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ARTICLE

Catalytic Efficiency of Phosphated Zirconia in Selected Organic Reactions

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ABSTRACT

The efficiency of phosphated zirconia as a catalyst for the selected organic reactions in the liquid phase was investigated in a self-modified batch type glass reactor. The PO_4^{3-}/ZrO_2 samples were prepared by treating zirconia with H_3PO_4 solution (0.5 M) followed by calcination at 523, 773 and 973 K. The prepared catalyst samples were characterized by XRD, SEM, EDX, BET surface area and pore size analyzer. The catalyst samples showed excellent catalytic activity for reactions such as ring-opening of epoxide with aniline, Aza-Michael addition reaction and Knoevenagel condensation reaction, at mild reaction conditions.

KEYWORDS

Phosphated zirconia, Liquid phase, Organic reactions.

INTRODUCTION

Acid catalysis has a vital importance for the development of chemical industries [1]. The petrochemical refining industries are always searching for the new alternatives to the current processes for the production of clean burning fuels. This in addition enables to the development of other promising fields such as the use of solid acids as a heterogeneous catalysts, which provides several advantages such as mild reaction conditions, high selectivity and ease of work-up procedures [2,3]. Solid acids catalyze many organic reactions like cracking, condensation, esterification and hydrocarbon isomerization [1,4]. Currently, most of these reactions are catalyzed by conventional acids such as H_2SO_4, HNO_3 and HF or Lewis acids such as $AlCl_3$, $CuCl_2$ and BF_3, *etc.* which exhibit substantial disadvantages in handling because of their toxicity and corrosive nature [1,5,6]. These conventional acids need to be replaced by solid acids because they have several advantages over the conventional acids, such as they are non-toxic, non-corrosive, easy to handle, low cost, easily recoverable and possess strong acid sites. A heterogeneous system not only minimize the production of wastes, but also exhibit activity and selectivity comparable or even superior to that of the existing homogeneous route [7,8]. Solid acid catalysts are prepared by combining two or more oxides or by impregnating metal oxide with sulphate or phosphate [9]. Arata *et al.* [10] have studied acidity and catalytic activity of zirconium sulphates for cracking of

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cumene and found that sulphated zirconia calcined at 973 K show high surface acidity and catalytic activity than SiO_2-Al_2O_3. Demirci and Garin [3] have studied that platinum, palladium and iridium promoted sulphated zirconia for cracking of higher alkanes and find significant results. Rosenberg and Anderson [11] reported that phosphated zirconia show high activity for alkane s isomerization reactions. Several studies suggested that phosphated zirconia calcined at low temperature show high surface area and accessible porosity [12,13]. Reddy *et al.* [4,14] have explored the efficiency of sulphated zirconia for Knoevenagel condensation and Aza-Michael addition reaction under solvent free condition with high yield and selectivity. Herein, the importance of the phosphated zirconia as a supper solid acid is reflected from its application to reactions such as Aza-Micheal addition reaction, Knoevenagel and ring opening reaction of epoxide. Different amines combine with the α-β unsaturated carbonyl compound resulting β-amino carbonyl ingredients, which have intense use because it is a key intermediates for various biologically active drugs such as anticancer agent and antibiotics. While β-lactams are synthesized by the aza micheal reaction [15] and Knoevenagel reaction is commonly employed for the synthesis of numerous active chemical and chemical intermediates [16,17]. These reactions also used for the synthesis of carbocyclic as well as heterocyclic compounds which are of prime importance and logical implication [18], calcium resistor [5], polymer [19], perfumes, cosmetics and pharmaceutical [5]. Synthetic intermediates such as α-aryaloxy alcohols have been used from decades for the synthesis of pharmacologically important compounds are usually synthesized by ring opening reaction of epoxide [20]. In this paper, we introduced phosphated zirconia as an efficient catalyst for the most commonly used reactions such as ring-opening of epoxide with aniline, Aza-Michael addition reaction and Knoevenagel condensation reaction with specific modification.

EXPERIMENTAL

All the chemicals used in this study were of research grade and used without further purification. N_2 gas was prepared by nitrogen generator and passed through a suitable filter.

