Available online at www.derpharmachemica.com

ISSN 0975-413X
CODEN (USA): PCHHAX

Der Pharma Chemica, 2016, 8(16):172-176
(http://derpharmachemica.com/archive.html)

Preparation of Co incorporated into the silicalite-1 and use as catalyst for epoxidation of cyclooctene

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ABSTRACT

CoS-1 catalyst was prepared via a hydrothermal treatment and synthesized from Ludox silica and cobalt nitrate as silicon and cobalt sources respectively. The prepared solid material was characterized using X-ray diffraction (XRD) , infrared (FT-IR) and UV-Vis spectroscopy techniques. The incorporation of divalent transition metal (Co) leads to the formation of the silicalite-1 with divalent cations on extra framework positions. A MFI structure with high crystallinity was obtained. The oxidation reaction of cyclooctene was carried out using CoS-1 as a catalyst and tert-butyl hydroperoxide (TBHP) as an oxidant.

Keywords: Zeolite, , Co-Silicalite-1, XRD, IR, UV-Vis ,incorporation ,catalyst, cyclooctene, epoxidation

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INTRODUCTION

Microporous materials have acid-base properties and adsorption that make suitable for industrial and laboratory applications, for research fields, such as medicine [1] [4] [5] and petrochemistry. [2] [3] These last years, attention was focused on the development of heterogeneous catalysts transition metals and operating under mild conditions.
The incorporation of the transition metals has made changes in physical and chemical properties that will give new catalytic properties maintaining the crystalline structure of the zeolite. Various metal elements such as Co [6], Cu [7], Mn [8], Ni [9], Sn [10], Ti [11], V [12], Zn [13] and Zr [14] have been incorporated into the zeolite framework.The transition metal incorporation into the zeolite networks has a great interest in the field of catalysis. MFI -type zeolite can be used as catalyst in the treatment of a variety of hydrocarbons and oxidation catalysis due to their good catalytic performance, chemical stabilities, excellent thermal and hydrothermal. [15] [16]

In this paper ,we report on the synthesis of CoS-1 using Ludox silica and cobalt nitrate as silicon and cobalt sources respectively, ,in the presence of template. The crystallization microporus material(CoS-1) was carried at 150°C for a period of 3 days.The resulting solid was characterized by XRD, FT-IR, UV-Vis and its catalytic performances evaluated by a test cyclooctene epoxidation. The progress of the epoxidation reaction is monitored by GC-MS.

MATERIALS AND METHODS

II.1. CoS-1 synthesis procedure

Cobalt silicalite was synthesized from Ludox silica and cobalt nitrate as silicon and cobalt sources, in the presence of template, tetraethylammonium bromide (TPABr),under hydrothermal conditions.

Hence, 7.5 g of Ludox (40 wt.% in H_2O) in 22.5 g of H_2O, 1.4 g of TPABr, 0.14 g of $Co(NO_3)_26H_2O$ and 0.55 g of NH_4F mixed in a flask were stirred for 2 h at room temperature. At this step, the reaction mixture had the following molar composition: $1SiO_2$, 0.01 $Co(NO_3)_26H_2O$, 0.0125TPABr,$0.03NH_4F$, $30H_2O$. The xerogel obtained was transferred into a stainless steel autoclave which was heated for 3days in an oven at 150°C.The autoclave mixture was filtered and washed several times with distilled water. The resulting powder was dried overnight at 90°C and calcined in air at 550°C for 6 h.

II.2.The used instrument of characterization

The sample was analyzed in its powder form. Quantitative data were determined using the Micro Powder method. X-ray diffraction patterns of the same material were recorded between 10 and 50° on a Bruker AXS D8 Advance diffractometer with a graphite monochromator using the Cu K radiation (λ = 1.5418 Å). The IR spectrum of CoS-1 (KBr pellet) was recorded with a Bruker Vector 22 spectrophotometer. The Diffuse Reflectance UV-Vis. spectrum was recorded at room temperature between 200 and 800 nm on a Varian Cary 5E spectrophotometer equipped with a double monochromator and an integrating sphere coated with polytetrafluoroethylene (PTFE) as reference.

II.III Catalytic reaction: Oxidation tests

Cyclooctene, *tert*-butyl hydroperoxide (5.5 M in decane) were purchased from Sigma-Aldrich and used as received. Oxidation reaction was carried out in a two-neck round-bottom flask equipped with a reflux condenser. The reaction system was magnetically stirred. The reaction progress was monitored by GC-MS (Trace GC equipped with a Optima 5 MS column (30 m length, 0.25 μm film thickness, 0.025mm internal diameter) coupled to a MS spectrometer). To identify the epoxidation products, 1 μL was taken from the crude reaction mixture after cooling and was injected into the GC/MS.

The flask was charged with 100 mg of CoS-1, then 10 mL of CH_3CN, 0.91 mL (7 mmol) of cyclooctene, 2.2 mL (11 mmol) of *tert*-butyl hydroperoxide (5.5 M in decane) were introduced. The mixture was heated at 70°C.

