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Sodium/fluorapatite as a new solid support for the synthesis of α,β-unsaturated arylsulfones

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The fluorapatite, both alone and doped with sodium nitrate, is a new basic catalyst for synthesis of α,β-unsaturated arylsulfones. Activation by water and benzyltriethylammonium chloride has also been investigated. When using an ammonium salt, fluorapatite modified with sodium nitrate is an excellent solid support for synthesis of α,β-unsaturated arylsulfones, leading to excellent yields in a few minutes.

KEY WORDS: fluorapatite; heterogeneous catalysis; arylsulfones; Knœvenagel; recyclable catalyst.

1. Introduction

The sulfones are important intermediates in organic synthesis [1]. Their importance is due to the fact that arylsulfonyl groups can stabilise adjacent carbanions [2] and may easily be removed by hydrolysis, reduction or elimination [3]. When it is appropriate, such groups can be eliminated to introduce carbon–carbon double bonds into organic molecules [4]. Thus they are useful temporary activating groups for alkylation [5], acylation [6] and addition reactions [7].

The Knœvenagel condensation of arylsulfones and aldehydes is a convenient route to the synthesis of unsaturated arylsulfones [8]. This condensation is normally carried out in the presence of a strong base to remove the somewhat acidic or "active" hydrogen atom. Often sodium hydride [9], butyl lithium [10] or lithium di-isopropylamide (LDA) [11] are used as the base. However, the deprotonation strongly depends on the presence of adjacent electron-withdrawing groups such as ester [2], nitrile or ketone [12]. Of late there has been of interest in carrying out synthetic organic reactions under conditions which do not require separation of the product from other organic materials (such as the base), which are fast, effective and which do not require heating or the use of large quantities of solvent.

In attempt to meet these conditions for the Knœvenagel reaction, attention has turned to the use of heterogeneous catalysts which can be removed from the reaction mixture by filtration. Zeolites [13], organic resins [14], mixed magnesium–aluminium oxides derived from hydrotalcites [15], sepiolites [16], aluminophosphonates oxynitrides (ALPON) [17], phosphate synthetic $Na_2CaP_2O_7$ [18] and more recently, natural phosphate both alone and doped with potassium fluoride [19] have been tested with success.

In a recent work, we have shown that doping with mineral salts increases the activity of solid catalysts [20]. We have also shown that the catalytic is intimately related to the structure of the solid catalyst [21]. Other researchers have increased the effect of the catalyst with the addition of ultrasound [22] and microwave radiation [23].

Here, we present results related to the use of fluorapatite modified with sodium nitrate (Na/FAP) activated by water or benzyltriethylammonium chloride (BTEAC), in the Knœvenagel condensation between phenylsulfonylacetonitrile 2 and benzaldehyde or 4-substitued benzaldehydes 1, at room temperature (Scheme 1).

2. Experimental

2.1. Preparation and characterisation of fluorapatite (FAP)

The synthesis of FAP in powder state is carried out by means reaction between diammonium phosphate, calcium nitrate and ammonium fluoride in the presence of ammonia (Scheme 2).

Scheme 2

FAP was obtained by co-precipitation: 250 mL of a solution containing 7.92 g of diammonium hydrogen phosphate and 1 g of ammonium fluoride, maintained at pH greater than 12 by addition of ammonium hydroxide (15–20 mL), were dropped under constant stirring into 150 mL of a solution containing 23.6 g calcium nitrate ($Ca(NO_3)_2{\cdot}4H_2O$). The suspension was

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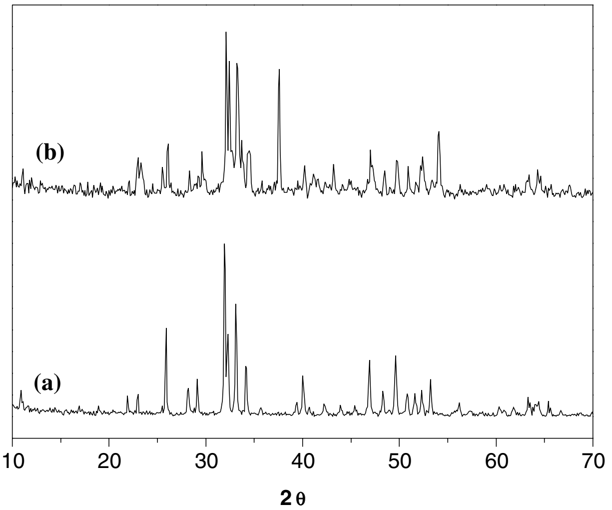

