# Catalytic application of CaO and ZnO nanoparticles for energy generation and viable waste management technique: A perspective for sustainable environment

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***Abstract*—**In the present era mankind needs the support of alternate renewable energy sources, while rise in use and disposal of polymeric commodities has raised the call for appropriate polymeric waste management techniques. The perspective presented here is centered on the design and application of nanocatalysis in the pyrolysis of waste polymeric materials as a valuable strategy for energy recovery and to deal with the current scenario of challenges for sustainable development following the principles of Green Chemistry. In this context it is emphasized that waste materials not only provide feedstocks but also can rather serve to construct the nanocatalysts especially of calcium and zinc metal oxides through chemical transformations proving cost effectiveness and atom efficiency.

***Keywords*—***nanostructured catalysts; nanoparticles; metal oxides; catalytic pyrolysis; wastes*

## I. INTRODUCTION

Catalytic technologies are indispensible parts of the past, present and future chemical processes, energy generation and environmental industries. Catalysts being the essential components and drivers for development, the demand for design of advanced catalysts include (i) cost-effectiveness with greater reuse and larger lifecycle, (ii) to produce high value added products using inexpensive feed-stocks and raw materials (iii) for energy efficient chemical conversion processes that are environmentally benign [1]. In this nano-age when size reduction of every device, object, matter and material is taking hype with their enhanced properties, nano-sized catalysts are emerging out as esteemed materials having enormous surface area offering expanded catalytic capabilities with intriguing research and developments [2]. Nanocatalysis, bridging the gap between homogenous and heterogeneous catalyses, is not new as its concept dates back to 1950s when even the term nanotechnology together with its multifaceted applications was not known [3]. Nanomatter, assigned for the domain of green chemistry catalysis, possessing intrinsic characteristic of high surface area to volume ratio, alters positively the inherent catalytic performance consisting important implications in favoring chemical reactions, due to the presence of increased number of surface active sites for reactants to adsorb, react and eventually desorb [4]. One of the most fruitful areas for application of nanostructured catalysts, much required for the benefit of mankind, is in the catalytic pyrolysis of polymeric wastes for the generation of energy products.

## II. POLYMERIC WASTES AND PYROLYSIS

Non-biodegradable polymeric materials or in general terms plastics are considered among the greatest innovations of this millennium because of its versatile innumerable uses, light weight, resistance to rust or rot, reusability and relative low cost. However, the huge rise in consumption of plastic commodities has caused an upstream of vast polymeric wastes casting a serious global environmental issue. Additionally, as petroleum is the chief source in plastic manufacturing their growth has led to depletion of petroleum vulnerably as a part of the non-renewable fossil fuel [5]. Thus, the need has arisen simultaneously for human beings to rely on alternative renewable energy sources. Since, plastics are petroleum based polymeric materials, pyrolysis technology to convert polymeric wastes into energy products such as liquid oil having high calorific value in comparable with the commercial fuels around 30-40 MJ/kg, briefly listed in Table 1, is conducive towards polymerc waste reduction and natural resource conservation

| **Oil Property** | **Polymer (Plastic Type)** | | | | | | **Commercial Standard Fuel Value (ASTM 1979)** | | |
|---|---|---|---|---|---|---|---|---|---|
| | ***Polyethylene terephthalate (PET)*** | ***Polyethylene (PE)*** | | ***Polyvinyl chloride (PVC)*** | ***Polypropylene (PP)*** | ***Polystyrene (PS)*** | ***Diesel*** | ***Gasoline*** | ***Liquified petroleum gas (LPG)*** |
| | | ***HDPE*** | ***LDPE*** | | | | | | |
| Calorific value (MJ/kg) | 28.2 | 40.5 | 39.5 | 21.1 | 40.8 | 43.0 | 43.0 | 42.5 | 46.1 |
| Density@15ºC ($g/cm^3$) | 0.90 | 0.89 | 0.78 | 0.84 | 0.86 | 0.85 | 0.807 | 0.780 | 0.525-0.580 |
| Viscosity@25-50ºC ($mm^2/s$) | -- | 5.08 | 5.56 | 6.36 | 4.09 | 1.4 | 1.9-4.1 | 1.17 | -- |

