

Direct use of mineral phosphate fertilizers MAP, DAP, and TSP as heterogeneous catalysts in organic reactions

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Abstract: In this paper, we reported the first use of phosphate fertilizers (MAP, DAP, and TSP) as heterogeneous catalysts for organic reactions. Their catalytic activities were investigated in the first time in Knoevenagel condensation of various aromatic aldehydes with malononitrile at room temperature. These minerals phosphate showed high catalytic activities and ability to be recovering and reusing without a significant loss in their catalytic activities. In order to reach the optimal reaction conditions for Knoevenagel condensation, we carried out a kinetic study of the effect of reaction time, the effect of solvent, the amount of catalysts and the variation of the range of the particles size the more active. The best conditions were obtained by the use of these fertilizers (MAP, DAP, and TSP) in their commercial status, simply crashed in powder, without any purification, using ethanol as solvent. These phosphate fertilizers prove to be very promising and effective heterogeneous catalysts for the condensation of Knoevenagel.

Keywords: Phosphate Fertilizers; MAP; DAP; TSP; Knoevenagel; Catalysis; Heterogeneous catalysts.

Introduction

The search for catalytic processes combined with the development of clean and environment-friendly strategies of synthesis ¹⁻³ is became one of the main purposes of chemists, since the environmental concerns hold constantly their attention. Recently, numerous phosphate-based catalysts have appeared and continue to arouse certain interest from organic chemists as justified by the number of the corresponding papers published in the last decade. Among these catalysts, we can mention natural phosphate ⁴⁻⁹, hydroxyapatites ¹⁰⁻¹³, fluoroapatites ¹⁴⁻¹⁶, solution of ammonium phosphate adsorbed in silica gel $\text{NH}_4\text{H}_2\text{PO}_4/\text{SiO}_2$ ¹⁷, $\text{NH}_4\text{H}_2\text{PO}_4/\text{MCM-41}$ prepared by mixing MCM-41 with a solution of ammonium phosphate ¹⁸ and copper salts with ammonium phosphate as base ¹⁹. Furthermore, many catalysts containing phosphate, such as KF/NP and NaNO_3/NP ²⁰ KF/HAP and NaNO_3/HAP ²¹ and $\text{Na}_2\text{CaP}_2\text{O}_7$ ²² were used as excellent catalysts for the reaction of Knoevenagel. We have consequently attempted to evaluate, through this study, the catalytic capacity of phosphate fertilizers mono-ammonium phosphate (MAP), di-ammonium phosphate (DAP) and triple super phosphate (TSP). For this purpose, we have chosen Knoevenagel condensation ²³ due to its importance in the production of fine chemicals ²⁴ and pharmaceuticals ²⁵, as support for this test.

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It has to be pointed out that Knoevenagel condensation served many years as model for the development of a wide array of catalysts such as, more recently, magnetic catalysts ²⁶⁻³¹, metal organic frameworks MOFs ^{32,33}, zeolite imidazole frameworks ZIFs ^{34,35}, KF-Clinoptilolite ³⁶, amine grafted on graphene oxide ³⁷, ionic liquids ³⁸⁻⁴¹, sevelamer ⁴², hydrotalcite ⁴³⁻⁴⁵, Lewis acid ⁴⁶ and base ⁴⁷, dolomite ⁴⁸, catalysts based on silica like TsOH-SiO_2 ⁴⁹, polyethylenimine- SiO_2 ⁵⁰ and Ni-SiO_2 ⁵¹, potassium-loaded MgAl oxide nK-MgAl(O) ⁵², urea derivative ⁵³, zeolites ⁵⁴⁻⁵⁶ and lipase ^{57,58}.

According to our humble knowledge, synthetic $\text{NH}_4\text{H}_2\text{PO}_4$ has been reported once as an homogeneous catalyst for the Knoevenagel condensation in water ⁵⁹, but this is the first time that phosphate fertilizers (MAP, DAP and TSP) were used directly as heterogeneous catalysts in their commercial form of granules.

Our work consists therefore in the direct use of fertilizers, MAP, DAP and TSP, as heterogeneous catalysts in organic reactions ⁶⁰.

