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Electronic Supplementary Information

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

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Methods and Materials

Synthesis of Hydroxyapatite (HAP) samples

In this synthesis, ammonium dihydrogen phosphate (BDH, a division of Glaxo Laboratories India Ltd.,) and calcium oxide (SD fine chemicals Ltd., Boisar) are used as the source for P and Ca respectively. Tii-block co-polymer (Sigma Aldrich) is used as template to create the meso/nano pores in the crystalline final material of calcium phosphate during hydrothermal synthesis. Poly (ethylene glycol)-poly (propylene glycol)-poly (ethylene glycol) (EO_{20}-PO_{70}-EO_{20}) is called P123 Tri block copolymer. Such materials have the tendency of micelle formation at lower temperatures and concentrations in aqueous solutions and can form homogenous mixture of micelle and calcium phosphate. The hydrothermal synthesis conditions adopted in the present study allows the crystallization of calcium phosphate material. The micelle part of the polymer becomes the integral part of the synthesized material. Calcination of the material at 5higher temperatures (550 C for 6h) causes decomposition and removal of micelle, leaving the corresponding void (meso/nano size) pores in the crystalline calcium phosphate

Typical synthesis method involves the admixing of 6.112 g of P123, 2.12 g of 1N HCl, 12.21 g of ammonium dihydrogenphosphate, 75 g of methanol followed by stirring of the resultant mixture at 60 °C for 2 hr until the formation of a clear solution (mixture A). Similarly 5.6 g of calcium oxide was mixed with 100 g distilled water with rigorous stirring to get a soluble suspension (mixture B). Now, mixture A is added slowly to mixture B with a continuous stirring (for 30 minutes). The final mixture having Ca/P mole ratio of 1, has exhibited the pH value of 7.81 and the mixture was charged into a Teflon-lined autoclave and treated at 150 ºC for 24 h for the hydrothermal synthesis of the crystalline calcium phosphate. At the end of the treatment, the compound was washed and collected by filtration, dried and calcined at 550 ºC for 6 hr. This sample is designated as Acid-base HAP

Two other materials with Ca/P molar ratios of 2 and 0.6 were also prepared by varying the amount of CaO in the initial mixture (CaO of 11.25 and 3 g respectively) following similar synthesis procedure described above. The synthesis mixtures exhibiting the pH values of 9.9 and 5.73 have been allowed for hydrothermal synthesis in the similar procedure mentioned above to obtain the basic HAP and acidic HAP samples respectively.

Physico-Chemical characterization of the materials

Powder X-ray diffraction patterns of the samples were recorded on D8 advance instrument, Bruker, Germany equipped with rotating anode and CuKα radiations. FE-SEM images were recorded on Quanta 200f instrument, Netherland, for obtaining particle morphology. Transmission Electron Microscopy (TEM) images were recorded on JEOL, JSM-2100F instrument, Japan. operated at 200 kV and equipped with a microprobe system. A small amount of each sample was lightly ground and subsequently dispersed ultrasonically in ethanol. A drop of suspension was deposited on a carbon film supported on a copper grid for TEM measurement. The measurements were conducted in continuous θ/2θ scan refraction mode. The anode was operated at 30 KV and 15 mA the 2θ angles were measured 5°–60° at the rate of 2°/min. The framework skeletal vibrations of zeolite samples were measured using the KBr pellet technique on Perkin Elmer-2000 FTIR (Fourier transform infrared) spectrometer.

The BET surface area, pore size and pore volume measurements of all the zeolite based catalysts were carried out using a standard adsorption equipment (ASAP 2020, Micromeritics Instruments Inc., Norcross, GA, USA) using N_2 gas (99.995% pure). For measuring above characteristics, 0.2g of the sample is taken in a specially designed sample tube and degassed at

300°C under vacuum of 1.3 x10^{-6} bar for 4h. A frit is attached to the mouth of the sample tube, so that when the sample tube is removed from the preparation mode, it does not allow the sample to expose in atmosphere. The sample is cooled to room temperature under vacuum and the sample tube is removed from the preparation port and attached to the analysis port of the instrument. For all the samples, N_2 adsorption desorption isotherms were obtained at 77K and the temperature was maintained constant by using liquid nitrogen, whereas helium gas was used for measuring the dead space. The surface area, pore volume and pore size distribution were obtained by measuring the volume adsorbed at different P/P_0 values and by applying different methods. Total pore volume was estimated by measuring the volume of gas adsorbed at P/P_0 of 0.99 whereas, t-plot method was used to calculate the micro pore surface area (0-20 Å) using the Harkins–Jura equation. The total micro pore volume (0-20 Å) was obtained by applying the Horvath–Kawazoe method (H-K).

