

Electronic Supplementary Information

Room temperature Baeyer-Villiger oxidation using molecular oxygen over mesoporous zirconium phosphate

Apurba Sinhamahapatra^a, Ankita Sinha^b, Sandip Pahari^a, Narottam Sutradhar^a, Hari C. Bajaj^a,
Asit Baran Panda^{a,*}

^aDiscipline of Inorganic Materials and Catalysis, Central Salt and Marine Chemicals
Research Institute, (Council of Scientific and Industrial Research, CSIR), G.B. Marg,
Bhavnagar-364 021, Gujarat, India.

^b Department of Applied Chemistry, Indian School of Mines, Dhanbad-826004, India.

S1. Detailed Characterization procedure and results of m-ZrP catalyst.

X-ray diffraction: The calcined m-ZrP was characterized by powder X-ray diffraction using Rigaku X-ray powder diffractometer (Ni-filtered Cu K α radiation, $\lambda = 1.5404 \text{ \AA}$, voltage: 30 kV, current: 15 mA) in the small ($2\theta=1-7^\circ$) as well as wide($2\theta=10-80^\circ$) angle region with a scan rate of 0.2° s^{-1} and scan width of 0.020.

Surface area measurement: The BET surface area, total pore volume, and average pore diameter were measured by N₂ adsorption–desorption method by ASAP 2010 Micromeritics, USA at -196°C . The sample was degassed under vacuum (10–2 Torr) at 300°C for 6 h before analysis. The surface area was determined by the BET (Brunauer–Emmett–Teller) equation. Pore size distributions were determined using BJH (Barrett–Joyner–Halenda) model of cylindrical pore approximation. Single point adsorption total pore volume was obtained at $P/P_0 = 0.97$.

Scanning electron microscopy: A scanning electron microscope (SEM) (Leo series 1430 VP) equipped with INCA was used to determine the morphology of sample and experiments was performed with an acceleration voltage 200 kV. The sample was supported on the aluminum stub and gold coated before microscopic observation.

Transmission electronic microscopy: Transmission electronic microscope (TEM) images were collected on JEOL JEM microscope with an acceleration voltage 200 kV. The sample was prepared by mounting the ethanol dispersed sample on carbon coated copper grid.

FTIR: The FTIR and DRIFT (diffuse reflectance FT-IR) spectra were obtained in a range of $400-4000 \text{ cm}^{-1}$ and $1200-1800 \text{ cm}^{-1}$, respectively on a Perkin-Elmer GX spectrophotometer. DRIFT experiment was carried out using pyridine as probe to identify the type of acid site present in catalyst. 20 mg of calcined sample placed in the sample holder of the instrument was degassed at 200°C for 1 h under nitrogen flow. After degassing, the sample was cooled down to room temperature and pyridine vapor with nitrogen flow was charged for 10 min. Nitrogen gas was flashed for another 30 min to remove the loosely attached pyridine. The FTIR spectrum was recorded in the temperature range from room temperature to 450°C .

Temperature-programmed desorption: NH_3 -TPD (temperature-programmed desorption) measurements were carried out on Micromeritics 2020 (USA) to measure the acid strength of m-ZrP. 200 mg of sample placed in a U-shaped sample tube was activated at 250 °C for 30 min in helium (35 mL min^{-1}) and then, 1 h at 350 °C and cooled to 100 °C. After that, ammonia (100 Torr) was adsorbed on the samples for 1 h. The physisorbed ammonia was removed by flushing the sample by helium for 1 h. The NH_3 desorption analysis was carried out in the temperature range of 100–900 °C.

Solid state NMR: ^{31}P MASNMR spectrum was recorded at 500 MHz on a Bruker Avance II-500 NMR spectrometer equipped with a magic angle spin probe at room temperature. 85% H_3PO_4 was used as external reference. The sample was rotated at 8 kHz and the spectrum was obtained from an average of 4000 scans.

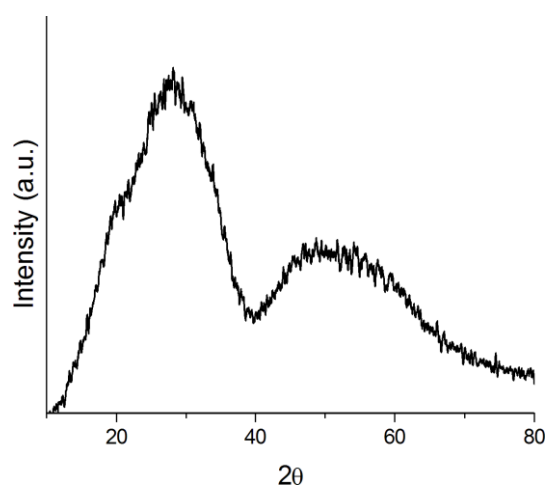


Fig. S1: Wide angle XRD of m-ZrP, calcine at 550°C for 6 h.

Presence of two broad peaks in 2θ ranges of 10–40° and 40–70° confirms the amorphous nature of synthesized m-ZrP catalyst.

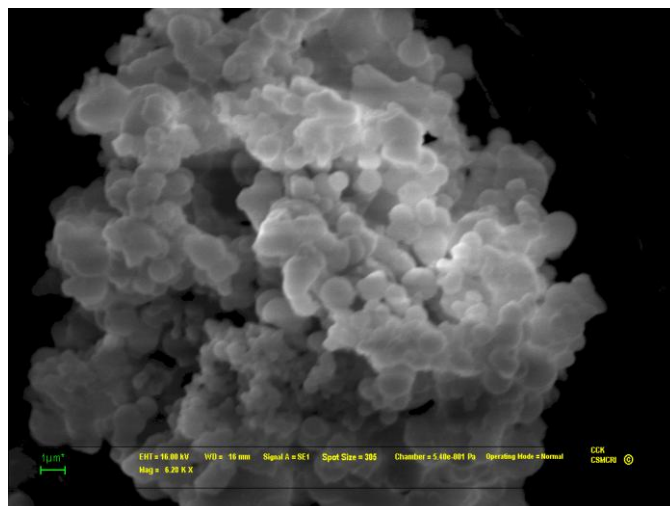


Fig. S2: SEM image of m-ZrP, calcine at 550°C for 6 h.