Preparation of phosphated zirconia: Zirconia was prepared by ammonolysis of 0.5 M Solution of $ZrOCl_2·8H_2O$ at pH 9. The precipitate was washed until a sample free of Cl^- was obtained. After that the sample was dried at 378 K in an oven, which was followed by grinding to fine powder. Finally, the sample was calcined at 973 K in order to obtain monoclinic zirconia. The prepared sample was immersed in 0.5 M H_3PO_4 solution in a ratio 1 g : 15 mL and sonicated for 30 min. The sample was then washed with hot distilled water, dried at 378 K for 24 h and calcined at temperatures 523, 773 and 973 K for 4 h under N_2 flow.

Characterization: Characterization of PO_4^{3-}/ZrO_2 was performed by SEM (JSM 5910, JEOL, Japan), XRD (X-ray diffractometer Rigaku D/Max-II, Cu tube, Japan) and Surface area and pore size analyzer (Quanta chrome Nova 2200e, USA).

Ring opening of meso-epoxides: 100 mg of PO_4^{3-}/ZrO_2 catalyst was added to a mixture (equimolar, 2 mmol) of meso-epoxides and aniline and magnetically stirred at room temperature in nitrogen atmosphere.

Aza-Michael addition: Amine and ketone in a ratio of 1:1.2 mmol with 100 mg of catalyst were stirred at room temperature.

Knoevenagel condensation: Aldehyde and malononitrile in a ratio of 1:1.2 mol were taken in a 25 mL round bottom flask, fitted with a reflux condenser. 100 mg of catalyst was added to it and stirred in nitrogen atmosphere under solvent-free condition.

These reactions were monitored by TLC. The catalyst was filtered out from the reaction mixture and reused. The products were separated with ethyl acetate from reaction mixture and purified by column chromatography on a silica gel column with ethyl acetate and *n*-hexane (3:4) solvent system. The products were analyzed by FT-IR, GC equipped with FID and UV-visible spectrophotometer and ^1H NMR.

RESULTS AND DISCUSSION

Characterization of PO_4^{3-}/ZrO_2: Fig. 1 shows XRD patterns of phosphated zirconia calcined at temperatures 523, 773 and 973 K. Usually, fresh ZrO_2 calcined at 773 K and 973 K has monoclinic geometry. However, in case of PO_4^{3-}/ZrO_2 sample calcined at 523 K has a tetragonal geometry while major fractions of the samples calcined at 773 and 973 K have tetragonal geometry, with monoclinic geometry exhibited by only a small fraction. The most probable reason for this behaviour is the changing of the phase of zirconia from monoclinic to tetragonal when it is immersed in the aqueous solution of phosphoric acid. This phase of zirconia is then stabilized by phosphate ions as shown in Fig. 1. The phase stabilization of zirconia by incorporation of anion is widely reported in the literature [5].

Table-1 shows the BET surface area, BJH surface area, pore volume, pore diameter and pore shape of phosphated zirconia. All the samples of phosphated zirconia have narrowed bottle necked shape pores and have larger surface area (64.46 m^2/g) because of porous surface.

Fig. 2 shows the SEM images of phosphate zirconia calcined at 923, 773 and 523 K. These images reveal smooth morphology, however, at higher temperature the presence of dust like particles can be seen on the surface, which could be due to the loss of water molecules during calcination [14].

Catalytic properties of PO_4^{3-}/ZrO_2: The catalytic activity of prepared catalysts was studied for the selected organic reactions.

TABLE-1
SURFACE CHARACTERISTICS OF PHOSPHATED ZIRCONIA

PO_4^{3-}/ZrO_2 calcinations (K)	Surface area BJH (m^2/g)	Pore volume (cc/g)	Pore diameter (Å)	Pore shape	Surface area BET (m^2/g)
523	48.67	0.14	141.90	Bottle neck	33.91
773	41.72	0.12	137.43	Bottle neck	26.84
973	64.46	0.18	128.33	Bottle neck	41.43

