Catalysis by phosphates: A simple and efficient procedure for transesterification reaction

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Abstract

Zinc chloride and potassium fluoride doped on natural phosphate (ZnCl₂/NP and KF/NP) and sodium nitrate modified natural phosphate (Na/NP) catalyze efficiently the transesterification reaction. The reaction proceeds in refluxing condition without remove of alcohol formed. Na/NP can be easily regenerated and reused.
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1. Introduction

Heterogeneous catalysis is widely applied in the organic synthesis. The transformation of homogeneous catalysis to heterogeneous catalysis, by supporting of the catalyst or by developing alternative solid catalysts, is a constant trend of the chemists. The nature of the support can exert a significant influence on the catalytic process. The activity enhancement is generally due to the intimate contact between the supported ions and the support surface. In recent decade, the use of natural phosphate (NP) in the organic transformation has been under attention [1–5] because this solid has several advantages, as it is cheap, readily available, stable, non-toxic, not a pollutant and recoverable and reusable. We have shown that its mild basic and acid properties can be exploited in many synthetic applications [1–5]. To improve the basic and acid activity of NP, we have doped it by zinc chloride (ZnCl₂/NP) and potassium fluoride (KF/NP) and modified by sodium nitrate (Na/NP). These new phosphates catalysts have been used to afford various organic transformations. Thus ZnCl₂/NP has been used as excellent acidic catalyst for Friedel-Crafts alkylation [6], 1,3-dipolar cycloaddition [7], acyclonucleoside synthesis [8] and 3,4-dihydropyrimdin-

2(*1H*)-one synthesis [9]. KF/NP catalyzed efficiently nitrile hydration [10], Michael addition [4,11–13], Knoevenagel condensation [5,14], flavanone synthesis [15], nucleobase alkylation [16] and nucleoside synthesis [17]. On the other hand, we have demonstrated that Na/NP, as strongly basic catalyst, can promote Knoevenagel condensation [14], alkene epoxidation [18], Claisen-Schmidt condensation [19,20] and Michael addition [21].

In continuation of our efforts to develop clean methods using Na/NP, KF/NP and ZnCl₂/NP as catalysts in organic synthesis, we decided to investigate its catalytic activity in the transesterification reaction. This reaction is an important organic transformation and provides essential synthons for a number of complex natural products, pheromones and additives for paints [22].

Acids and bases are known to accelerate the rate of transesterification. In this regard, various catalysts have been recently reported to effect this reaction as indium triiodide [23], diphenylammonium triflate [24], amberlyst-15 [25] yttria–zirconia [26] Mo-ZrO₂ [27], lithium perchlorate [28], polymer-supported lipase [29], envirocat EPZG [30], hydrotalcite [31], clays [32] and zeolites [33]. Some of these catalysts are difficult to prepare and toxic. Recently, we have shown that natural phosphate alone can catalyze the transesterification reaction [34].

Here, we report on the efficient heterogeneous transesterification between a methyl benzoate **1** and various alcohols **2** using ZnCl₂/NP, KF/NP and Na/NP as catalysts (Scheme 1).
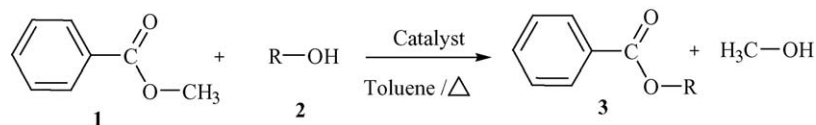
Scheme 1.