RESULTS AND DISCUSSION

III.1. Characterization of TS-1

III.1.1. X-Ray Diffraction (XRD)

XRD patterns of the Co-silicalite-1 synthesized in this study are shown in Figure 1. The XRD patterns of the material show 10°and 30° (2θ values). The patterns show the crystalline nature of zeolite with no amorphous phase [17] and no additional peaks due to the presence of cobalt. Also show that the cobalt oxide Co_3O_4 phase was formed at 2θ = 21.8°,31.8°and 45°.[18] [19]

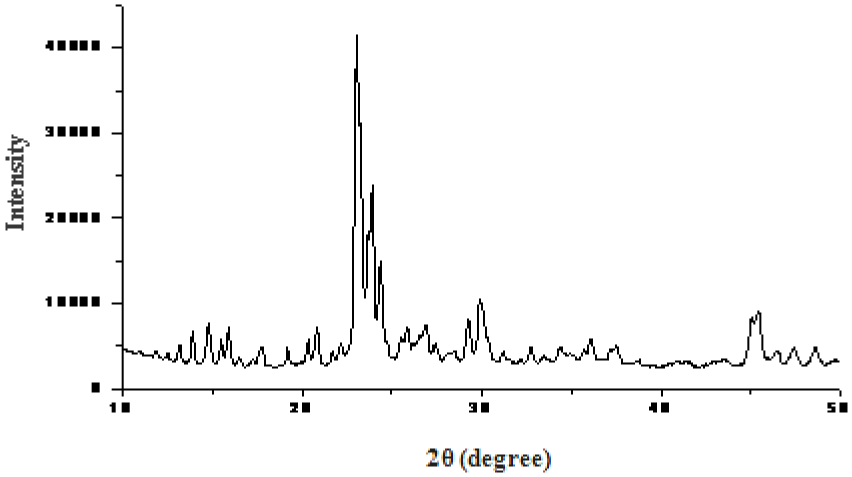


Fig 1: XRD patterns of CoS-1

III.1.2. IR spectroscopy

In Figure 2, the FTIR vibration spectra shows the absorption bands of tetrahedral structure typical of MFI zeolite at 1228, 1103, 798, 551 and 451 cm^{-1} [20]. The absorption band at 798 cm^{-1} is for the stretching/bending symmetry vibration of the Si-O-Si bridge. The preferential sitting of Co ions as coordinated bonding to the framework oxygen atoms was observed at 556 and 798 cm^{-1}. Moreover, the absorption band at 1365 cm−1 can be attributed to the location of cobalt as coordinated framework Co^{2+} ions. [21]

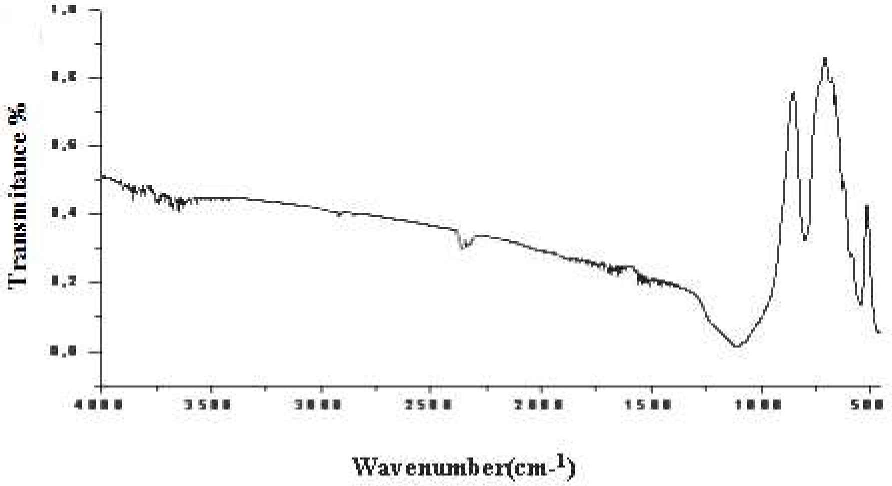


Fig 2: IR spectrum (transmission) of CoS-1

III.I.3. UV-Vis. spectroscopy

UV-vis spectra of CoS-1 is shown in Figure 3, three bands at 220 nm [22], 250 and 550 nm for CoS-1 catalyst . The absorption bands which are at 250-270 nm and 350-560 nm correspond to tetrahedral Co^{2+} and Co^{3+} ions or Co-complexes octahedral. [23][24]

