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 malonitrile at room temperature. These minerals 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 NH₄H₂PO₄/SiO₂ 17, NH₄H₂PO₄/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 NaNO₃/NP 20, KF/HAP and NaNO₃/HAP 21 and Na₂CaP₂O₇ 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-SiO₂ 49, polyethyleneimine-SiO₂ 50 and Ni-SiO₂ 51, potassium-loaded MgAl oxide nK-MgAl(O)₅ 52, urea derivative 53, zeolites 34-36 and lipase 54-56.

According to our humble knowledge, synthetic NH₄H₂PO₄ 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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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 (\(H_3PO_4\)) \(^{61,62}\) (Scheme 1).

\[
\begin{align*}
\text{NH}_3 (g) & \quad + \quad \text{H}_3\text{PO}_4 (aq) \quad \rightarrow \quad \text{NH}_4\text{H}_2\text{PO}_4 (s) \\
2 \text{NII}_3 (g) & \quad + \quad \text{H}_3\text{PO}_4 (aq) \quad \rightarrow \quad (\text{NH}_4)_2\text{H}_2\text{PO}_4 (s)
\end{align*}
\]

**Scheme 1.** Synthesis of MAP and DAP from ammonia

The basic chemical reactions involved in TSP manufacture from the Phosphate rock \(^{63}\) are shown in scheme 2.

\[
\begin{align*}
\text{Ca}_3(\text{PO}_4)_2 & \quad + \quad 4 \text{H}_3\text{PO}_4 & \quad + \quad \text{H}_2\text{O} \quad \rightarrow \quad 10 \text{CaSO}_4\cdot2\text{H}_2\text{O} & \quad + \quad 3 \text{Ca}(\text{H}_2\text{PO}_4)_{2}\cdot\text{H}_2\text{O} \\
\text{Ca}_{16}\text{F}_2(\text{PO}_4)_6 & \quad + \quad 14 \text{H}_3\text{PO}_4 & \quad + \quad 10 \text{H}_2\text{O} \quad \rightarrow \quad 10 \text{CaSO}_4\cdot2\text{H}_2\text{O} & \quad + \quad 10 \text{Ca}(\text{H}_2\text{PO}_4)_{2}\cdot\text{H}_2\text{O} & \quad + \quad 2 \text{HF}
\end{align*}
\]

**Scheme 2.** Synthesis of TSP from Phosphate rock.

**Experimental Section**

**Materials**

Different fertilizers used are marketed as \(^{61}\):
- Mono-Ammonium Phosphate: MAP 11-52-00, binary Fertilizer, complex granule with Nitrogen: 11 % N and Phosphorus: 52 % P\(_2\)O\(_5\).
- Di-Ammonium Phosphate: DAP 18-46-00, binary Fertilizer, complex granule with Nitrogen: 18 % N and Phosphorus: 46 % P\(_2\)O\(_5\).
- Triple Super Phosphate: TSP 00-46-00, simple granule Fertilizer with Phosphorus: 46 % P\(_2\)O\(_5\).

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 (\(\lambda = 1.54178 \text{ Å} \)).

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 (3 mmol) 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>
<thead>
<tr>
<th>Fraction number</th>
<th>Particle size range</th>
<th>Medium diameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10-71 µm</td>
<td>53.5 µm</td>
</tr>
<tr>
<td>2</td>
<td>71-90 µm</td>
<td>80.5 µm</td>
</tr>
<tr>
<td>3</td>
<td>90-120 µm</td>
<td>105 µm</td>
</tr>
</tbody>
</table>

**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

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 λ = 1.5418 Å.

The diffractogram of X-ray (Figure 1) presents characteristic peaks of pure synthesized MAP. Its crystal structure was found to be tetragonal in the space group I-42d with lattice parameters of a = b = 7.5021 Å, and c = 7.5541 Å.

![Figure 1. X-ray diffraction pattern of MAP fertilizer](image)

SEM spectroscopy

![Figure 2(a). SEM images of MAP fertilizer](image)

![Figure 2(b). SEM images of DAP fertilizer](image)
With respect to the particle size, the SEM micrographs in Figure 2 (a), (b), and (c) display 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. The EDXA spectrum also showed the presence of Ca in the TSP fertilizer, which confirms its chemical composition.

