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website:- www.journalofchemistry.org**Microwave assisted synthesis of highly crystalline nano CaO from waste egg shells-A low temperature record activity in glycerol carbonate**BHAGYALAKSHMI H¹, VEERABHADRASWAMY M.^{1*} and VENKATESHA N.J^{2*}¹Green Chemistry Centre, PES University, BSK 3rd Stage, Bengaluru, Karnataka (India)²Chemistry Research Centre, Bangalore Institute of Technology, K.R. Road, V.V. Purm, Bengaluru, Karnataka (India)*Corresponding author email: ybs@pes.edu<http://dx.doi.org/10.22147/juc/140401>

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Abstract

The renovation of eggshell wastage into nanocrystalline CaO by solution combustion method under microwave irradiation is vital process. Microwaves influenced to get high surface area, increase in active sites density with morphological difference than the conventional calcinations method. Accordingly various types of catalysts from egg shells such as CaO-M (microwave combustion), CaO-F (combustion in furnace), CaO-C (calcinations of waste egg shells) were synthesized. The obtained catalyst were characterized using XRD, SEM, TPD-CO₂, TGA and BET surface area instruments to know the physico-chemical characteristics. The catalytic evolution of these catalysts showed record activity and recyclability at lower temperature for the glycerol carbonate synthesis under the microwave irradiation method. Under the optimize reaction condition CaO-M showed maximum yield of glycerol carbonate of 94%. Thereby catalytic activity of CaO-M showed better performance when compared with CaO-F, CaO-C and commercially obtained CaO. Better catalytic activity of CaO-M is due to higher surface area with lower particle size and increase in active sites. CaO-C showed decreased in activity due to mask of active sited by CO₂. The term active site approach was coined; this concept is to develop the catalysts for the industrial applications. Accordingly, various factors such as surface area, particle size and active sites were compared and correlated with the yield of glycerol carbonate. The distribution of active sites on the each nano particle confirms more activity for CaO-M of 93%. and the r value 0.97 showed better correlation within active site approach influence on the product formation.

Key words: Waste Egg shell, CaO, Glycerol carbonate, Active site approach

Introduction

Chicken eggs are favourite nutritious food athwart the globe¹. The utilization of eggs fallout in the creation of huge egg shell waste bio-material that has to be disposed, creating environmental problems. Companies spend huge amount of money towards disposal of waste egg shells². To lessen the saddle attempts were made towards their potential applications³. Currently, waste eggshells are utilized in the field of agriculture as fertilizers, industrial goods via medicine, cosmetics, paints, and manufacturing materials⁴. Waste egg shells are major bio-ceramic composite consisting 95% of calcium carbonate⁵. Commercially CaO is produced from the egg shells by calcination method⁶⁻⁸. Effective utilization of eggshell has opened up a broad view towards waste management. The obtained CaO have been used as heterogeneous catalyst towards biodiesel production⁹⁻¹⁰. In this venture for the wellbeing of the ecosystem and finding an alternate to fossil based fuels, biodiesel has gained its importance. Tons of glycerol is obtained as by-product from biodiesel industry which has to be efficiently utilized¹¹. Rapidly production of biodiesel has made glycerol a low-cost feedstock chemical. Utilization of glycerol has motivated researches towards glycerol transformation to obtain value added commodity chemicals¹². Extensive and comprehensive literature review on commodity chemicals synthesis from glycerol has been studied. Glycerol carbonates, acetals, ethers, acetins, among these carbonates are one such central derivative obtained from transesterification of glycerol¹³.

Transesterification of glycerol to glycerol carbonate (GC) is one of the significant promising paths for glycerol valorization. GC is an important bi-functional chemical intermediate has potential industrial applications. GC is extensively used in synthesis of technologically important polymers, surfactants, lubricating oils, emulsifiers and moisturizers¹⁴⁻¹⁵. It has been evidenced that on the conversion of glycerol into various products and intermediates using different reactants like urea¹⁶⁻¹⁷,

CO₂¹⁸, carbonates¹⁹⁻²⁰, acetone, acetic acid using base or acid catalyst such as Clays, Zeolites, Metal oxides²¹⁻²². However, yield of glycerol carbonate was too low as reaction was carried out at elevated temperature and pressure making reaction less feasible²³⁻²⁴. In comparison with all possible reactants alkyl carbonates was found to give best results for glycerol carbonate synthesis using K₂CO₃/MgO, CaO²⁵⁻²⁶.

