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Mineral oil Shale Part Based-support as Heterogeneous Catalyst for Organophosphorus Synthesis, Assisted by Ultrasounds

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ABSTRACT

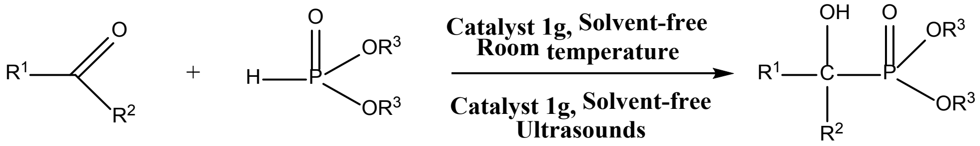
A new heterogeneous catalyst has been developed based on moroccan oil shale raw matter. This new support was used in the α-hydroxyphosphonates synthesis by Pudovik pathway using dialkylphosphites and carbonyls compounds. The transformation was performed by using oil shale-based catalyst under room temperature and by ultrasound-assisted synthetic approach. Both approaches have been found to be efficient in this organophosphorus synthesis. The reaction was carried out with a high yield in dry media, the catalyst is separated easily and reused several times without losing its activity.

Keywords: α-hydroxyphosphonate, Oil shale, Heterogeneous catalysis, Ultrasound.

INTRODUCTION

One of the important classes of organophosphorus there is α-hydroxyphosphonates which have attracted an immense attention due to their biological activities such as enzymes inhibitors[1], anti-bacterial and anti-fungal[2,3], anti-cancer[4,5], and anti-HIV activities[6]. Adding to that best-known example of phosphonates activity is their potent insecticidal activities[7]. Moreover, α-hydroxyphosphonates are synthetic intermediates to achieve a wide important phosphorus compounds of alpha and beta functionalized phosphonates such α-keto[8,9], α-acetoxy[10,11] β-malono[12,13] and α-aminophosphonates[14-16]. Many synthetic pathways are used in α-hydroxyphosphonates synthesis, the two main routes are the addition of dialkyl or trialklphosphite to an oxo compound, these methods were described for the first time by Pudovik and Abramov[17]. Since then, this reaction got the attention of chemists, a numerous of different catalysts were used to obtain the α-hydroxyphosphonates such as guanidine hydrochloride[18], Amberlyst-15[19], natural phosphate[20], KH_2PO_4[21], oxalic acid[22] MoO_2Cl_2[23], $MgCl_2/Et_3N$[24], K_3PO_4[25], Na-FAP[26], MNPs-Guanidine[27], and $CeCl_3{\cdot}7H_2O$[28].

On the other hand, Oil shale raw matter is considered as an energy source by conversion this matter to energy and chemical products through the thermochemical conversion technology[29]. A number of environmental alternatives have also been developed using Moroccan oil shale as adsorbent material to remove industrial dyes, heavy metals, and radioactive elements[29-36]. In this paper, we present the use of this raw matter as heterogeneous catalyst. We present here a simple, rapid, environmentally friendly and high yielding protocol for the synthesis of α-hydroxyphosphonates in in dry media at room temperature or under ultrasonic irradiations (Scheme 1), this elaborated support has been used successfully in Knoevenagel reaction[37].



Scheme 1. Synthesis of -hydroxyphosphonates in the presence of the oil shale catalyst

EXPERIMENTAL

Generalities

The raw matter comes from the Tarfaya region, Morocco, the catalyst has been prepared as described previously[37]. The structural and textural proprieties of the obtained catalyst have been studied using X-ray diffraction, FX, MEB-EDS and BET-BJH analysis.

The isolated synthesized compounds were identified using IRTF on a Bruker tensor 27 FTIR spectrometer and nuclear magnetic resonance analysis performed on a Bruker ADVANCE II NMR spectrometer, using $CDCl_3$ as a solvent.

