Research article

Investigation of the basis for catalytic activity of expanded Perlite in Knoevnagel condensation

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Abstract

The expanded Perlite was prepared by calcinations of natural Perlite and was characterised by X-ray diffraction, BET surface area, BJH total pore volume and scanning electron microscopy (SEM). The condensation reaction between benzaldehyde and ethyl cyanoacetate was chosen as model substrates to understand the catalytic activity of expanded Perlite. This catalyst bring advantages such as high catalytic activity, easy separation of the catalyst by simple filtration, possible recycling of the catalyst, use of non-toxic and inexpensive catalysts and especially, elimination of salts and by-product pollutants. It is these hydroxyl groups and the multiple porous structure of the expanded Perlite that give the catalytic property to this catalyst.

Keywords: The expanded Perlite, Knoevnagel condensation, Heterogeneous catalysis, Recyclable catalyst.

Introduction

Perlite is a glassy volcanic rock [1]; commonly light gray, with a rhyolitic composition and 2–5% of combined water. Commercially, the term perlite includes any volcanic glass that will expand or ''pop'' when heated quickly,

1

forming a lightweight frothy material. The temperature at which expansion takes place ranges from 1400 to 2000 F (760-1100°C); a voluminous increase of 10-20 times is common.

In Morocco, the largest deposit of perlite is the mines of Jbel Tidiennit located 17 km SW of Nador and possesses about 38×10^6 tons of reserves of perlite [2]. The uses of the expanded Perlite are many and varied, and are based primarily upon its physical and chemical properties.

Recently, the Moroccan Authors have directed our interest to feasibility of adsorption of chromium (III) onto expanded Perlite [3]. This study shown that, the expanded Perlite (EP) is a very good adsorbent for chromium (III).

In the present work, our goal is to understand the catalytic activity of the EP catalyst towards the Knoevenagel reaction between benzaldehyde and ethyl cyanoacetate.

Materials and Method

Preparation of expanded Perlite

The Perlite samples were obtained from Jbel Tidiennit Perlite mines locates in Nador, Morocco. The Perlite was expanded in the Laboratory of the Office of Research and Mineral Participation. Perlite is an inert glassy volcanic ryholitic rock which will expand when quickly heated to above 870°C. It expands up to 20 times its original volume.

Characteristics of expanded Perlite

The EP was first studied by X-ray diffraction (Figure **1**). This analysis indicated that the EP was amorphous. This result agrees well with literature [4]. Figure **2** shows that EP is porous, and these pores vary in size, and the edge is obvious.