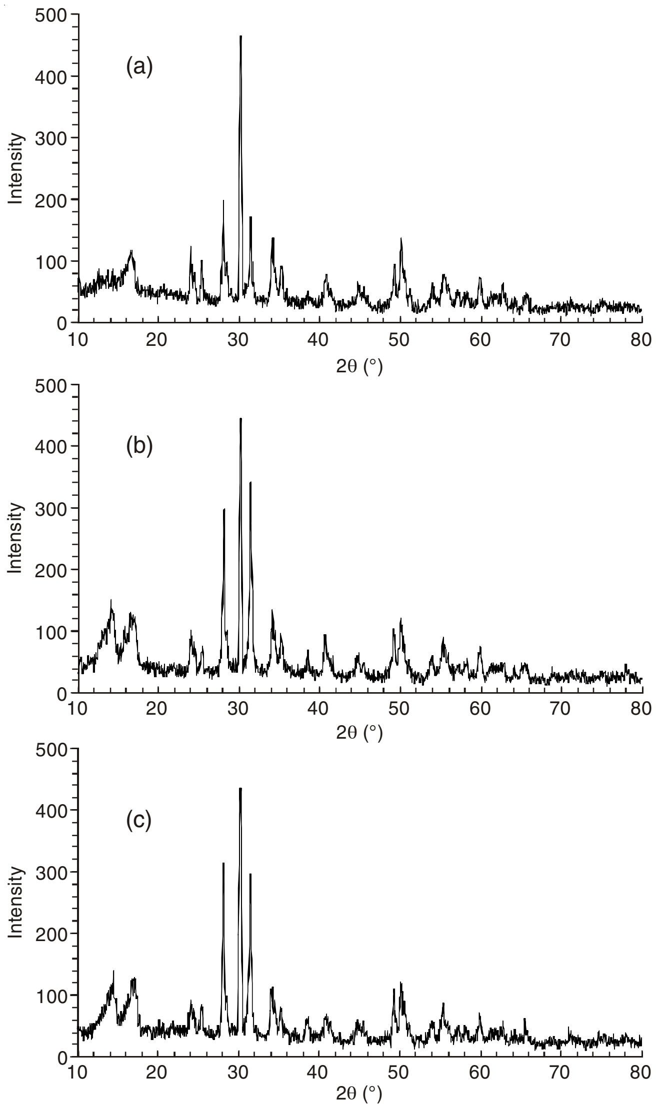


Fig. 1. XRD of phosphated zirconia calcined at (a) 523 K, (b) 773 K and (c) 973 K

Ring opening of meso-epoxides with aniline: The catalytic activity of phosphated zirconia was studied for ring opening of meso-epoxides with aniline as shown in Table-2. The reaction of meso-epoxides with aniline is significantly fast and forms the addition products with high selectivity and yield (86-97 %) generally in 1 h, under solvent free condition, at room temperature. The reaction was also carried out in dichloromethane but the result was not very satisfactory, probably due to the interference of the solvent with active surface sites on the catalyst. After the completion of reaction, the solid catalyst was removed by simple filtration from the reaction mixture. The wet catalyst was recycled several times and found to be effective for several runs without loss of any significant catalytic activity. ^{1}H NMR and FT-IR results are consistent with literature [21].

(1S,2S)-1,2-Diphenyl-2-(*o*-tolylamino)ethanol (2a): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.19 (s, 3H), 4.56 (d, *J* = 5.2 Hz, 1H), 4.96 (d, *J* = 5.2 Hz, 1H), 6.28 (d, *J* = 8.0 Hz, 1H), 6.56-6.59 (m, 1H), 6.87-6.90 (m, 1H), 7.01 (d, *J* = 7.2 Hz, 1H), 7.22-7.29 (m, 10H). FT-IR (cm^{-1}): 3420, 3061, 3029, 2888, 2855, 1607, 1587, 1508, 1453, 1316, 1266, 1048, 749, 700.

(1S,2S)-2-(4-Isopropylphenylamino)-1,2-diphenylethanol (2b): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.14 (d, *J* = 6.4 Hz, 6H), 2.70 (br, 1H), 2.71-2.75 (m, 1H), 4.47 (d, *J* = 6.0 Hz, 1H), 4.84 (d, *J* = 6.4 Hz, 1H), 6.48-6.50 (m, 2H), 6.92-6.94 (m, 2H), 7.20-7.26 (m, 10H). FT-IR (cm^{-1}): 3410, 3060, 3028, 2884, 1606, 1585, 1504, 1451, 1312, 1263, 1174, 1088, 1045, 813, 752, 700.