Figure 1. X-ray diffraction patterns of (a) FAP and (b) $NaNO_3$/FAP calcined at 900 °C.

refluxed for 4 h. Doubly distilled water (DDW) was used to prepare the solutions. The FAP crystallites were filtred, washed with DDW, dried overnight at 80 °C and calcined in air at 700 °C for 30 min before use. The final product is identified by X-ray diffraction (space group hexagonal system; $a = 9.364$ Å and $c = 6.893$ Å), infrared spectra IR and chemical analysis (Ca = 38.29%, P = 17.78% and Ca/P = 1.66). The BET specific surface area was found to be $S = 15.4$ m^2/g. The total pore volume was calculated by the BJH method at $P/P_0 = 0.98$ ($V_t = 0.0576$ cm^3/g).

2.2. Preparation and characterisation of Na/FAP

The modified FAP (Na/FAP = 1/2 w/w) was prepared by addition of FAP (10 g) to an aqueous sodium nitrate solution (50 mL, 1.17 M). The mixture was stirred at room temperature for 15 min and then the water evaporated under vacuum. The resulting solid was calcined under air at 900 °C. The XRD patterns of calcined Na/FAP showed the apparition of new phases, so the CaO phase ($2\theta = 32.2$, 37.5 and 54.0) is clearly identified (figure 1). Two new phases are probably $CaNaPO_4$ and $Na_2Ca_4(PO_4)_3F$ obtained by an exchange of sodium with calcium. No crystalline phases of Na_2O and CaF_2 were observed. The surface area of the new catalyst Na/FAP was determined by the BET method as $S = 5.4$ m^2/g and the total pore volume obtained by BJH method is 0.0032 cm^3/g.

2.3. General procedure for the syntheses of α,β-unsaturated arylsulfones (3a–e).

To a flask containing an equimolar mixture (1 mmol) of aldehyde **1** and phenylsulfonylacetonitrile **2** in solvent (methanol or ethanol : 1 mL), phosphate catalyst (FAP or Na/FAP) 0.1 g was added and the mixture was stirred at room temperature for a specified time (table 1). The reaction mixture was filtered and the catalyst washed with dichloromethane. After concentration of the filtrate under reduced pressure the residue was subjected to chromatography or distillation under vacuum leading to the Michael adduct as a solid. The same procedure was used for the reactions carried out with Na/FAP (0.1 g) activated with water or BTEAC (0.05 g). Water or BTEAC was always added in the last place, respectively. In the case of BTEAC, the products were washed with water to eliminate the ammonium salt before purification. The product structure was analysed by ^{1}H, ^{13}C-NMR, mass spectroscopy and IR spectrometry.

Table 1
Synthesis of products **3** by Knœvenagel condensation using FAP and Na/FAP

Entry	Products	R	Yield/% (time/h)[a]	
			FAP	Na/FAP
1	3a	H	78(48)	95(17)
2	3b	OMe	70(48)	91(17)
3	3c	Me	75(48)	93(17)
4	3d	Cl	80(16)	90(9)
5	3e	NO_2	92(6)	92(2)

[a] Yields of pure products isolated by distillation under vacuum and identified by ^{1}H, ^{13}C-NMR, mass spectroscopy and IR spectroscopy.

^{1}H and ^{13}C-NMR spectra were recorded at 400 and 100 MHz, respectively, on a Bruker DRX-400 spectrometer in $CDCl_3$, using $CDCl_3$ as internal standard. The chemical shifts (δ) are expressed in ppm relative to $CDCl_3$ and coupling constant (*J*) in Hertz. Mass spectra were obtained on VG ZAB-HS mass spectrometer. IR spectra were obtained on a FTIR (ATI Mattson-Genesis Series) and reported in wave numbers (cm^{-1}). Surface area and pore size analysis were carried out at 77 K on a Micromeritics ASAP2010 instrument using nitrogen as adsorbent. X-ray diffraction patterns of the catalysts were obtained on a Philips 1710 diffractometer using CuK$_\alpha$ radiation and SEM images were taken on a Hitachi S-2400 microscope. Melting points were determined with a "Thomas Hoover" melting (capillary method) apparatus and are uncorrected. Flash column chromatography was performed using Merck silica gel 60 (230–400 mesh ASTM).