In the present study, utilization of waste materials for the catalysts synthesis such as egg shells for CaO catalysts by conventional and microwave method and glycerol for the fuel additive as well as polymers precursors has been investigated. CaO prepared under microwave method by solution combustion method showed good physico-chemical properties including the catalytic activity for the glycerol valorization. One such process includes cyclic carbonates synthesis using glycerol with lower alkyl carbonates under mild conditions for maximum conversion with good reproducibility; hence this process effectively raised the importance of the present work and highlights the feasibility of green chemistry for sustainable growth.

Materials and Methods

Chemicals and reacting conditions :

Glycerol (C₃H₈O₃), n-pentanol (C₅H₁₂O) were purchased from Merck India Ltd. Dimethyl carbonate (C₃H₆O₃), Nitric acid (HNO₃), Urea (CH₄N₂O) were of analytical grade and was purchased from SD fine Chemicals India. All the chemicals were of research grade and used without any further purification.

Preparation of catalyst :

Waste eggshells were collected from neighborhood bakeries in Bengaluru, India. Initially eggshells were cleaned to remove impurities under running water; dried out and then pulverized using mortar and pestle further ball milled to get fine powder. The obtained egg shell powder (CaCO₃) was digested in concentrated nitric acid to obtain a apparent yellow color solution of calcium nitrate (Ca(NO₃)₂). Stoichiometric quantity of urea was dissolved in 50 ml of Merck millipore water. The redox mixture was taken

in a Pyrex dish and kept in pre-heated muffle furnace at 500°C with heating rate 5°C per minute. Product obtained was further heated at 450°C for 4hrs, the obtained sample was named as CaO-F. Similar solution was prepared and kept for combustion in modified domestic microwave oven (koryo, KMC 2523, 900 W), product obtained was highly porous, foamy and non-flame dense fumes were observed during microwave combustion. Further product was heated to 450°C for 4hrs in muffle furnace. Obtained sample was named as CaO-M. The well grinded egg shell powder was heated to 200°C for 6 hrs the obtained sample was named as ES. For comparison, CaO was also synthesized by calcination methods wherein powdered eggshells was placed in an industrial furnace at 900°C for 4 hrs and obtained samples was named as CaO-C.

Catalyst characterization :

The above samples were subjected to physico-chemical characterization to know the structural integrity, composition, functional group, surface characteristics and morphology using various techniques such as XRD, SEM-EDXA, BET surface area, TGA and TPD-CO₂ was performed. The structural integrity of all the samples were obtained using Bruker AXS (model D8) powder XRD, the patterns were recorded by 2 θ range of 10–80° by per step up scan 0.02 with graphite mono chromatized Cu-K α radiations of $\lambda=1.5406$ Å. Morphology of the samples was recorded by Leica S440iINCA X-sight Scanning electron microscope attached with an EDX analyzer was used to know the chemical composition. Surface area and total pore volume was analyzed using Quanta chrome auto sorb IQ instrument, initially samples are degassed at 400°C for 6 hrs. Nitrogen adsorption and desorption studies were carried out and BET (Bruner-Emmett-Teller) method was applied to adsorption data to obtain surface area measurements, total pore volume was analyzed from liquid nitrogen temperature.

Total basicity of the samples were found using CO₂ as probe molecule by temperature-programmed desorption experiments; it was carried out using (BELCAT-II, BEL, Japan, Inc.). Typically, 100mg of calcinated sample was placed between quartz wool in a U-shaped quartz tube. The sample was thermally treated under an Ar stream at 400 °C for 2 hrs to remove

physics orbled water and other gaseous impurities. The catalysts were cooled to room temperature under Ar gas and the samples was treated with mixture of CO₂ in He (10%) was passed at the rate of 30 cm³ min⁻¹ at 150°C for 1 hr. then the sample was flushed with He (30 cm³ min⁻¹) at 150 °C for 1 hr. to remove physisorbed CO₂, the chemisorbed CO₂ desorption measurements carried out between the range of 100–600 °C at a heating rate of 10 °C min⁻¹. CO₂ concentration in the effluent was measured using gold-plated filament attached thermal conductivity detector.

