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Synthesis of [Zr] ZSM-5 with Ludox silica by a hydrothermal process, and application as oxidation catalyst of 2-Mercaptobenzimidazole

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ABSTRACT

The objective of this work is studied in particular the synthesis of MFI-type material microporous as catalysts incorporated with the zirconium. The [Zr] ZSM-5 was synthesized in succession without organic template by a hydrothermal process. X-ray diffraction (XRD) confirmed the ZSM-5 crystal phase. Fourier Transform Infrared (FTIR) analysis showed a band at 962 cm^{-1} , probably because Si-O-Zr links, in addition to other characteristic bands of MFI structure of [Zr]-ZSM-5. In this aim, we tested different types of treatments without and in the presence of a catalyst for the oxidation of sulfur heterocyclic, 2-Mercaptobenzimidazole with H_2O_2 as oxidant.

Keywords: Zeolites, MFI, [Zr] ZSM-5, Catalysis, Oxidation, 2-Mercaptobenzimidazole.

INTRODUCTION

For several economic and ecologic factors, the use of zeolites is the best choice for a regular application in environment (1). zeolites are currently the important class of inorganic materials which is used for the development of functional materials and nanotechnology because of their multiple applications not only as ion exchangers and molecular sieves, but also as catalysts in organic chemistry and industrially (2) zeolites can be obtained from commerce or can be synthesized, The synthesis of Microporous Zirconium Silicates is not available in literature. In this work, we present an original method to synthesis acrySTALLINE zirconium Silicates having the type of MFI structure which is characterized by X-ray diffraction (XRD), infrared spectroscopy (FTIR), UV-Vis. spectroscopy and catalytic studies that confirm the zirconium incorporation in the MFI network. The under free air Calcination causes a structural change in crystal symmetry from orthorhombic to monoclinic framework. (3)

In this study, we have chosen an organic molecule, 2-Mercaptobenzimidazole which is biodegradable (4) (5) and harmful for environment (6), and important heterocyclic (7) systems with varied new biological activities such as antibacterial (8), antifungal (9), and anti-inflammatory (10) activities. This synthesis of oxidation compounds was checked by melting point and TLC and their structure was established by various analytical techniques such as IR and ¹HNMR spectral studies.

MATERIALS AND METHODS

II.1 Synthesis of Zr-ZSM-5

The synthesis was performed without organic template by a hydrothermal process using the following experimental protocol. In a beaker containing a solution which contains: 7.85 g deionized water, 0.123 g of

zirconium (IV) oxide and under stirring, 0.64g of sodium hydroxide and 0.164 g aluminium source Al_2O_3 75.6% and 7.5g source silica Ludox (40% in H_2O) was added. Stirring was continued at room temperature until the obtaining of a homogeneous gel. The mixture 1SiO_2 , $0.02\text{Al}_2\text{O}_3$, $0.16\text{Na}_2\text{O}$, 0.02ZrO_2 $25\text{H}_2\text{O}$ formed was heated in an autoclave at 150°C for 48 h. after crystallization, the autoclave is cooled and the product was washed with H_2O and dried for 6 hours in air. The synthesized sample was calcined in air at 550°C for 6 hours.

II.II the used instrument of characterization

The diffraction pattern of the X-ray powder zeolite samples [Zr] ZSM-5 has been recorded on a diffractometer Bruker AXS D8 Advance with a graphite monochromatic over the range 2θ of 10° to 50° to a scan rate of 2° (2θ) by minute preparation of the samples for analysis to soft X-rays involved grinding the solid to a fine powder in a sample holder with a slight compression to make it flat and tight. IR framework spectra ($400\text{-}1300\text{ cm}^{-1}$) of sample were recorded with spectrophotometer Bruker Vector 22(KBr pellet). Diffuse reflectance UV-VIS spectra of the samples Was Recorded on Varian spectrometer dual beam UV-Visible a Cary 5E equipped with an integrating sphere coated with polytetrafluoroethylene (PTFE) at 200 and 800 nm. The synthetic zirconium silicate sample was determined using X-ray fluorescence spectroscopy of dispersive spectrometer XEPOS energy (Ametek Spectro).