All reactions were carried out under atmosphere air. Solvents and starting materials (Aldrich) were used without further purification.

2.4. Spectroscopic-spectrometry data of the reaction products

α-Phenylsulfonyl cinnamonitrile, 3a. White solid; mp 130–132 °C; R_f (20% AcOEt/hexane) 0.46; ^{1}H-NMR ($CDCl_3$) δ: 8.24 (1H, s, =C*H*); 8.03 (2H, d, $J = 8.4$ Hz, *H*Ar); 7.92 (2H, d, $J = 8.8$ Hz, *H*Ar); 7.74–7.70 (1H, m, *H*Ar); 7.64–7.57 (3H, m, *H*Ar); 7.50 (2H, t, $J = 8.0$ Hz, *H*Ar). ^{13}C-NMR ($CDCl_3$) δ: 151.5; 137.8; 134.6; 134.1;

131.0; 130.1; 129.7; 129.5; 128.7; 114.8; 113.1; $\nu_{\max}$ (KBr): 3031; 2218 ; 1578 cm^{-1}. *m/z* (EI): 271 (M^{2+}, 5), 269 (M^{+}, 63); 128 (100); 101 (10); 77 (100); 51 (36%); HRMS (EI): M,$^{+}$ found 269.0506. $C_{15}H_{11}NO_2S$ requires 269.0511.

α-Phenylsulfonyl 4-methoxycinnamonitrile, ***3b***. White solid; mp 113–115 °C; ^{1}H-NMR (CDCl$_3$) δ: 8.14 (1H, s, =C*H*Ar); 8.01 (2H, d, *J* = 7.6 Hz, *H*Ar); 7.92 (2H, d, *J* = 8.8 *Hz*, *H*Ar); 7.69 (1H, t, *J* = 7.6 Hz, *H*Ar); 7.60 (2H, t, *J* = 7.6 *Hz*, *H*Ar); 6.98 (2H, d, *J* = 8.8 Hz, *H*Ar); 3.89 (3H, s, OC*H*$_3$). ^{13}C-NMR (CDCl$_3$) δ: 164.5; 151.0; 138.5; 134.3; 133.7; 129.6; 128.4; 122.9 ; 115.0; 113.7; 110.9; 55.7. IR (KBr): 3022; 2218; 1589 cm^{-1}. *m/z* (EI): 301 (M^{2+}, 10); 299 (M^{+}, 44); 157 (100); 77 (33); 51 (10); 40 (16); HRMS (EI): M^{+}, found 299.06608. $C_{16}H_{13}NO_3S$ requires 299.0616.

α-Phenylsulfonyl 4-methylcinnamonitrile, ***3c***. White solid; mp 144–146 °C; ^{1}H-NMR (CDCl$_3$) δ: 8.20–7.20 (m, 9H, Ar*H* and 1H, *H*C=C); 2.4 (s, 3H, C*H*$_3$). ^{13}C-NMR (CDCl$_3$) δ: 159.0, 139.9, 138.2, 135.2, 132.4, 131.3, 131.2, 129.3, 129.2, 114.9, 99.1, 21.5. IR (KBr): 3030.75; 2226.83; 1596.48 cm^{-1}. *m/z* (EI): 285 (M^{2+}, 20); 283 (M^{+}, 100); 142 (29); 115 (27); 77 (100); HRMS (EI): M^{+}, found 283.0669. $C_{16}H_{13}NO_2S$ requires 283.0664.

