

Research article

$K_2CaP_2O_7$, a new catalyst for Knoevenagel reaction

Younes Abrouki^{1,*}, Abdelkader Anouzla¹, Hayat Loukili¹, Ahmed El Khadir¹, Aicha El Jourahri¹, Jamal Bennazha¹, Ahmed Rayadh¹, Saïd Sebti², and Mohamed Zahouily¹

¹Department of Research, Faculty of Science and Technology, Mohammedia, Morocco ²Department of Chemistry, Faculty of Science Ben M'Sik, Casablanca, Morocco *Corresponding author (E-mail: younesabrouki@gmail.com)

Abstract

The pyrophosphate catalyst $K_2CaP_2O_7$ is a new basic catalyst for Knoevenagel reaction of aldehydes with active methylene in the ethanol at room temperature. The pyrophosphate catalyst bring advantages such as easy separation of the catalyst by simple filtration, possible recycling of the catalyst, use of non-toxic and inexpensive catalysts and especially, elimination of salts and by-product pollutants.

Keywords: Knoevenagel reaction, Heterogeneous catalysis, $K_2CaP_2O_7$, Carbon-carbon bond formation.

Introduction

Surface-mediated solid phase reactions are of growing interest [1] because of their advantages of ease of set up, mild conditions, rapid reactions, selectivity, increased yields of the products and low cost compared with their homogeneous counterparts.

The Knoevenagel reaction is one of the most important C-C bond forming reactions available, because the alkenes synthesized are very useful intermediates in organic synthesis [2]. In recent years, this reaction has been carried out

in heterogeneous media in the presence of several solids such as alumina [3], Hydroxyapatite [4], fluorapatite [5] and Natural phosphate [6].

In continuation of our investigations on the use of heterogeneous catalysts for fine chemicals preparation, we wish to report here a mild, heterogeneous catalytic method for the Knoevenagel condensation between an aldehyde and an activated methylene catalyzed by synthetic potassium pyrophosphate $K_2CaP_2O_7$ in mild reaction condition.

Materials and Method

Chemicals and instrumentations

All commercial reagents and solvents were used without further purification. Potassium pyrophosphate $K_2CaP_2O_7$ is prepared in powder state. X-ray diffraction (XRD) patterns of the catalysts were obtained on a Philips 1710 diffractometer using $Cu-K\alpha$ radiation. Surface areas were determined at 77 K using a Coulter SA 31000 instrument with an automated gas volumetric method employing nitrogen as the adsorbate. NMR spectra were recorded on a Bruker ARX 300 spectrometer. Mass spectra were recorded on a VG Autospec spectrometer. FTIR spectra were recorded on an ATI Mattson-Genesis Series spectrophotometer using the KBr disc method.

Preparation of the catalyst and structural characteristics

The Potassium pyrophosphate $K_2CaP_2O_7$ [7] was synthesized by heating stoichiometric quantities of K_2CO_3 , $CaCO_3$ and $NH_4H_2PO_4$ (purity greater than 99%). The starting materials were carefully mixed in an agate mortar and heated by steps of $150^\circ C$ in a porcelain crucible up to $800^\circ C$. This solid state technique allows ammonia, water and carbon dioxide to evolve progressively according to the following equation (Figure 1).

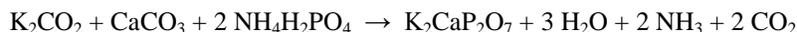


Figure 1. Preparation of potassium pyrophosphate

After the final grinding, the powder is heated at $820^\circ C$ for 48 hours. The purity of the final powder was controlled by X-ray diffraction, using a D 500 Diffractometer (CuK_α radiation, $1,540 \text{ \AA}$).

The powder pattern of $K_2CaP_2O_7$ available in the literature (monoclinic system, space group $P2_1/n$, $a = 9.79 \text{ \AA}$, $c = 12.97 \text{ \AA}$, $\beta = 104.3^\circ$), and by comparison to those of its two isomorphous diphosphates $Cs_2CaP_2O_7$ and $Rb_2CaP_2O_7$ [8]. The powder was dried for 2 hours at $100^\circ C$ before use in order to eliminate possible water molecules adsorbed on the surface of the sample which may affect catalytic.

General Procedure

The general procedure is a flask contain an equimolar mixture (1mmol) of aldehyde **1** and active methylene compound **2** in ethanol (1.5 ml), $K_2CaP_2O_7$ (0.1g) was added and the mixture stirred at room temperature for specified time (Figure 2).