II.III Catalytic reaction: Oxidation of 2- Mercaptobenzimidazole

The catalytic protocol for oxidation of 2- Mercaptobenzimidazole is carried out using aqueous H_2O_2 (30% aq.sol) as an oxidant. In a 100 ml flask, 0.5 g of 2- Mercaptobenzimidazole 16 ml of acetone with stirring .We added 0.05g of catalyst and 6 ml H_2O_2 was added to the reaction mixture Bring the mixture in an ice bath (exothermic) and the reaction was continued for 10 minutes each and follow the reaction by TLC. The obtained product was analysed with the HPLC method is developed as described above (as stated in the section) Using water 90-10 MeOH as the mobile phase and leads to a chromatographic separation. Figure shows the UV-chromatogram of the mixture were taken 1 ml of the solution (an amount of product soluble in THF and insoluble in acetone) was then injected using a micro syringe, 20 μl of the sample in the HPLC chromatogram is obtained .

RESULTS AND DISCUSSION

III.I Catalyst characterization [Zr] ZSM-5

III.I 1 Chemical analysis by XRF

The $\text{Na}_2\text{O} / \text{SiO}_2$ ratio from 0.033 to 0.167 has a clear effect on the purity of phase [Zr]ZSM-5 formed (11). [Zr] ZSM-5 was synthesized in the optimal conditions $\text{Na}_2\text{O} / \text{SiO}_2$ ratio = 0.16 and $\text{SiO}_2 / \text{ZrO}_2$ ratio = 50. The elemental composition of the [Zr]ZSM-5: 1SiO_2 , $0.02\text{Al}_2\text{O}_3$, $0.16\text{Na}_2\text{O}$, 0.02ZrO_2 $25\text{H}_2\text{O}$ was analysed on zirconium silicate powder. The sample synthesized have 45.82 wt% of Si, 1.247 wt.% of Al, and 16520 mg / kg of Zr suggesting isomorphous substitution of Si^{+4} in the Zr^{4+} tetrahedral sites. the samples have an orthorhombic crystalline form on calcinations in air around 550°C , [Zr] ZSM-5 is transformed into the monoclinic form (12).

III.I 2 Powder X-Ray Diffraction

Synthetic zeolite XRD pattern is shown in Fig. 1. The peaks at $2\theta = 20.28, 20.84, 22.17, 23.09, 23.86, 24.37, 29.23^\circ$ confirmed zeolite ZSM-5 (13). The fig 1 shows XRD pattern of the sample which was crystallized by the crystallization temperature of 150°C and the crystallization time from 48 hours to a $\text{Na}_2\text{O} / \text{SiO}_2$ ratio 0.16. The XRD pattern clearly indicates that the [Zr] ZSM-5 synthesized pentasil has the frame structure and orthorhombic symmetry (14).

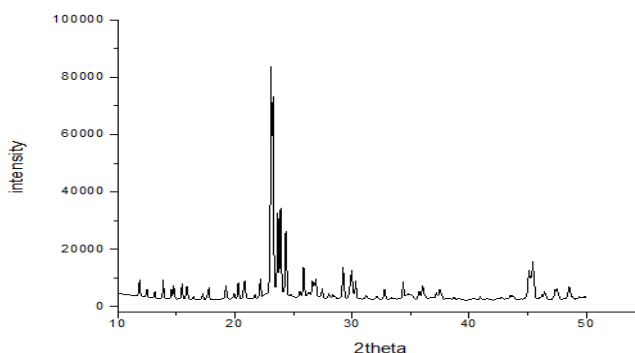


Fig 1: XRD patterns of [Zr] ZSM-5

III.I 3 FTIR Spectroscopy

The crystalline framework of spectra containing Zr in the MFI structure shown ZrZSM-5. A structure, under vibration band region ($450\text{-}1300\text{ cm}^{-1}$) are compared with that of MFI (15) the strong absorption band at 1320 cm^{-1} was assigned to the internal and the asymmetric stretching vibration of SiO_4 , AlO_4 tetrahedral.