The SEM micrograph shows spherical morphology with very smooth surface of the synthesized m-ZrP particles.

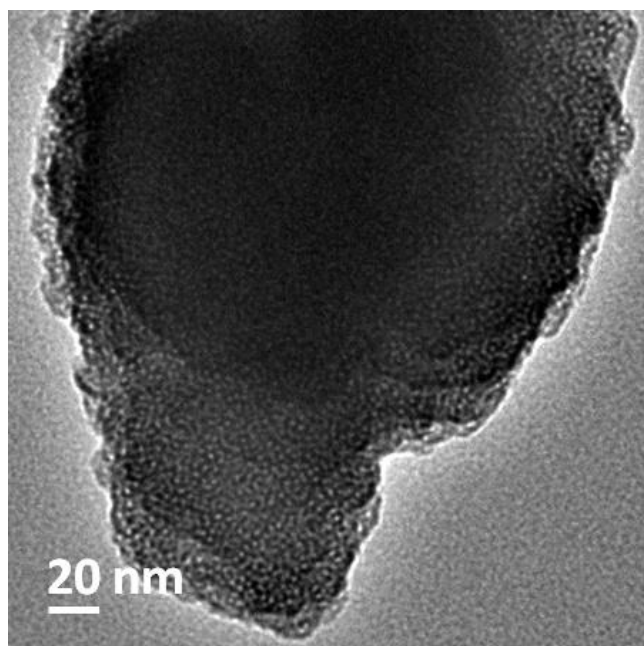


Fig. S3: TEM image of m-ZrP, calcine at 550°C for 6 h.

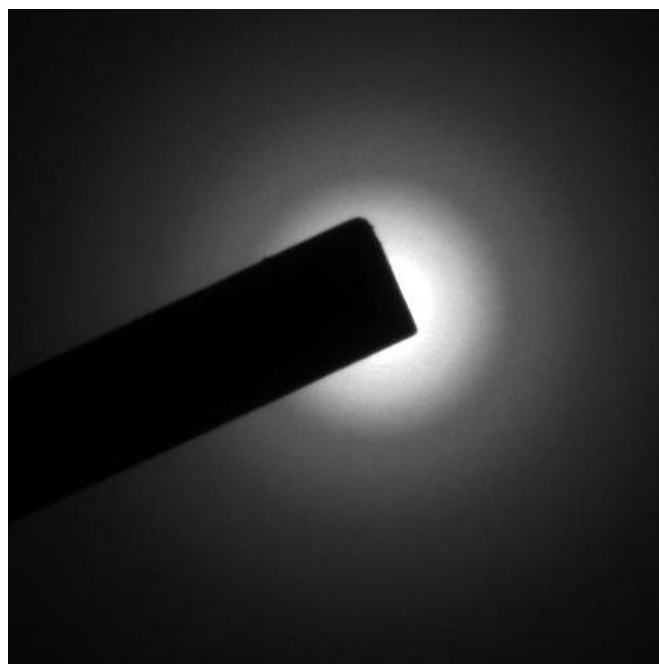


Fig. S4: SAED pattern of m-ZrP, calcined at 550°C for 6 h.

The TEM images exhibited mono-dispersed porous nature of the synthesized m-ZrP catalyst with worm like pore structures and an average pore size of ~3 nm. The SAED pattern of m-ZrP resembled amorphous nature of the synthesized m-ZrP which supports the wide angle XRD result.

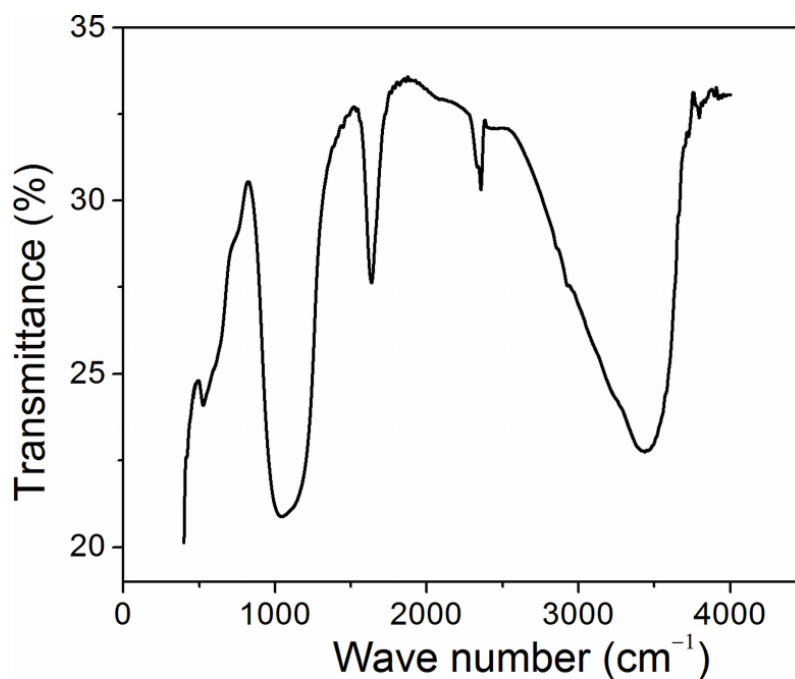


Fig. S5: FT-IR spectrum of m-ZrP, calcined at 550°C for 6 h.

In the FTIR spectra of m-ZrP the strong and sharp band centred at 1046 cm^{-1} corresponds to P–O stretching vibration. The broad peak at 2352 cm^{-1} corresponds to the (P)–O–H stretching vibration. The broad band around 3445 cm^{-1} may be attributed to OH stretching of water molecule and the weak peak at 1634 cm^{-1} indicates the bending mode of water molecule, which is not proportionate with the total intensity of the corresponding stretching band.