The ammonium phosphates are produced in industrial quantities and are used mainly in agriculture as nutrient sources for nitrogen and phosphorus.

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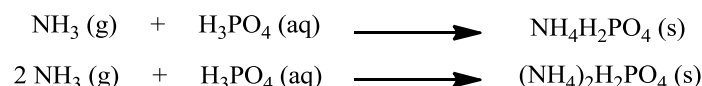
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Currently, Morocco, China and United States are the most important players in phosphate industry. However, Morocco has most important phosphate world-wide reserves and is thus a major actor for the production of phosphate fertilizers whose physicochemical characteristics are shown in the

website of the OCP (Office Cherifien des Phosphates)⁶¹, the first Moroccan company.

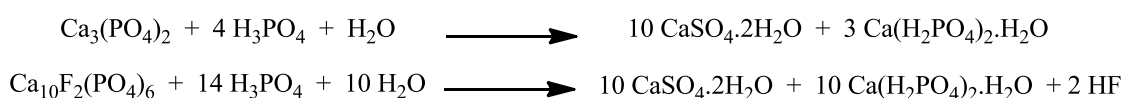
The ammonium phosphates are the important compound of phosphate fertilizer family, they are formed by the reaction of anhydrous ammonia with orthophosphoric acid (H₃PO₄)^{61,62} (Scheme 1).



Scheme 1. Synthesis of MAP and DAP from ammonia

The basic chemical reactions involved in TSP manufacture from the Phosphate rock⁶³ are shown in scheme 2.

Two mechanisms of granule formation for granular MAP, DAP, and TSP are known: agglomeration-type and accretion-type processes⁶³.



Scheme 2. Synthesis of TSP from Phosphate rock.

Experimental Section

Materials

Different fertilizers used are marketed as⁶¹:
 -Mono-Ammonium Phosphate: MAP 11-52-00, binary Fertilizer, complex granule with Nitrogen: 11 % N and Phosphorus: 52 % P₂O₅.
 -Di-Ammonium Phosphate: DAP 18-46-00, binary Fertilizer, complex granule with Nitrogen: 18 % N and Phosphorus: 46 % P₂O₅.
 -Triple Super Phosphate: TSP 00-46-00, simple granule Fertilizer with Phosphorus: 46 % P₂O₅.

All these commercial fertilizers were used without further purification; they were just ground into powder completely.

Catalysts Characterization

The X-ray powder diffraction patterns of the catalysts with particle size less than 71 μm were recorded on a PANalytical X'Pert 3 Powder diffractometer equipped with Cu Kα radiation source (λ = 1.54178 Å).

The scanning electron Microscopy (SEM) and energy dispersive X-ray analysis (EDXA) were carried out using

Catalysts evaluation

General procedure for Knoevenagel condensation

In a typical experiment, aromatic aldehyde (2 mmol) and malononitrile (3mmol) were dissolved in 3 ml of Ethanol. 4 mol % of catalyst was then added and the solution was stirred at ambient temperature (25°C) and constant agitation speed (700 rpm). When the reaction is completed, the product of Knoevenagel condensation was washed one time with ethanol, then dissolved in THF and filtered off in order to separate it from the catalyst. The organic phase was compressed under vacuum. The data of the obtained products were authenticated by comparison with data shown in the literature.

Effects of catalyst particle size

In order to compare between catalytic activities of different catalyst particle size ranges in the reaction of Knoevenagel, the catalyst was ground, sieved, and separated into three fractions in the ranges of 10-71 μm, 71-90 μm, and 90-120 μm, respectively. The medium diameters of each fraction were calculated from the average pore sizes of the two adjacent sieves (Table 1).

Table 1. Medium diameter of different catalysts particle size ranges

Fraction number	Particle size range	Medium diameter
1	10-71 μm	53.5 μm
2	71-90 μm	80.5 μm
3	90-120 μm	105 μm

Recyclability and reusability studies of catalysts

The recoverability and reusability of the catalyst were investigated under similar reaction conditions.

After dissolving products in THF, the catalyst was recovered, washed with ethanol (2×5mL), dried at 70°C and reused for a new Knoevenagel condensation.

