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OIL SHALE DOPED BY ZINC CHLORIDE: NEW ECOLOGICAL AND EFFICIENT CATALYST FOR THE ACETYLATION OF ALCOHOLS AND PHENOLS

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Abstract: The main objective of this work concerns the upgrading of oil shale rocks through the development of a new heterogeneous catalyst.
Initially, we developed a simple method for preparing catalysts based on Moroccan oil shale from the TARFAYA region, using mechanical and thermal treatment. Stable, recyclable catalyst supports - oil shale alone (SB) or doped with Zinc Chloride (Zn/SBc) were characterized by various analytical methods. Next, we demonstrated the catalytic activity of Zn/SBc in the acetylation of alcohols and phenols, via a clean and ecological method that fits in with green chemistry concepts, and quantitative yields were obtained under mild conditions.

Keywords: Heterogeneous catalysis, Oil shale, Acetylation, Alcohol, Phenol, valorization of natural resources.

1.INTRODUCTION

Oil shale is a natural resource for Morocco. As such, it represents a strategic national challenge to develop them in several fields, especially in the energy sector. They are sedimentary rocks with an organic and mineral matrix, and are distributed over several sites, the two main ones being the Tarfaya and Timahdit deposits. According to estimates by the World Energy Council in 2010, oil shale reserves in the two deposits of Tarfaya and Timahdit, combined with other deposits located in northern and central Morocco, could lead to the production of 8,167 million tonnes of oil in place, or around 53,381 million barrels of oil [1,2].

Numerous studies [3-10] have been devoted to the development of Moroccan oil shales, in particular their exploitation for energy production by direct combustion in power plants, or by pyrolysis to produce oils from shale rocks. We also note that oil shales have been developed in various fields, such as the preparation of new adsorbent materials [4,5] and the elaboration of carbon fibers from kerogen derived from Tarfaya oil shales [11].

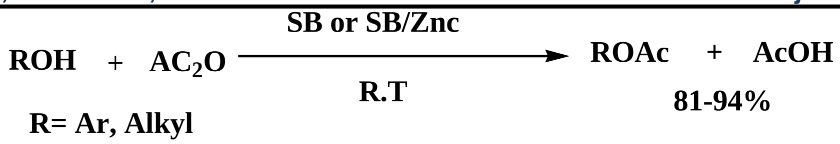
Recently, our team has focused on the valorization of Tarfaya oil shale as a catalyst for organic synthesis [12-14].

With the aim of developing clean processes through the search for new catalytic applications of oil shale alone or doped in organic synthesis, we turned our attention to the acetylation reaction of alcohols and phenols by acetic anhydride (Scheme 1). This reaction is of interest to many researchers [15-24].

Traditionally, this reaction is carried out in a homogeneous medium using catalysts [15-20]. These have a number of drawbacks: they are difficult to handle, and harmful to humans and the environment.

In recent years, several solid catalysts have been used to solve the main problems mentioned above [21-24].

In this context, we have developed a new, simple, efficient and environmentally friendly method using Zinc Chloride-doped oil shale as a stable and regenerable catalyst for the protection of alcohols and phenols by acetic anhydride.



Scheme 1

2.EXPERIMENTAL

2.1- preparation of SB and Zn/SBc catalysts

Oil Shale was ground, the fraction recovered between 50 and 200 microns was calcined for 2h at 900°C.

The doped Zn/SBc catalyst was prepared by adding 10 mmol $ZnCl_2$ and 10 g SB in 100 mL water. The mixture was evaporated and dried, then calcined at 900°C for 30min (Zn/SBc-900°C). The prepared supports were characterized by various analytical methods [12-14].

2.2- Acetate synthesis

2 mmol alcohol (phenol) is mixed with 2.5 mmol acetic anhydride in the presence of 4 mL dichloromethane solvent. SB (0.5) or Zn /SBc/ catalyst (0.1g) is added to the resulting solution. The mixture is stirred at room temperature for the duration of the reaction. After filtration and evaporation of the solvent under reduced pressure, the crude product obtained is purified by a silica gel chromatography column (20% ethyl acetate and Hexane), and identified by IR, 1H NMR and mass spectroscopy (MS).