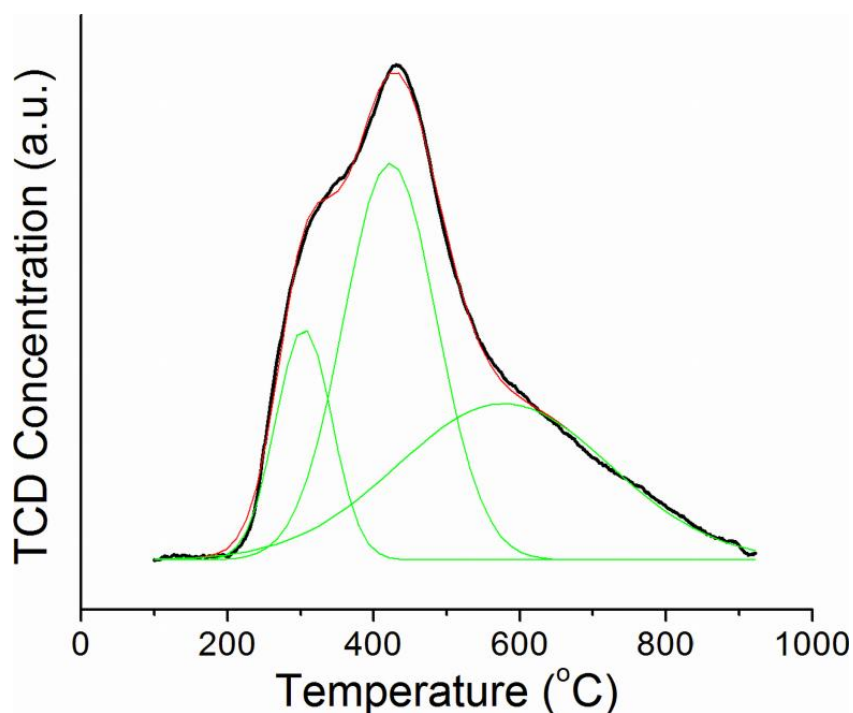


Fig. S6: NH_3 -TPD pattern of m-ZrP, calcine at 550°C for 6 h.

One distinct peak centre at 433°C with a hump at $\sim 326^\circ\text{C}$ was observed in the NH_3 -TPD profile and desorption of NH_3 continued even at 900°C , confirmed the presence of significant amount of strong acidic sites. The total amount of desorbed NH_3 was found to be $\sim 1.8\text{ mmol NH}_3$ per gram of catalyst. The de-convoluted plot shows three different strength acid sites present in synthesized m-Zrp.

S2: Calculation of the conversion and selectivity.

GC (Varian-450 GC, fitted with flame ionization detector, VS-5 factor 4 30 nm capillary column) was used for conversion and selectivity studies of the corresponding products. n-Tetradecane was used as the internal standard to calculate the initial and final mole percentage of the cyclohexanone. The blank reaction performed in absence benzaldehyde, and m-ZrP and molecular oxygen for comparison. The reaction also carried out using other oxidant using m-ZrP as catalyst.

The conversion of ketones and selectivity of corresponding ester or lactone (for cyclic ketone) was calculated using GC data as follows:

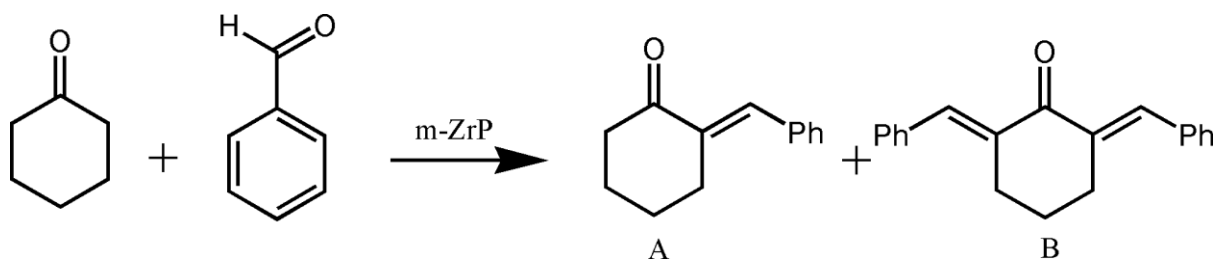
$$\% \text{ Conversion} = [100 \times (\text{Initial mole of ketone} - \text{Final mole of ketone})] / \text{Initial mole of ketone}.$$

$$\% \text{ Selectivity} = 100 \times [\text{mole of lactone or ester}] / (\text{Initial mole of ketone} - \text{Final mole of ketone}).$$

S3. Study of solvent free Claisen-Schmidt (CS) condensation the reaction of cyclohexanone and benzaldehyde.

Procedure for CS Condensation of cyclohexanone:

In typical procedure for CS Condensation of cyclohexanone was carried out in a two neck round bottom flask (50 ml) fitted with a condenser, magnetic stirrer, oil bath on a thermostat and attached with a nitrogen cylinder for maintain the inert atmosphere. m-ZrP as catalyst, benzaldehyde and cyclohexanone were added into the reactor under nitrogen atmosphere. The reaction was performed at desired temperature using a preheated oil bath for desired time with continuous air bubbling. After the completion of reaction, the products were extracted by acetone and analyzed by gas chromatography (GC) on the Varian-450 GC fitted with flame ionization detector (FID), VS-5 factor 4 30 nm capillary columns. In the reactions, two product were formed i.e. 2-benzylidene cyclohexanone [product (A)] and 2, 6-di-benzylidene cyclohexanone [product (B)] ([Scheme S1](#))



Scheme S1: CS condensation of cyclohexanone and benzaldehyde over m-ZrP.

Effect of substrate (cyclohexanone:benzaldehyde) ratio:

In the first set of reactions the molar ratio of was varied from 1:1 to 1:3 employing the other parameters as catalyst loading = 10 wt%, reaction temperature 120°C and reaction time = 3h. The results are in presented in Fig. S7.