General procedure for the synthesis of the α-hydroxyphosphonates in dry media

Equimolar mixture (2.5 mmol) of carbonyl compound and dialkylphosphite, 1 g of the support was added in the absence of solvent at room temperature without stirring or under ultrasound irradiation. After completion of the reaction, the mixture was extracted with 15-20 mL of ethyl acetate to give a residue which is purified by chromatographic column (hexane/ethyl acetate), the support recovered off by simple filtration, and the products were identified by their melting points, IRTF and NMR spectroscopy. The recovered support was washed with water and ethanol, then dried at 150°C for 2 h before reuse or washed with water and ethanol dried and calcined at 900°C for 30 min to regenerate it.

RESULTS AND DISCUSSION

Catalyst characterization

The characterization of the support was carried out by XRD which showed that it formed principally of different oxides such as CaO and MgO, also the presence of alumina and silice were identified. The surface area of the catalyst was determined by BET method from the adsorption-desorption isotherm using nitrogen as adsorbent at 77.373 K, the surface area of 3.3103 m^2/g was found. According to the IUPAC classification, the isotherm of catalyst is assigned to type (IV) with a distinct hysteresis loop of type H3 and reversible adsorption–desorption process, which is characteristic of mesoporous materials. Furthermore, the pore size distribution curve determined by (BJH) method shows the pore size distribution is centered approximately at 25.20 Å. In addition, the total pore volume is VT= 0.004440 cm^3/g.

In the regard to broaden the application of this new catalyst, a green protocol was adopted for the synthesis of α-hydroxyphosphonates via Pudovik pathway under solvent-free at room temperature with no agitation.

Further it was studied the influence of the catalyst weight on diethyl (hydroxy(phenyl) methyl) phosphonate synthesis. The obtained results have shown that the optimum catalyst weight should be 1 g (Figure 2).

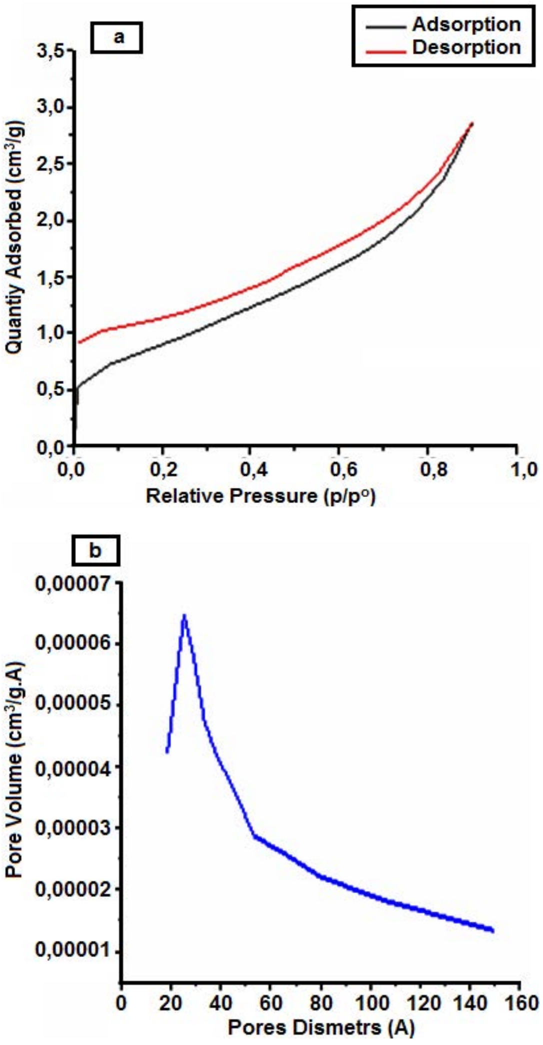


Fig. 1. Catalyst nitrogen adsorption/desorption isotherms (a) and BJH pore size distribution (b)

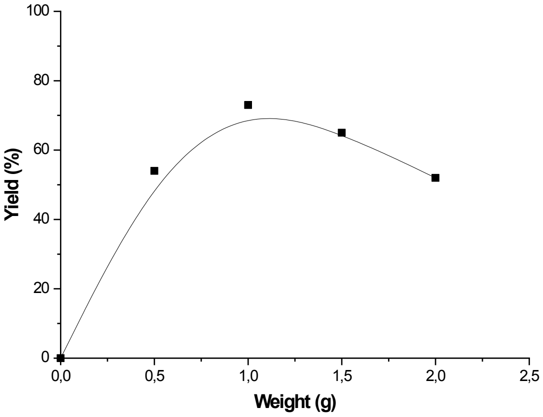


Fig. 2. Catalyst weight influence on diethyl (hydroxy(phenyl) methyl)phosphonate synthesis

