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COMMUNICATION

Nano porous hydroxyapatite as a bi-functional catalyst for bio-fuel production†

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Nano porous hydroxyapatite possessing acid-base functionality has been successfully synthesized by a simple
10 **hydrothermal method using P123 tri-block co-polymer as structure directing agent. The material exhibited excellent catalytic activity for the production of solketal (100% selectivity) from bio-glycerol (90% conversion)**

15 Calcium phosphate compounds are of vital importance due to their biochemical nature such as in bone formation and their long time stability.[1] Synthesis of high quality calcium phosphates is of considerable interest for its applications in important areas of biology, medicine and geology. [2] Hydroxyapatite (HAP) is the
20 most stable among the known calcium phosphates and hence suitable for exploring for various applications.[3] The material with its general composition of Ca_{10} $(PO4)_6(OH)_2$ possesses a special property of exhibiting both acid (PO_4^{-2} ion) and base (Ca^{+2} ion) active sites together. Due to this reason, the material has been
25 recently gaining special importance in catalysis for selective reactions where the synergetic functioning of acid-base active site pair facilitates the molecular transformations.[4] The tunable ratio of Ca/P in on one hand and the presence of ion exchange positions at Ca, PO_4 and OH regions of the material on the other
30 make it convenient for the synthesis of wide variety of acid-base pair, metal functionalized materials.[5] With their flexibility in properties the materials have been successfully employed for various reactions such as oxidation of alkanes, water gas shift reaction, Knoevenagel condensation, Friedel-Crafts alkylation
35 reaction, dehydrogenation and dehydration of alcohols.[4-7]

The production of oxygenates from glycerol gains much importance due to the excellent diesel-blending property of the oxygenates that not only improve the quality of the fuel but also increases the overall yield of the biodiesel. This reaction also
40 helps to meet the target for energy production for transport from renewable sources. Olefins such as isobutene or alcohols such as tertiary butyl alcohol are commonly used as etherifying agents of glycerol. But the use of olefins create the problem of undesired di-olefin formation, while the alcohols can cause the formation of
55 huge amount of water.[8,9] Esterification with low molecular weight acids, transesterification with low molecular weight esters and acetalization with aldehydes or ketones are the other promising and economically viable alternative routes for the conversion of glycerol.[10-14]
60 Acetalization with ketones, especially acetone is gaining importance due to the fact that acetone is widely produced from biomass conversion as well as from the chemical process of cumene cracking. Hence, facilitating reaction between two biomass derived products glycerol and acetone is advantageous as
65 they constitute an excellent component for the formulation of gasoline, diesel and biodiesel fuels.[15,16] These oxygenated compounds, when incorporated into standard diesel fuel, have led to a decrease the undesired emissions of particles, hydrocarbons, carbon monoxide and aldehydes. Likewise, these products also
70 can act as improvers of cold flow and flash point properties of biodiesel along with simultaneous reduction its viscosity desirable for fuel applications.[17]

Continuous processes for the formation of solketal employing heterogeneous catalysts, such as the commercial macro porous
75 acid resins of the Amberlyst family, have been described in the literature. More recently, G. Vicente *et al.*[6] reported the suitability of sulphonic meso-structured silica as a catalyst for the acetalization of glycerol. The acid functionalized C-Si composite materials have also been successfully employed for acetalization
80 of glycerol and to the best of our knowledge, acid-base functionalized materials have not been studied for this reaction. On the other hand, the acid-base site bearing HAP has been used as a catalyst for dehydrogenation and hydrogen transfer reactions of alcohols, and for catalytic intra-molecular dehydration of lactic
85 acid to acrylic acid. In the present study, the lab synthesized nano particles of HAP (CaP) material possessing both acid and base sties has been first time employed for the inter-molecular dehydration (condensation) from glycerol and acetone to produce solketal at solvent-free reaction conditions.
90 Herein we report a simple hydrothermal method for the synthesis of crystalline calcium phosphate nano particles exhibiting acid-base dual functionality suitable for effective catalytic applications related to biomass conversion by using P123 tri-block copolymer (Poly (ethylene glycol)-poly (propylene
95 glycol)-poly (ethylene glycol) (EO_{20}-PO_{70}-EO_{20}) as an organic template . The typical synthesis method involves (ESI) the admixing of P123 block co-polymer, 1N HCl, ammonium dihydrogenphosphate, methanol followed by stirring of the resultant mixture at 60 °C for 2 hr until the formation of a clear

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†Electronic supplementary information (ESI): Experimental details, wide angle XRD, EDX, SEM images, IR spectra, TG/DTA, TPD etc.

solution to which added the calcium (water solution) drop-wise with rigorous stirring to get a soluble suspension. The resultant mixture was charged into a Teflon-lined autoclave for hydrothermal synthesis and treated at 150 °C for 24 h. At the end of the treatment, the compound was washed and collected by filtration, dried and calcined at 550 °C for 6 hr.