Thermo gravimetric analysis (TGA) was carried out by TGA850-model, Mettler, and the sample weight of 20 milligrams at the temperature range of 30 -900° C under nitrogen flow.

Results and Discussion

X-ray diffraction :

XRD patterns of eggshells (ES), CaO-F and CaO-M are shown in Fig. 1, diffraction pattern of ES sample showed main peak at 2 θ values 29.39(104), minor peaks 22.02(012), 37.08(110), 42.12(113), 47.02(202), 52.15(018), 54.06(116) and 65.08(112) for hydrated CaCO₃ with rhombohedral phase and rhombo-centred lattice (JCPDS 05-586)²⁷. The XRD pattern of both CaO-F and CaO-M shows the peaks at 32.19(111), 37.35(200), 53.84 (220), 64.12(311), 67.34(311), and 80.88(400) corresponds to the calcium oxide of FCC phase (JCPDS: 4-777). In addition XRD Pattern of CaO-F and CaO-M shows very small peaks at 17.93, 28.61 and 33.12 corresponds to calcium hydroxide of the hexagonal phase (JCPDS: 86-0174), due to hygroscopic nature of the sample. The crystallite size of CaO-F and CaO-M samples were found by using De-bye Scherer equation is to be 74 and 42 nm respectively.

SEM and EDX :

Surface morphology of all the samples ES, CaO-C, CaO-M and CaO-F were provided in the Fig. 2. Egg shell derived nano-crystalline CaO-F and CaO-M are crystalline nano rod structures, but the CaO-M showed average particles size of 42 nm and for the CaO-F average particle size found to be 74 nm. The crystal growth is in form of rod is due to the non-

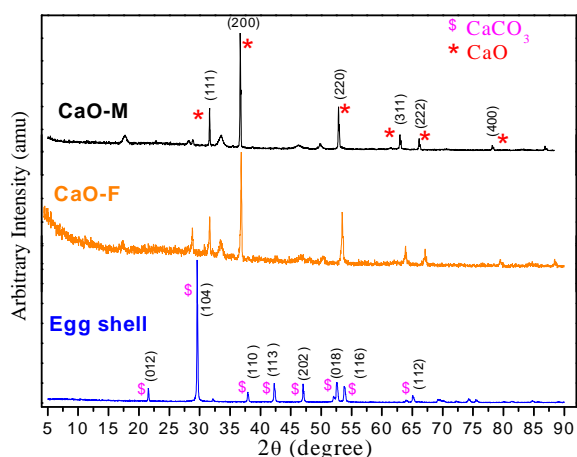


Fig. 1: Diffraction pattern of ES (Egg shell powder), CaO-F and CaO-M

flammable combustion offered by the microwave caused the uniform crystal growth like nano rods with

smaller size, whereas, the combustion process carried by furnace cause increased particle size. The shape and size may be correlated to the distribution of temperature in furnace and microwave oven these results were good agreement with the XRD results. The CaO-C cause irregular shaped particle with higher size of 225 nm which well matched with the literature²⁸. Comprehensive literature studies on CaO obtained by calcination method shows irregular dumbly shape particles²⁹⁻³⁰. Comparing CaO obtained from solution combustion (method followed in the present work) and CaO obtained by calcination method shows huge difference in the morphology. EDX spectra of natural egg shell powder shows the clear presence of carbon and CaO-F and CaO-M represents the absence of carbon and presence of Ca and O as shown in figure 3. Impurities P, and C may be found in EDX but might have been detached during the combustion process.

