Nano particles of $ZrPO_4$ for green catalytic applications

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Materials synthesis

The typical synthesis method involves the admixing of 6.102 g of P123, 2.12 g of HCl, 12.21 g of ammoniumdihydrogenphosphate and 75 g of methanol at 60 °C for 2 hr followed by vigorous stirring of the mixture until clear solution obtained (solution A). Similarly 28.26 g of zirconium acetylacetonate and 75 g of methanol are mixed and stirred at 45 ºC until clear solution obtained (solution B). Now, the mixture A is added to mixture B in a bit-wise-manner for 30 min with a continuous stirring to make the precipitate. The resultant mixture is allowed to react at the room temperature for 24 h. At the end of the treatment, compound was washed and collected by filtration, dried and calcined at 500 ºC for 5 hr. Similar procedure is followed for the synthesis of aluminumphosphate with the only difference being the use of aluminumisopropoxide in place of zirconium acetylacetonate. The resultant materials are denoted as ZP (zirconium phosphate) and AP (aluminumphosphate) samples

Characterization

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. TEM images were recorded on Tecnai-12 model, FEI, Netherland and GC equipped with the EQUITY column and FID detector

Application of materials for the CO_2 fixation on aniline

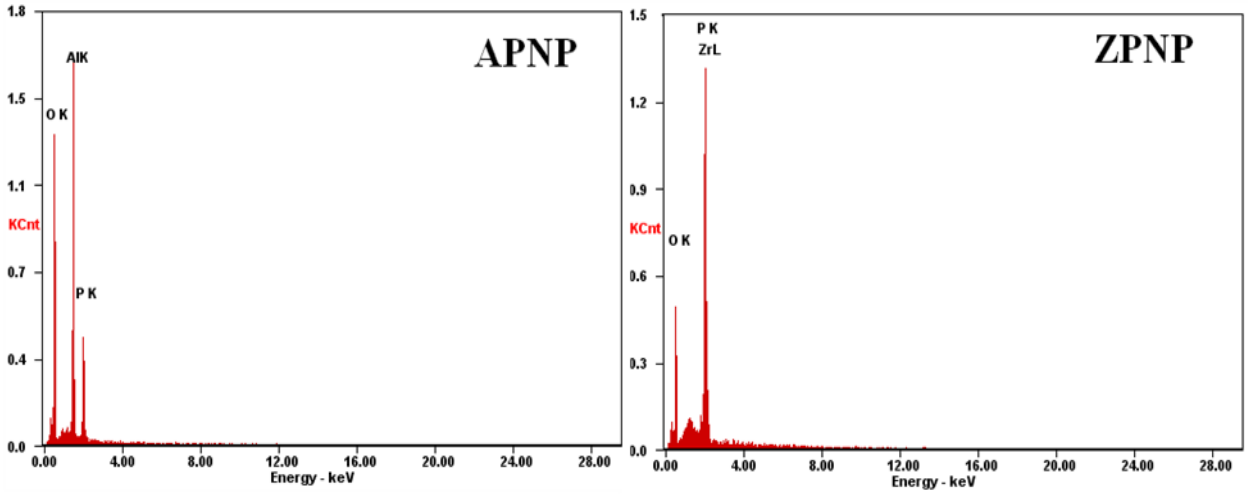
The catalyst performance studies of the materials were conducted in the present work towards the production of acetanilide from aniline using the green house gas CO_2 as carbonyl source. In a typical reaction procedure, 10 gm

aniline was added to a 2 gm of methanol, 8 gm acetonitrile and 1 gm of catalyst. The whole mixture was transferred in to a 160 ml volume capacity Parr reactor autoclave, sealed tightly and pressurized by CO_2 up to 150 Psi. The reaction was conducted at 150 °C for 7 h and the product obtained at the end of the run was filtered and analyzed by GC equipped with an EQUITY column and flame ionization detector (FID)**.** GC-Mass is used for the qualitative analysis while the GC is used for the quantitative estimation of the individual products.

