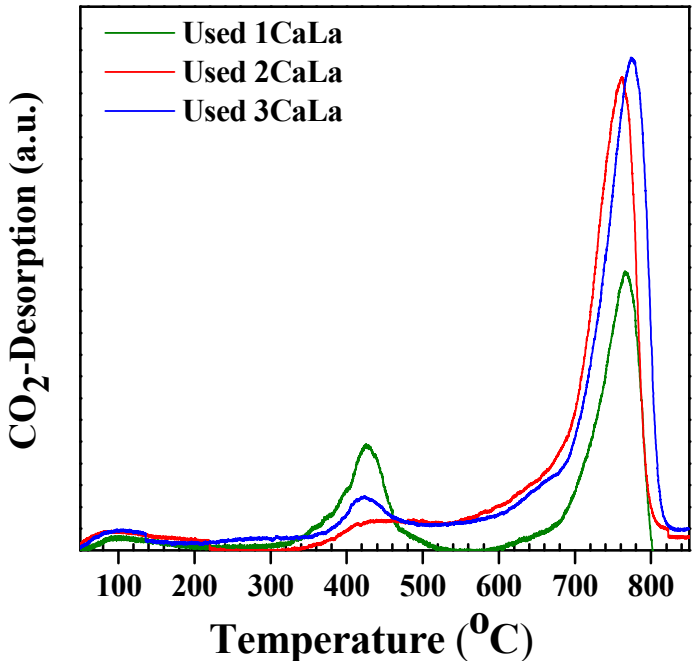


Fig. S6. CO_2-TPD of CaLa Catalysts after 4 cycles of usage for different catalysts.