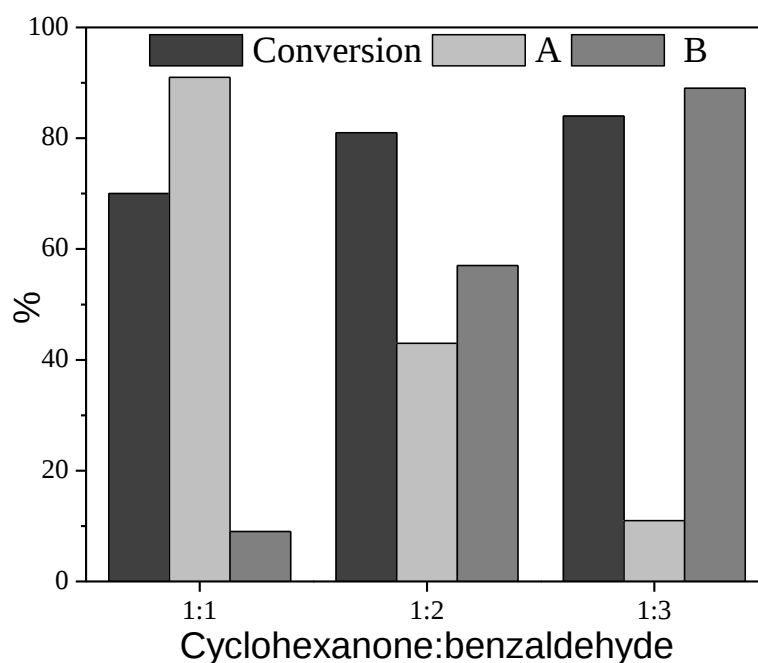


Fig. S7: Effect of molar ratio of cyclohexanone and benzaldehyde on the CS condensation over m-ZrP. Reaction condition: catalyst loading=10 wt%, temperature =120°C, and time =3h.

The conversion of cyclohexanone was increased from 70% (1:1) to 84% (1:3) with the increase of the ratio from 1:1-1:3. However, the selectivity of the two products were changed with the different molar ratio of cyclohexanone: benzaldehyde. When the ratio was 1:1 the product (A) was the major product (91%). As the amount of benzaldehyde was increased the selectivity of product (B) was increased and when the ratio was 1:3 it is 89%. Thus, the selectivity of product was highly dependent on the availability of benzaldehyde.

Effect of catalyst loading:

The catalyst loading was varied from 5 wt% to 20 wt% with respect to the amount of cyclohexanone (Fig. S8) employing the ratio of cyclohexanone to benzaldehyde of 1:3 and other parameter were same.

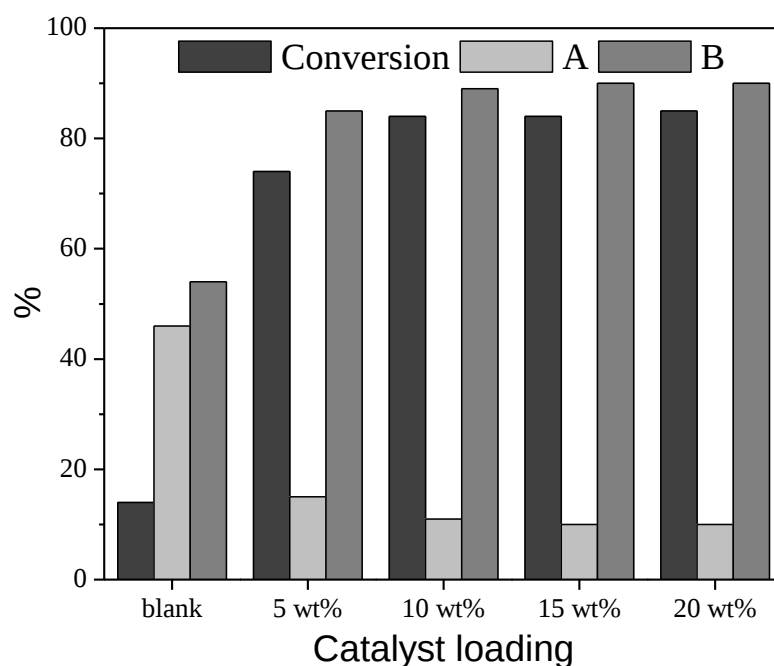


Fig. S8: Effect of catalyst loading on the CS condensation of cyclohexanone and benzaldehyde reaction over m-ZrP. Reaction condition: cyclohexanone:benzaldehyde 1:3, temperature =120°C, and time =3 h.

The conversion of cyclohexanone was increased from 74% (5 wt%) to 84% (10 wt%). The conversion remained almost constant on with further increase in the amount of catalyst. The selectivity scenario of the two products was almost same for the different amount of catalyst loading. In blank reaction, i.e without catalyst, only 18% conversion was observed and the selectivity was 14% for A and 86 % for B.

Effect of reaction temperature and time:

To know the influence of temperature on conversion and selectivity the reaction was performed in temperatures in the range of RT (29°C) to 150°C (Fig. S9), keeping the other parameter constant.

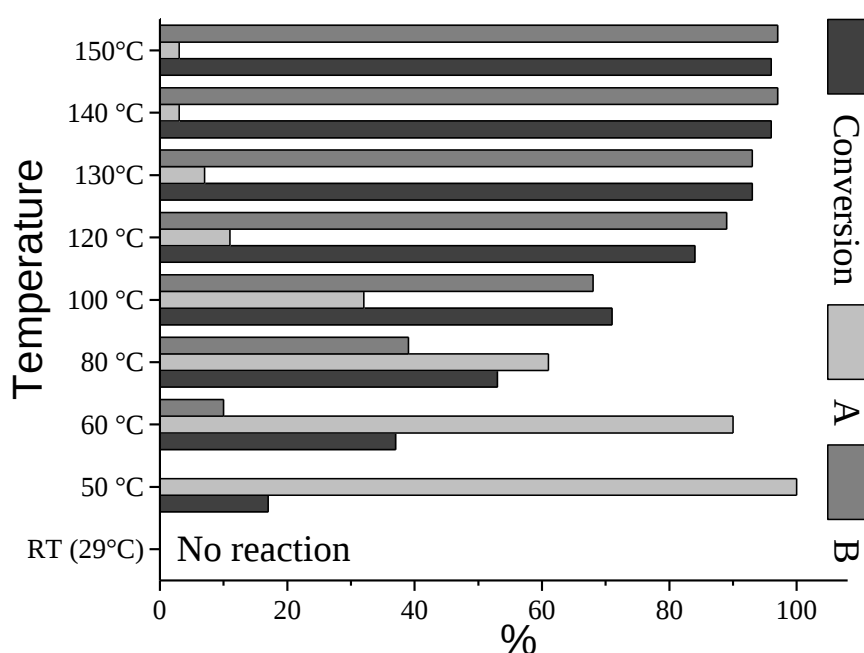


Fig. S9: Effect of temperature on the CS condensation of cyclohexanone and benzaldehyde reaction over m-ZrP. Reaction condition: cyclohexanone: benzaldehyde 1:3, catalyst loading =10 wt%, and time =3 h.