*TABLE I. PROPERTIES OF LIQUID OBTAINED FROM PYROLYSIS OF POLYMERIC WASTES AND COMMERCIAL STANDARD FUELS [6]*

Pyrolysis is the process of controlled thermal decomposition in an air deficient/oxygen starved chamber, whereby chemical degradation of organic compounds takes place leading to the production of gaseous, liquid and solid high value added products as potential fuels or sources of chemicals. Catalyst loading in the pyrolysis of waste plastic fragments or segregates, influences upon the optimization of product distribution and selectivity for obtaining hydrocarbons, olefins and liquid oil having similarity to conventional fuels (diesel and gasoline) which are in great demand by the petrochemical industry. Catalysts (i) significantly lowers the activation energy, thus speeds up reaction rate while reduces pyrolysis process time and optimum degradation temperatures, this is crucial as low thermal conductivity of polymers and highly endothermic feature of pyrolysis renders heat as the most expensive cost required for combustion/conversion, (ii) enhances rate of conversion, improves control over the hydrocarbon yield and upgrades fuel quality while narrows the product distribution [8].

### *A. Catalysts in Pyrolysis*

There are mainly two kinds of catalyst: homogeneous, involving one phase and heterogeneous involving two or more phases. Homogeneous catalyst applied for waste polymeric pyrolysis usually have classical Lewis acid sites (electron pair acceptors) such as $AlCl_3$ $FeCl_3$, $TiCl_3$, $TiCl_4$ and fused metal tetrachloroaluminate compexes of types $M(AlCl_4)_n$ or $MCl_n$–$AlCl_3$ (M = Li, Na, K, Mg, Ca, Ba & n = 1–2) [9]. However, heterogeneous catalysts have been used widely since for the ease of separation of the fluid product mixture from the solid catalyst, and can be broadly classified as conventional solid acids such as silica-alumina, alumina, FCC catalysts (Fluid Catalytic Cracking), zeolites; nanocrystalline zeolites e.g. n-HZSM-5, HUSY, Hβ, HMOR, HY-zeolite, etc.; mesostructured catalysts e.g. MCM-41 etc.; metal oxides e.g. $K_2O$, MgO, CaO, $TiO_2$, ZnO, etc.; alkali or alkaline metal carbonates, metal supported on activated carbon; reforming catalysts; among other catalytic materials are clays such as montmorillonite and saponite [10]. Although numerous zeolites of the types ZSM-5, ZSM-11, REY, USY, Y-zeolite, Beta, Mordenite, etc., [11] are extensively used due to their feature of proper acid strength, pore structure and pore size, however the catalyst activity increases with increase in the number of acid sites, therefore nanocrystalline zeolites have shown comparatively superior performance at relatively milder operating conditions than their ordinary bulk zeolite counterparts in the catalytic pyrolysis of various polymeric materials, Table 2 compares the product yield.

### *B. Trends of nanocatalysis*

Besides, efficiency of HZSM-5, HMOR and HUSY was investigated on HDPE pyrolysis with 40 wt% of catalyst to polymer ratio [22]. Studies have put forth that HZSM-5 displayed very high catalytic activity along with very good exhibition by HUSY and HMOR, in terms of the very less left over residue. This denotes that these nanocrystalline zeolites are able to maximize total product conversion in catalytic pyrolysis of polymeric wastes. While, trends of product selectivity depend on product preferences of different zeolite based catalysts. This was proven by experimental evidences of using HUSY and HZSM-5 on HDPE and LDPE pyrolysis with 10 wt% of catalyst to polymer ratio at 550 $^oC$ in a batch reactor [17]. Use of HUSY nanocatalyst yielded higher liquid oil, HDPE = 41.0 wt% and LDPE = 61.6 wt%, while, HDPE = 17.3 wt% and LDPE = 18.3 wt% from HZSM-5 nanocatalyst, conversely higher gaseous fraction was recovered catalyzed by HZSM-5, HDPE = 72.6 wt% and LDPE = 70.7 wt%. Effects of HZSM-5 in catalytic pyrolysis of HDPE reported by researchers [23, 24], with 20 wt% of catalyst to polymer ratio, at 450-500 $^oC$, resulted liquid yield of around 35 wt%