The acidic properties of zeolite samples were studied by means of temperature programmed desorption of ammonia (TPD of NH_3). using a Micromeritics 2750 pulse chemisorption system. 0.1g sample was used for each TPD experiment. It was carried out after of the catalyst sample was dehydrated at 500°C in helium gas (30 cm^3 min^{-1}) for 1h. The temperature was decreased to 100°C and NH_3 was adsorbed by exposing sample treated in this manner to a stream containing 10% NH_3 in helium for 1h at 100°C. It was then flushed with helium for another 1h to remove physicosorbed NH_3. The desorption of NH_3 was carried out in helium gas flow (30 cm^3 min^{-1}) by increasing the temperature upto 950°C at 100C min^{-1} heating rate, measuring NH_3 desorption using TCD detector. Similarly, the basic properties of the samples were measured by using CO_2- TPD following the similar procedure as that of NH_3-TPD.

Reaction Studies:

The high purity glycerol (99.9%) obtained from Mrek was used as reactant. Liquid phase acetalization of glycerol was conducted without using any solvent in a in magnetically stirred two necked round bottom flask. The reaction temperature was maintained at 90°C by using oil bath and reaction mixture stirred at 550 RPM for 4h. In a typical reaction procedure, 0.25 g of the catalyst (5% glycerol weight) was taken in a round bottom flask and 18.9 g of acetone and 5 g of glycerol with glycerol to acetone molar ratio 1:6 was added to it and refluxed at 60°C. At the end of the reaction, the catalyst (solid particles) was recovered from the reaction mixture via centrifugation, washed thoroughly with acetone and reused for multiple cycles. The desired product is solketal,(five-membered oxygenate) but the formation of acetal (six-membered oxygenate) was also reported to obtain as side product on some acid catalysts. The products were analyzed using a gas chromatograph (GC, PerkinElmer) connected with a EQUITY column and a flame ionization detector (FID).

Fig. S1 Low angle XRD pattern of the acid-base HAP

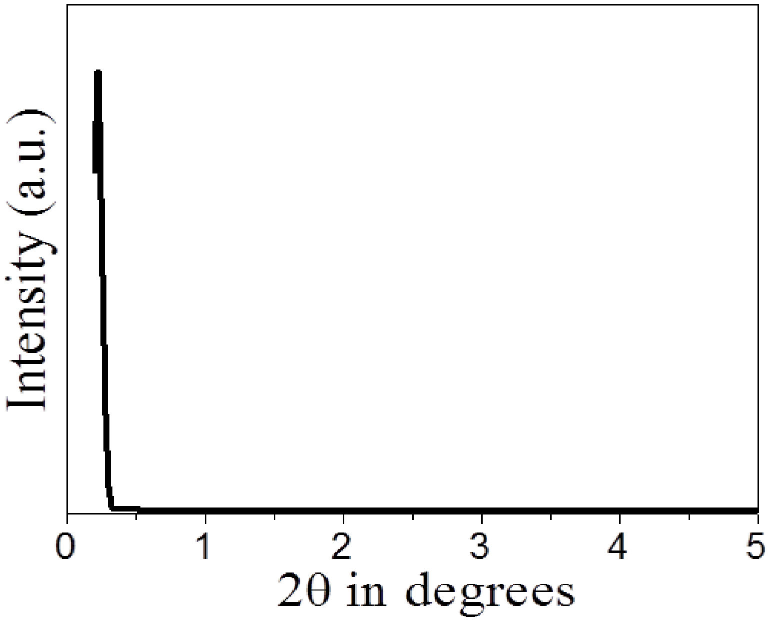
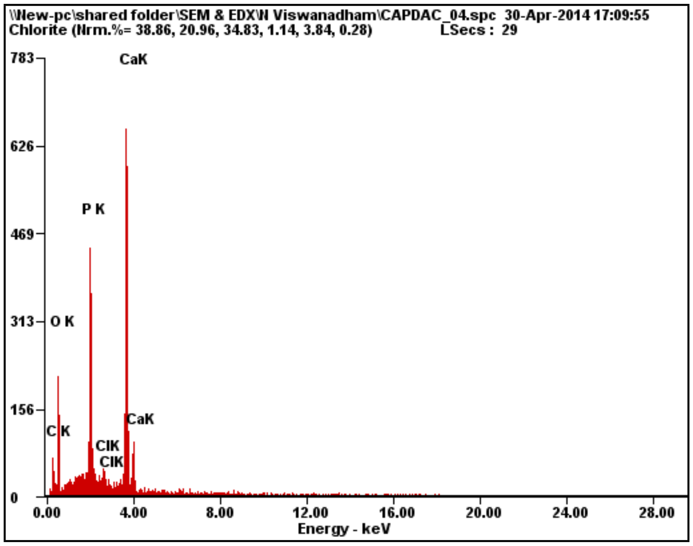