Additionally, it was studied the effect of the reaction time with the purpose to identify the minimum time which could lead to the optimum yield (Fig. 3). The results showed that the optimum time to achieve the maximum yield was observed and fixed at 60 minute. After this time, the yield presents the same values indicating on the possibility of catalyst poisoning, which could happen when dealing with phosphorous reagents such phosphites. That idea will impose itself when was studied the kinetic of this reaction between dimethylphosphite and acetophenone.

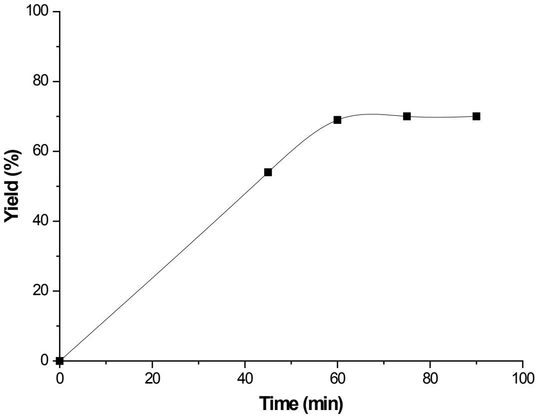


Fig. 3. Reaction time influence on the synthesis of diethyl (hydroxy(phenyl) methyl)phosphonates

Furthermore, (Fig. 4) of the kinetic study of the reaction between dimethylphosphite and acetophenone showed that despite the progressive increase in the reaction time, the yield remains unchanged with no significant improvement, the results achieved after 6 and 18 h respectively gives a yield of 59% and 71%. To improve the used catalytic system, the model reaction was conducted under ultrasonic irradiations, solvent-free conditions, and 1 g of the catalyst (Fig. 5). The reaction proceeds smoothly and the formation of the targeted products was accelerated by ultrasounds within a short reaction time, a yield of 77% achieved after 8 min, the large gap of reaction time between room temperature and ultrasounds conditions showed the positive effect of this last.

Studying the recyclability of the catalysts considered as the most important feature of this last. In fact, a catalyst will preferably be chosen if after several re-uses its activity stays unchanged or slightly modified. For this and depending on the encouraging obtained results, the reusability and regeneration of the catalyst have been examined, the synthesis was carried out under similar conditions previously used.

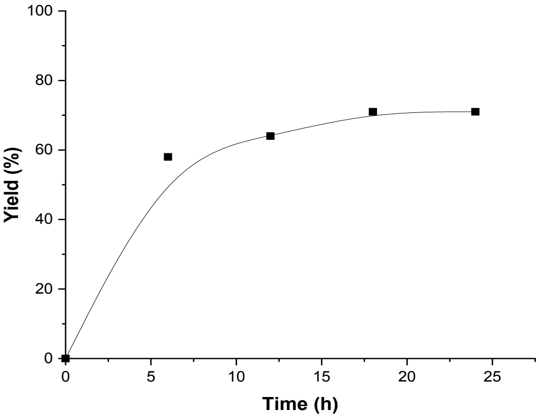


Fig. 4. Kinetic study on the synthesis of dimethyl (1-hydroxy-1-phenylethyl)phosphonates

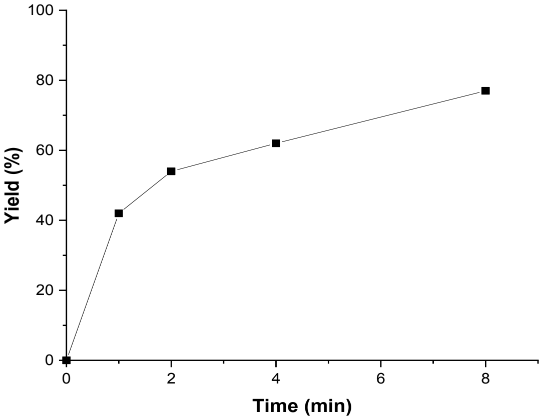


Fig. 5. Kinetic study on the synthesis of diethyl (hydroxy(phenyl) methyl)phosphonates under ultrasound irradiation