*TABLE II. ANALYSIS OF APPROXIMATE PRODUCT YIELDS OF ZEOLITES VERSUS NANOCRYSTALLINE ZEOLITES FROM CATALYTIC PYROLYSIS OF POLYMERIC MATERIALS*

| **Catalyst** | | **Polymeric feedstock** | **Product yield (%wt)** | | | **References** |
|---|---|---|---|---|---|---|
| | | | ***Gas fraction*** | ***Liquid fraction*** | ***Solid fraction*** | |
| Zeolites | ZSM-5 | HDPE | 63.5 | 35 | 1.5 | [12] |
| | | PET, PE, PVC, PP, PS | 40.4 | 56.9 | 3.2 | [13] |
| | Y-zeolite | PE wax | 28.95 | 66.98 | 4.08 | [14] |
| | | Municipal plastic waste | 36 | 52 | 12 | [15] |
| | USY | HDPE/LDPE/PP/PS | 87.5 | 3.7 | 8.8 | [16] |
| | Mordenite | HDPE/LDPE/PP/PS | 90.2 | 4.3 | 5.5 | [16] |
| | | PE wax | 15.11 | 82.59 | 2.3 | [14] |
| | Natural zeolite | Municipal plastic waste | 34 | 50 | 16 | [15] |

| | | | | | | |
|---|---|---|---|---|---|---|
| Nanocrystalline zeolites | HZSM-5 | HDPE | 72.6 | 17.3 | 0.7 | [17] |
| | | LDPE | 70.7 | 18.3 | 0.5 | [17] |
| | | PE wax | 51.04 | 47.18 | 1.78 | [14] |
| | | PP | 94.77 | 2.31 | 3.92 | [18] |
| | HY-zeolite | PE | 46 | 42 | 8 | [19] |
| | | PP | 52 | 44 | 10 | [19] |
| | | PS | 24 | 71 | 5 | [19] |
| | HUSY | HDPE | 93.2 | 4.9 | 1.9 | [20] |
| | | PE/PVC/PP/PS | 85.6 | 3.3 | 4.1 | [21] |
| | HMOR | PP | 88.29 | 4.54 | 4.96 | [18] |
| | HBeta | HDPE | 95.7 | 2.4 | 1.9 | [20] |

having gaseous fraction of 63.5 wt% and lower liquid yield of around 4.4 wt% but high gaseous products of 86.1 wt%, respectively [23, 24]. Also applying HUSY and HZSM-5 zeolite nanocatalysts, very minute amount of liquid product was obtained 3.75 wt% and 2.31 wt% respectively, in PP pyrolysis with 40 wt% of catalyst to polymer ratio, at 360 $^{o}$C [18]. Above all, it was further proved that nanocrystalline zeolites such as HZSM-5 have high resistance to coking