Spectra [Zr]-ZSM-5 shows an absorption band at 962 cm^{-1} in addition to other bands characteristic of the MFI structure. this group probably comes (SiO_4) tetrahedral disturbed by the presence of zirconium ions in the vicinity

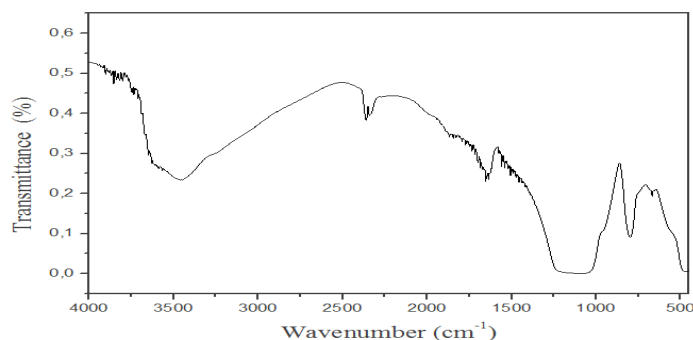


Fig 2: IR spectrum (transmission) of [Zr]ZSM-5

III.I 4 UV-Vis. Spectroscopy

The UV-VIS spectrum of [Zr]ZSM-5 shows a strong band of 212 nm (16). The solid ZrZSM-5 transition band has been allocated to the transition having a charge transfer character having sites Zr (IV), while pure silicalite does not give such a signal.

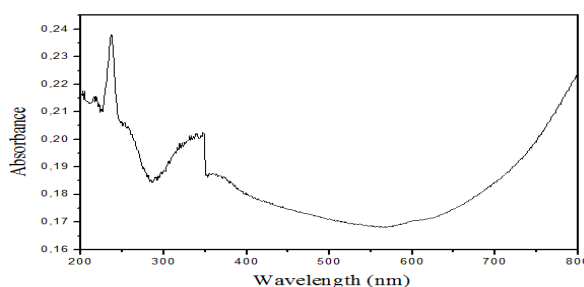


Fig 3: Diffuse reflectance UV-Vis. spectrum of ZrZSM-5

III.II Catalytic reaction: Oxidation of 2- Mercaptobenzimidazole

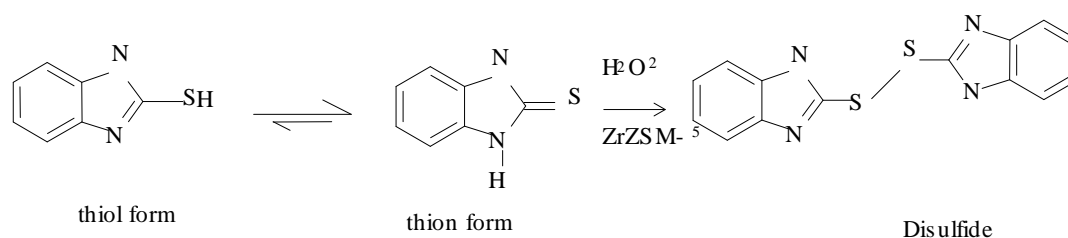
2- Mercaptobenzimidazole used as a pollutant model with $\text{C}_7\text{H}_5\text{N}_2\text{S}$ as Empirical formula and a Molecular weight $M = 150\text{ g / mole}$ soluble in acetone. These small molecules exist in equilibrium tautomeric thione / thiol bearing a $-\text{NH}-\text{C}=\text{S}$ and $-\text{N}=\text{C}-\text{SH}$ groups in a thione-thiol equilibrium (17), (18) this product is yellowish crystal with a pungent odor and is slightly soluble in water. The 2- Mercaptobenzimidazole is relatively very slightly soluble in a non-polar organic solvent, this experiment results concord the results of several studies found in the literature.

The spectrum showed the following characteristic band 2- Mercaptobenzimidazole s (cm^{-1}). (19) (20)

1.	3037.96 cm^{-1}	C-H aromatic
2.	3109.81 cm^{-1}	N-H secondary
3.	2835.89 cm^{-1}	S-H
4.	1595.65 cm^{-1}	C=N aromatic
5.	$1425.75, 1496.48\text{ cm}^{-1}$	C=C aromatic
6.	1319.88 cm^{-1}	C=S

2- Mercaptobenzimidazole has a thiol group, which can be used in several reactions (21), the mechanism of this reaction and the contributing factors for the light, oxygen and heat are evaluated. 2- Mercaptobenzimidazole is easily oxidized in order to obtain disulfide molecule via free radicals, Benzimidazole are an important class of heterocyclic compounds which have a wide range of biological properties In many research works, a series of new 2-substituted derivatives benzimidazole are synthesized and evaluated as improved antioxidant and antimicrobial agents .It was observed that the derivatives of 2-substituted benzimidazole confirmed the antioxidant and antimicrobial activities (22).