At RT, no progress of reaction was observed. At 50 °C conversion was only 17% with 100 % selectivity of product (A). As the temperature was increased the conversion was increased, but gradually the selectivity of product (A) decreased with increased selectivity of product (B). At 140°C, the conversion was 96% and selectivity of the product (B) was 97%. Further increase in temperature no change in the scenario was observed. From the above results, it can be concluded that at lower temperature predominantly mono-substituted product was formed and at higher temperature the mainly di-substituted product was formed on expense mono-substituted product and transformation of cyclohexanone to product (A) to product (B) was concerted. The progress of the reaction at 140°C was monitored time to time (Fig. S10). From the reaction progress study, it was observed that conversion was continuously increases up to 3h and the selectivity of the product (B) is 90% only after 15

min of reaction and it increases to 96 % after 3 h. This result supports that the reaction follows almost concerted pathway.

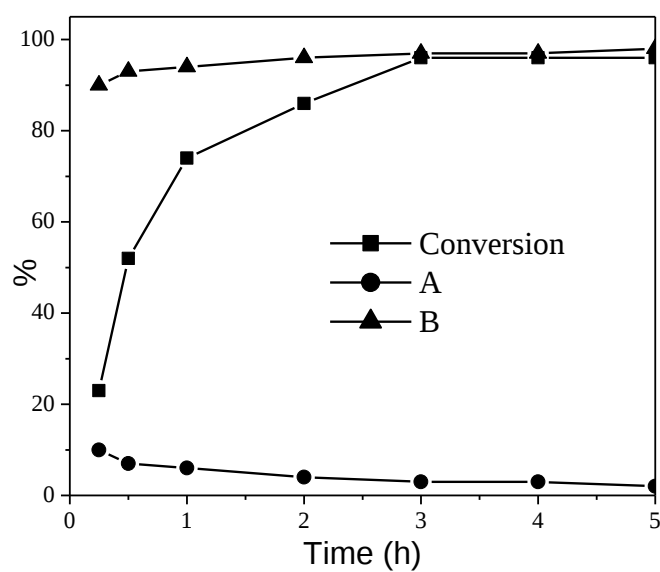


Fig. S10: Reaction profile of the CS condensation of cyclohexanone and benzaldehyde reaction over m-ZrP. Reaction condition: cyclohexanone:benzaldehyde 1:3, catalyst loading =10 wt%, and temperature =120°C.

Effect of cyclohexanone and benzaldehyde

Inspiring from the above results, the effect of temperature was again performed with a varying ratio of cyclohexanone to benzaldehyde of 1:1, 1:1.5 and 1:2 (Fig. S11).

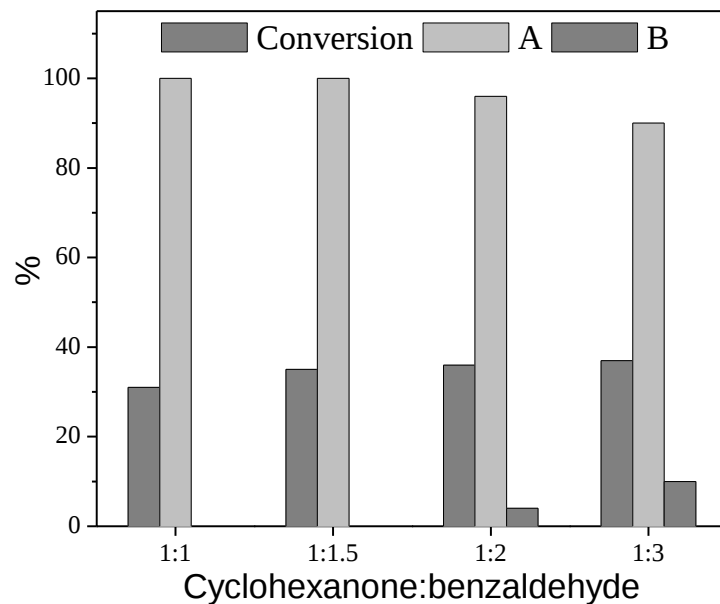


Fig. S11: Effect of molar ratio of cyclohexanone and benzaldehyde on the CS condensation over m-ZrP. Reaction condition: catalyst loading=10 wt%, temperature =60°C, and time =3 h.

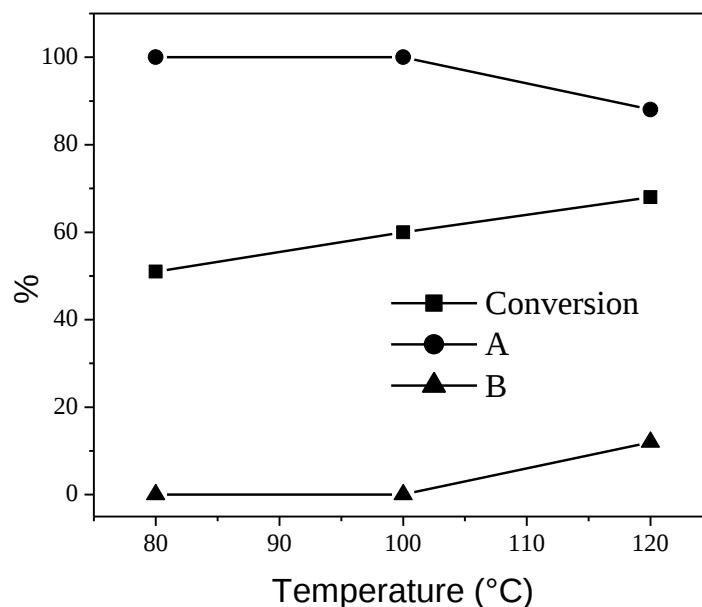


Fig. S12: CS condensation of cyclohexanone and benzaldehyde reaction over m-ZrP. at different temperature when cyclohexanone:benzaldehyde 1:1.5. Reaction condition: catalyst loading =10 wt%, temperature =120°C, and time =3 h.