## III. Metal Oxides as Catalysts for Polymeric Waste Recycling

Investigations indicate that degradation by pyrolysis of polyethylene using solid bases (MgO, CaO, BaO, ZnO, $TiO_2$) as catalyst yield more liquid oil (tar) than on solid acids, even though the degradation completion time on solid bases is of much longer duration than on solid acids [5, 10]. Also, in the current research scenario the obtained oil composition consisting mainly of olefins fail to fulfill the needs to stand as fuel oil due to their polymerization characteristic during transportation and preservation. Moreover, the liquid oils produced over these metal oxides chiefly contain straight chain hydrocarbons, rich in n-paraffins and 1-olefins while poor in aromatics and branched isomers, expecting low octane number to comply with the present standards of fuels. For example catalytic degradation of waste polystyrene carried out separately by dispersing powdered metal oxide catalysts ($K_2O$, MgO, CaO, BaO), solid acids (viz. $SiO_2/Al_2O_3$, HZSM5) and active carbon as catalysts, reported effect of solid bases exhibit more yield of styrene, around 80-90 wt% both monomer and dimer of styrene at 623 K, which could be even recycled for polystyrene production.

There have been even successful investigations of catalytic hydrolysis of waste polycarbonates (PC) in the presence of metal oxide catalysts MgO and CaO leading to the formation of high value products [25]. Thus these basic oxides, such as BaO found to be most effective while CaO more desirable, are catalyst models holding dual potentiality from technology point of view for dealing with the issue of environmental polymeric waste to energy recovery as well as saving carbon resources by transforming recyclable polymers [5, 10, 26], and should be focused for extensive study. Experimental studies involving zinc for catalytic cracking of polymeric materials such as polystyrene report product yield containing 2.5-9.9 wt% of gaseous matter, 89-97 wt% of liquid oil (tar) and 0.5-0.6 wt% of solid residue (char), at temperatures ranging from 425-581 $^{o}$C, with the obtained tar comprising 64.9 wt% of styrene. Whereas, thermogravimetric methods have been adopted to study the influence of the presence of metal oxides on the product structure and yield from thermal degradation of PVC [27]. Catalytic cracking of waste polymeric materials like PET, PE, PP, PS have been carried out applying activated carbon, activated carbon with granulated charcoal and activated carbon with calcium oxide, which proved to be efficacious approach for conversion into low-emissive hydrocarbon fuel [28]. Conversion have been also tested involving $Ca(OH)_2$, $Al_2O_3$, and ZnO for catalytic thermal cracking of PE based plastic materials and highest liquid yield of lower molecular weight compounds ($C_5$-$C_{22}$, MW=100-300) was obtained for $Ca(OH)_2$ [29]. Scarcely available literatures regarding the application of basic metal oxides in catalytic pyrolysis clearly indicates that they have not been properly explored for this aspect and their prospective latent capability still lies dormant and is yet to hike.

### *A. Importance of Calcium and Zinc in Generation of Energy Products*

Calcium oxide apart from being an inexpensive chemical compound can be abundantly obtained from natural sources e.g. limestone, egg shell, snail shell, crab shell, other crustacean and mollusk shells, fish scales, etc., having porous structure and nontoxic nature. These raw materials as catalysts which are chiefly composed of calcium carbonate are partially converted to CaO after calcination (above 1000 K around 2 h). The heat treatment produces smaller particles of $CaCO_3$ and CaO responsible for catalytic activity under optimized reaction conditions [30]. CaO may be later converted to calcium hydroxide $Ca(OH)_2$ by simple hydration method. Also the catalytic activities and high conversion have been successfully characterized through FTIR, XRD, XPS, TG/DTA, $CO_2$-TPD, SEM, BET techniques and evaluated in the reactions when product stream like isobutane and isopentane remain unaffected all through the process while there is increase in butane and pentene olefins. Inspite of the fact that zeolite based catalysts achieve greater conversion than non-zeolitic ones, there exists intense need for innovation of more efficient catalysts for pyrolysis process of waste polymeric materials, with foremost focus on being cost-effective and easily obtainable for commercial scale.

of the kind transesterification of vegetable oil such as sunflower oil, palm oil, etc., for biodiesel production. Experiments carried out revealed that hydration followed by thermal decomposition (calcination-hydration-dehydration treatment) of natural calcium sources developed novel CaO solid consisting surface area twice than the value from conventional thermal decomposition of CaO. The water treatment did not significantly alter the pore characteristics even though it intensively increased the surface area and pore volume [31, 32]. The calcium oxide based catalyst thus prepared having high basicity and employed for the transesterification reaction of palm oil showed that highest biodiesel conversion of 98% was achieved by limestone with highest calcium content (99.98%). Its reusability was also maintained up to three consecutive times which was established by carrying subsequent examination of reaction cycles. The first run gave 98% of biodiesel conversion while the second and third run attained 96% and 88%, respectively, decreasing dramatically thereafter [33].