2. Experimental

2.1. Preparation and structural characteristics of the catalysts

2.1.1. NP

Natural phosphate (NP) used in this work was obtained in the Khouribga region (Morocco). Prior to use this material requires initial treatments such as crushing and washing. For use in organic synthesis, the NP is treated by techniques involving attrition, sifting, calcinations (900 °C), washing, and recalcination. These treatments lead to a fraction between 100 and 400 μm that is rich in phosphate and has the following chemical composition P (34.24%), Ca (54.12%), F (3.37%), Si (2.42%), S (2.21%), C (1.13%), Na (0.92%), Mg (0.68%), Al (0.46%), Fe (0.36%), K (0.04%) and several metals (Zn, Cu, Cd, Cr, ...) in the range of ppm. The structure of NP is similar to that of fluoroapatite ($Ca_{10}(PO_4)_6F_2$). In sedimentary rocks, phosphates are formed from compounds derived from apatite by partial isomorphic substitution: Ca^{2+} ions by Na^+, Mg^{2+}, Co^{2+}, Fe^{3+}, or Al^{3+}, PO_4^{3-} ions by VO_4^{3-}, SO_4^{2-}, CO_3^{2-} or MnO_4^-, and F^- by HO^- or Cl^-. These different substitutions cause distortions of the structure which depends on the nature and the radii of the ions involved. NP presents a very low surface area (BET, $1.4 \, m^2 \, g^{-1}$) as well as a total pore volume (BJH, $0.0055 \, cm^3 \, g^{-1}$).

2.1.2. ZnCl₂/NP

The preparation of $ZnCl_2$/NP was as follows: 10 mmol of $ZnCl_2$ and 10 g of NP were mixed in 100 mL of water and then evaporated to dryness and dried for 2 h at 150 °C before use. The modification of the apatite structure solid by $ZnCl_2$ impregnation does not change the crystalline structure of the solid material. It should be noted that no $ZnCl_2$ phases were detected on the doped materials, indicating that $ZnCl_2$ were highly dispersed in the solid. The surface area (BET, $1.3 \, m^2 \, g^{-1}$) and total pore volume (BJH, $0.0045 \, cm^3 \, g^{-1}$) of $ZnCl_2$/NP are similar to that of NP. Interestingly, some changes of structure of doped catalysts were observed in scanning electron micrographs (SEM). Thus, the comparison of the images of $ZnCl_2$/NP with NP (Fig. 1) shows some modification in the particle morphology of doped materials. This result suggests that $ZnCl_2$ interacted with the surface of NP.

2.1.3. KF/NP

KF/NP has been prepared by adding NP (8 g) to aqueous solution of KF (1 g). The mixture stirred, evaporated to dryness and dried at 150 °C for 2 h. The IR data shows the presence of some additional H-bonded water at $3250 \, cm^{-1}$ and $1636–1675 \, cm^{-1}$ for the supported solid. The X-ray diffraction of KF/NP gives a diffraction pattern almost identical to that of NP itself [15]. It appears that the basic structure of NP is not destroyed, indicating a less profound interaction of KF with NP than is the case with alumina.

2.1.4. Na/NP

Na/NP was prepared by adding a mass (m_0) of natural phosphate to an aqueous solution of a mass ($m_0/2$) of sodium nitrate. The mixture was stirred vigorously at room temperature, evaporated to dryness and dried at 100 °C for 2 h. The solid obtained was calcined for 1 h to give a new modified phosphate. The X-ray diffraction pattern of the modified phosphate calcined at 900 °C, showed the apparition of two new phases witch can be attributed to sodium phosphate and calcium oxide [20]. This phenomenon can be due to possible reaction in the solid state between sodium nitrate and natural phosphate. The surface area and total pore volume of Na/NP calcined at 900 °C are low ($0.66 \, m^2 \, g^{-1}$ and $0.0045 \, cm^3 \, g^{-1}$, respectively). It is clear that this solid is basic, as indicated by its catalytic activity, observed in the epoxidation of electron-deficient alkenes with H_2O_2 [18], a reaction that needs the presence of basic centers.
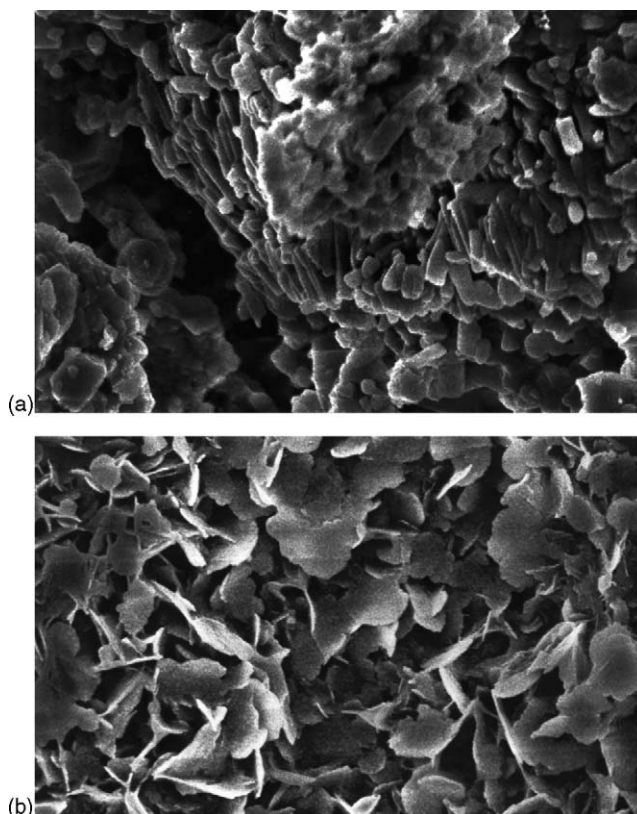
Fig. 1. Scanning electron micrograph (SEM) images of (a) NP and (b) ZnCl₂/NP.