Results and Discussion

Catalysts characterization X-ray diffraction analysis

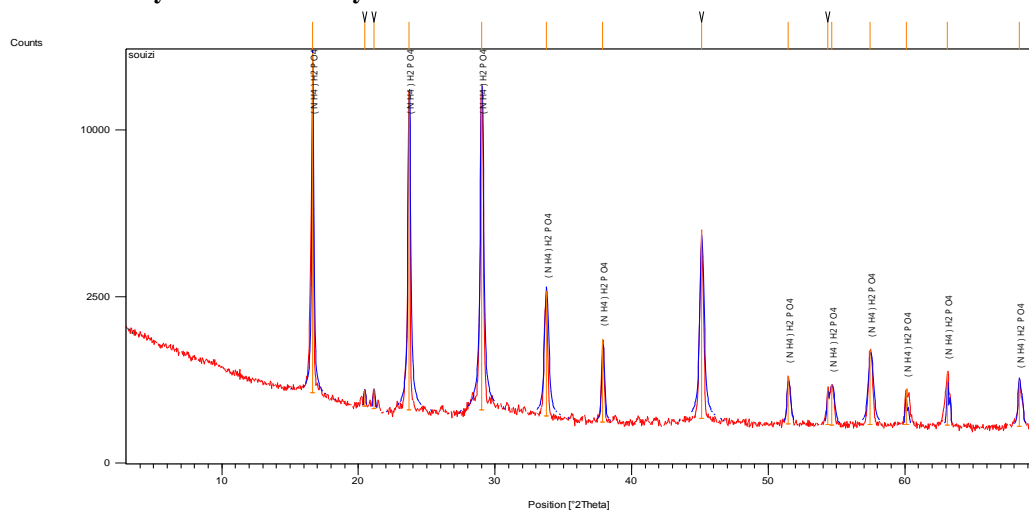


Figure 1. X-ray diffraction pattern of MAP fertilizer

SEM spectroscopy

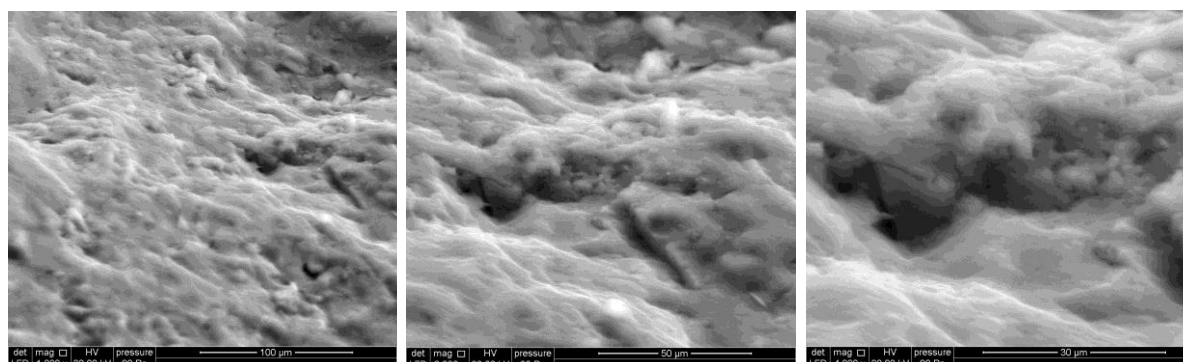


Figure 2(a). SEM images of MAP fertilizer

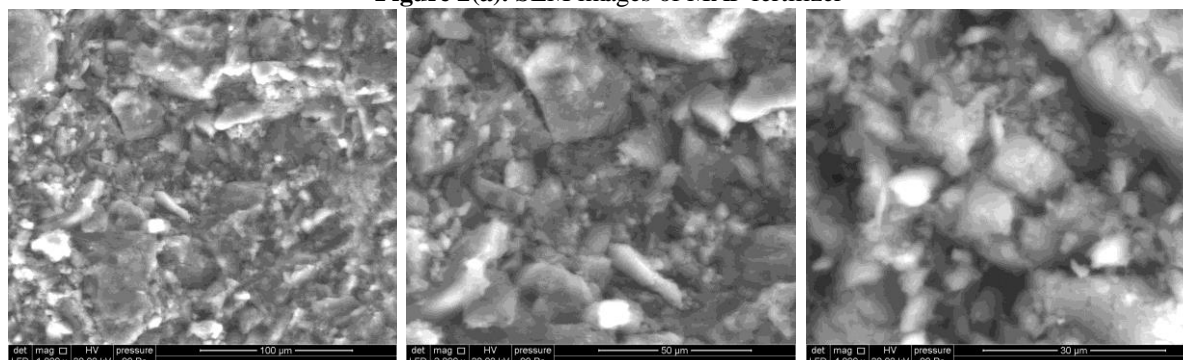


Figure 2(b). SEM images of DAP fertilizer

XRD patterns of the catalysts powders were recorded at ambient condition of temperature and pressure using PANalytical X'Pert 3 Powder diffractometer with Cu-K α radiation $\lambda = 1.5418 \text{ \AA}$.

The diffractogram of X-ray (Figure 1) presents characteristic peaks of pure synthesized MAP^{64,65}. Its crystal structure was found to be tetragonal in the space group I-42d with lattice parameters of $a = b = 7,5021 \text{ \AA}$, and $c = 7,5541 \text{ \AA}$.