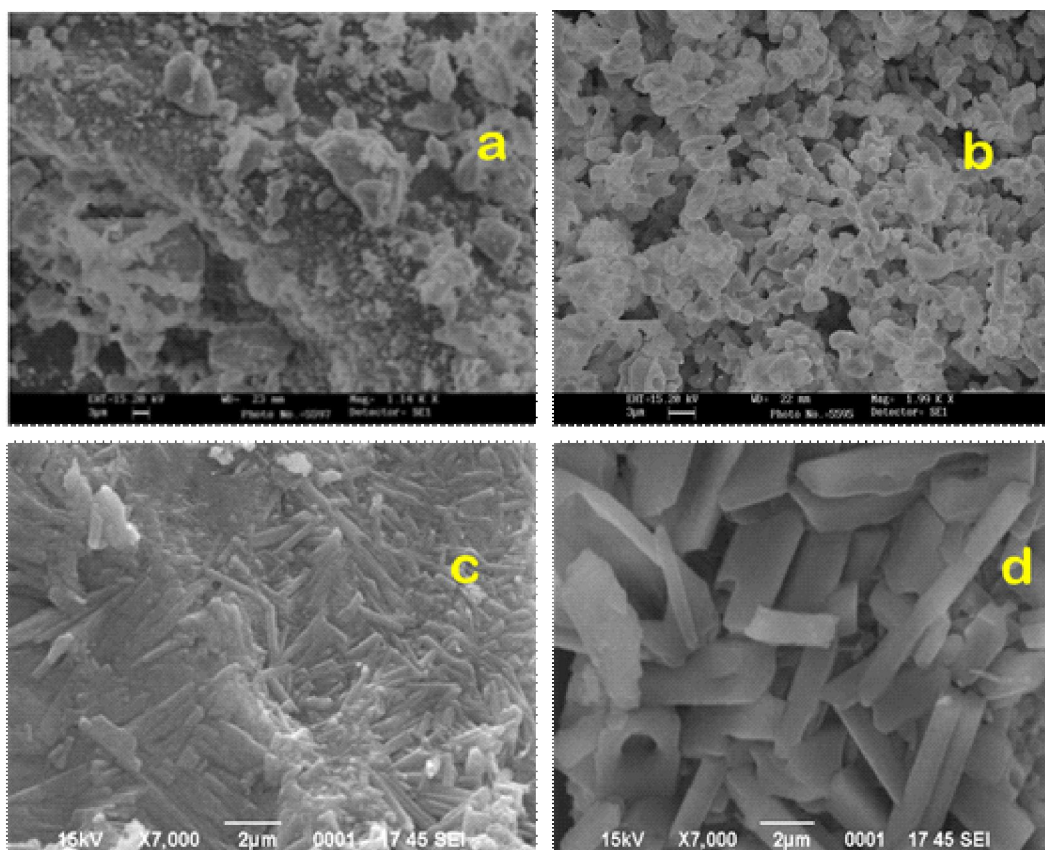


Figure 2: SEM images of (a) ES, (b)CaO-C, (c) CaO-M and (d) CaO-F

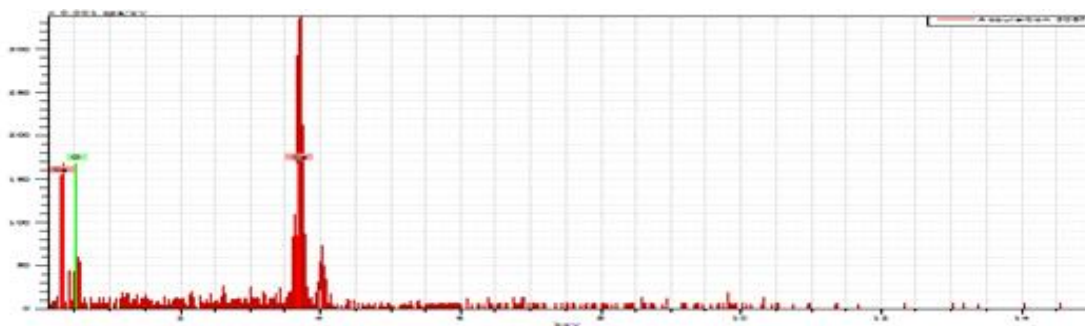


Fig 3: EDXA images of CaO

BET Surface area :

Performance of heterogeneous catalyst depends on the surface parameters such as surface area, pore volume, pore diameter. The N_2 adsorption-desorption isotherms and BJH plots for egg shell, CaO-F and CaO-M are shown in figure 4 and 5 respectively. Accordingly surface area, pore volume and pore diameter were tabulated in table 1. BET surface area analysis implies CaO-M ($26.85 \text{ m}^2 \text{ g}^{-1}$) has got more compared to CaO-F ($18.86 \text{ m}^2 \text{ g}^{-1}$) and CaO-C ($16.91 \text{ m}^2 \text{ g}^{-1}$). BJH plots showed that samples are in mesoporous nature with less pore diameter, with more pore volume for the CaO-M and CaO-F showed slightly more than the CaO-C and less than the ES. BJH plots showed that samples are in mesoporous nature with less pore diameter, with more pore volume for the CaO-M and CaO-F showed slightly more than CaO-C. But the all the samples showed mesoporous characteristics.