The efficiency of the recovered catalyst was checked, the results show that the product yield has dramatically decreased after the 2nd cycle as it shown in Fig. 6. These results can be explained in this kind of solid catalysts by the exhaustion of the active sites of the surface by reagents or the products, the thing that prevents contact between the reagents and these active sites. These unsatisfactory lead toward finding the total regeneration of the catalyst, which has been achieved by the thermal treatment of the recoverable catalyst, the results presented in Fig. 6 confirm the positive effect of this treatment, and showed that the catalyst can be reused until 4 cycles without any loss of its activity.

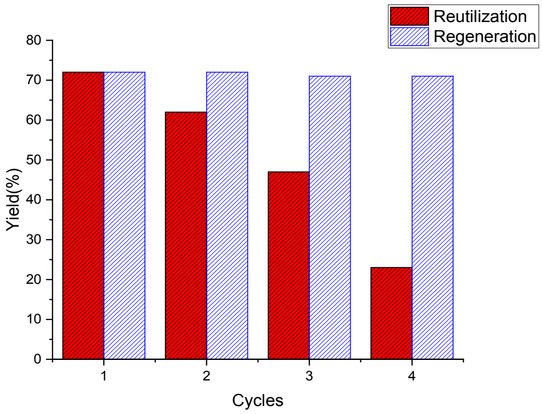


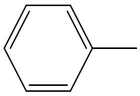
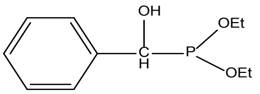
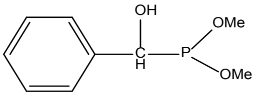
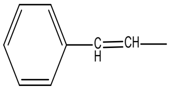
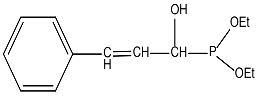
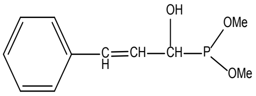
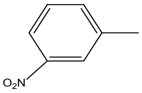
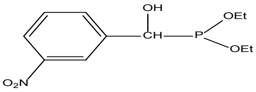
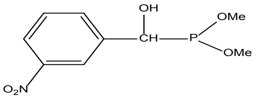
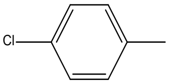
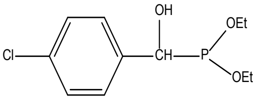
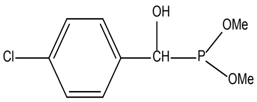
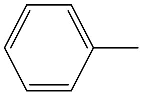
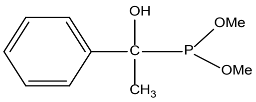
Fig. 6. Recyclability and the regeneration of the catalyst in the synthesis of diethyl (hydroxy(phenyl) methyl) phosphonates

To demonstrate the scope of applicability of the catalyst, different derivatives of α-hydroxyphosphonates have been synthesized using the optimized reaction conditions which already in hand. This scope was explored using various aromatic carbonyl compounds bearing substitutions at meta and para positions with a dialkylphosphite compound. As shown in Table 1, when the reaction is carried out at room temperature it affords the corresponding products in good yields (65-86%) within 60 minute. The condensation is preceded easily when the aldehydes are used instead of ketones, the thing that has been observed in the case of acetophenone when a yield of 59% and 71% has been achieved respectively after 6 and 18 hours. The efficiency of the catalyst improved when the catalytic system has been assisted by ultrasound irradiations, the formation of the desired compounds was accelerated by ultrasounds irradiation with equal or higher yield compared to the conventional method. These results accentuate the positive effect of ultrasound on the reaction outcome.