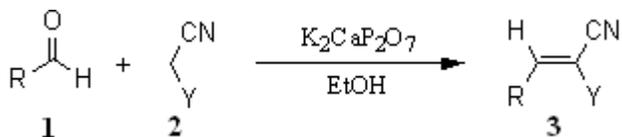


Figure 2. Knoevenagel reaction catalyzed by $K_2CaP_2O_7$

The mixture was filtered, dried and the solvent evaporated. The residue was purified by distillation under vacuum and identified by ^1H , ^{13}C NMR and IR spectrometry.

Results and Discussion

In this study, the Knoevenagel reaction between Benzaldehyde and Malononitrile was chosen as model substrates to understand the catalytic activity of $\text{K}_2\text{CaP}_2\text{O}_7$ catalyst.

In the presence of ethanol at room temperature, the $\text{K}_2\text{CaP}_2\text{O}_7$ promotes the Knoevenagel condensation but the reaction rate is relatively slow (38% (10min)). The yield becomes (92% (40min)) when the reaction times are prolonged. Indeed, the addition of a small quantity of water in ethanolic solution to the $\text{K}_2\text{CaP}_2\text{O}_7$ notably improves the results obtained in the synthesis of product **3e** (64% (10min)). The simultaneous additions of water and benzyltriethylammonium chloride (BTEAC) in ethanolic solution show a clear superiority in the activation of the $\text{K}_2\text{CaP}_2\text{O}_7$. The yield of product is obtained in with very high yields (93% (10min)).

To determine the scope and limitation of Knoevenagel reaction, the optimum reaction conditions were applied to other substrates for this condensation between aldehyde (Furfural, Benzaldehyde or Cinnamaldehyde) with activated methylene (Methyl cyanoacetate, Malononitrile or Ethyl cyanoacetate) as shown in Table 1.

Table 1. The synthesis of alkenes **3** catalyzed by $\text{K}_2\text{CaP}_2\text{O}_7$ at room temperature.

Products	R_1	R_2	Yield % (time min)		
			a	b	c
3a		—CO ₂ Me	34(5)	81(5)	91(5)
3b		—CO ₂ Me	22(20)	63(20)	86(20)
3c		—CO ₂ Me	28(15)	76(15)	95(15)
3d		—CN	51(5)	84(5)	90(5)
3e		—CN	92(40) 38(10)	86(20) 64(10)	93(10)
3f		—CN	46(10)	87(10)	94(10)
3g		—CO ₂ Et	26(10)	72(10)	92(10)
3h		—CO ₂ Et	14(30)	57(30)	90(30)
3i		—CO ₂ Et	20(15)	68(15)	96(15)

a (0.1 g $\text{K}_2\text{CaP}_2\text{O}_7$, 1 ml EtOH).

b (0.1 g $\text{K}_2\text{CaP}_2\text{O}_7$, 1 ml EtOH, 0.1ml water).

c (0.1 g $\text{K}_2\text{CaP}_2\text{O}_7$, 1 ml EtOH, 0.1ml water, 40mg CBETA).

This result shows that the $K_2CaP_2O_7$ possesses a basic character and can be used in heterogeneous synthesis solid/liquid. It is worth noting that, in the same conditions and in absence of the $K_2CaP_2O_7$, water, BTEAC or both do not promote this reaction.

The mechanism of the Knoevenagel condensation involves abstraction of one the active methylene protons by a base, followed by attack of the resulting anion on the carbonyl carbon of benzaldehyde. The resulting negatively charged oxygen atom abstracts a hydrogen atom from the base. Elimination of a molecule of water results in the formation of a system of extended conjugation (Figure 3).