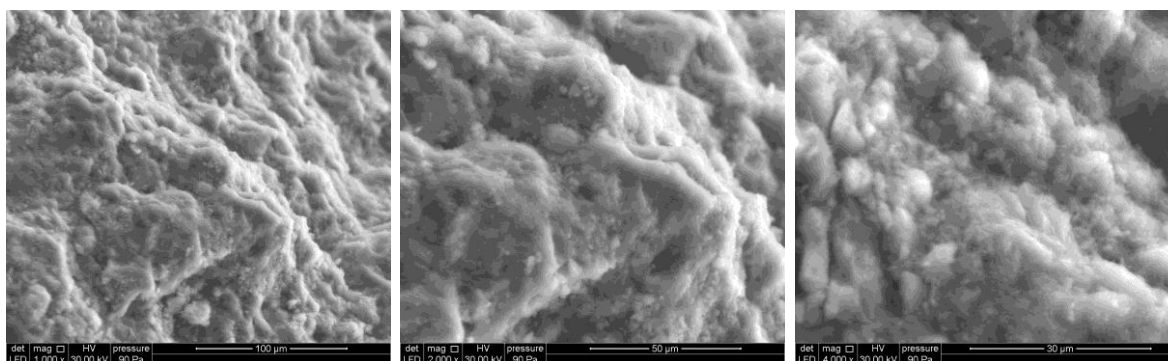


Figure 2(c). SEM images of TSP fertilizer

With respect to the particle size, the SEM micrographs in Figure 2 (a), (b), and (c) displays that the three samples are composed of microparticles of various sizes ranging from 70 to 10 micrometers.

EDXA analysis

The EDXA analysis data in Figure 3 shows the elemental composition of MAP, DAP, and TSP

fertilizers. It can be clearly seen that MAP (Fig. 3(a)), DAP (Fig. 3(b)) and TSP (Fig. 3(c)) are composed of N, O, and P, primary elements of these fertilizers^{61,64}. The EDXA spectrum also showed the presence of Ca in the TSP fertilizer, which confirms its chemical composition⁶¹.