**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).
Scheme 3. Knoevenagel condensation of aromatic aldehydes with malononitrile.

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

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Catalyst amount (mol%)</th>
<th>Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Blank</td>
<td>-</td>
<td>55</td>
</tr>
<tr>
<td>2</td>
<td>MAP</td>
<td>0.01 g (3.76 mol%)</td>
<td>91</td>
</tr>
<tr>
<td>3</td>
<td>DAP</td>
<td>0.01 g (4.35 mol%)</td>
<td>93</td>
</tr>
<tr>
<td>4</td>
<td>TSP</td>
<td>0.02 g (4.27 mol%)</td>
<td>75</td>
</tr>
</tbody>
</table>

Reaction conditions: 3 mmol malononitrile, 2 mmol 4-chlorobenzaldehyde, (~4 mol%) 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, ~4 mol% (0.01 g MAP, 0.01 g DAP, 0.02 g 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: 3 mmol malononitrile, 2 mmol 4-chlorobenzaldehyde, 3 ml EtOH, t.a.; Reaction time for MAP: 30 min, 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 solvents. In fact, strong effects of solvent polarity have been observed for catalytic Knoevenagel reactions.

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: 0.01 g, 30 min; Cat. DAP: 0.01 g, 25 min; Cat. TSP: 0.02 g, 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.

<table>
<thead>
<tr>
<th>Reactants(a)</th>
<th>Particle size range</th>
<th>Yield %</th>
<th>MAP(b)</th>
<th>DAP(c)</th>
<th>TSP(d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a + 2</td>
<td>&lt; 120 µm</td>
<td>89</td>
<td>88</td>
<td>84</td>
<td></td>
</tr>
<tr>
<td>1a + 2</td>
<td>71-10 µm</td>
<td>91</td>
<td>95</td>
<td>97</td>
<td></td>
</tr>
<tr>
<td>1a + 2</td>
<td>90-71 µm</td>
<td>90</td>
<td>93</td>
<td>87</td>
<td></td>
</tr>
<tr>
<td>1a + 2</td>
<td>120-90 µm</td>
<td>87</td>
<td>91</td>
<td>85</td>
<td></td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Entry</th>
<th>Structure</th>
<th>Catalyst</th>
<th>Yield %</th>
<th>mp °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td><img src="image1.png" alt="Structure" /></td>
<td>MAP</td>
<td>91</td>
<td>161-2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DAP</td>
<td>95</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>TSP</td>
<td>97</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Blank</td>
<td>55</td>
<td></td>
</tr>
<tr>
<td>3b</td>
<td><img src="image2.png" alt="Structure" /></td>
<td>MAP</td>
<td>96</td>
<td>152-4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DAP</td>
<td>95</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>TSP</td>
<td>91</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Blank</td>
<td>31</td>
<td></td>
</tr>
<tr>
<td>3c</td>
<td><img src="image3.png" alt="Structure" /></td>
<td>MAP</td>
<td>94</td>
<td>159-160</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DAP</td>
<td>97</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>TSP</td>
<td>92</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Blank</td>
<td>44</td>
<td></td>
</tr>
<tr>
<td>3d</td>
<td><img src="image4.png" alt="Structure" /></td>
<td>MAP</td>
<td>66</td>
<td>141-2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DAP</td>
<td>83</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>TSP</td>
<td>72</td>
<td></td>
</tr>
<tr>
<td></td>
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<td>25</td>
<td></td>
</tr>
<tr>
<td>3e</td>
<td><img src="image5.png" alt="Structure" /></td>
<td>MAP</td>
<td>51</td>
<td>113-4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DAP</td>
<td>72</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>TSP</td>
<td>63</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Blank</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td>3f</td>
<td><img src="image6.png" alt="Structure" /></td>
<td>MAP</td>
<td>73</td>
<td>133-4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DAP</td>
<td>84</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>TSP</td>
<td>67</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Blank</td>
<td>42</td>
<td></td>
</tr>
<tr>
<td>3g</td>
<td><img src="image7.png" alt="Structure" /></td>
<td>MAP</td>
<td>71</td>
<td>80-1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DAP</td>
<td>92</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>TSP</td>
<td>77</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Blank</td>
<td>29</td>
<td></td>
</tr>
</tbody>
</table>

**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.
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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