TPD- CO_2 :

Basicity of the catalyst is another vital role played for the samples to show catalytic activity, the active sites were found by CO_2 -TPD and are presented in Table 1 and the patterns were provide in the fig 6. Accordingly, CaO-M sample showed highest active sites with bimodal curve in the pattern of the temperature range 50-180 °C and another between 230-

530 °C with higher strength of the active sites, due to the higher surface area and smaller particles size. while CaO-F showed broader peak in the middle temperature range cause intermediate strength of the active sites with less amounts due to the lesser surface area and bigger particle size. But the ES gives single peak in the lower temperature range with too less amount of active sites in it.

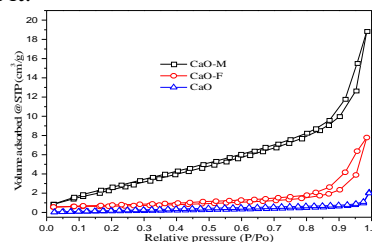
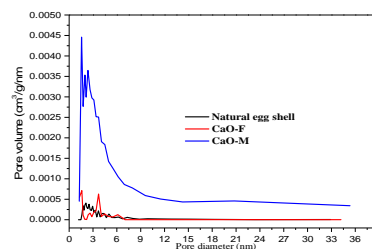
Figure 4: N_2 adsorption –desorption isotherm for samples CaO, CaO-F and CaO-M.

Figure 5: Pore size distribution of samples ES, CaO-F and CaO-M.

Table 1: BET surface area, pore volume, pore diameter and CO_2 -TPD.

Sample	SSA ($\text{m}^2 \text{ g}^{-1}$)	Vp (ccg^{-1})	Dp (nm)	TPD CO_2 (mmol g^{-1})
Egg shell powder	16.32	0.006	1.869	0.015
CaO-M	26.85	0.028	1.566	0.398
CaO-F	18.86	0.016	1.791	0.325
CaO-C	16.91	0.011	1.687	0.266

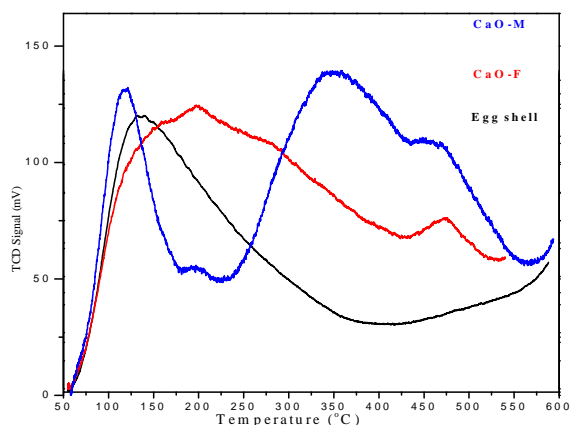
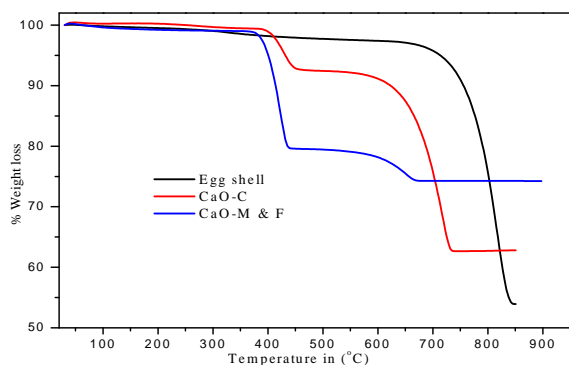
Figure 6 : CO₂-TPD curve of ES, CaO-F and CaO-M

Figure 7 – TGA cure of natural ES, CaO-C, CaO-F and CaO-M.