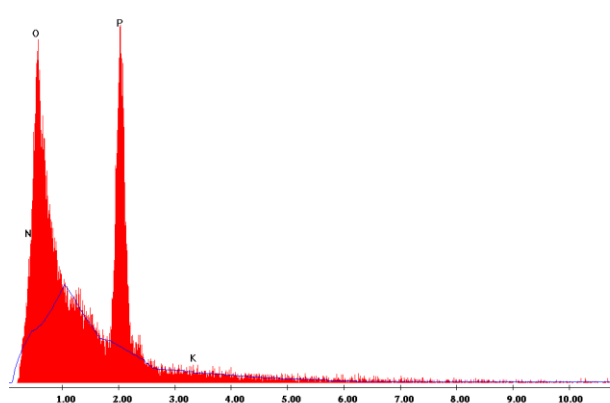


Figure 3(a). EDXA spectrum of MAP fertilizer

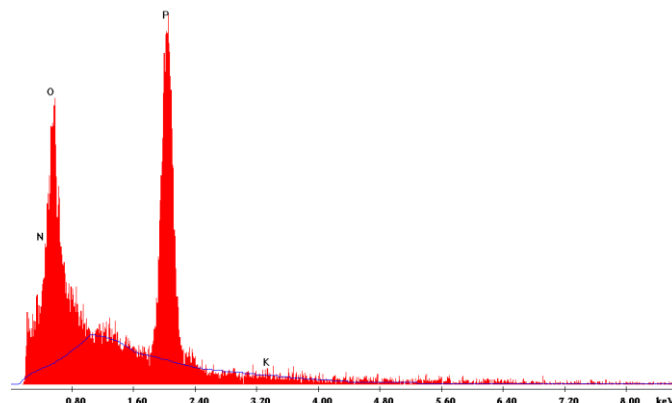


Figure 3(b). EDXA spectrum of DAP fertilizer

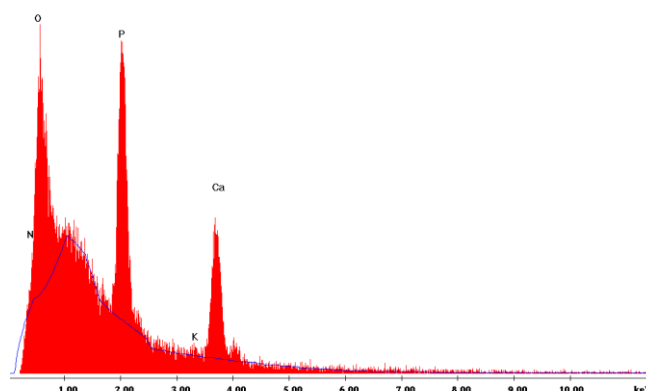
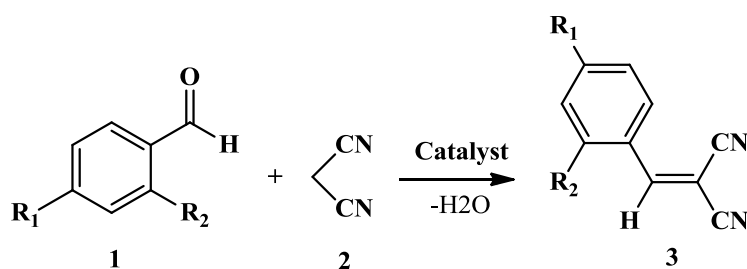


Figure 3(c). EDXA spectrum of TSP fertilizer

Catalytic activity evaluation of MAP, DAP, and TSP: Synthesis of 4-chlorobenzylidene-malononitrile

The catalytic activities of phosphate fertilizers MAP, DAP, and TSP were evaluated based on the Knoevenagel condensation between 4-chlorobenzaldehyde with malononitrile at ambient conditions of temperature and pressure using

absolute ethanol (Scheme 3). In the absence of catalysts, the conversion of 4-chlorobenzaldehyde was limited to 55% toward 4-chlorobenzylidene-malononitrile. However, in the presence of approximately 4 mol% of phosphate fertilizers catalysts, the reaction leads to much higher yields of the Knoevenagel adduct (Table 2).



a: $R_1 = \text{Cl}$, $R_2 = \text{H}$; b: $R_1 = \text{Cl}$, $R_2 = \text{Cl}$; c: $R_1 = \text{NO}_2$, $R_2 = \text{H}$; d: $R_1 = \text{OCH}_3$, $R_2 = \text{OCH}_3$
 e: $R_1 = \text{OCH}_3$, $R_2 = \text{H}$; f: $R_1 = \text{CH}_3$, $R_2 = \text{H}$; g: $R_1 = \text{H}$, $R_2 = \text{H}$

Scheme 3. Knoevenagel condensation of aromatic aldehydes with malononitrile.