(1S,2S)-2-(3-Chlorophenylamino)-1,2-diphenylethanol (2c): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.33: (d, *J* = 2.8 Hz, 1H), 4.52-4.53 (m, 1H), 4.83 (br, 1H), 4.89-4.91 (m, 1H), 6.35-6.37 (m, 1H), 6.48 (s, 1H), 6.59 (d, *J* = 9.6 Hz, 1H), 6.92-6.96 (m, 1H), 7.23-7.32 (m, 10H). FT-IR (cm^{-1}): 3403, 3061, 3029, 2883, 1598, 1497, 1453, 1400, 1316, 1295, 1260, 1177, 1090, 1050, 816, 768, 700.

(1S,2S)-2-(3-Bromophenylamino)-1,2-diphenylethanol (2d): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.30 (d, *J* = 2.8 Hz, 1H), 4.50-4.52 (m, 1H), 4.81 (d, *J* = 4.4 Hz, 1H), 4.90 (dd, *J* = 5.2 Hz, *J* = 3.2 Hz, 1H), 6.38-6.40 (m, 1H), 6.65 (s, 1H), 6.73 (d, *J* = 8.0 Hz, 1H), 6.86-6.90 (m, 1H), 7.23-7.25 (m, 3H), 7.29-7.32 (m, 7H). FT-IR (cm^{-1}): 3406, 3062, 3028, 2882, 1593, 1494, 1453, 1396, 1316, 1295, 1260, 1179, 1073, 1051, 814, 768, 700.

Aza-Michael addition reaction: PO_4^{3-}/ZrO_2 efficiently catalyzed the Aza-Michael addition reaction of aniline with ketone at ambient temperature, under solvent free condition. The product of these reaction is quite excellent (80-96 % yield) as given in Table-3. After completion of reaction, the catalyst was recovered from the reaction mixture by simple filtration, recycled and reused for 5 subsequent trials. Both activity and selectivity of the catalyst were remarkable. ^{1}H NMR and FT-IR results are in good agreement with literature [14].

4-(Phenylamino)pentan-2-one (3a): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.25 (d, *J* = 6.4 Hz, 3H), 2.16 (s, 3H), 2.55 (dd, *J* = 16.4, 7.1 Hz, 1H), 2.76 (dd, *J* = 16.4, 4.8 Hz, 1H), 3.67 (s,

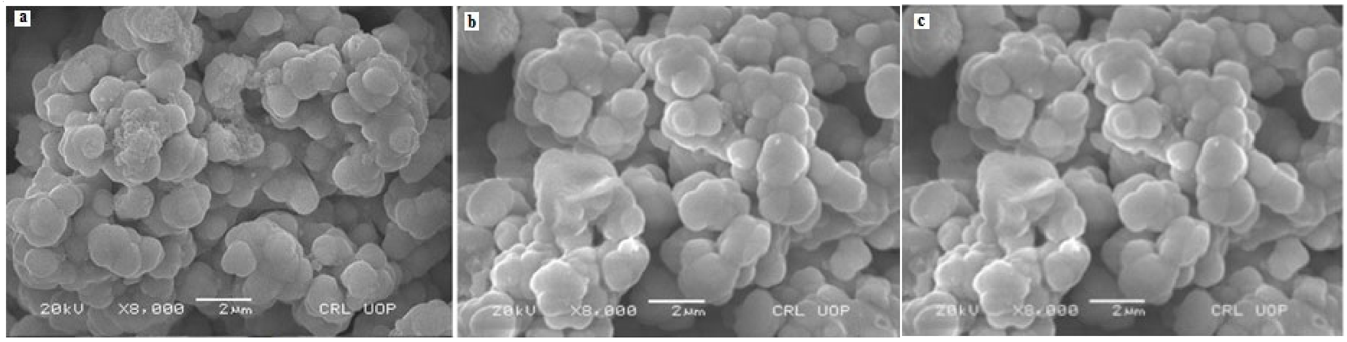
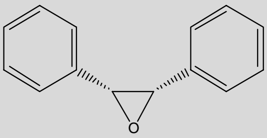
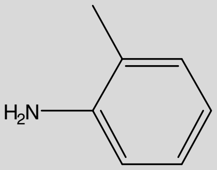
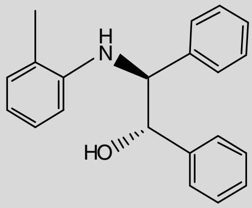
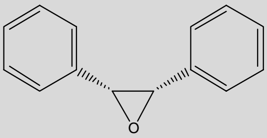
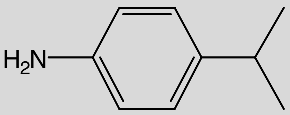
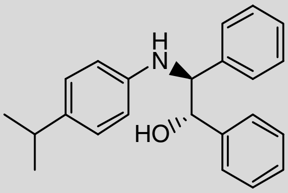
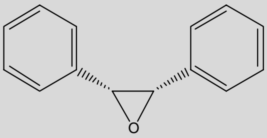
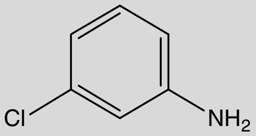
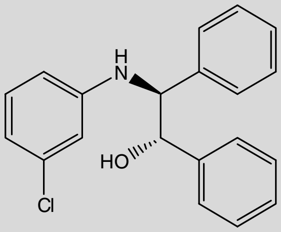
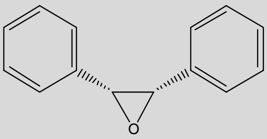
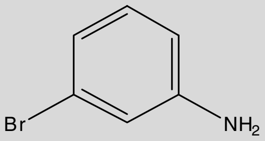
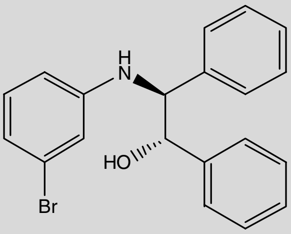