TGA analysis

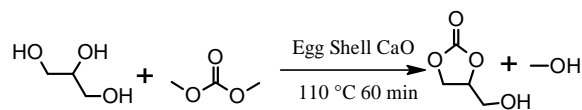
Thermo gravimetric analysis (TGA) was performed for the samples and showed in figure 7, nature egg shell (ES) was showed drastic weight loss of 44% between the temperature 660-850 °C due to decomposition of CaCO₃ into CaO, whereas CaO-F and CaO-M were loosed those weight in the temperature range of 370 to 720 °C. It depicts that decomposition (20%) of Ca(OH)₂ to CaO at the temperature 370-410 °C due to hygroscopic nature CaO readily converted to Ca(OH)₂, in addition to this some of the carbonates present in the samples was dissociated into CaO at the temperature range 510-640 °C (3%). Higher temperature needed for the decomposition of the CaCO₃²⁵. The calcined ES samples (CaO-C) also showed some weight at two staged one is at the 370-

410 °C (7% loss) and the 510-640 °C (26%) for decomposition of CaCO₃, it may due to calcined samples showed more affinity towards the CO₂ than the processed samples like CaO-F and CaO-M had less affinity towards the CO₂, otherwise sample will not act as catalysts. Due to the affinity towards the CO₂, CaO-C samples showed less surface area as well as active sites than the CaO-M and CaO-F.

Catalytic activity test :

The activity evaluation of the CaO samples were studied under microwave irradiation using Milestone, “START-S” microwave lab station for synthesis, Italy. The equipment enables the control of reaction mixture temperature and power output through aid of infrared sensor.

Typically 10mmol of glycerol and 20mmol of dimethyl carbonate were mixed with 300mg catalyst in a 15 ml microwave reactor vessel with a magnetic stirring bar. Initial power of 1100 W was applied for 30 seconds to attain the reaction temperature of 120 °C with stirring speed of 750 rpm. The reaction temperature was then maintained for 29.5 minutes by applying variable power of 300–800 W. The reaction mixture was cooled to lab temperature; the reaction mixture was then extracted by stirring with 5ml of n-pentanol for 10 minutes. The reaction mixture (scheme1) was analyzed using Chemito GC-1000 gas chromatograph with TR-Wax capillary column with a FID using methyl benzoate as internal standard. The products were also confirmed by GC-MS.



Scheme 1 – Transesterification of glycerol to glycerol carbonate

Reaction parameter study- Influence of reaction parameters on glycerol carbonate formation was studied. Effect of reaction setting like mole ratio, temperature, time and catalyst concentration were considered.

Effect of temperature:

The outcome of temperature on the glycerol

transesterification is shown in figure 8. Reaction temperature is also one of the major factors upsetting the transesterification reaction because the inbuilt rates constant are study functions of temperature. In this flow of transesterification reaction was carried out with glycerol: DEC mole ratio of 1:2 in the presence of 0.3% catalyst in 30 minutes reaction at different temperature from 70 to 120 °C. Glycerol conversion and GC yield increased with increase in temperature and remained nearly same for temperature above 100°C. Thereby 100°C is selected as optimum temperature for transesterification of glycerol to glycerol carbonate.

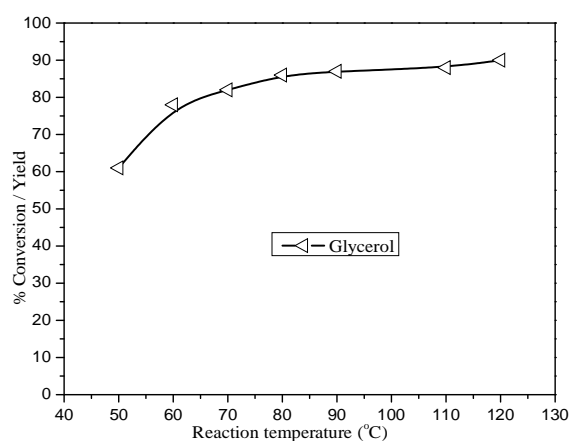


Figure 8 Effect of temperature on the glycerol carbonate synthesis

Reactions conditions: reaction time- 30 min; catalysts amount- 0.3 g; molar ratio of G: DMC-1:2.

Effect of reaction time :

The reaction time was also investigated by varying the reaction time from 10 to 60 minutes, whereby the Glycerol: DEC molar ratio, catalyst amount and reaction temperature was preset at 1:2, 0.3 % and 100 °C. The outcome obtained from the effect of reaction time on glycerol conversion and GC yield is illustrated in figure 9. it showed that initially 61% conversion & yield of GC at 5 min, further increase in the time caused increase upto 90 % at 60 min beyond that no increase in conversion or yield due to stabilization.