Table 2. Synthesis of 4-chlorobenzylidenemalononitrile (3a) using fertilizers MAP, DAP, and TSP

Entry	Catalyst	Catalyst amount(mol%)	Yield %
1	Blank	-	55
2	MAP	0.01g (3.76mol%)	91
3	DAP	0.01g (4.35mol%)	93
4	TSP	0.02g (4.27mol%)	75

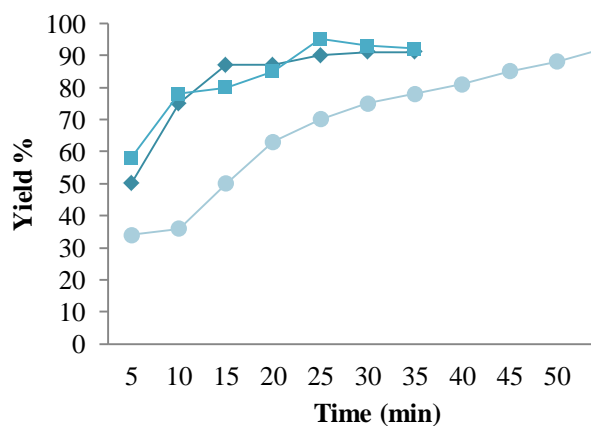
Reaction conditions : 3 mmol malononitrile, 2 mmol 4-chlorobenzaldehyde, (~4mol%) of catalysts, 3 ml EtOH, 30 min, t.a.

Optimization of reaction conditions for Knoevenagel condensation

The positive results obtained in the evaluation of the catalytic activity of phosphate fertilizers MAP, DAP, and TSP encouraged us to undertake a study on the influence of various parameters Knoevenagel condensation for each of the three catalysts. We, therefore, examined, respectively, the effect of reaction time, the effect of the catalyst amount, the effect of solvent, in an attempt to improve catalyst activity and to optimize the reaction conditions.

The effects of reaction time

The kinetic study of the synthesis of 4-chlorobenzylidenemalononitrile according to the reaction time showed that the conversion of 4-chlorobenzaldehyde increases gradually as the reaction time increases until equilibrium is reached within 30 min for MAP catalyst, 25 min for DAP catalyst and 60 min for TSP catalyst (Figure 4).



Influence of different catalyst amounts

To determine the optimal amount of each catalyst MAP, DAP, and TSP for the Knoevenagel condensation, we took the 4-chlorobenzaldehyde as a model substrate and then we have generalized the results to other aromatic aldehydes. Reaction of 4-chlorobenzaldehyde with malononitrile was performed on each of the catalysts by varying the mass of 0.01 g to 0.04 g. Figure 5 shows that the catalysts are active from an amount equal to 10 mg and that increasing the amount of the catalyst has no effect on improving the conversion of the benzaldehyde, since the reaction product yields remain almost constant. A remarkable increase in the reaction yield was observed for the TSP catalyst by varying the amount of catalyst from 0.01 to 0.02 g. Thus, 0.01 g of catalysts MAP and DAP, and 0.02 g of the catalyst TSP were chosen as the optimized amounts of these catalysts for the rest of our experiments.

Figure 4. Optimization of reaction time for Knoevenagel condensation of 4-chlorobenzaldehyde with malononitrile

Reaction conditions: 3 mmol malononitrile, 2 mmol 4-chlorobenzaldehyde, ~4mol% (0.01g MAP, 0.01g DAP, 0.02g TSP) of catalyst, 3 ml EtOH, t.a.

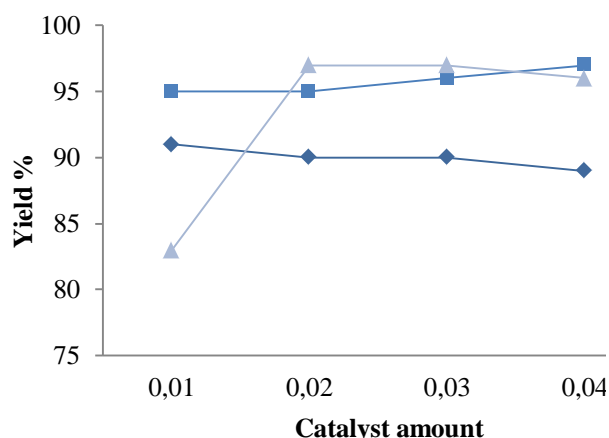


Figure 5. Optimization of amount of catalyst for Knoevenagel condensation of 4-chlorobenzaldehyde with malononitrile.