α-Phenylsulfonyl 4-chlorocinnamonitrile, ***3d***. White solid; mp 152–154 °C; ^{1}H-NMR (CDCl$_3$) δ: 8.18 (1H, s, =C*H*Ar) ; 8.02 (2H, d, *J* = 8.8 *Hz*, *H*Ar) ; 7.87 (2H, d, *J* = 8.8 *Hz*, *H*Ar); 7.75–7.71 (1H, m, *H*Ar); 7.65–7.60 (2H, m, *H*Ar); 7.51–7.46 (2H, m, *H*Ar). ^{13}C-NMR (CDCl$_3$) δ: 149.9; 140.5; 137.6; 134.8; 132.1; 129.9; 129.5; 128.7; 128.5; 115.2; 112.9. IR (KBr): 3031; 2227; 1596 cm^{-1}. *m/z* (EI): 305 (M^{2+}, 30); 303 (M^{+}, 57); 162 (100); 126 (28); 77 (56); 51 (54); 40 (53); HRMS (EI): M^{+}, found 303.0117. $C_{15}H_{10}ClNO_2S$ requires 303.0126.

α-Phenylsulfonyl 4-nitrocinnamonitrile, ***3e***. White solid; mp 140–142 °C; ^{1}H-NMR(CDCl$_3$) δ: 8.34 (2H, d, *J* = 8.8 Hz, *H*Ar); 8.30 (1H, s, =C*H*Ar); 8.08 (2H, d, *J* = 8.8 Hz, *H*Ar); 8.04 (2H, d, *J* = 7.6 Hz, *H*Ar); 7.77 (1H, t, *J* = 7.6 Hz, *H*Ar). ^{13}C-NMR (CDCl$_3$) δ: 151.0; 148.0; 137.4; 136.0; 135.2; 131.5; 129.9; 129.0; 124.5; 115.5; 112.3. IR (KBr) : 3112.97; 2217.69 ; 1596.48 cm^{-1}. *m/z* (EI): 314 (M^{+}, 13); 181 (5); 141 (53); 77 (100); 51 (22); 40 (36%); HRMS (EI): M^{+}, found 314.0345. $C_{15}H_{10}N_2O_4S$ requires 314.0361.

3. Results and discussions

The results for a variety of α,β-unsaturated arylsulfones prepared by Knœvenagel condensation catalysed by FAP and Na/FAP are summarised in table 1. In general the use FAP alone as heterogeneous catalyst in the Knœvenagel reaction allowed the isolation of α-phenylsulfonyl cinnamonitrile with modest yields (table 1). The yields seem to be limited even if the time of the reaction is prolonged. However, for all cases the reaction rate is very long. Only the isomer of configuration *E* has been isolated [18,19].

To improve the reactivity of the FAP, we used sodium nitrate supported on FAP in different proportions. To determine the best weight report (*r* = NaNO$_3$/FAP), we carried out the synthesis of α,β-unsaturated arylsulfone **3a** at room temperature using the weight report of *r* = 0.1; 0.25; 0.5; 0.75 and 1. The best yield in unsaturated arylsulfone *3a* is obtained with *r* = 0.5 (figure 2). In the presence of 0.034 g of NaNO$_3$ alone or calcined (the present quantity in NaNO$_3$/FAP : 1/2 catalyst) has no activity in the Knœvenagel reaction.

The best conditions for synthesising the alkene **3a** are generalised to **3b**, **3c**, **3d** and **3e** (table 1). The use of FAP modified by NaNO$_3$, remarkably, increases the catalytic activity and decreases the reaction time in the Knœvenagel reaction (table 1).

Solid catalysts become particularly interesting when they can be regenerated. Indeed, in our case, Na/FAP was recovered quantitatively by simple filtration and regenerated by calcination for 15 min at 700 °C. The recovered catalyst was reused several times without loss of activity, even after the seventh cycles product **3a** was obtained with the same yield.

We have reported previously that addition of small amounts of water to reaction mixtures can increase the catalytic activity of natural and synthetic phosphates [19,24]. We tested this approach in the synthesis of α,β-unsaturated arylsulfone **3a** using Na/FAP in the presence of different amounts of water in conjunction with methanol or ethanol as solvents (figure 3). The best result was then obtained with 0.1 mL of water in 1 mL of ethanol (figure 3). If a large amount of water is used a thin film of water will be formed between the organic reagents and catalyst which explain the decreasing of the yields (figure 3).