The presence of Ca, P and O in the sample was confirmed from EDX analysis (ESI Fig S1). The XRD patterns of the sample (Fig 1) are in good agreement with those reported for hydroxyapatite (HAP) and confirm that the sample is in crystalline HAP structure. The three major intense peaks appeared at ~31.6, ~32 and ~33 2θ in XRD are known to be characteristic bands of HAP.[4, 19] The structure of the HAP material is also confirmed by FTIR (Fig S3), where, the presence of broad band at about 1000-1000 cm^{-1} represents the formation of HAP. Splitting of this broad band at around 1090 cm^{-1} corresponds to the splitting of the γ3 fundamental vibrational mode of the tetrahedral phosphate group. Accordingly, the γ1 and γ4 symmetric stretching vibrations of P-O bond in phosphate group were identified by the prominent adsorption bands at 960 and 565 cm^{-1} respectively. The other two prominent bands appeared at ~3500 cm^{-1} and 630 cm^{-1} represent the stretching modes of the –OH groups in the HAP sample.[4, 20]

The SEM images of the CaP (Fig. 2a,b) indicate the presence of wafers like crystals of the material accumulated together. The material also exhibited porous nature on the surface of the crystals in SEM. Further, TEM images (Fig 2c) reveal the presence of uniform size nano particles (~30 nm) of HAP. The HRTEM also show the porous nature of the sample having the uniformly distributed pores (Fig 2d). The hysteresis loop obtained with steep increase in pore volume at P/P0 ~1.0 in N_2 adsorption isotherm clearly indicates the presence of nano range pores (Fig 3). The BJH pore size distribution of the sample (shown in inset) indicates the maximum population of pores with pore diameter of ~25 nm. The sample exhibits 73 m^2/g surface area, a typical character of nano particles. The presence of nano pores reflected in the high pore volume (0.7978 cm^3/g) along with mean pore diameter of 43.65 nm (ESI Table 1 and Fig 3). The presence of nano pores and the resultant pore volume exhibited by the sample can be ascribed to the structure directing and void-filling property of the P123 tri-block co-polymer used in the hydrothermal synthesis, which decomposes to leave pores in the material up on calcinations. The removal of the template is further confirmed from TGA analysis of the as-synthesized sample (ESI Fig S2), where, the sample exhibited initial weight loss of ~2-7 % at below 200 °C related to the removal of water followed by another weight loss at ~ 350 °C related to the removal of P123 block polymer. The major weight loss of 10-15wt% related to the decomposition of phosphate moiety is observed at temperature range of 600-700 °C that clearly envisions the high temperature stability of the CaP sample and its suitability for material applications up to 600 °C.[18]

The sample possessing both phosphate and calcium ion is expected to exhibit both acidic and basic nature of the active sites. The acid sites and base sites have characterized by employing temperature programmed desorption measurements of NH_3 and CO_2 gases respectively. The sample exhibited a very strong ammonia desorption peak at ~ 400 °C related to strong
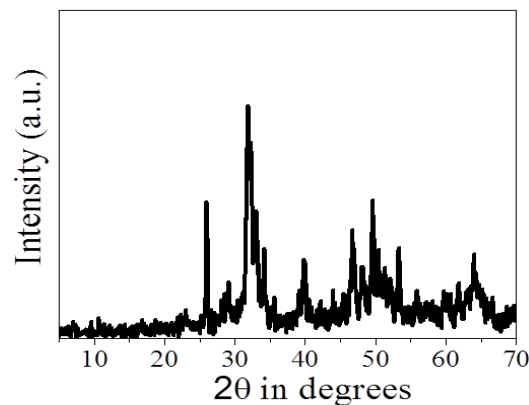