Fig. S2 EDEX analysis of acid-base HAP



Element	*Wt %*	*At %*
C K	17.93	29.55
O K	37.66	46.59
P K	12.75	08.15
ClK	01.17	00.66
CaK	30.49	15.06

Fig. S3 FT-IR spectra of acid-base HAP

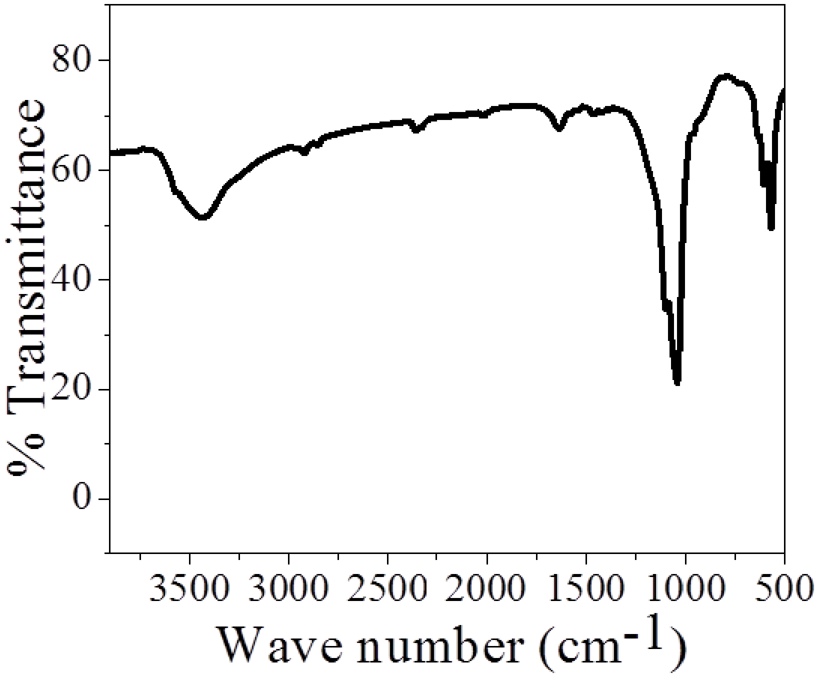


Fig. S4 TGA analysis of acid-base HAP

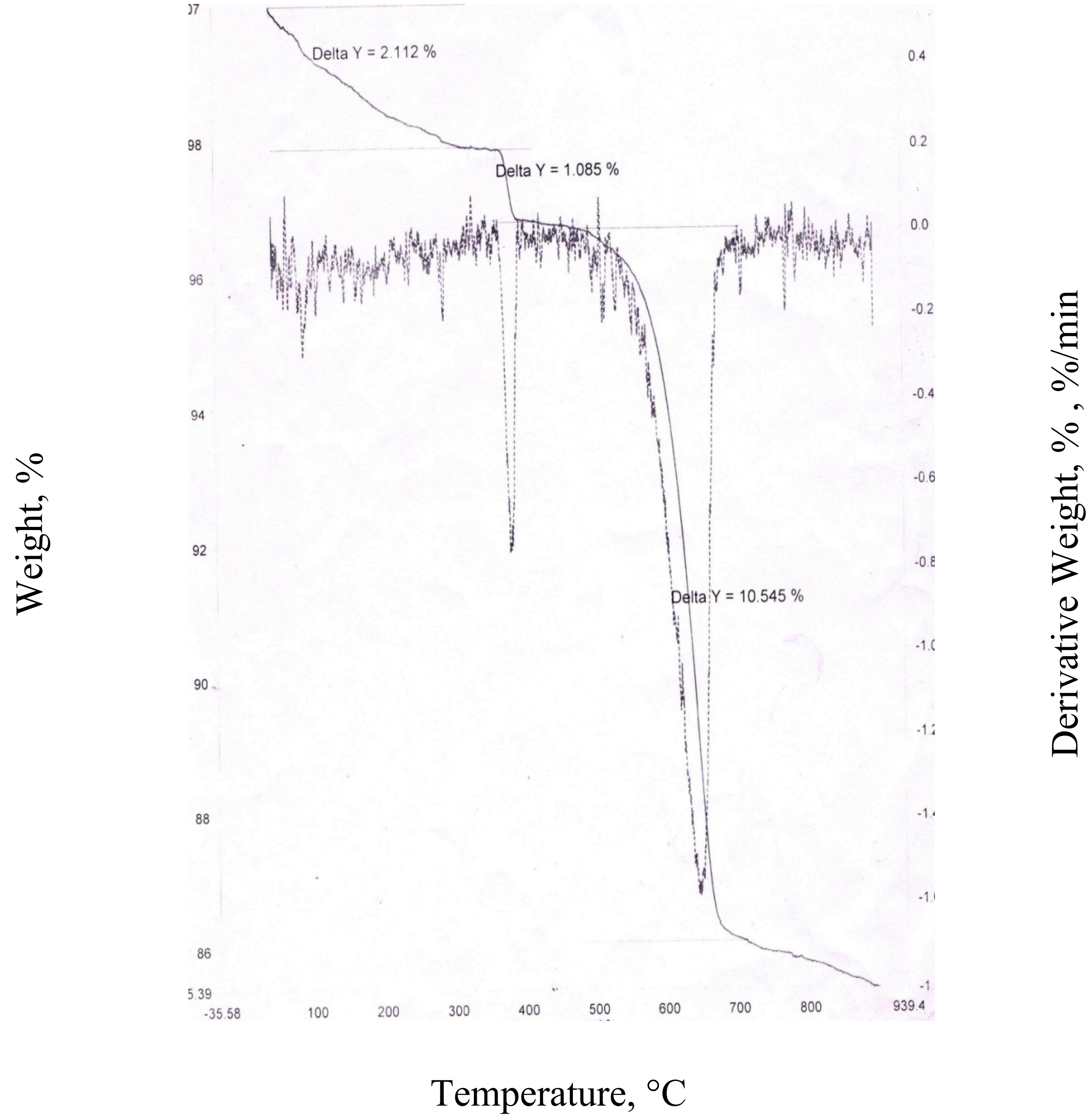