Fig. 2. SEM images of phosphated zirconia calcined at (a) 973 K, (b) 773 K and (c) 523 K

TABLE-2
RING OPENING OF MESO-EPOXIDE WITH ANILINE CATALYZED BY PHOSPHATED ZIRCONIA

Entry	Reactants		Products	Time (h)	Yield (%)
2a				1	97
2b				1	86
2c				1	90
2d				1	89

1H), 3.89-4.02 (m, 1H), 6.60 (dd, *J* = 8.6, 0.9 Hz, 2H), 6.67-6.76 (m, 1H), 7.13-7.22 (m, 2H). FT-IR (cm^{-1}): 2911, 1626, 1578, 1514, 1451, 1287, 1195, 1025, 931, 757, 697.

4-(*p*-Tolylamino)pentan-2-one (3b): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.16 (s, 3H), 2.24 (s, 3H) 2.73 (t, *J* = 6.1 Hz, 2H), 3.39 (t, *J* = 6.1 Hz, 2H), 3.83 (s, 1H), 6.54 (d, *J* = 8,4 Hz, 2H), 6.99 (d, *J* = 8.3 Hz, 2H). FT-IR (cm^{-1}): 3426, 2917, 2885, 1629, 1582, 1524, 1290, 1195, 1027, 758, 700.

2-[(Phenylamino)methyl]cyclohexanone (3c): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.48 (dq, *J* = 12.7, 3.8 Hz, 1H), 1.59-175 (m, 2H), 1.84-95 (m, 1H), 2.09 (ddd, *J* = 8.9, 5.9, 2.8 Hz, 1H), 2.16 (ddd, *J* = 12.2, 5.7, 2.7 Hz, 1H), 2.31 (ddd, *J* =