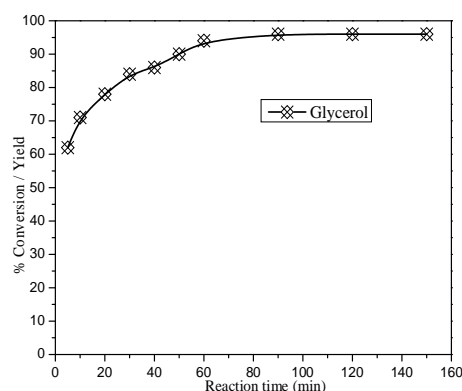


Figure 9 Effect of reaction time on the glycerol carbonate synthesis

Reactions conditions: temperature- 100 °C; catalysts amount- 0.3 g; molar ratio of G:DMC-1:2.

Effect of catalyst amount :

The effect of catalyst amount on the glycerol conversion and GC yield was studied. The amount of catalyst is another vital aspect under study. At lower catalyst amounts, the conversion and yield showed lesser at beginning (0.1 g) more than this increase in catalyst amounts showed increased conversion as well yield (85%) up to 0.3 g, further increase in catalyst amount from 0.4 to 1.0 g only 8 % increase was observed. At lower catalyst amounts the number of active sites is less for the approach of reactant molecules, whereas at higher amounts enough number of active sites is possible to adsorb the reactant molecules on it and get converts into products. At once enough number of active sites reached further conversion not increased due to stabilization or equilibrium.

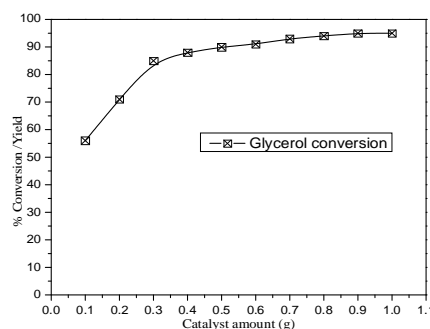


Figure 10 Effect of catalyst amount on the glycerol carbonate synthesis

Reactions conditions: temperature- 100 °C; reaction time- 30 min; molar ratio of G:DMC-1:2.

Effect of molar ratio :

The influence of molar ratio of glycerol:DMC were examined. Although scheme showed equimolar reactant ratio required. But the increase or decrease of any one of the reactant among directly influence on the reaction rate. So at equimolar ratio 82% yield was observed and increased molar ratio towards DMC causes increased conversion only 8% due to more of DMC available to the alkoxy anion formed after deprotonation by the catalyst, readily attacks to the electrophilic center presents in the DMC. Whereas increase in glycerol cause slight decreased conversion of glycerol due less amount of electrophilic centers (DMC) in the mixture. So 1:2 ratio of Glycerol to DMC showed more of conversion as well products yields as shown in Table 2.

Table 2. Effect of glycerol to DEC molar ratio on the Glycerol conversion is shown

Mole ratio G:DMC	% Glycerol conversion	% DMC conversion
1:1	82	82
1:2	90	-
1:3	88	-
2:1	-	76
3:1	-	74

Reactions conditions: temperature- 100 °C; reaction time- 30 min; catalysts amount- 0.3 g

Comparison of different catalysts :

The reaction conditions were optimized to get appropriate conversion and yield. Under the optimized conditions, catalytic performance all the different catalysts were examined to evaluate better catalyst. The samples such as CaO-F, CaO-M, CaO-C, CaO and ES, the results were provided in the figure 11, it showed that maximum yield 94% in the presence of CaO-M, due to high surface area, more active sites and less particle size influence on the higher conversion and yield of GC. In case of CaO-F showed 74% glycerol conversion and yield, reduced conversion compared to CaO-M due to slightly less

surface area and active sites with increased particle size. Whereas CaO-C showed still less activity than former and ES powder samples gives least activity may due to the least surface area and higher particle size with least active sites, least active sites due to hydration and adsorption atmospheric moisture and CO₂ masks the active sites, caused reduced activity to 36%.