Figure 1. X-ray diffraction of the expanded Perlite

2
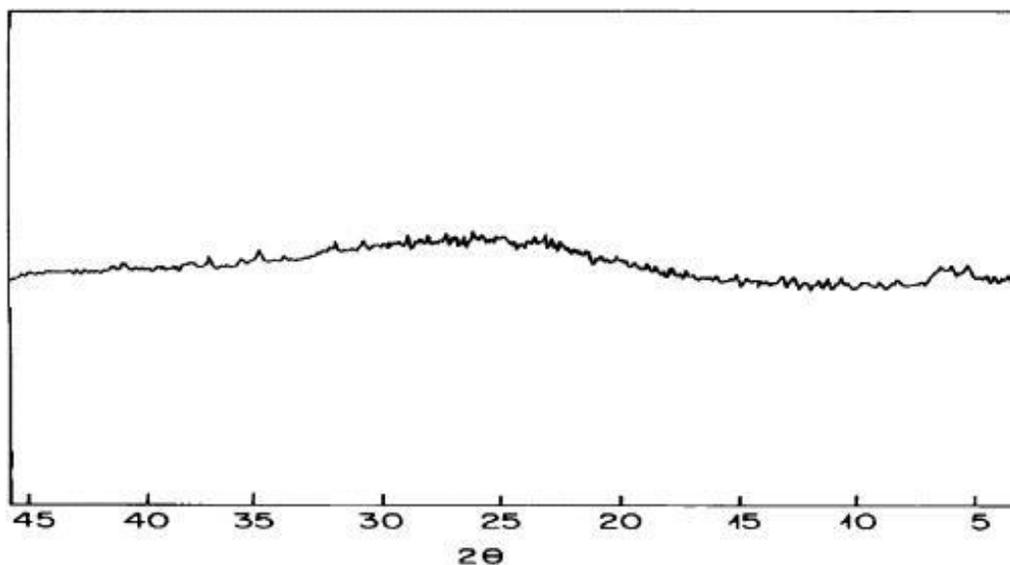
Figure 2. SEM image of the expanded Perlite
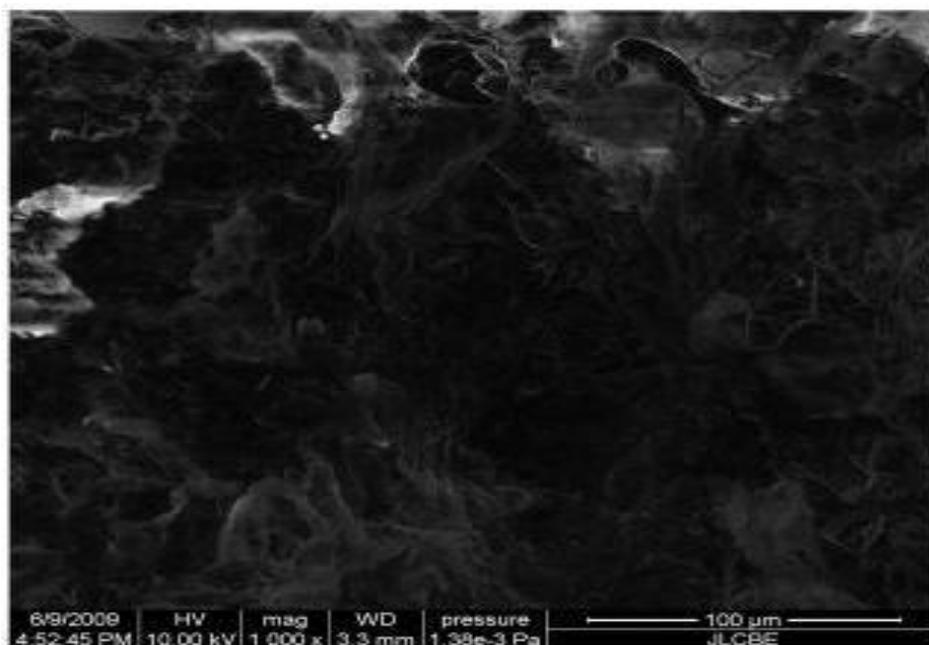
The chemical composition of the EP used in this study is summarised in table **1**. It can be noted that EP is natural alumino-silicate rich in SiO_2 and Al_2O_3.

Table 1. Chemical analysis of Expanded Perlite

Constituent	Percentage (%)
SiO_2	75.22
Al_2O_3	13.08
Fe_2O_3	01.83
P_2O_5	00.02
TiO_2	00.13
CaO	01.43
MgO	00.10
MnO	00.06
K_2O	04.95
Na_2O	03.00

However, XPS analysis of the extreme surface of EP shows considerable enrichment in aluminium species (Si/Al= 4.65) compared to X-ray fluorescence results where atomic ratio of Si/Al =13. The only contaminant detected by XPS on the surface of EP was carbon (Figure **3**). The percentage and binding energy of elements presented at the EP surface are summarised in table **2**. The specific surface area of EP is $1.726 m^2/g$ and the particle size for this solid state ranged between 7.0 and 65.7 μm, 50% were 30.3 μm.