3. Results and discussion

3.1 Characterization of SB and Zn/SBc

Comparison of DRX spectra (Philips 1710 diffractometer), using Cu-Kα (λ = 1) of SB and Zn/SBc calcined at 900°C (**Figure 1**), shows the appearance of new ZnO peaks (2Theta =36,32,47,60,57), in the doped catalyst. We also note that the SB catalyst impregnated with uncalcined $ZnCl_2$ gives peaks similar to those of SB [14].

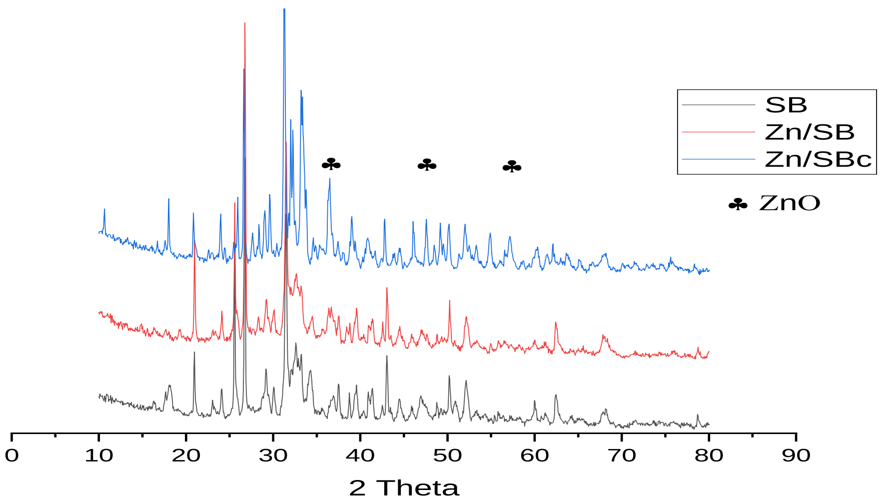


Figure.1. XRD patterns of (a) SB and (b) Zn/SB (c) Zn/SB 900

The specific surface area of Zn/SBc was determined by the BET method (S = 5.44146 m2 g1). The specific surface area is higher than that of SB (3.313 m^2g-1).
Analysis of scanning electron microscopy (SEM) images of Zn/SBc, shown in **Figure 2**, and comparison with those of SB, reveals a slight change in particle morphology. Analysis of the EDS results reveals the presence of elements such as Ca, Mg, Si, Al, C, O...