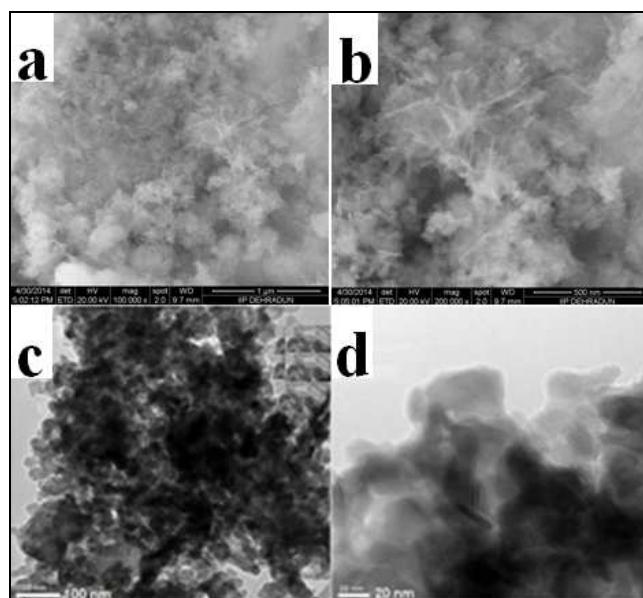**Fig. 1 (**a) XRD pattern of the aicd-base HAP material

Fig. 2 a ,b are SEM images and c,d are TEM and HRTEM images of the synthesized acid-base HAP.
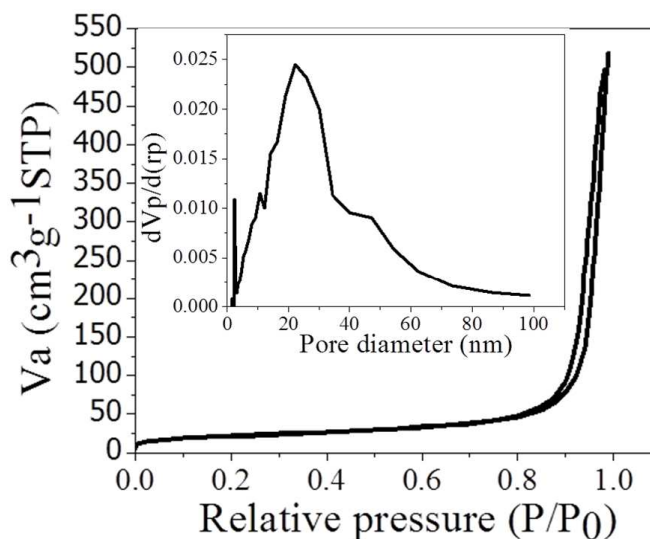

Fig. 3 N_2 adsorption-desorption isotherms and the BJH pore size distribution (inset) of the acid-base HAP.

Table 1. Acid- base properties of synthesized HAP materials

sample	Ca/P mol ratio≠	Acidity (m.mol NH$_3$/g catal)	Basicity (m.mol CO$_2$/g.catal)
Acid-base HAP	1.0	0.14	0.30
Acidic HAP	0.6	0.26	0.08
Basic HAP	2.0	0.05	0.34

≠calculated based on the chemicals taken during the synthesis

acid sites (ESI, Fig S4), along with a low intensity low temperature peak at ~100 °C related to weak acidity. As predicted by the presence of Ca, the CaP sample also exhibited the presence of good amount of basic sites. The spectra (ESI, Fig S5) indicates a strong desorption peak of CO$_2$ related to strong base sites at ~450 °C along with a low temperature CO$_2$ desorption peak at ~150 °C. Overall, the TPD studies indicate the presence of both strong acid and strong base sites in the HAP (Table 1).

The CAP sample possessing acid and base functions (bi-functional HAP) is expected to act as efficient bi-functional catalyst transformations and was explored towards the acetalization of glycerol in the present study. The data given in table 1 indicates high conversions of glycerol facilitated at solvent-free reaction conditions on this catalyst. The glycerol conversion was low (77%) at first 30 min of reaction time but was increased to 90 % (steady state) quickly within 60 min reaction time (entries 2-4). The selectivity to solketal was always 100% and there was no side product obtained except water during the reaction that makes the overall solketal yield of 90 wt.%. The other two HAP samples synthesized by taking higher (basic HAP) and lower amounts of CaO (acidic HAP) were also tested for the reaction. The data given in table 1 indicates that the acidic HAP also exhibited some basicity and the basic HAP also exhibited some acidity. But, based on the dominating property, the HAP are named as acidic HAP and basic HAP samples.