3

Figure 3. XPS spectrum of of the expanded Perlite
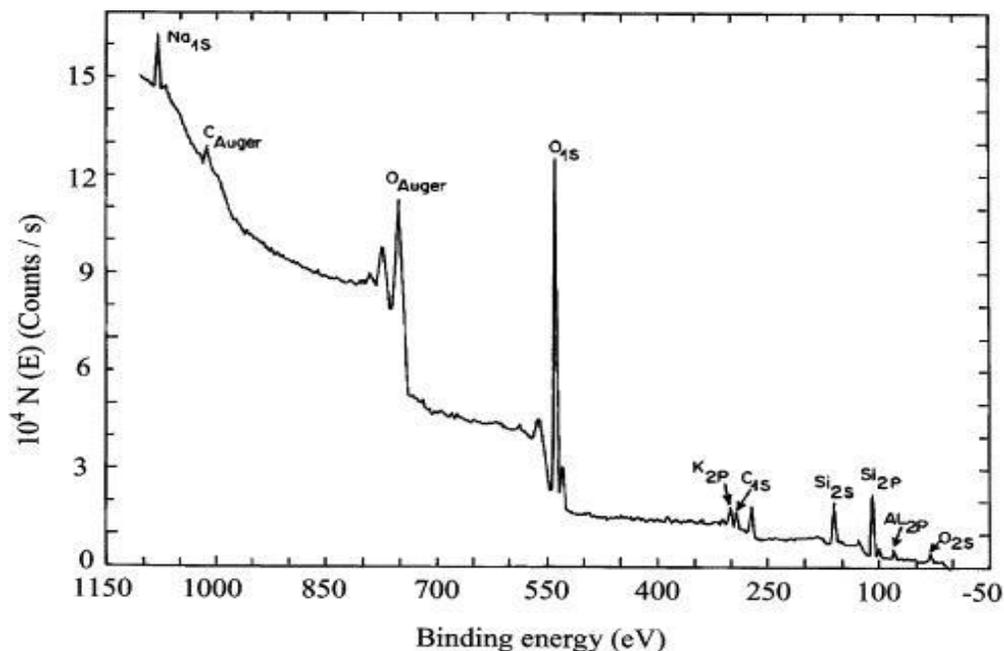
Table 2. Binding energy and Percentage of elements present in the surface of catalyst

Constituent	Binding Energy (eV)	Percentage (%)
Si_{2p}	0102.68	23.7
O_{1s}	0532.00	55.9
Na_{1s}	1072.48	06.1
C_{1s}	0284.60	07.0
K_{2p}	0293.36	02.3
Al_{2p}	0073.92	05.1

General Procedure

The general procedure was as follows. To a flask containing 100 mg of the EP were added, successively, benzaldehyde (3 mmol), ethyl cyanoacetate (3.2 mmol) and the solvent (ethanol: 1.6 ml). The mixture was then stirred vigorously at room temperature for 35 min. At the end of the reaction time, the catalyst was removed by gravity filtration and washed with 6 ml of ethanol. The product was purified by distillation under vacum and identified by ^{1}H NMR, ^{13}C NMR and IR spectrometry.

Ethyl (*E*)-α-cyanocinnamate : mp =50–51°C. IR: 2230 (C≡N), 1730 (C=O), 1610 (C=C) cm^{-1}. ^{1}H NMR spectrum: 1.40 (t, 3H ethyl), 4.40 (q, 2H ethyl), 7.50 (m, 3H m- and p-aromatic protons), 8.00 (d, 2H *o*-aromatic protons), 8.25 (s, 1H alkene proton). Varian Gemini 300 mH NMR spectrometer. ^{13}C NMR spectrum: 14.09 (ethyl), 62.67 (ethyl), 102.96 (CN), 115.42 (CH=CCN), 129.22, 131.01, 131.42, 133.24 (aromatic carbon atoms), 155.28 (Ph-CH=C), 162.42 (C=O). Mass spectrum: M^{+} 201, 156, 172, 128, 200, 102.

4

Results and Discussion

The Knoevenagel condensation is one of most important methods in the synthesis of functionalised alkenes [5]. It consists of condensation between a carbonyl compound and an activated methylene. In homogeneous media, this reaction requires a weakly basic catalyst such pyridine, or primary and secondary amines. It is necessary to remove the water formed during the synthesis by using a specific installation. In heterogeneous media [6], several solids supports have been used including the Alumina [7], Potassium Fluoride-Alumina [8], Aluminium Phosphate-Alumina [9], Zeolite [10], Silica Gel Functionalised [11], Natural Clinoptilolite [12], Natural Phosphate [13], Fluorapatite [14], Hydroxyapatite [15], $Na_2CaP_2O_7$ [16], Quaternary ammonium-Silicate Composite Materials [17], Xonoltite [18], animal bone meal [19] and other catalysts [20].

In this study, the Knoevenagel reaction between benzaldehyde and ethyl cyanoacetate was chosen as model substrates to understand the catalytic activity of the EP catalyst (Figure **4**).