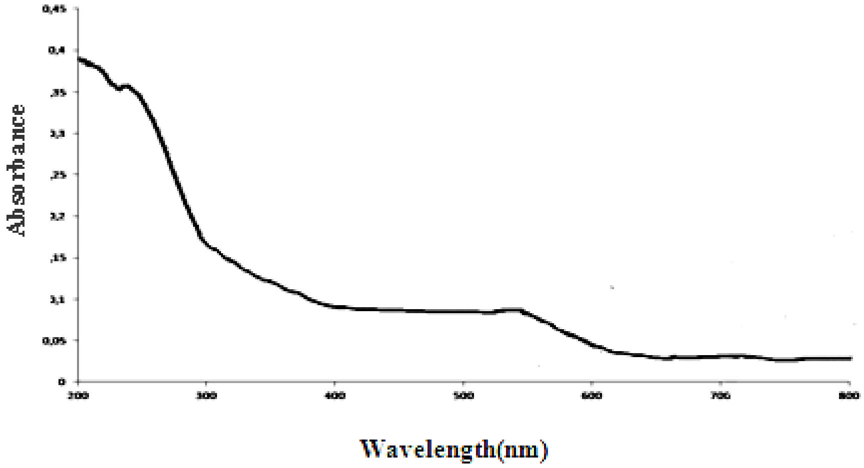
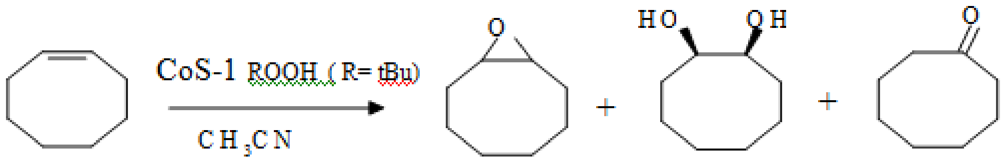


Fig 3: Diffuse reflectance UV-Vis. spectrum of CoS-1

III.II. Catalytic reactions:

The CoS-1 sample was tested in the catalytic epoxidation of cyclooctene in acetonitrile using *tert*-butyl hydroperoxide in decane (TBHP) at 70°C. (scheme 1).



Scheme 1: Oxidation of cyclooctene

Due to its stability to oxidation processes, acetonitrile was selected as solvent. Its rather high polarity allows the miscibility of the oxidizing agent in the reaction mixture and, therefore, favors the access of the oxidant and of cyclooctene to the active sites. [25] T*ert*-butyl hydroperoxide interacts with Co-O-Si affording Si-O-Co-OOR (R = t-Bu).

Using TBHP as oxidant, the reaction had to be performed at 70°C and lead to a mixture of compounds. Among the various products, cyclooctene oxide was found to be formed with the highest selectivity (Table 1). TBHP is advantaged compared to hydrogen peroxide due to the absence of water formation resulting from the reduction of this oxidant. Water is indeed considered to be at the origin of the CoS-1 catalyst deactivation.

Table 1: Relative areas of compounds detected by GC-MS for TBHP / CoS-1 vs.time

Compounds	RT (min)	A_i/A_{is}*	m/z
cis cyclooctene	4.35	4.93	110
cyclooctene oxide	10.23	1.48	126
2-cyclooctene-1-one	11.46	0.24	125.3 ; 124 ; 110
2-OH-cyclooctanone	16.46	0.19	141,9 ; 137.9 ; 123.9 ;110.10 ; 108 ; 125,9 ;
trans 1,2-cycloctanediol	18.55	0.09	145.2; 143.9;142.7;126.1;124.9;108.4

**A_i and A_{is} correspond to the area of the studied compound and the internal standard, respectively.*

Besides cyclooctene oxide, trans 1,2-cycloctanediol, 2-hydroxy-cyclooctanone, 2-cyclooctene-1-one were also produced (Table 1). The diol is probably derived .from the hydrolysis of cyclooctene oxide due to the presence of some water molecules coordinated to the CoS-1 centers in an acidic environment. Other compounds mentioned before are resulting from dehydration of the diol and/or over-oxidation.

The weak catalytic performances of CoS-1 synthesized in this work are related to the use of cyclooctene as a substrate. This molecule has a relatively high kinetic diameter (5.5Å) [26] and does not easily reach the cobalt species included in the pores. Therefore, only those located on the external surface of the crystals are involved here. The higher temperature of the test performed with TBHP leads to a higher yield of epoxide due to side reactions not involving cobalt. In the latter case, tert-butoxyl (*t*-BuO$^{\cdot}$), hydroxyl (HO$^{\cdot}$) then *tert*-butylhydroperoxyl (*t*-BuOO$^{\cdot}$) radicals may be produced by thermal decomposition of TBHP. [27] The latter are able to produce cyclooctene oxide from cyclooctene.

CONCLUSION

CoS-1 was synthesized by hydrothermal method from silicate, cobalt nitrate and characterized as tetrahedral structure typical of MFI zeolite (FT-IR,UV-vis) with no amorphous phase and no additional peaks(XRD).The epoxidation reaction in the presence of TBHP as oxidant and CoS-1 as catalyst gave mixtures consisting in the epoxide, allylic compounds and products derived from the opening of the oxirane ring. The good results of the oxidation with this oxidant can be explained by a non-metalled centered mechanism.

In the future, we are interested to synthesize new microporous materials with different templates and study the influence of these templates on the synthesis of these materials and used as a catalyst in various applications.

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