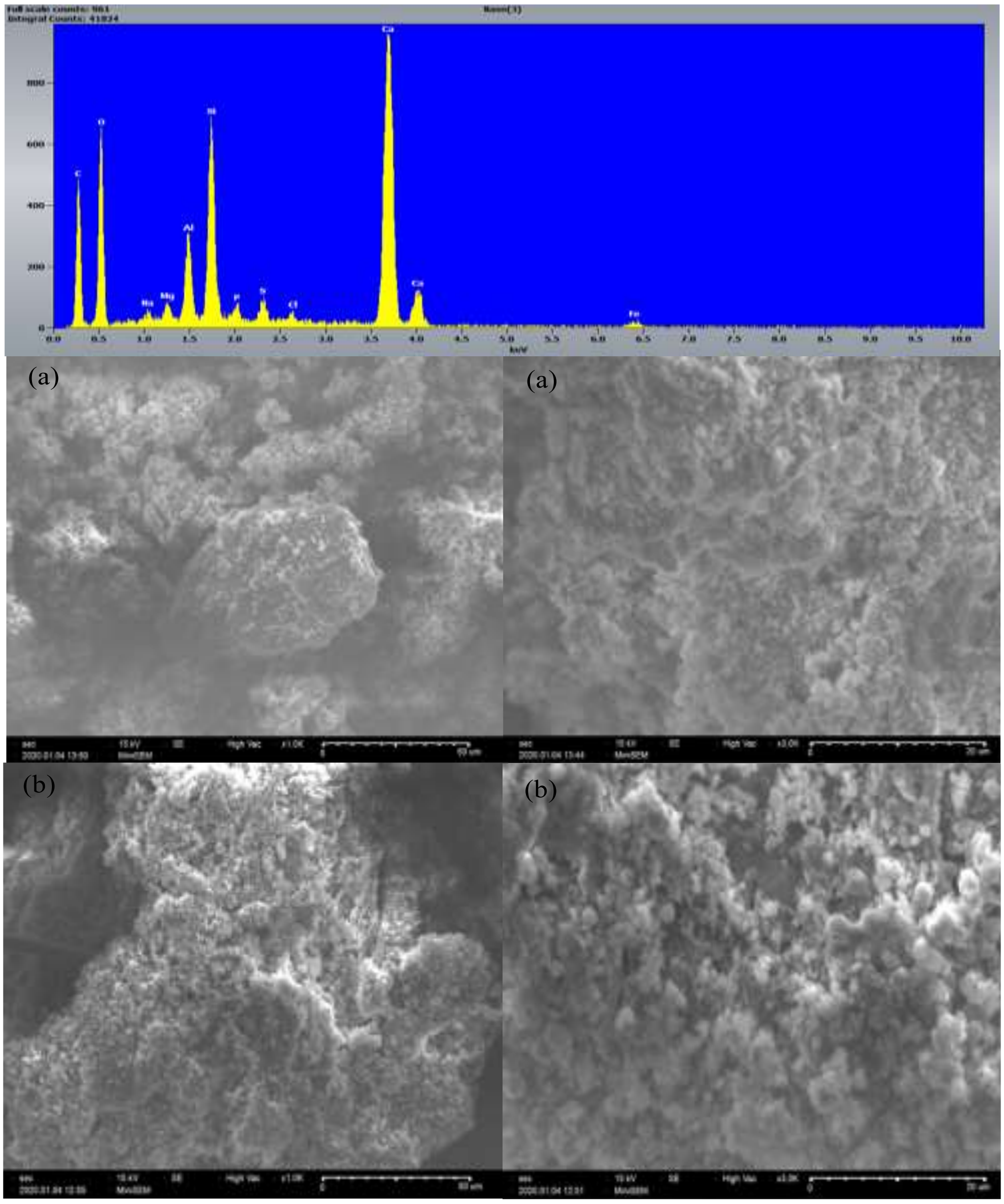
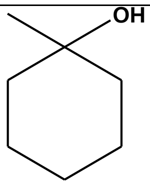
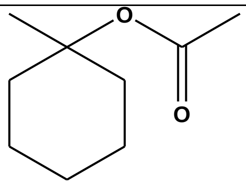
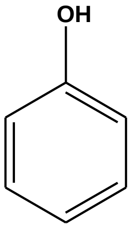
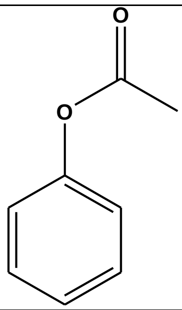
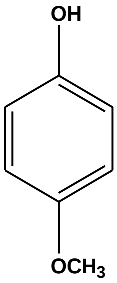
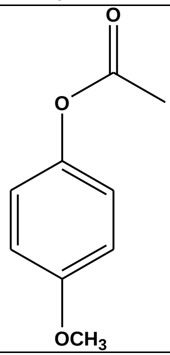
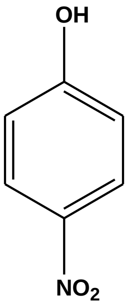
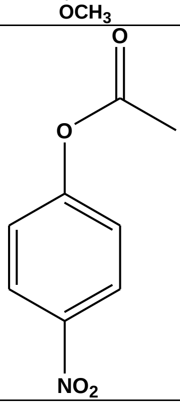
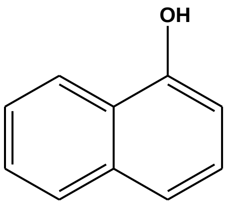
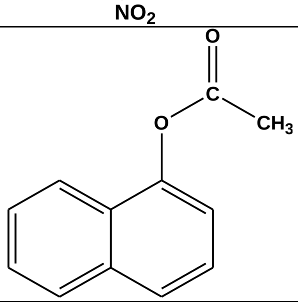
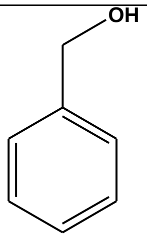
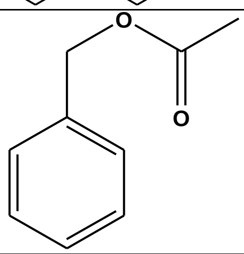