TABLE-3
REACTION OF AMINE WITH KETONE CATALYZED BY PO_4^{3-}/ZrO_2

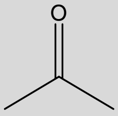
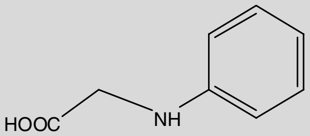
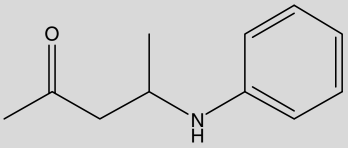
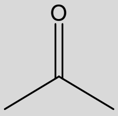
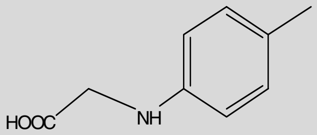
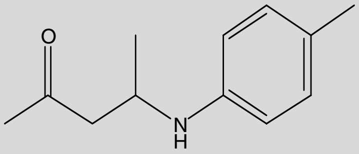
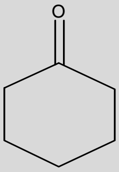
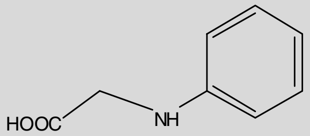
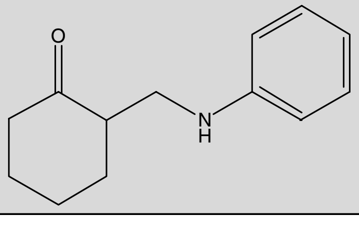
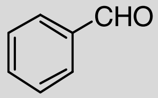
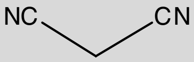
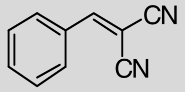
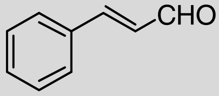
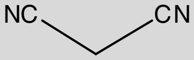
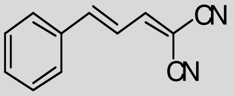
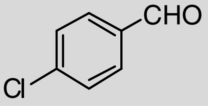
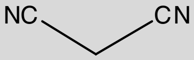
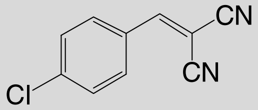
Entry	Reactants		Products	Time (h)	Yield (%)
3a				1.5	96
3b				1.5	85
3c				2.0	80

TABLE-4
REACTION OF ALDEHYDES WITH MALONONITRILE CATALYZED BY PHOSPHATED ZIRCONIA

Entry	Reactants		Products	Time (h)	Yield (%)
4a				3	89
4b				1	90
4c				2	87

18.8, 9.6, 3.5 Hz, 1H), 2.37-2.44(m, 1H), 2.67 (dq, J = 7.8, 4.6 Hz, 1H), 3.12 (dd, J = 13.5, 4.6 Hz, 1H), 3.43 (dd, J = 13.5, 7.8 Hz, 1H), 6.63- 6.68 (m, 2H), 6.73 (t, J = 7.3 Hz, 1H), 7.15-7.20 (m, 2H). FT-IR (cm^{-1}): 3385, 3264, 2943, 2889, 1589, 1567, 1523, 1445, 1238, 1178, 1026, 698.

Knoevenagel condensation reaction: The catalytic activity of PO_4^{3-}/ZrO_2 was also tested for Knoevenagel condensation reaction of aldehydes with malononitrile. The experiments were performed for time spans ranging from 1-3 h to obtained yield ranging from good to excellent (87-95 % yield) as given in the Table-4. The catalytic activity of the catalyst for the Knoevenagel condensation reaction may be attributed to the strong acidic sites on the surface. The catalyst was recycled several times and was found to show the same efficiency in the subsequent runs. ^{1}H NMR and FT-IR results are consistent with literature [22].

2-(Phenylmethylene)malononitrile (4a): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.57 (t, J = 8.0 Hz, 2H), 7.67 (t, J = 7.2 Hz, 2H), 7.82 (s, 1H), 7.94 (d, J = 7.6 Hz, 2H). FT-IR (cm^{-1}): 2198, 1589, 1566.

2-[(E)-3-Phenylallylidene]malononitrile (4b): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.27-7.35 (m, 2H), 7.46-7.52 (m, 3H), 7.62-7.66 (m, 3H). FT-IR (cm^{-1}): 2215, 1600, 1510, 956.

2-(4-Chlorobenzylidene)malononitrile (4c): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52 (d, J = 8.4 Hz, 2H), 7.75(s, 1H), 7.86 (d, J = 8.8 Hz, 2H). FT-IR (cm^{-1}): 2223, 1580, 1520, 710-725.

Conclusion

Zirconia (ZrO_2) impregnated with H_3PO_4 shows excellent catalytic activity for the synthesis of β-amino alcohol from ring-opening of epoxide with aniline, β-amino ketones from the addition reaction of amine with α,β-unsaturated carbonyl compound and Knoevenagel condensation reaction of various aldehydes with malanonitrile, at room temperature under solvent free condition. The catalyst was found to be superior to other reported catalysts, due to high its catalytic activity, affordability, feasibility and reusability. PO_4^{3-}/ZrO_2 are thus an excellent and green alternative for the existing classical catalysts, used for the selected organic reactions.

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