Reaction conditions: 3mmol malononitrile, 2 mmol 4-chlorobenzaldehyde, 3 ml EtOH, t.a.; Reaction time for MAP: 30min, DAP: 25 min and TSP: 60 min.

The effects of solvent on the reaction

To construe the solvent effects for these fertilizers, we performed the reaction in different solvents (Figure 6). It was observed that the catalysts have the highest activity in ethanol and methanol which are protic and polar solvents, by contrast,

aprotic and less polar solvents, including THF, CH₃CN and dioxane are not good media.

The effects can be explained probably by the stabilization of the charged transition-state complex of the Knoevenagel reaction by polar solvents⁶⁶. In fact, strong effects of solvent polarity have been observed for catalytic Knoevenagel reactions³².

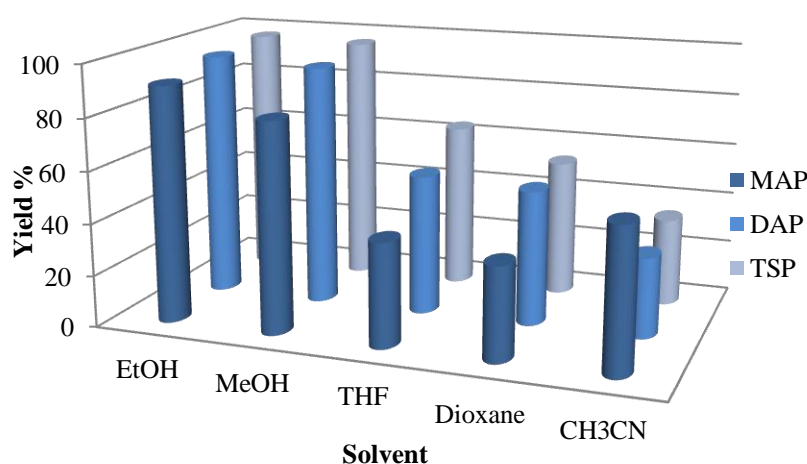


Figure 6. Optimization of solvent reaction for Knoevenagel condensation of 4-chlorobenzaldehyde with malononitrile.

Reaction conditions: 3 mmol malononitrile, 2 mmol 4-chlorobenzaldehyde, 3 ml Solvent, t.a.; Cat. MAP: 0.01g, 30 min; Cat. DAP: 0.01g, 25 min; Cat. TSP: 0.02g, 60 min.

The effects of particle size

Different fractions of catalysts MAP, DAP, and TSP with precise particle sizes have been used to examine their activity on the reaction. The results shown in Table 2 indicate that the catalysts maintain

their catalytic activity even when used directly in commercial form (Particle size less than 120 μm). It should be noted, however, that the best yields were obtained by the fraction 71 to 10 μm.

Table 2. Comparison between the different fractions of catalysts MAP, DAP, and TSP.

Reactants ^(a)	Particle size range	Yield %		
		MAP ^(b)	DAP ^(c)	TSP ^(d)
1a + 2	< 120 μm	89	88	84
1a + 2	71-10 μm	91	95	97
1a + 2	90-71 μm	90	93	87
1a + 2	120-90 μm	87	91	85

Reaction conditions: (a) 3mmol malononitrile, 2 mmol 4-chlorobenzaldehyde, 3 ml EtOH, t.a., (b) 0.01 g, 30min ; (c) 0.01 g, 25 min ; (d) 0.02 g, 60 min.