Figure.2. Scanning electron micrograph (SEM) images of (a) SB and (b) Zn/SBc and EDS

3.2. Acetylation catalysis of alcohols and phenols using SB alone

The first tests we carried out in our laboratory on the possibilities of synthesizing acetates in the presence of SB (Scheme 2), led to the conclusion that it was necessary to employ a mass of the order of 0.5 g of catalyst and a quantity of 4 mL of dichloromethane as solvent (Table1).

Table 1. Catalysis of the acetylation of alcohols and phenols by SB

Substrat	Product	Yield % [Time (h)]
		16 (24h)
		24 (24h)
		40 (24h)
		19 (24h)
		21 (24h)
		26 (24 h)

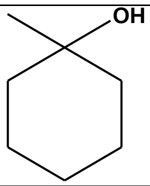
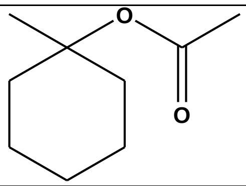
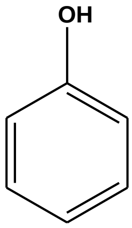
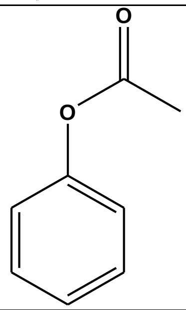
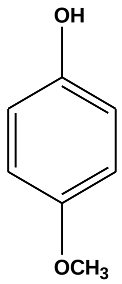
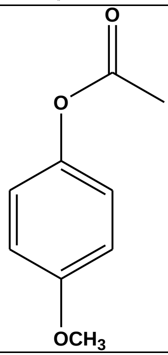
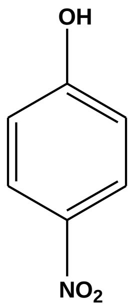
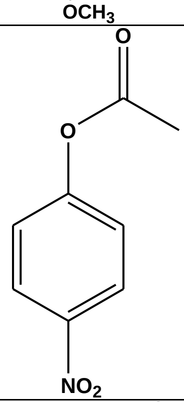
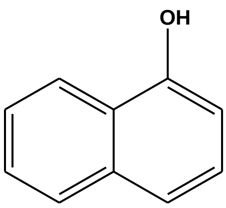
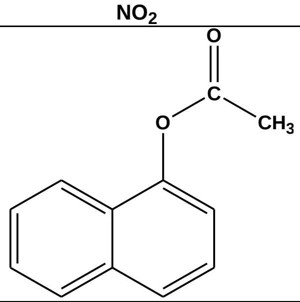
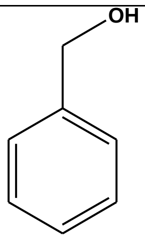
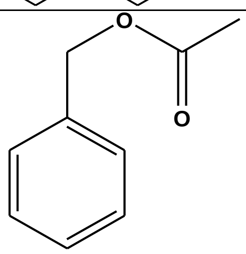
The results obtained show that Bituminous Shale alone (SB) can catalyze the acetylation reaction. Nevertheless, the reaction is slow (24h) and the yields obtained are low (16-40%). In view of these results, we decided to improve the conditions of this synthesis by using Zinc Chloride (Zn/SBc)-doped Bituminous Shale, whose catalytic activity has been demonstrated [14].

3.3.Acetylation catalysis of alcohols and phenols using $ZnCl_2$-doped Oil Shale (Zn/SBc)

Optimization of the operating conditions for this reaction in the presence of Zn/SBc shows that the use of a 0.1g mass is capable of achieving good yields in short times compared with the use of SB alone.

Thus, we carried out the acetylation of alcohols and phenols (2mmol) with acetic anhydride (2.5mmol) and 4mL of dichloromethane in the presence of 0.1g of Zn/SBc. The products obtained were isolated and identified by IR, 1H NMR and mass spectroscopy (MS).