Scheme 1: Oxidation of 2- Mercaptobenzimidazole



Oxidation of 2- Mercaptobenzimidazole using hydrogen peroxide gave the title compound. (23) The structure of this compound was confirmed on the basis of its melting point of 202° C and the spectral data shown in Fig 4 this compound was prepared by oxidation of the - Mercaptobenzimidazole using hydrogen peroxide. Hydrogen peroxide 4ml with continuous stirring for 30 minutes, yellow precipitate was formed, which was collected by filtration, washed with distilled water and dried to give the -disulfide compound

The oxidation of 2- Mercaptobenzimidazole in disulfide using H₂O₂ (24) under mild conditions has also been demonstrated. The structures of the obtained products have been proven by the spectroscopic methods FTIR and HPLC.

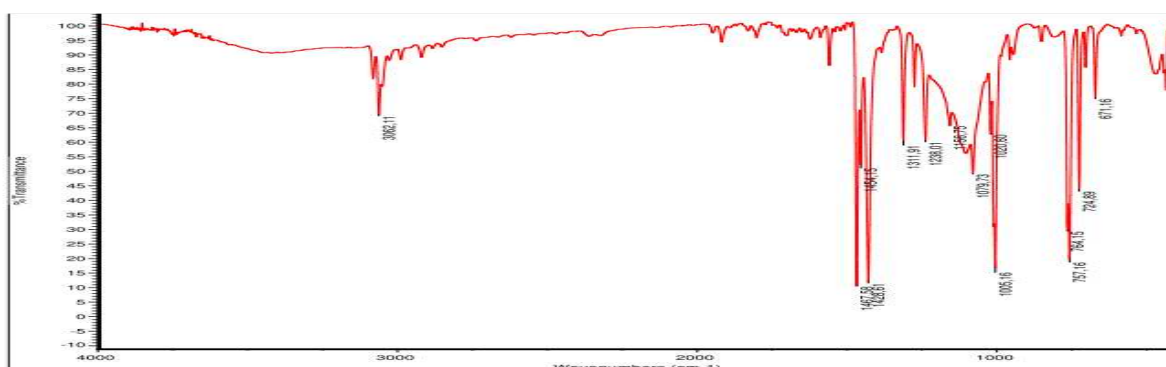


Fig4: The FTIR spectrum of Disulfide

Analytical and spectral data

Yield: 81% , crystal mp: 202-204°C; White solid; IR (KBr, cm⁻¹): 3062.11 cm⁻¹ (C-H aromatic), 1600 cm⁻¹ (C=N aromatic), 1428.61, 1467.58 cm⁻¹ (C=C aromatic) · 724,89cm⁻¹ (C-S) ,671.16 cm⁻¹ (S- S)

High performance liquid chromatography (HPLC):

The disulfide compounds studied was analyzed by high performance liquid chromatography (HPLC) with a Waters apparatus consists of:- A sample changer -a UV-visible absorption detector.- Flow rate: 1mL / min- Mode: isocratic- Eluent: water / MeOH 90/10- Column: C18- Length of the column: 12cm- Oven temperature: 40 ° C. The injection volume used for analysis is 20 µL .The product separation was performed on a column: C18 as a mobile phase consisting of a mixture of water / methanol with a flow of 1 ml / min.

Table1: analytical requirement implemented for HPLC analysis of compounds models

Compose analyzes	mobile Phase	Detection	
		UV Absorption	retention time (min)
Disulfide	90 /10 water / méthanol	$\lambda_{\text{abs}} = 254 \text{ nm}$	6.34 (25)

CONCLUSION

we have prepared [Zr] ZSM-5 with an MFI structure The Na₂O / SiO₂ from 0.167 to 0.033 using a hydrothermal synthesis .XRD, IR, UV-VIS and elemental analysis were conducted to assess its physical and chemical properties, and evidence of Zr⁴⁺ incorporation into the skeleton of the zeolite were provided: For the catalytic reaction trial in the liquid phase oxidation of 2-mercaptobenzithiazole using hydrogen peroxide as an oxidant was performed. Oxidative disulfide 2- Mercaptobenzimidazole transformation was observed while the use of hydrogen peroxide as oxidants with Zr ZSM-5 as catalystr. the important finding of our results is that disulfide is a stable product of 2-

Mercaptobenzimidazole oxide in aquatic environment. Oxygen cannot be excluded, as there are many C = S, the benzimidazole2-substituted derivatives are valued as improved antioxidant and antimicrobial agents.

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