Table 2. Performance evaluation of HAP catalysts in solketal production

Entry	Reaction Time (min)	Glycerol conversion (wt.%)	Solketal selectivity (%)	Acetal selectivity (%)
Catalyst: Acid-base HAP				
1	30	77	100	nil
2[a]	60	90	100	nil
3	120	91	100	nil
4	240	88	100	nil
5[b]	60	91	100	nil
6[c]	60	88	100	nil
7[d]	60	89	100	nil
8[e]	60	90	100	nil
9[f]	60	88	100	nil
Catalyst: Basic HAP				
10	60	50	66	34
Catalyst: Acidic HAP				
11	60	83	75	15

[a] represents the data obtained on fresh catalyst, while b,c,d,e and f represent the data obtained after consecutive reaction cycles

At the similar reaction conditions, the basic HAP as well as acidic HAP have exhibited lower glycerol conversions (50 wt% and 83% respectively) and solketal selectivity (92% and 85% respectively). The formation of 8% (selectivity) acetal as side product was observed on the basic HAP, while, the formation of 10% acetal (selectivity) along with some unidentified lower molecular weight products (5%) was observed on acidic HAP catalyst. The better performance of acid-base HAP when compared to acidic HAP and basic HAP, in terms of glycerol conversion and solketal selectivity clearly emphasizes the positive role of bi-functional reaction mechanism facilitated on this catalyst to drive the formation of five-membered oxygenate solketal. The performance of the acid-base HAP of the present study is comparable and better than those reported earlier on the other catalyst systems (ESI, table 2), perhaps due to the complimentary role played by acid and base sites present in the catalyst adjacent to each other.

The proposed mechanism suggests the dissociative adsorption of acetone on the CaP as an acetate ion on the Ca site and the carboxylic proton on phosphate oxygen, (scheme1). The resultant adsorbed species with its positive charge on the acetonic carbon along with a negative charge on the phosphate may polarize the glycerol molecule for its dissociative adsorption followed by intra-molecular dehydration to produce solketal. In the entire reaction, the first step requires base sites, while the final dehydration step is facilitated by acid sites of the catalyst. In the final step of reaction, the removal of hydroxyl group preferably from secondary carbon rather than from the primary carbon of the intermediate seems to be facilitated in presence of acid sites for the selective production of solketal (five-membered ring) rather than acetal (six-membered ring). The presence of weak acidity or weak basicity in other two catalysts encouraged the formation of six-membered oxygenate acetal. The glycerol conversion was also lower on these catalysts due to the lack of either strong acid sites or basic sites. The catalyst was further studied for its reusability up to several reaction cycles (Table 2, entries 5 to 9), where the catalyst exhibited excellent stability in activity in terms of glycerol conversion as well as solketal selectivity in the studied course of 5 reaction cycles.
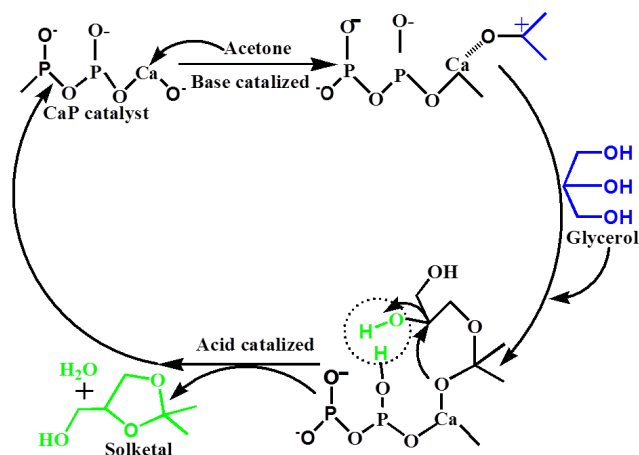
Scheme 1. Proposed reaction path for solketal production

In summary, the present study provides a simple and novel method for the synthesis of uniform size nano particles of HAP material possessing excellent pore volume contributed by nano size pores, crystallinity along with the presence of acid and base sites to facilitate promising catalytic activity towards bi-functional and bulky molecular transformations. The material exhibited high conversion, product selectivity and reusability in the glycerol acetalization reaction. The subject opens up a new property of the HAP materials as suitable catalysts for acid-base catalyzed reactions and has scope in improvement of the catalytic activity through the optimization of the acid-base sites more quantitatively through optimized synthesis procedure (especially by varying the Ca/P ratio) for expansion of its applications to other reactions. The HAP materials possessing significant pore volume contributed by nano pores along with acidity or basicity can be suitable materials for the selective adsorption of acidic or basic nature gases, storage and delivery of bulky organic molecules required for biological and drug delivery applications.

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Graphical Abstract

Nano porous hydroxyapatite as a bi-functional catalyst for bio-fuel production†

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Nano porous hydroxyapatite possessing acid-base functionality selectively produces 100% solketal at higher glycerol conversions (~90%)