Table 2. Catalysis of the acetylation of alcohols and phenols by Zn/SBc

Substrat	Product	Yield % [Time (h)]	
		SB	Zn/SBc
		16 (24h)	81 (18h)
		24 (24h)	92 (6h)
		40 (24h)	90 (1h30)
		19 (24h)	97(14h)
		21 (24h)	94(6h)
		26 (24h)	92 (6h)

- These results show that Zn/SBc is an effective catalyst for the cross-aldolization reaction, compared with SB alone. Yields generally exceed 80%.
- The difference in results obtained in the presence of Zn/SBc and SB is notable. Indeed, yields and reaction rates are improved in the presence of Zn/SBc, leaving no doubt as to the positive effect of doping SB with zinc chloride.
- On the other hand, the variation in reaction yields and times from one phenol to another is due in particular to the electronic effects of substituents on the aromatic ring.

3.4. Study of Zn /SBc reuse and regeneration

Catalyst recyclability is an important aspect in the development of sustainable chemical processes. It refers to the ability of a catalyst to maintain its catalytic activity after being used in a reaction, thus enabling it to be reused. To determine the recyclability of the Zn/SBc catalyst, we adopted two procedures: reuse and regeneration.

Reuse is carried out by direct recycling of the catalyst without any prior treatment, with only the moisture removed by drying at 150°C. In the case of regeneration, the recovered Zn/SBc is washed with an organic solvent (CH_2Cl_2), dried and calcined at 900°C. The results obtained are shown in Figure 3.

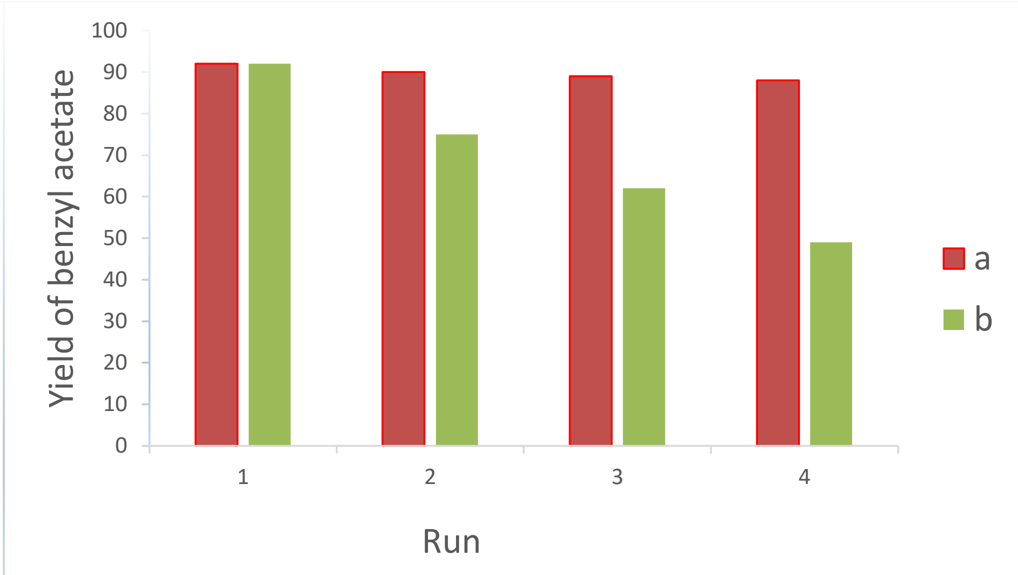


Figure 3: Study of regeneration (a) and reuse (b) of Zn/SBc

The study of catalyst reuse revealed a gradual decrease in yield, which can be explained by the occupation of the catalyst's active sites by organic compounds. In the case of regeneration, yields remain virtually unchanged. Regeneration is therefore necessary to activate the Zn/SBc.

4.Conclusion

In this work, we have shown for the first time that oil shale alone can be used as an environmentally-friendly catalyst in the acetylation reaction of alcohols and phenols, but the yields obtained are very low even after a reaction time of 24 h. Doping oil shale with zinc chloride has enabled us to demonstrate a high-performance, regenerable and recyclable catalyst system for this reaction. Acetate yields and reaction times were significantly improved.

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