2.2. General procedure for the transesterification reaction

A mixture of the methyl benzoate **1** (2 mmol), butanol (11 mmol) and catalyst (0.1 g) in the toluene (3 mL) was refluxed for the specified time. The progress of the reaction was monitored by G.C. Workup comprises of the simple filtration followed by evaporation under reduced pressure and purified by column chromatography (hexane/ethylacetate, 98/2, V/V) to afford **3**. The product was analyzed by ^{1}H NMR spectroscopy.

3. Results and discussion

Reaction of methyl benzoate and butanol was chosen as the model reaction to evaluate the catalytic activity of phosphate materials. The kinetic curves of these reactions as shown in Fig. 2 indicate clearly the promoting effect of all doped and modified phosphates. In this reaction, Na/NP and ZnCl$_2$/NP appears to be relatively more active than KF/NP. In the absence of any catalyst, the desired butyl benzoate (**3c**) was obtained in a very low yield 14% even after being stirred for 2 days.

For second evaluation we examined the weight effect of the phosphates in this reaction. Because KF/NP is low reactive, in this reaction, than Na/NP and ZnCl$_2$/NP, we have used 6 h (Fig. 3) and 4 h (Fig. 4) of reaction time, respectively. The conversion of methyl benzoate **1** increased as catalyst weight increased. This result indicates the positive effect of the catalyst in this transformation. We have chosen 0.1 g of the catalyst for further study in order to avoid diffusion control of reactions at increased catalysts weights.

We have carried out some control experiments in order to verify that the reaction is a heterogeneous one. Thus, we carried out the reaction as follows: 0.1 g of KF/NP was added to a mixture of butanol (11 mmol) and toluene (5 mL) and was refluxed during 4 h, then the solid catalyst was separate and methyl benzoate (2 mmol) was added to the liquid phase and was still heated during 12 h, then the reaction was continued as indicated in the Section 2. The butyl benzoate was isolated with a yield of 37% while 93% were obtained in heterogeneous medium. This result indicates that the reaction was essentially heterogeneous.
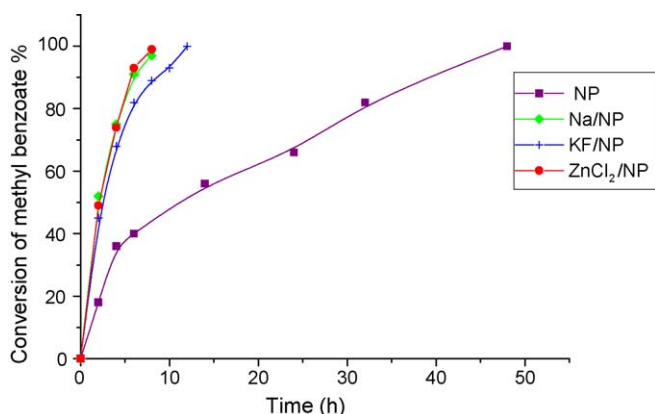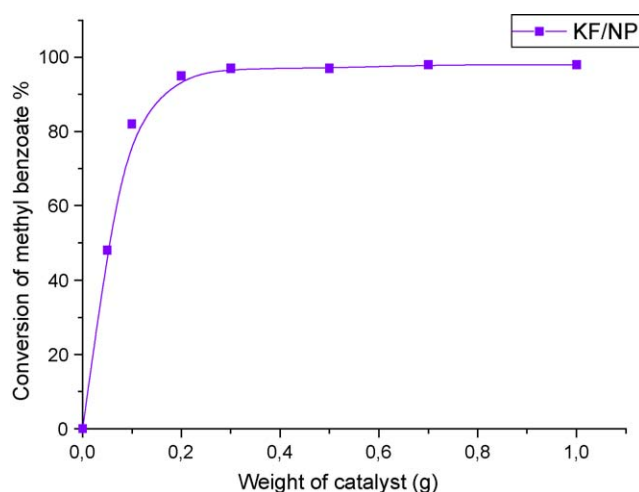