Fig. S5 Ammonia desorption TPD spectra of acid-base HAP

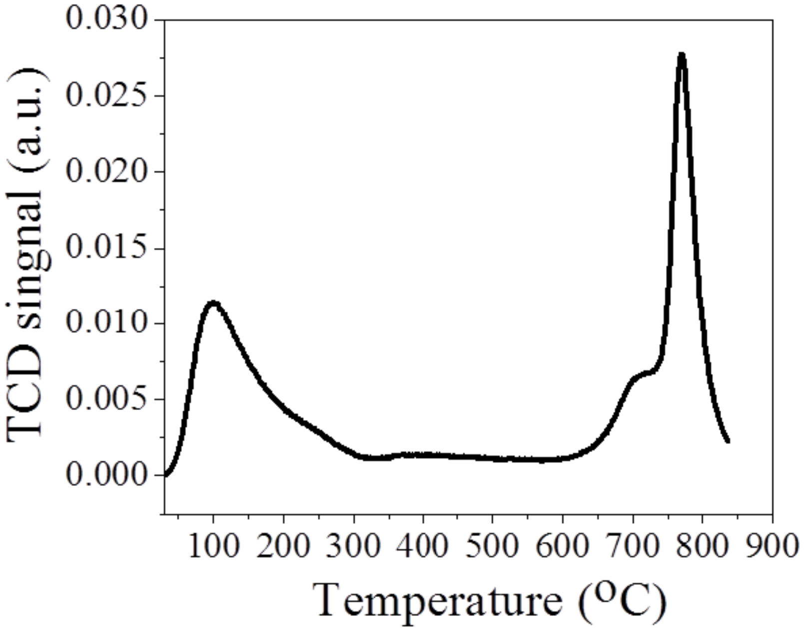


Fig. S6 CO_2, TPD spectra of the acid-base HAP

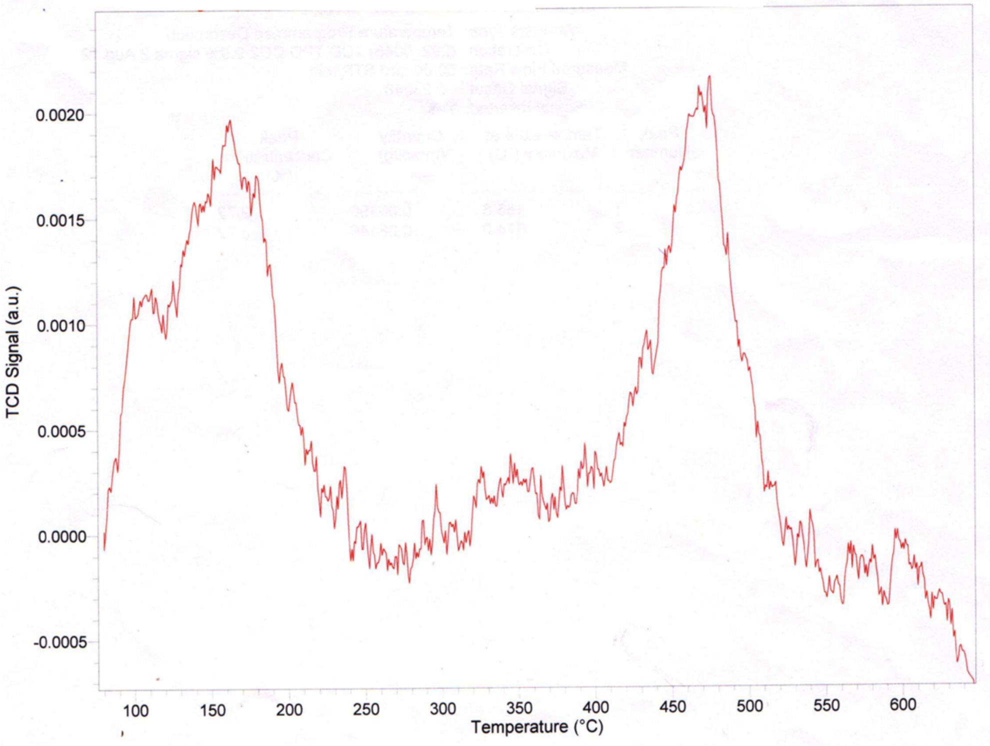


Figure S7, NH_3-TPD of acidic HAP

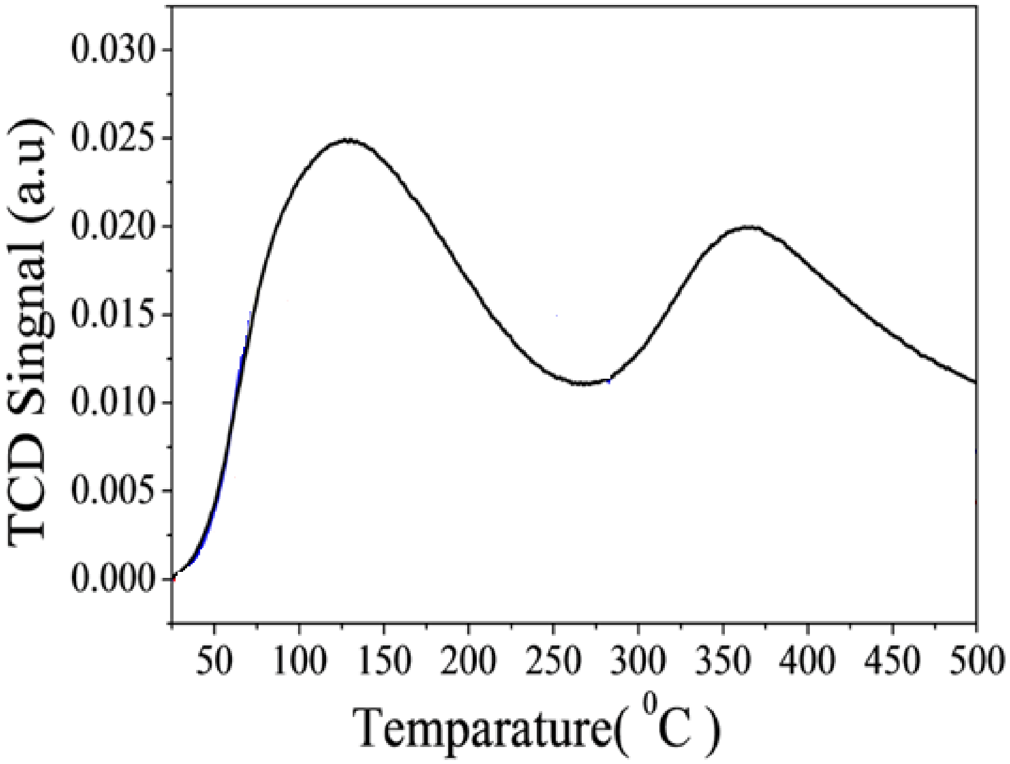


Fig S8, CO_2-TPD of basic HAP

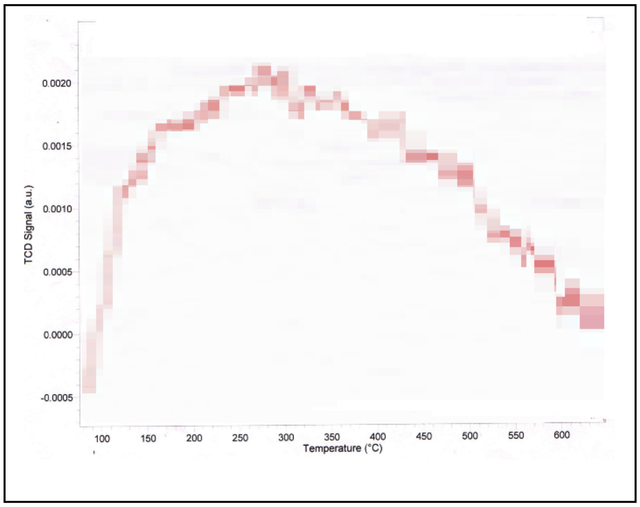


Table S1 Textural properties of HAP samples

Samples	BET Surface Area(m2/g)	Total Pore Volume(cm3/g)	Mean Pore Diameter (nm)
Acid-base HAP	73	0.7978	43.65
Acidic HAP	65	0.7540	39.50
Basic HAP	76	0.6990	41.25

Table S2. Performance comparison of catalysts in glycerol to solketal reaction

Catalyst	**Conversion %**	**Solketal Selectivity(%)**	**Ref**
Hf-TUD-1	65	----	1
Amberlyst-15	85.1	----	2
$NiAlPO_4$	75.44	75.12	3
AC1 supported Bi/Pt	87-97	50-88	4
$CuCr_2O_4$	----	73	5
Fe/Al-SBA-15	58	99	6
$SnCl_2$	81	98	7
Sulphated C-Si-composite	82	99	8
0.8%Ce- 1.5%Bi-0.75%Pt-3%Pd/C	100	58	9
CAP	90	100	Present Work

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