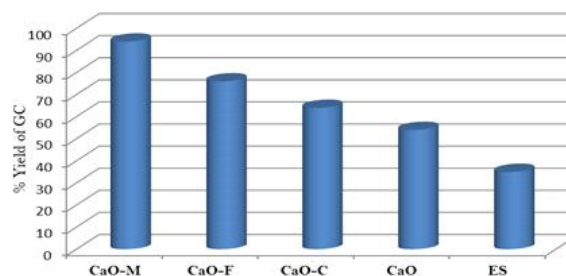


Figure 11: catalytic activities of different catalysts for the glycerol carbonate synthesis.

Reactions conditions: temperature- 100 °C; reaction time- 30 min; catalysts amount- 0.3 g; molar ratio of G:DMC-1:2.

Correlations study :

To know the exact physico-chemical factors influence on the conversion and the yield. The various factors such as surface area, particle size and active sites were compared and correlated with the yield of GC, the results were provided in the table4, and it showed that the correlations between the individual factors with yield of GC. The correlation factor for the active sites was 0.83 as the active sites decreased with yield also decreased, because glycerol carbonate formation takes place under influence of basic sites, more the number of active sites more will be the formation of alkoxy compounds, whereas correlation with particle size gives 0.88, the particle size also quite important for the distribution of active sites on the surface of the materials as well surface area also be the somehow important, due to the population density of active sites per surface area be a part of the catalytic activity (0.90). All the three factors are equally influence on the activity, variation of any one of the factor causes variation in the yield of GC. So the factor called active site approach which is ratio of product of surface area and active sites with particles size, because active sites

Table 4- Correlations study of different catalyst with yield of glycerol carbonate.

Samples	SA	PS	AS	Yield of GC	Active site approach
CaO-M	26.85	46	0.398	93	0.232
CaO-F	18.86	62	0.325	72	0.099
CaO-C	16.91	84	0.266	60	0.052
CaO	18.15	126	0.256	50	0.037
ES	16.32	104	0.015	36	0.002
r	0.83	-0.87	0.90	—	0.97

SA- Surface area ($\text{m}^2 \text{g}^{-1}$), PS= Particle size (nm), AS- active sites ($\mu\text{mol g}^{-1}$)

density on each nano particles. From the factor, it was found that lower the particle size more will be the surface area. The distribution of active sites on the each nano particle will show more activity 93% as CaO-M, and the r value 0.97 showed better correlation within active site approach influence on the product formation.

Reusability of the catalyst :

One of the most key factors of a good heterogeneous catalyst is the capability of reuse for a long time period. Reusability of the catalyst (CaO-M) was observed for 5 cycles as shown in figure 12 for 0.5% catalyst, G:DMC ratio 1:2 at temperature 100°C for 30 minutes. Under the same conditions catalyst sample was recovered and calcined at 400°C for 4 hours and used for further. It showed good performance upto 5 cycles on its reuse without further deactivation and loss of active sites.

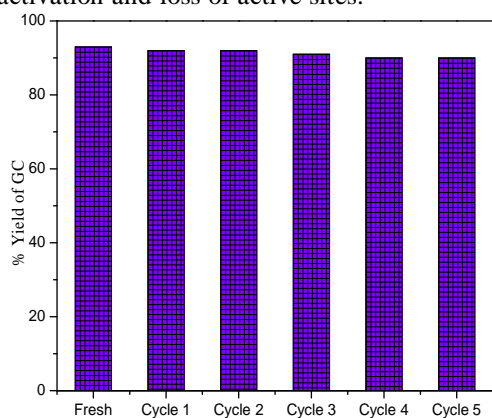


Figure 12: Reusability of CaO-M catalyst
Reactions conditions: temperature- 100°C ; reaction time- 30 min; catalysts amount- 0.3 g; molar ratio of G:DMC-1:2.

Conclusions

The utilization waste egg shells into catalytic material by solution combustion process by microwave irradiation method to obtain mesoporous CaO catalysts having high surface area and active sites density with good morphology compared to conventional heating mode. The evaluation of catalytic of all the samples showed bare results, whereas CaO-M samples showed better catalytic activity compared commercial CaO in all aspects without deactivation and steady state reactivity was observed for the glycerol carbonate synthesis under moderate temperature. Reusability of catalyst exhibits good performance. An important concept was developed based on the physico-chemical characteristics influence on the catalytic activity and coined the term active site approach; it will be a good concept to develop the catalysts for the industrial applications. It could be better and further needs to explored. On the whole present research has been worked towards sustainable method in reaction design and performance.

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