It has been shown previously that the addition of an ammonium salt to natural phosphate [19], fluorapatite [25], or hydroxyapatite [24a] increases the activity of

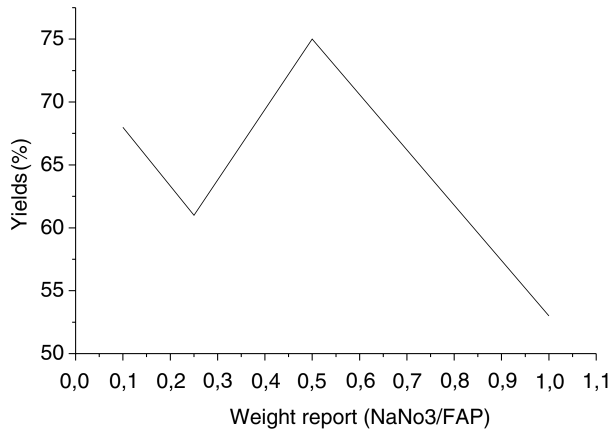

Figure 2. Influence of weight report NaNO$_3$/FAP on the yield in α,β-unsaturated arylsulfone **3a** after 12 h of reaction.

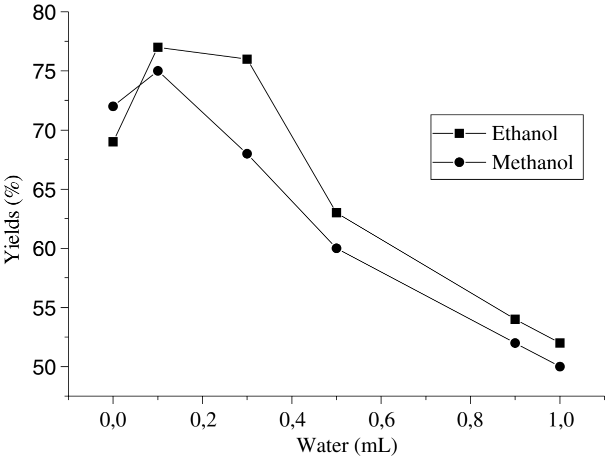

Figure 3. Influence of water with methanol or ethanol as solvent in the synthesis of **3a** after 9 h of reaction.

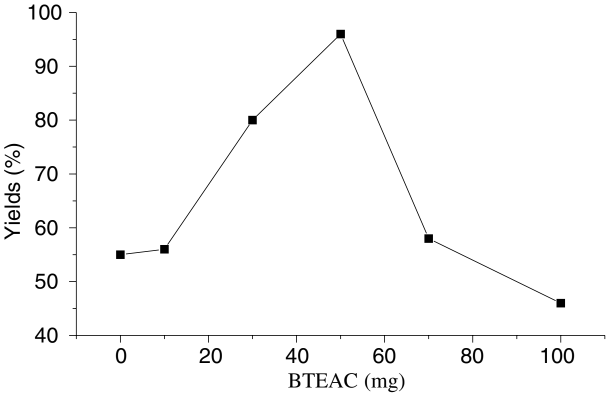

Figure 4. Influence of BTEAC with Na/FAP as catalyst in the synthesis of **3a** after 4 h of reaction.

these catalysts. Therefore, we carried out the synthesis of the α,β-unsaturated arylsulfone **3a** with Na/FAP in ethanol using different amounts of BTEAC. The results obtained after 4 h show that the best yields are obtained with 0.05 g of BTEAC (figure 4). Moreover, the kinetic curves for the synthesis of the alkene **3a** in the absence and in the presence of BTEAC clearly show the improvement of the catalytic activity of Na/FAP by addition of the ammonium salt. The yields obtained after 1, 2, 3 and 4 h are 50%, 60%, 76%, and 96% in the presence of BTEAC and 24%, 30%, 44%, and 50% without BTEAC.

Finally, this method was extended to the preparation of several α,β-unsaturated arylsulfones (table 2). The addition of BTEAC lead to a significant decrease in the reaction time (table 2). For example, the reaction time of alkene **3a** decreases from 17 to 4 h in ethanol when using Na/FAP/BTEAC. In all cases the reaction afforded the product **3** in high yields. It is important to note that BTEAC itself has no catalytic activity and seems to act as a phase transfer catalyst.