All the three reaction were carried out at 60°C for 3h. 31 and 35% conversion with 100% selectivity was observed with a ratio of 1:1 and 1:1.5 respectively. However, the in case of 1:2 the conversion and selectivity was 36% and 96% respectively. Then, the reaction was carried out at 80°C and 100°C, and 120°C with a ratio of 1:1.5 (Fig. S12). The observed conversions were 51% and 60% with 100% selectivity of product (A) when the reaction temperature was 80 and 100°C respectively. But with increase in tempereature from 100 to 120 °C the conversion was increased to 68% with a decreased selectivity of 88%. For the more transparency, the progress of the reaction was studied at 100°C with a ratio of 1:1.5 (Fig. S13).

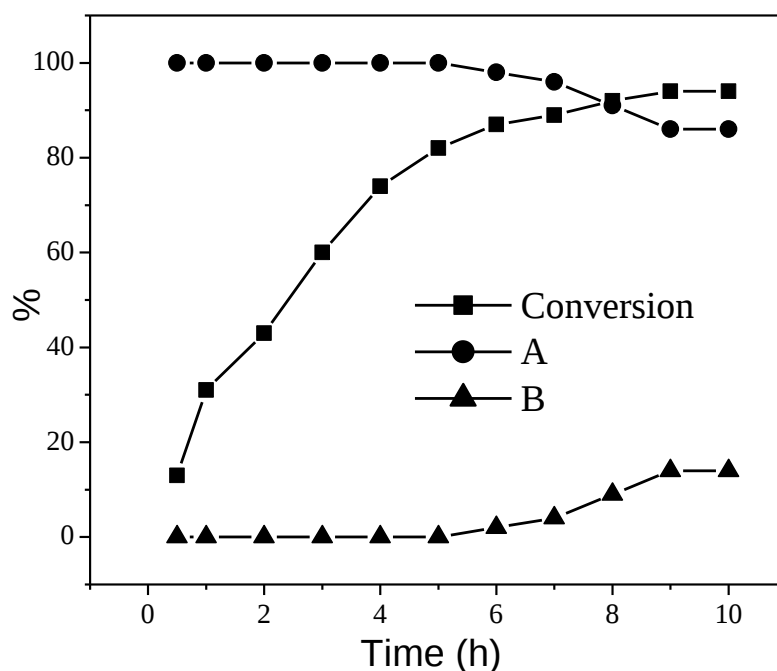


Fig. S13: Reaction profile of the CS condensation of cyclohexanone and benzaldehyde reaction over m-ZrP at 100°C. Reaction condition: cyclohexanone:benzaldehyde 1:1. 5, catalyst loading =10 wt%.

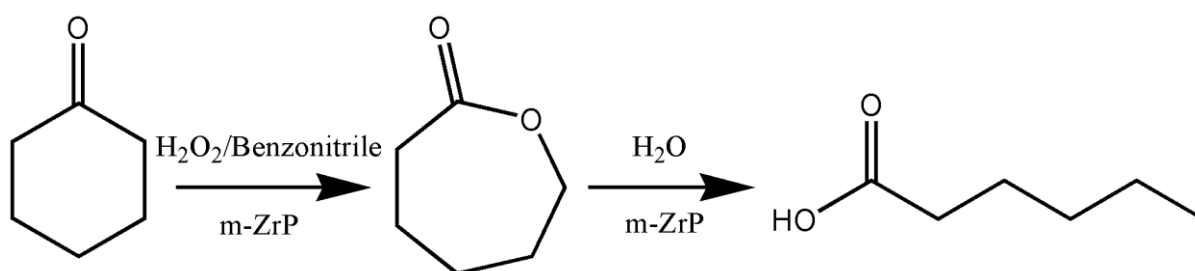
A maximum 82 % conversion of cyclohexanone with 100% of selectivity of product (A) was obtained after 5h of reaction. Further increase in time the conversion was increased to 94% with a selectivity of 86% for product (A) and 14% for product (B) and reaction was almost completed at 9h.

Thus, from the above discussion it was concluded that formation of product (A) and product (B) product can be controlled by controlling the reaction parameters. The m-ZrP catalyst was reused for the CS condensation upto four times for the reaction condition as follows, molar ratio of cyclohexanone and benzaldehyde=1:3 catalyst loading=10 wt% , and temperature =140°C, Time =3h. At the fourth cycle, the conversion of cyclohexanone was 95% and selectivity of product (B) product was 96%.

S4: BV Oxidation using hydrogen peroxide

General procedure of BV Oxidation using hydrogen peroxide:

In a typical procedure, to a two necked round bottom flask (50 mL) fitted with a condenser, magnetic stirrer, oil bath and a thermostat, m-ZrP (98 mg), benzonitrile (30 mmol, 3 ml) and H_2O_2 (4.53 ml 30 wt %) were charged. After 20 min stirring, cyclohexanone (10 mmol) was added. Reaction was carried out at 120°C for desired time. After the completion of reaction, the products were extracted in ethyl acetate from aqueous layer and analyzed by gas chromatography and the conversion was calculated as stated above from the GC data. The reaction was also carried out in absence of benzonitrile for comparison.



Scheme S2: BV oxidation of cyclohexanone using molecular H_2O_2 in presence of benzonitrile over m-ZrP as catalyst.

Effect of temperature:

Since at room temperature only 37% conversion was observed, the influence of temperature, on the reaction was evaluated at different temperatures (Fig S14) in the range of RT to 120 °C. The conversion of cyclohexanone was gradually increases with the increase in temperature. On the other hand, the selectivity for ϵ -caprolactone decreased due to formation of hydrolysis product, 6-hydroxyhexanoic acid. 89% of conversion with a 47% selectivity of ϵ -caprolactone and 53% selectivity of 6-hydroxyhexanoic acid were observed at 120 °C after 3 h.