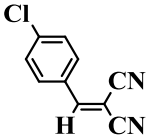
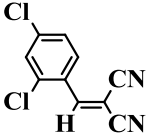
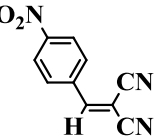
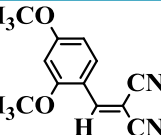
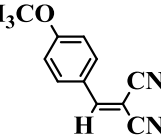
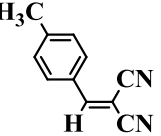
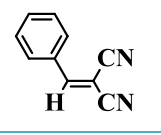
Results of Knoevenagel condensation of benzaldehydes using MAP, DAP, and TSP at optimum conditions

After optimization of the reaction conditions, the condensation of malononitrile with various aldehydes was examined in the presence of almost 4

mol% of catalyst at room temperature in 3 ml of ethanol as solvent, in order to assess the scope and the generality of the catalysts. The results are

displayed in Table 3. As it is shown, a large difference in the yields of the reaction appears in the presence of MAP, DAP, and TSP catalysts.

Table 3. Knoevenagel condensation of aromatic aldehydes using MAP, DAP, and TSP at optimum conditions.

Entry	Structure	Catalyst	Yield %	mp °C
3a		MAP	91	161-2
		DAP	95	
		TSP	97	
		Blank	55	
3b		MAP	96	152-4
		DAP	95	
		TSP	91	
		Blank	31	
3c		MAP	94	159-160
		DAP	97	
		TSP	92	
		Blank	44	
3d		MAP	66	141-2
		DAP	83	
		TSP	72	
		Blank	25	
3e		MAP	51	113-4
		DAP	72	
		TSP	63	
		Blank	18	
3f		MAP	73	133-4
		DAP	84	
		TSP	67	
		Blank	42	
3g		MAP	71	80-1
		DAP	92	
		TSP	77	
		Blank	29	

Recyclability studies of MAP, DAP, and TSP

The ability of catalyst to be recycled was also evaluated in this work. The study was performed after determination of optimum reaction conditions.

The results are shown in Figure 7. This study revealed that the catalysts could be reused without considerable decrease in their catalytic activities.

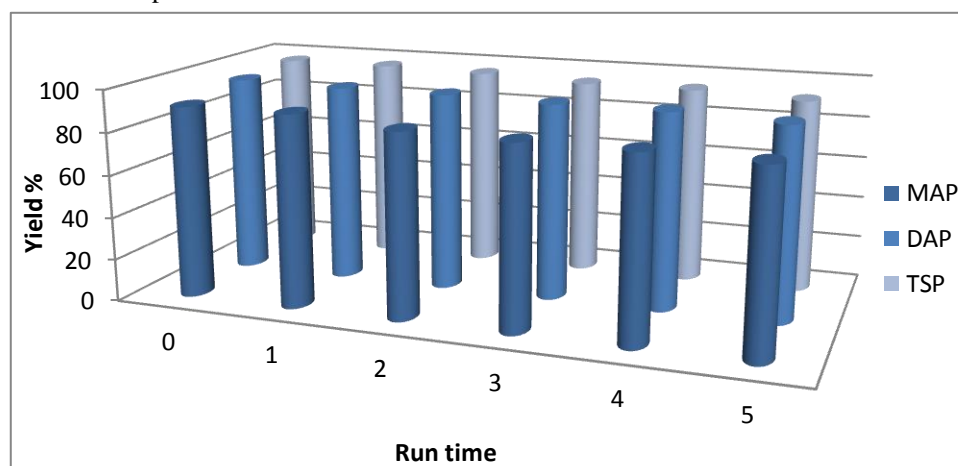


Figure 7. Recyclability of catalysts MAP, DAP, and TSP at optimum reaction conditions.

Conclusion

Fertilizers MAP, DAP, and TSP served as excellent catalysts in the reaction of Knoevenagel, as shows the object of our study. We will generalize their use in other organic reactions cited in the literature.

The use of fertilizers MAP, DAP, and TSP opens a new way of strategy of organic synthesis by the use of many other fertilizers.

These novel heterogeneous catalysts are not only cheap and easily available but exhibit remarkable catalytic activity and good recyclability.

In this regard, the catalysis from fertilizers might be an effective method to solve the drawbacks of expensive catalysts.

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