*B. Effect of CaO and ZnO in Nanodimensions*

There are experimental evidences of CaO and ZnO nanoparticles being employed in the generation of biofuels suggesting superior yield results. Nanoparticles of CaO synthesized from calcium nitrate and snail shell powder as $CaCO_3$ source, have been used as active as well as stable catalyst and their performance tested via transesterification process for biodiesel production resulting 93-96% yield with 8wt% of catalyst loading.

The characteristic results show that nanoparticles of CaO developed from snail shell hold excellent catalytic activity and potentiality for use as solid base nano catalyst with examined moderate reusability having further scope of enhancing its regeneration, realizing the great importance of catalyst recyclable efficiency for industrial application from economic point of view [34]. Diverse forms of nano CaO such as pellets, powder and granules, as catalyst have been studied by co-workers and 99% biodiesel yield have been reported from soybean oil. The high yield obtained through transesterification is considered due to the larger surface area associated with nano crystallite size and defects. Also, utilization of ZnO nanorods as catalyst yielding 94.8 % displayed better performance than conventional bulk ZnO with 91.4% yield of biodiesel from olive oil. The nano metal oxides mostly used for biodiesel production are of Mg, Ca, Zn, Zr, individually or supported on other materials, with highest biodiesel yield obtained using Li-CaO and CaO nanocatalysts, under milder operating conditions giving rise to lower energy consumption for process feasibility [35], summarized in Table 3. The nanocatalysts reduce reaction temperatures in biomass liquefaction which causes an increase in the liquid yield as higher temperature during the liquefaction process promotes gaseous products.

The effect of catalysts on biomass gasification is important in reducing the tar formation while improving the conversion efficiency along with the quality of gas products which mainly include a combustible mixture of carbon dioxide, carbon monoxide, methane and hydrogen referred as synthesis gas (syngas). Effective gasification catalysts holding the criteria of being deactivation resistant as a result of sintering or carbon fouling and can be easily regenerated are calcined rocks, olivine, clay minerals, activated alumina, transition metal oxides e.g. NiO, FeO, $CeO_2$, ZnO, $SnO_2$, alkali metal carbonates and FCC catalysts while successful nanocatalysts are nano-$SnO_2$ and nano-ZnO structures. In hydrothermal conversion of cellulose remarkable catalytic activity was illustrated by nanosized ZnO of twelve times higher than that of nano $SnO_2$ whereas the bulk ZnO was only five times ahead of the bulk $SnO_2$ in catalytic conversion [35].

*TABLE III. COMPARISON OF LIQUID FUEL OBTAINED WITH THE APPLICATION OF METAL OXIDE CATALYSTS (CaO AND ZnO) IN MULTIPLE FORMS ON DIFFERENT TARGETS*

| Catalyst | Feedstock | Technique | Liquid Fuel Yield (%) | References |
|---|---|---|---|---|
| $Ca(OH)_2$ | LDPE | Catalytic cracking (pyrolysis) | 95.9 | [29] |
| CaO + activated carbon | Mixed plastics PET/PE/PP/PS | Catalytic cracking (pyrolysis) | 75.5 | [28] |
| CaO from limestone | Palm oil | Transesterification (biodiesel production) | 98 | [33] |
| CaO from eggshell, crabshell | Sunflower oil | Transesterification (biodiesel production) | 97.75, 83.1 | [30] |
| Nano CaO | Soybean oil | Transesterification (biodiesel production) | 99 | [34] |
| ZnO | LDPE | Catalytic cracking (pyrolysis) | 96.1 | [29] |
| ZnO | Olive oil | Transesterification (biodiesel production) | 91.4 | [36] |
| ZnO nanorods | Olive oil | Transesterification (biodiesel production) | 94.8 | [36] |
| Nano ZnO | Palm oil | Transesterification (biodiesel production) | 83.2 | [37] |