Finally, the efficiency of the catalyst was compared with that of other catalysts reported previously in the literature, the synthesis of diethyl (hydroxy(phenyl) methyl)phosphonate as a model product compound was chosen. The comparison targeted the catalysts performed in this synthesis under quite similar conditions.

The data summarized in Table 2 clearly shows that this catalyst has an activity similar or high over to other compared catalysts. The method is also effective for a variety of aromatic carbonyls and achieved the products in good yields and in a short time, therefore it's a novel, environmentally friendly and economically viable method for the synthesis of α-hydroxyphosphonates in dry media. The application of ultrasound and solvent-free methodology makes this protocol a green chemistry approach.

Table 1: α-Hydroxyphosphonates synthesis by Pudovik pathway over oil shale catalyst alone and assisted by ultrasounds oil shale catalyst/ultrasounds

R^1	R^2	R^3	Product	Catalyst Yield(h)	Catalyt/US Yield(min)	m.p°C Found	m.p°C lite
	H	Et		72(1)	83(12)	74-75	75-76[40]
				71(1)	88(12)	84-85	86-87[42]
	H	Me					
	H	Et		65(1)	74(15)	91-92	104-107[43]
	H	Me		73(1)	78(15)	80-82	82-83[22]
	H	Et		85(1)a	90(12)[a]	84-85	81-82[40]
	H	Me		86(1)a	91(12)[a]	81-82	-
	H	Et		65(1)	76(18)	66	67-68[40]
	H	Me		69(1)	81(18)	84-86	70-71[44]
	CH_3	Me		59(6) 71(18)	66(60)	132-134	137-138[41]

[a] 1mL of ethylacetate is added to the mixture

Table 2: Comparison of the efficiency of oil shale catalyst over to other catalysts

Catalyst	Conditions	Yield (min)	References
Oil shale catalyst 1 g	2.5 mmol Dry media	72(60)	This work
Oil shale catalyst 1 g,<))))	2.5 mmol Dry media	83(12)	This work
NP 1g	2.5 mmol Dry media	93(15)	[20]
FAP 1g	2.5 mmol Dry media	50(60)	[26]
HAP 1g	2.5 mmol Dry media	59(60)	[38]
Na_2CO_3 1g, MW900W	5mmol Dry media	75(2)	[39]
CaO 1g,MW900W	5mmol Dry media	70(2)	[39]

CONCLUSION

In this work, it was demonstrated that a solid elaborated depending on the mineral part of oil shale could be considered as an active and promising solid heterogeneous catalyst. XRD and chemical analysis confirmed that the prepared material contains essentially a variety of oxides such as CaO, SiO_2, Al_2O_3 and MgO, which formed due to the thermal treatment of the raw matter (fresh oil shale). Moreover, the textural analysis showed an isotherm of the catalyst which is assigned with characteristics of mesoporous materials.

The obtained catalyst was effectively used in the synthesis of a variety of α-hydroxyphosphonates via Pudovik pathway, easily separated from the reaction mixture, and was reused several times without any loss of activity. In addition, it was demonstrated that the effect of ultrasound led to a decrease in the reaction time and an increase in the yield of the reactions. These results open a way for the use of this inexpensive solid as a catalyst for other transformations.

Physical and Spectral Data of model compound Diethyl (hydroxy(phenyl) methyl)phosphonates

White solid; Yield : 72% (Method A), 83% (Method B); Melting point : 74-75°C; ^{1}H NMR: (500 MHz, Chloroform-d) δ 7.50–7.40 (m, 2H), 7.31 (t, *J* = 7.4 Hz, 2H), 7.28–7.20 (m, 1H), 4.99 (dd, *J* = 11.1, 7.2 Hz, 1H), 4.07–3.89 (m, 4H), 1.18 (dt, *J* = 21.9, 7.1 Hz, 6H); ^{13}C NMR : (151 MHz, Chloroform-d) δ. 16,48 ; 63.39, 78 ; 127.13 ; 128.05 ; 128.34 ; 136.78 ; 31P NMR : (202 MHz, Chloroform-d) δ 22.00; IR (KBr) : v cm^{-1} = 1220 (P=O); 3260 (OH).

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Conflicts of interest

The authors declares no conflict of interest

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