Figure 4. Condensation reaction between benzaldehyde and ethyl cyanoacetate catalyzed by the expanded Perlite
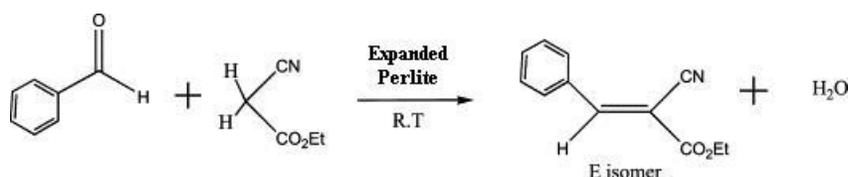
In the presence of ethanol at room temperature, the EP promotes the Knoevenagel condensation but the reaction rate is relatively slow (10%). The yield becomes 26% when the reaction times are prolonged (60 min). This result shows that the EP possesses a basic character and can be used in heterogeneous synthesis solid/liquid. Indeed, the addition of a small quantity of water in ethanolic solution to the EP notably improves the results obtained in the synthesis of Ethyl (*E*)-α-cyanocinnamate (52%). The simultaneous additions of water and benzyltriethylammonium chloride (BTEAC) in ethanolic solution show a clear superiority in the activation of the EP. The yield of product is obtained in with very high yields (94%). It is worth noting that, in the same conditions and in absence of the EP, water, BTEAC or both do not promote this reaction.

The mechanism of the Knoevengel condensation involves abstraction of one the active methylene protons by a base, followed by attack of the resulting anion on the carbonyl carbon of benzaldehyde. The resulting negatively charged oxygen atom abstracts a hydrogen atom from the base. Elimination of a molecule of water results in the formation of a system of extended conjugation (Figure **5**).

Figure 5. Catalytic mechanism of condensation reaction catalyzed by the expanded Perlite
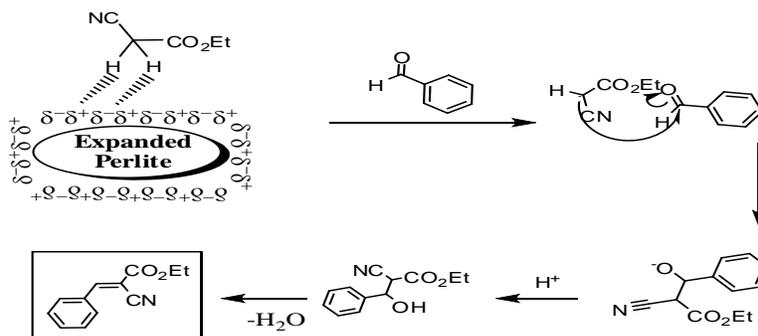
Indeed, we estimate that the surface of the EP presents certainly multicatalytic active sites. Thus, the role of the EP can be presumed to be the initial abstraction of proton from the active methylene group of the ethylcyanoacetate by negatively charged oxygen atom of an oxide group. The origin of this charge is still a controversial issue, but the majority of evidence suggests that this charge arises from structural hydroxyl groups (Figure **6**). In the surface this hydroxyl groups, the silicon atoms at the surface tend to maintain their tetrahedral coordination with oxygen. They complete their coordination at room temperature by attachment to monovalent hydroxyl groups, forming silanol groups.

Figure 6. Hydroxyl groups in surface of the expanded Perlite
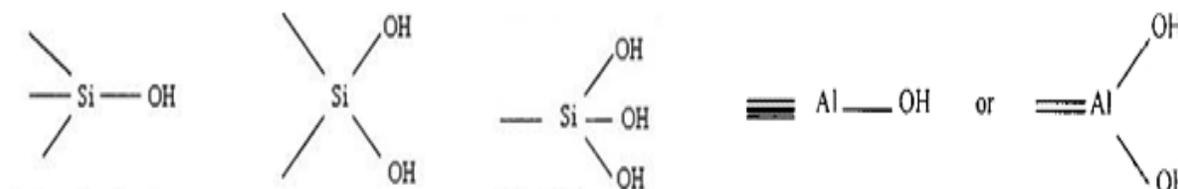
Another hand, the multiple porous structure of the EP provides the mechanical strength for the whole composite and prevents the leakage of the melted Water-BTEAC due to the effect of capillary and surface tension forces between the Water-BTEAC and the porous EP. It is these hydroxyl groups and the multiple porous structure of the EP that give the catalytic property to this catalyst.

Conclusion

In summary, we have reported an efficient heterogeneous catalyst for condensation reaction between benzaldehyde and ethyl cyanoacetate in mild reaction condition. The EP catalyst bring advantages such as easy separation of the catalyst by simple filtration, possible recycling of the catalyst.

Acknowledgement

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