Table 2
Synthesis of products **3** by Knœvenagel condensation using Na/FAP, in the absence and in the presence of BTEAC

Entry	Products	R	Yield/% (time/h)[a]	
			Na/FAP	Na/FAP/ BTEAC[b]
1	3a	H	55(4); 95(17)	96(4)
2	3b	OMe	50(4); 91(17)	92(4)
3	3c	Me	53(4); 93(17)	93(4)
4	3d	Cl	58(4); 90(9)	96(4)
5	3e	NO_2	80(1); 92(2)	96(1)

[a] Yields of pure products isolated by distillation under vacuum and identified by ^1H, ^{13}C-NMR, mass spectroscopy and IR spectroscopy.
[b] BTEAC 0.05 g.

Table 3
Influence of the presence of electron acceptor or donor on the aromatic ring of benzaldehyde on the yield in α,β-unsaturated arylsulfones **3**

Entry	Products	R	Yield/% (time/h)	
			Na/FAP (9 h)	Na/FAP/ BTEAC (1 h)
1	3a	H	69	64
2	3b	OMe	c58	56
3	3c	Me	60	60
4	3d	Cl	90	70
5	3e	NO_2	92[a]	96

[a] The reaction is total just after 2 h.

The effect of electron acceptor or donor substituents on the aromatic ring of benzaldehyde in the Knœvenagel condensation was carried out in the reaction of phenylsulfonylacetonitrile **2** and substituted benzaldehyde derivatives (**1a–e**) using Na/FAP/ and Na/FAP/BTEAC as catalysts. Results from table 3 show that the presence of electron acceptor groups on the aromatic ring increases the reaction rate proportionally to the value of the Hammet constant. Meanwhile, the presence of electron donor groups decreases the reaction rate, demonstrating the participation of the aldehyde in the controlling step of the reaction.

For the catalytic activity of Na/FAP in this Knœvenagel condensation we suppose that the reaction occurs at the surface rather than inside tunnels of the catalyst. The dimensions of the tunnels in our catalyst are not large enough compared to those of zeolites [26]. Thus, we estimate that probably the surface of Na/FAP presents multicatalytic active sites. The basic sites (CaF_2 and oxygen of PO_4 group) polarize the C–H bond of the active methylene compound and the acidic sites (Ca^{2+}, Na^+ and phosphorus of PO_4 group) probably coordinate with the oxygen of the carbonyl carbon on which a partial positive charge appears. Consequently, the C–C bond formation is facilitated

Table 4
Comparison of Na/FAP/BTEAC with several heterogeneous catalysts in the synthesis of product **3a** by Knœvenagel condensation

Entry	Solid catalyst	Yields (time) [(%) (time/h)] **3a**
1	Na/FAP/BTEAC	64(1)/96(4)
2	FAP	78(48)
3	NP [19]	58(5)
4	NP/BTEAC [19]	75(5)
5	KF/NP [19]	60(1)
6	$Na_2CaP_2O_7$ [18]	58(1)
7	Zeolite-CsX [17]	35(2)
8	Mg–Al-hydrotalcite [17]	71(2)
9	MgO [17]	86(2)
10	KF/NP/ BTEAC [24]	91(1)
11	ALPON [17]	95(2)[a]

[a] Atomic ratio Al : P : N = 1 : 0.95 : 0.42.

and the final alkene is obtained by the transfer of a proton followed by dehydration.

The results obtained in this reaction with Na/FAP/BTEAC as catalyst were compared to those using other catalysts (table 4). Thus, the reactivity of Na/FAP/BTEAC was higher than FAP, natural phosphate (NP) [19], NP/BTEAC [19], natural phosphate doped by potassium fluoride (KF/NP) [19], $Na_2CaP_2O_7$ [18], Zeolite-CsX [17] and Mg–Al-hydrotalcite [17] and slightly lower than KF/NP/BTEAC [19] and ALPON (atomic ratio Al : P : N = 1 : 0.95 : 0.42) [17].

In summary, the activity of fluorapatite has been improved by doping with sodium nitrate. The good conditions to promote the synthesis α,β-unsaturated arylsulfones are obtained by addition of BTEAC. The yields obtained are very high. This catalyst can be regenerated and reused without lost of activity which make it attractive alternative to homogeneous basic reagents.

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