# Synthesis of orderly nanoporous aluminophosphate and zirconium phosphate materials and their catalytic applications

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# 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 DB wax column and FID detector

## **BET Analysis**

The N2 adsorption desorption isotherms were measured at 77 K on ASAP (Model 2010) Micrometrics USA instrument. Before measurement the samples were evacuated overnight at 250 °C. The BET surface area was calculated from linear part of plot according to IUPAC recommendations.

#### **Ammonia-TPD**

The acidity of the catalysts were measured by temperature programmed desorption of NH<sub>3</sub> (NH<sub>3</sub>-TPD) using a Micromeritics chemisorbs 2750 pulse chemisorbs 2750 pulse chemisorption system. 0.1 g sample was used for each TPD experiment. It was carried out after of the catalyst sample was dehydrated at 300 °C in helium gas (30 cm<sup>3</sup> min<sup>-1</sup>) for 1 h. The temperature was decreased up to 30 °C and NH<sub>3</sub> was absorbed by exposing sample treated in this manner to a stream containing 10% NH<sub>3</sub> in helium for 1 h at 30 °C. It was then flushed with helium for another 1 h to remove physicosorbed NH<sub>3</sub>. The desorption of NH3 was carried out in helium gas flow (30 cm<sup>3</sup> min<sup>-1</sup>) by increasing the temperature up to 950 °C at 10 °C min<sup>-1</sup> heating rate, measuring NH<sub>3</sub> desorption using TCD detector. Here the ammonia desorbed at lower reaction temperatures represent the weakly bound ammonia (weak acidity) and the ammonia desorbed at higher temperatures represent the strongly bound ammonia (strong acidity).

# **Pyridine FT-IR**

For acidity evaluation, about 14 mg of the sample was pressed to obtain a 13 mm disk. The sample was introduced in the infrared cell with KBr windows. The sample was heated at 200 ° C in vacuum condition for 3 h. The infrared spectra were recorded at room temperature using Thermo Nicolet Nexus 670 FTIR spectrometer at 4 cm<sup>-1</sup> resolution. The types of acid sites were determined using pyridine as a probe molecule. Pyridine was allowed to absorb at room temperature for five minutes, continued by desorption

of the physisorbed pyridine at  $150^{\circ}$  C for an hour. The chemically adsorbed pyridine on the catalyst sample was then treated for assessing the strength of the acid sites. Being the strong acid sites, the Lewis acid sites evolve the pyridine at lower wave number of IR (~1450 cm-1) while the Bronsted acid sites evolve the corresponding band at ~1550 cm<sup>-1</sup>.

### Application of materials for the cyclohexylation of phenol

The catalyst performance studies of the materials were conducted in the present work towards the alkylation of phenol. In a typical reaction procedure, 1 mol of phenol was added to a 1 mol of cyclohexanol and 0.5 g of catalyst. The whole mixture was transferred in to a 25 ml volume capacity Parr reactor autoclave, sealed tightly and pressurised by  $N_2$  up to 1 bar. The reaction was conducted at 150 °C for 4 h and the product obtained at the end of the run was filtered and analyzed by GC equipped with a DB wax column and flame ionization detector (FID)





Fig-S2: TGA/DTA curve of the AP and ZP samples



Fig-S3: Low angle XRD patterns of AP and ZP samples and Zoomed XRD (Inside)



Fig-S4: Wide angle XRD of the AP and ZP samples



Fig-S5: SEM images of A) AP and B) ZP samples



Supporting Table 1: Performance comparison of various catalysts with AP and ZP samples

Catalyst	Cyclohexanol	Products Selectivity (%)		Ref
	Conversion (%)	<b>O-Alkylation</b>	C-Alkylation	
APa	68	100.0		Present work
AP <sup>ab</sup>	67	100.0		Present work
ZP <sup>a</sup>	100	7.0	93.0	Present work
ZP <sup>ab</sup>	98	10.0	90.0	Present work
Na-Y	97.5	12.0	28.4	1
HY	97.9	3.0	76.5	1
U-550	99.9	4.1	76.2	1
U-700	99.9	3.7	75.1	1
U-850	97.7	8.7	62.8	1
V-Al <sub>2</sub> O <sub>3</sub>	98.1	1.7	5.0	1
Silica-alumina	81.9	28.9	10.0	2
H-M	96.6	2.0	81.3	2
Η-β	98.9	0.3	88.6	2
H-ZSM-5	98.6	1.9	13.5	2
H-FER	91.0	3.9	2.7	2

1) R. Anad, K. U. Gore, and B. S. Rao, *Cata. Let.*, 2002, **81**,33

2) R. Anad, T.Daniel, R. J. Lahoti, K. V. Srinivan, and B. S. Rao, Cata. Let., 2002, 81,241.

Supporting Table 2: Reaction cycles of the AP and ZP samples.

Cycles	Catalyst	Cyclohexanol Conversion (%)	Product Selectivity (%)		
			<b>O-Alkylation</b>	C-Alkylation	
1	AP	68	100		
2		69	100		
3		67	100		
4		68	100		
5		66	100		
1	ZP	100	7	93	
2		100	9	91	
3		98	10	90	
4		97	9	91	
5		99	9	91	

Temparature= 150 °C, Time= 4 h, Phenol= 1 mol, Cyclohexanol=1 mol, Catalyst= 0.5 g.