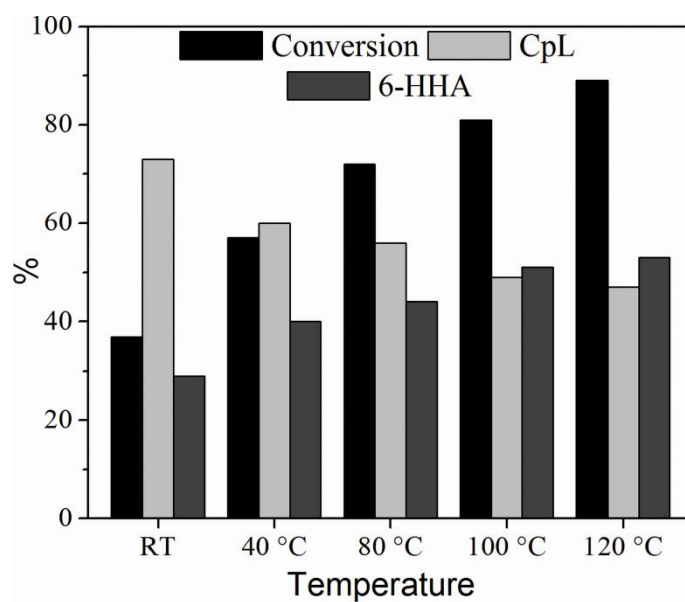


Fig. S14: BV oxidation cyclohexanone using H_2O_2 in presence of benzonitrile over m-ZrP at different temperature. Reaction condition: molar ratio of cyclohexanone and H_2O_2 and benzonitrile =1:44:3, catalyst loading=10 wt%, and time=3 h. CpL= selectivity of ϵ -caprolactone and 6-HHA=selectivity of 6-hydroxyhexanoic acid.

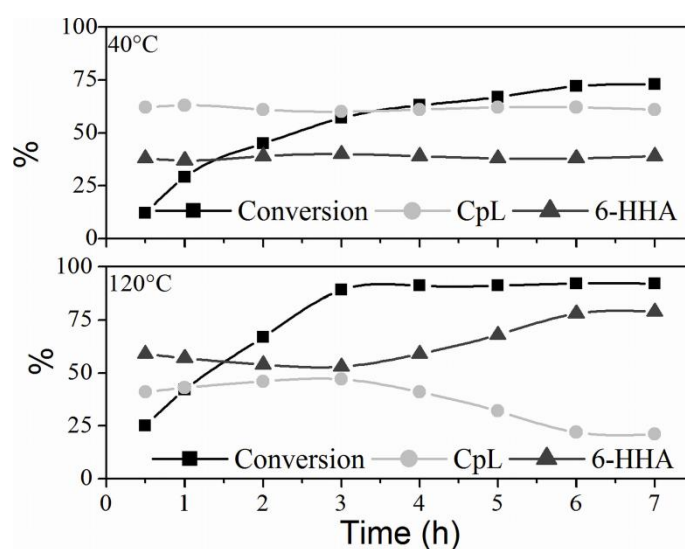


Fig. S15: Reaction profile of BV oxidation cyclohexanone using H_2O_2 in presence of benzonitrile over m-ZrP at 40 and 120 °C. Reaction condition: molar ratio of cyclohexanone and H_2O_2 and benzonitrile =1:44:3, catalyst loading=10 wt%. CpL= selectivity of ϵ -caprolactone and 6-HHA=selectivity of 6-hydroxyhexanoic acid.

The results clearly indicated that with an increase of temperature, both the reaction lactonisation and hydrolysis of lactone are facilitated. Along with the temperature, the time of reaction is also a controlling factor. For this, reaction profile of the same reaction was monitor in two different temperatures (120 and 40 °C) for 6 h (Fig S15). At 40 °C, the conversion of cyclohexanone was found to increase with the time (72% conversion after 6 h). Whereas, maximum 91% conversion was observed in 4 h, after that there was no significant change in conversion. Although at 40 °C the selectivity of both the product was almost identical throughout reaction but the selectivity of the 6-hydroxy hexanoic acid continuously increased with time at 120 °C and reached 79% after 6 h. Thus from the above results and discussions one can concluded that the high acidity of the m-ZrP influences the hydrolysis of the lactone even after completion of the lactonization reaction at high temperature.

Effect of amount of H₂O₂:

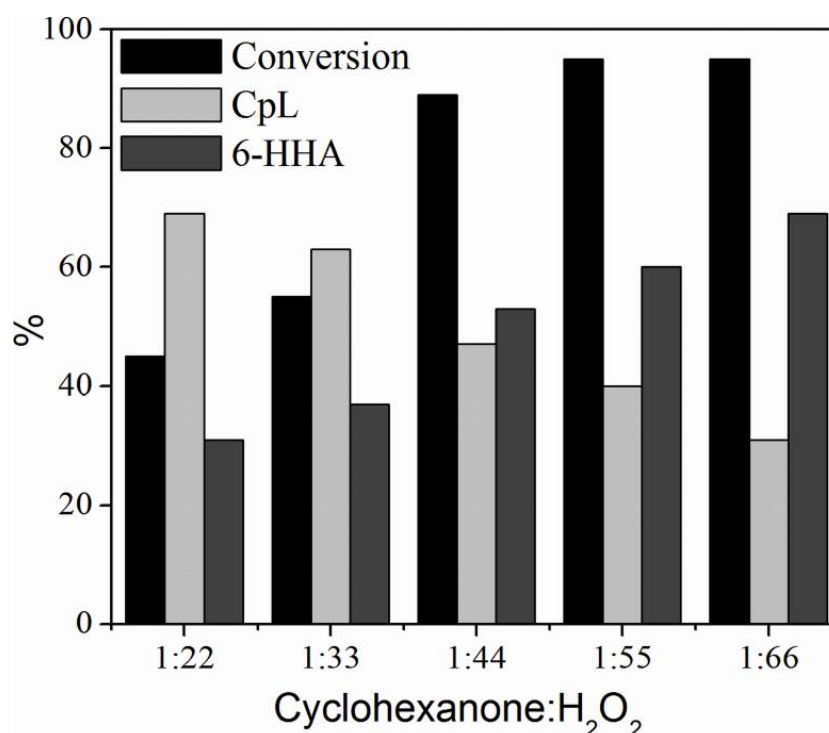


Fig. S16: BV oxidation cyclohexanone using H₂O₂ in presence of benzonitrile over m-ZrP at different molar ratio of cyclohexanone and H₂O₂. Reaction condition: temperature = 120°C, catalyst loading=10 wt% , and time=3 h. CpL= selectivity of ϵ -caprolactone and 6-HHA=selectivity of 6-hydroxyhexanoic acid.