*C. Prospective Catalyst Materials from Wastes*

With growing scientific effort and appreciation for targeting waste materials as renewable feedstock for transformations into fuels and value added products as energy sources [38],

in this context a variant form of waste materials have been also discovered to be resources for developing the catalysts which would further serve to curb out the expenses significantly while enhancing atom-efficiency and energy of the overall process. Catalysts though required in small amounts its cost is consequentially expressive in the industrial scale therefore creation of catalyst from continually produced anthropogenic livestock wastes without raising ecological questions for concomitant conversion of other sorts of wastes into valuable energy products is a leap towards sound economical and environmental system. There exist numerous reports of solid base heterogeneous catalysts derived from waste materials more extensively of CaO due to the existent wealth of broad range calcium rich wastes as well as minerals, along with regeneration possibilities of the deactivated catalysts through easy re-calcination at 900 $^{o}$C [39]. Novel catalytic technologies may arise with the large scale production of such calcium based excellent solid base catalysts from animal bones, shells, seafood wastes, mining and construction wastes, readily collected from slaughterhouses, fisheries and processing plants. Superbasic MgO–CaO/$SiO_2$ obtained from calcined waste slag, utilized for rapeseed oil transesterification achieved 98% yield, being active as much as lab grade CaO but only at one tenth cost [39]. Minerals of calcium e.g. dolomite requiring less processing and purification often generate equally and more active catalysts. Furthermore, facile, feasible and low cost protocols for green synthesis of nano ZnO [40-42] and CaO nanoparticles [43-45] are presented by the researchers in myriad numbers being environmentally benign and applicable for nanocatalysis [46-51].

## IV. CONCLUSION

Nanocatalysts have proven role in achieving improved product quality and yield efficiency at optimal operating conditions in comparison to the catalysts having bulk dimensions. Their huge specific surface area renders high catalytic activity, imparting manifold catalyst-reactant interaction and other beneficial characteristic features of homogenous catalysis, whereas removing the drawbacks of heterogeneous catalysis such as time consumption, mass transfer resistance, fast deactivation and inefficiency while retaining ease of separation from the reaction mixture due to insolubility, thus bridging the gap between the two catalysis types. Regarding this, attempts to develop novel nanocatalysts have drastically increased in various sectors citing examples especially in biofuels rather more attention to biodiesel production from different edible and non-edible biomass feedstock. Same set of hypothesis and theory applies to justify the postulation and perspective of favourable catalytic activity for the objective of enhanced efficiency of the overall polymeric pyrolysis process influenced by metal oxide nanoparticles such as CaO and ZnO as nanostructured catalysts. The nanostructured properties may hold promising viabilities to overcome the shortcomings consisted in the bulk metal oxide catalysts which might have restricted their use in the catalytic pyrolysis of non-biodegradable waste polymers and hindered the achievement of desired product selectivity and percent yield. There exists research gap in the catalytic application of CaO and ZnO nanoparticles in the pyrolysis process of waste polymeric materials in an era where atom efficiency, cost effectiveness and catalyst regeneration, for the generation of energy products, are matters of great concern. The motto intended consecutively is to proceed and reach the completion of the pyrolysis process with haste to make waste into value added products and energy sources. Thus there is essential requirement to bring forth the fruitful utilization of these metal oxide nanocatalysts in the section of catalytic pyrolysis of polymeric wastes for energy recovery through extensive experimental studies, from the perspective of exponential sustainable development of our environment.

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