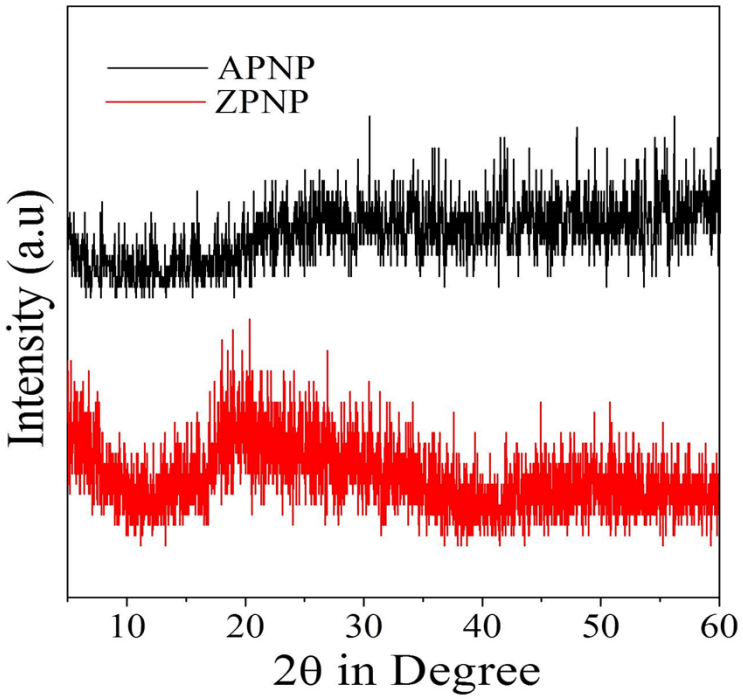
Supporting Table1: Elemental composition of the materials.

Samples	**Elements (Wt%)**			**Al/P or Zr/P**
	Zr	**P**	**Al**	
APNP	-------	11.93	30.65	2.57
ZPNP	35.75	14.27	--------	2.51

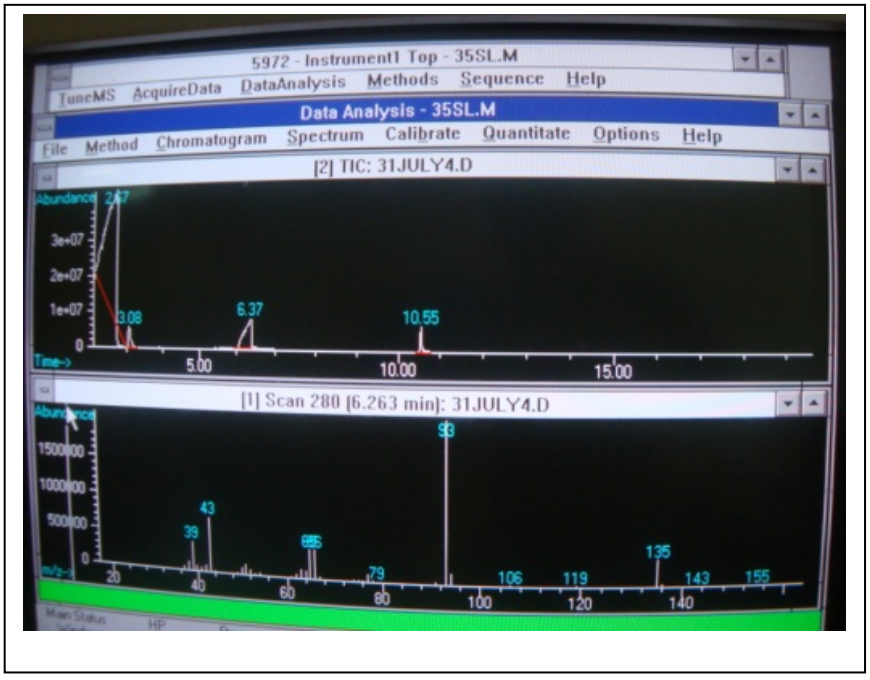
Supporting Figure1: EDX Spectra of the APNP and ZPNP samples.



Supporting Figure2: Wide angles XRD of the APNP and ZPNP



Supporting Figure3: GC-Mass spectra indicating acetanilide formation on ZPNP catalyst



Supporting Table 2: Effect of solvent on the performance of ZPNP catalyst

Solvent	**Aniline Conversion (%)**	**Product Selectivity (%)**	
		N-Methyl Aniline	**Acetanilide**
Acetonitrile	13.0	15	85
Toluene	11.8	12	88
m-Xylene	12.5	18	82
Temperature= 150 °C, CO_2 Pressure= 150 Psi, Time= 7 hr, Aniline= 10 g, Solvent= 8g and Methanol =2g.			