Fig. 3. Weight effect of KF/NP in the synthesis of product **3c** (6 h).

In the other hand, we have carried out the transesterification of methyl benzoate with butanol in presence of 0.0125 g of KF (the same quantity of KF contained in 0.1 g of KF/NP). The yield obtained after refluxing for 12 h was 56%.

Furthermore, we have tested the transesterification of methyl benzoate in presence of KF/NP using a methanol removal process. In this case, the methanol was continuously distilled away and the reaction became much faster, the total conversion (91% yield of isolated product) was obtained after only 3 h of reaction time.

The increase in activity of Na/NP is attributed to the apparition of new phases. These phases appear after calcination of Na/NP at 900 °C, because of the decomposition of nitrate. It should be noted that the use of other calcination temperatures (treatment at 150, 300 and 500 °C) led to catalysts with poor activities (Table 1).

To evaluate the use and regeneration of phosphates catalysts, we have carried out the synthesis of ester **3c** using Na/NP and ZnCl$_2$/NP in toluene and 8 h of reaction time. The isolated

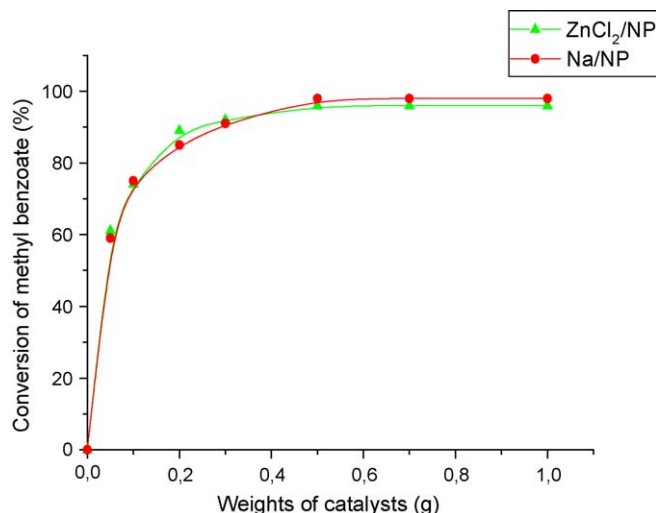Fig. 2. Kinetic curves of the ester **3c** synthesis catalysed by NP, KF/NP, ZnCl$_2$/NP and Na/NP.

Fig. 4. Weight effect of Na/NP and ZnCl$_2$/NP in the synthesis of product **3c** (4 h).

Table 1
Reaction of methylbenzoate and butanol catalysed by $NaNO_3/NP$ calcined at various temperatures