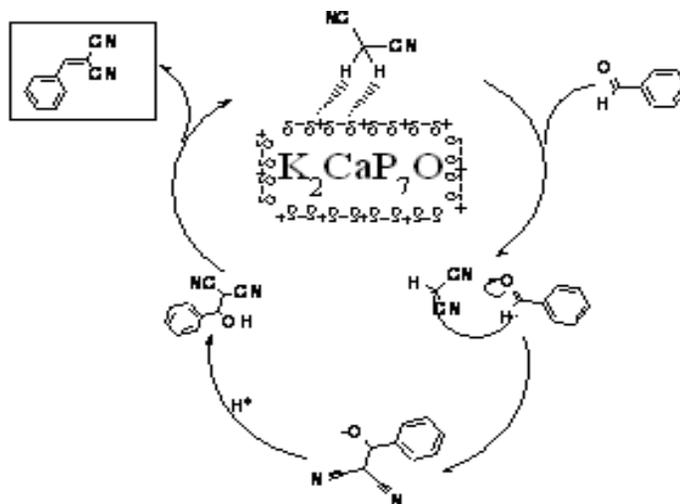


Figure 3. Catalytic mechanism of Knoevenagel reaction catalyzed by $K_2CaP_2O_7$

Indeed, we estimate that the surface of the $K_2CaP_2O_7$ presents certainly multicatalytic active sites; the basic sites (oxygens of P_2O_7 group and CaO_6 octahedra) and the acidic sites (phosphorus of P_2O_7 group, K^+ and Ca^{2+} cations). It is these multiple active sites in the surface of $K_2CaP_2O_7$ that give the catalytic property to this catalyst.

We next investigated the stability of the catalyst in order to recycle it. The used and recovered $K_2CaP_2O_7$ has been shown to be reusable after drying at 150 °C in vacuum, and more efficiently after washing with acetone followed by calcinations at 600 °C. In the last case, the catalyst can be recovered and reused at least five times without appreciable loss of activity.

Conclusion

In summary, we have reported an efficient Knoevenagel condensation catalyzed by the $K_2CaP_2O_7$ in mild reaction condition, this catalyst bring advantages such as high catalytic activity under mild reaction conditions, easy separation of the catalyst by simple filtration, possible recycling of the catalyst, use of non-toxic and inexpensive catalysts and especially, elimination of salts and by-product pollutants. This new solid base catalyst becomes then a practical alternative to soluble bases.

Acknowledgement

The support of the International Foundation of the Sciences Swede is gratefully acknowledged.

References

- [1] Abrouki, Y., Anouzla, A., Loukili, H., Saida, K., Bennazha, J., Loukili, A., Rayadh, A., Sebti, S., and Zahouily, M., 2013, Sodium Pyrophosphate: A Novel and Efficient Catalyst for Sulfa-Michael additions., *American Journal of Biological Chemical and Pharmaceutical Sciences*, 1(5), 16-21.
- [2] Balalaie, S., Bararjanian, M., Hekmat, S., and Salehi, P., Novel, 2006, *Synthetic Communications*, Efficient, and Green Procedure for the Knoevenagel Condensation Catalyzed by Diammonium Hydrogen Phosphate in Water., 36(24), 3703-3711.
- [3] Balalaie, S., and Nemati, N., 2000, Ammonium Acetate-Basic Alumina Catalyzed Knoevenagel Condensation Under Microwave Irradiation Under Solvent-Free Condition., *Synthetic Communications*, 30(5), 869-875.
- [4] Sebti, S., Tahir, R., Nazih, R., Saber, A., Boulaajaj S., 2002, Hydroxyapatite as a new solid support for the Knoevenagel reaction in heterogeneous media without solvent, *Applied Catalysis A: General* 228, 155-159.
- [5] Smahi, A., Solhy, A., El Badaoui, H., Amoukal, A., Tikad, A., Maizi, M., Sebti, S., 2003, Potassium fluoride doped fluorapatite and hydroxyapatite as new catalysts in organic synthesis., *Applied Catalysis A: General*, 250, 151-159.
- [6] Sebti, S., Smahi A., and Solhy A., *Tetrahedron Letters*, 2002, Natural phosphate doped with potassium fluoride and modified with sodium nitrate: efficient catalysts for the Knoevenagel condensation., 43, 1813-1815.
- [7] Brown, EH., Lehr, JR., Smith, JP., Frazier, AW., and Agr, J., 1963, Preparation and characterization of some calcium pyrophosphates., *Agricultural and Food Chemistry*, 11, 214-222.
- [8] Song, HJ., Yim, DK., Cho, IS., Roh, HS., Kim, JS., Kim, DW., and Hong, KS., 2012, Luminescent Properties of Phosphor Converted LED Using an Orange-emitting $\text{Rb}_2\text{CaP}_2\text{O}_7:\text{Eu}^{2+}$ Phosphor., *Materials Research Bulletin*, 47(12), 4522-4526.