The amount of H₂O₂ (cyclohexanone: H₂O₂) was also varied in the range of 1:22 to 1: 66 to know the effect of H₂O₂ (Fig S16). The conversion of cyclohexanone was increased with the increasing amount of H₂O₂, but the selectivity of ϵ -caprolactone was decreased from 69% (1:22) to 29% (1: 66). The conversion was increased due to the increased availability of oxygen with the increased amount of H₂O₂. With the increased amount of H₂O₂ the presence of total water in the reaction medium was also increased which leads to the hydrolysis of ϵ -caprolactone to 6-hydroxyhexanoic acid. The maximum 89% conversion of cyclohexanone with 29% selectivity of ϵ -caprolactone and 71% of 6-hydroxyhexanoic acid was observed at 120 °C with a ϵ -cyclohexanone to H₂O₂ ratio of 1:66. Thus, the above results clearly depict the high catalytic activity of m- ZrP towards the lactonization of cyclohexanone but the water present in H₂O₂ leads to the hydrolysis of lactone. To understand the effect of water presence an additional reaction was performed using ϵ -cyclohexanone to H₂O₂ ratio of 1:22 with addition of 2 ml of water. The selectivity of ϵ -caprolactone was evidently decreased to 42% from 69% due to hydrolysis reaction.

Effect of Catalyst loading:

Besides the presence of water, the high acidity of synthesized m-ZrP may also affects the ring opening hydrolysis of ϵ -caprolactone. To investigate the influence of acid sites, the amount of catalyst loading was varied from 0 to 20% with respect to the amount of cyclohexanone (Fig S17). With the increase in amount of catalyst loading the selectivity of 6-hydroxy hexanoic acid was increased along with increase in conversion (14-89%) of cyclohexanone. 36% of 6-hydroxy hexanoic acid was observed when the catalyst loading was 2 wt% and it was 68% when catalyst loading was 20 wt%. Thus it can be conclude that the acidity of m-ZrP assist the ring opening of lactone on hydrolysis in presence of water. The result (78% of ϵ -caprolactone) of blank reaction (i.e. without m-ZrP) supports the above discussion.

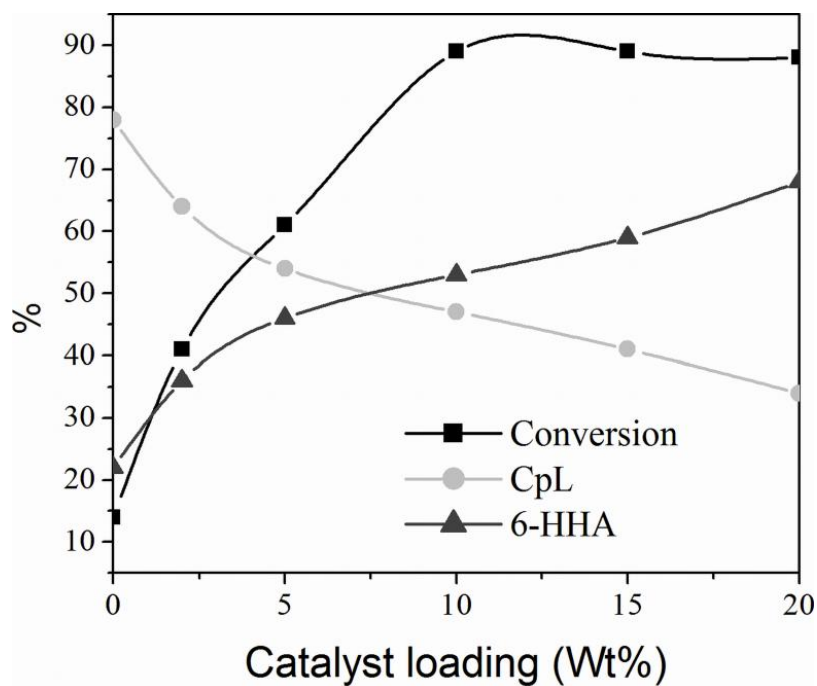


Fig. S17: BV oxidation cyclohexanone using H_2O_2 in presence of benzonitrile over m-ZrP at different catalyst loading (0-20 wt%). Reaction condition: molar ratio of cyclohexanone and H_2O_2 and benzonitrile =1:44:3, temperature = 120°C , , and time=3 h. CpL= selectivity of ϵ -caprolactone and 6-HHA=selectivity of 6-hydroxyhexanoic acid.

S4: BV Oxidation using benzaldehyde and molecular oxygen with different addition time of cyclohexanone

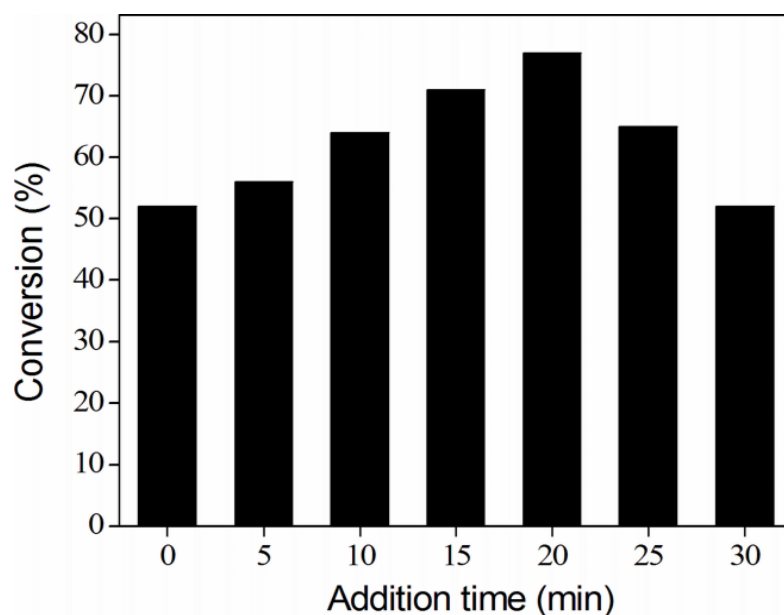


Fig. S18 Variation of addition time on the BV oxidation using molecular oxygen and benzaldehyde over m-ZrP. Reaction condition: molar ratio of cyclohexanone and benzaldehyde, 1:1.75; catalyst loading, 10 wt%; RT and time, 1.5 h.