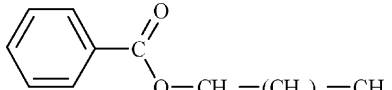| Temperature of calcinations of $NaNO_3/NP$ (°C)	150	300	500	900
Conversion of **1** after 8 h of reaction time (%)	38	40	35	97
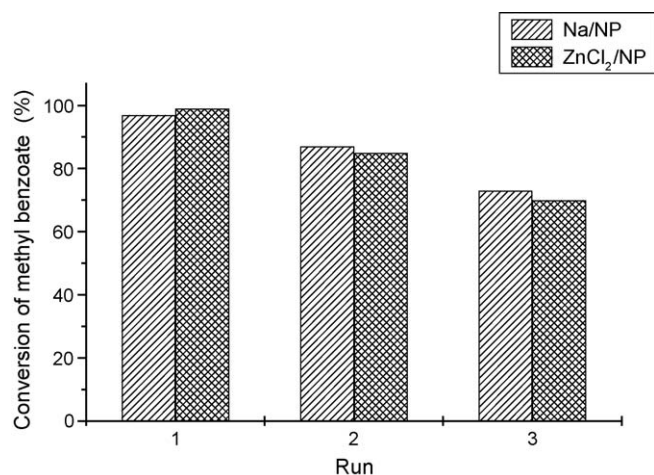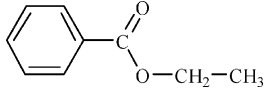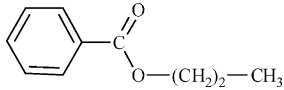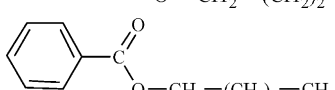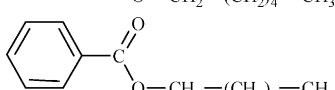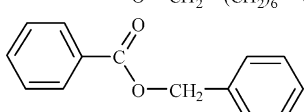
Fig. 5. Reusability of Na/NP and $ZnCl_2/NP$ catalysts in the synthesis of ester **3c**.

Fig. 6. Recycling of the Na/NP catalyst in the synthesis of **3c**.

catalyst was washed with dichloromethane and dried at 150 °C for 2 h before reuse. For both catalysts (Fig. 5), the conversion of methyl benzoate decreases slowly. This result demonstrates that the catalyst can be reused for tree time with a low cost of the activity.

It should be noted that the activity was almost completely recovered when the catalyst Na/NP was washed with dichloromethane and calcined at 900 °C for 1 h. Investigations by using methyl benzoate and butanol as model substrates showed that successive reuse of the recovered catalyst in the same reaction gave the product with a yield almost as high as that of the first cycle (Fig. 6).

The results for variety of ester prepared by the conversion of methyl benzoate catalyzed by NP, KF/NP, $ZnCl_2/NP$ and Na/NP are summarized in Table 2. It's shown that NP used in toluene can promote the transesterification reaction with moderate to good conversions. The same conversions of methyl benzoate were obtained when we carried out the reaction without solvent (toluene). The reaction is relatively slow and needs a long time

Table 2
Synthesis of products **3** by transesterification using NP, Na/NP, $ZnCl_2/NP$ and KF/NP as catalysts

Entry		Products	Conversion of ester **1** (%) [time (h)][a]			
			NP	Na/NP	$ZnCl_2/NP$	KF/NP
1	**3a**	(benzoate) $O-CH_2-CH_3$	57 (48)	72 (8)	41 (8)	79 (12)
2	**3b**	(benzoate) $O-(CH_2)_2-CH_3$	74 (48)	76 (8)	75 (8)	80 (12)
3	**3c**	(benzoate) $O-CH_2-(CH_2)_2-CH_3$	100 (48)	97 (8)	99 (8)	100 (12)
4	**3d**	(benzoate) $O-CH_2-(CH_2)_4-CH_3$	97 (48)	97 (8)	98 (8)	99 (12)
5	**3e**	(benzoate) $O-CH_2-(CH_2)_6-CH_3$	98 (48)	99 (8)	99 (8)	99 (12)
6	**3f**	(benzoate) $O-CH_2-$(phenyl)	100 (48)	98 (8)	97 (8)	98 (12)

to afford the total conversion. However, under the same conditions used for NP, the use of NP doped with KF, $ZnCl_2$ and modified with $NaNO_3$ remarkably increases the catalytic activity and decreases the reaction time. Products **3a** and **3b** were isolated with moderate to good yield whereas total conversion was obtained with **3c–f**. The difference of conversion can be caused by the low boiling point of ethanol and propan-1-ol. It is worth noting that no conversion was observed using isopropanol and terbutanol. The secondary and tertiary alcohols are known to be low reactive than primary alcohols. $ZnCl_2$/NP and Na/NP gave similar results in terms of reaction time and conversions except for the product **3a**, and seem to be more reactive than KF/NP. A facile regeneration and reuse of Na/NP gives this catalyst some advantages.

We believe that these efficient doped and modified phosphates $ZnCl_2$/NP, KF/NP and Na/NP represent an important breakthrough in the development of solid catalysts. The high reactivity of these catalysts coupled with their ease of use makes them attractive alternatives to homogeneous acidic and basic reagents.

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