

Oxidation of an organic molecule using a purely silicic zeolite as a catalyst

^[1] Affaf Tabti*, ^[1] Abderazzak Baba Ahmed and ^[1] Fathi Boudahri

^[1] Faculty of science and technology, Relizane University - Relizane, Algeria

^[1] affaf.affaf@yahoo.fr, ^[1] abderrazak_baba@yahoo.fr, ^[1] fethi.boudahri@cu-relizane.dz

Abstract— *The aim of this work is to study the catalytic performance of synthesized zeolite materials in an oxidation reaction of an organic molecule. The synthesis of these zeolites was carried out by following protocols and under precise temperature and crystallization time conditions. The materials obtained are characterized using different characterization techniques, X-ray fluorescence (XF), X-ray diffraction (XRD), infrared spectroscopy (IR) and visible UV spectroscopy (UVvis). The oxidation reaction was carried out in the presence of tert-butyl hydroperoxide (TBHP) as oxidant and zeolites incorporated with transition metals as catalyst. The progress of this reaction was followed by gas chromatography coupled to mass spectrometry (GC-MS), this reaction gave products consisting of the epoxide.*

Index Terms— *CrS-1, epoxidation, incorporated silicalite-1, incorporated zeolites, VS-1.*

I. INTRODUCTION

The oxidation of organic substrates represents one of the most important industrial chemical reactions [1], explaining the importance of the efforts invested in the research and development of new heterogeneous catalysts with the increase in activities and selectivities in these types of reactions. In particular, the epoxidation of alkenes which is the epoxidation of olefins is a reaction of great relevance both in industry and in academia. Epoxides are very important intermediates in the chemical industry, in particular for the synthesis of various polymers (polyglycols, polyamides, polyurethanes, etc.) [2], but they are also used in the synthesis of fine chemicals such as pharmaceuticals, perfume and fragrance additives [3].

With the growing interest in using zeolites as catalysts, increased attention has been paid to modifying zeolite properties by incorporating transition metals into the zeolite structure. This modification aims to cause changes in the chemical and physical properties and to induce new catalytic properties maintaining the original crystal structure of the zeolite. Subsequently, various elements such as Co[4], Cu[5], Mn[6], Ti[7], V[8], Zn[9], were incorporated as part of zeolite.

Catalysts derived from solid acids and bases play an important role with regard to economic and ecological aspects [10]. Both are widely applied in various chemical reactions [11],[12], but, so far, the number of processes using solid acid catalysts is massively larger than those considering solid bases [13]. Among solid acids, natural and synthetic zeolites have attracted great interest due to their catalytic and exchange properties. These microporous materials have also shown great potential for the epoxidation of various olefins [14]. Isomorphic substitution of various transition metals (Ti, Zr, Fe, Co, V, Cr, etc.) has been attempted to obtain catalytic functionalities in zeolites [15],[16].

Vanadium-incorporated zeolites are found to be active catalysts in selective oxidation reactions of organic compounds [18],[17], such as the oxidation of alcohol

hydrocarbons and the selective oxidation of benzene to phenol [19], the epoxidation of olefins and adsorption of dyes[40].

Using aqueous hydrogen peroxide and TPHB as the oxidant. The activity and selectivity of the vanadium silicalite catalyst depends on the nature of the vanadium species in the matrix, i.e. oxidation state, coordination number, stability and choice of solvent.

The incorporation of transition metal ions such as Ti and V makes zeolite oxidation catalysts active in liquid phase reactions with hydrogen peroxide and TPHB as the oxidant. However, due to the catalytic properties of chromium, several attempts have been made to introduce chromium cations into zeolites (Huang et al.[20], Sugimoto et al.[22], Mambrim et al.[21] and Chapus et al.[23].

Sugimoto et al. [24] reported that chromium atoms exist in a highly dispersed state on chromium silicates, Anpo and coworkers reported the photo-catalytic activity of chromium-incorporated ZSM-5 zeolites [24] for oxidation selective. The results clearly showed the photocatalytic efficiency of Cr(IV) in the context of silica and silica-alumina supports.

In the present work, we will study the catalytic performance of zeolites incorporated with transition metals (CrS-1 and VS-1) in the epoxidation reaction of a cycloalkene (cyclooctene), this reaction led to a mixture of compounds. Among the various products the cyclooctene oxide which was formed.

II. Experimental

II.1 Synthesis of incorporated zeolites

VS-1 and CrS-1 synthesized from a gel containing reagents, Ludox as silicon source, in the presence of structuring agent tetrapropylammonium hydroxide (TPAOH), metal source and water. These mixtures are stirred for 2 hours at room temperature (25°C) until homogeneous mixtures (gel) are obtained. These gels of molar composition are transferred into reactors and then placed in an oven heated to 175°C:

-KF-0.08TPAOH-SiO₂-0.01VOSO₄-20H₂O

-KF-0.08TPAOH-SiO₂-0.01Cr(NO₃)₃-20H₂O

After a crystallization period of 24 hours, the autoclaves are removed from the oven. The recovered products are filtered, washed several times with distilled water and dried at 80°C. The products obtained are calcined at 550° C for 6 hours. The synthesized materials are characterized by different techniques, X-ray fluorescence, X-ray diffraction, IR spectroscopy and UVvis spectroscopy.

II.2 Oxidation tests

The oxidation reactions were carried out in a two neck round bottom flask equipped with a reflux condenser. The reaction system was magnetically stirred. The progress of the reaction was followed by GC-MS (Trace GC equipped with an Optima 5 MS column (30 m length, 0.25 m thickness, 0.025 mm internal diameter) coupled to an MS spectrometer). To identify the epoxidation products, after cooling 1L was taken from the crude reaction mixture and then it was injected into the GC/MS apparatus.

III. Results and discussion

III.1 Characterization of incorporated materials

III.1.1 X-ray fluorescence

X-ray fluorescence of silicalite-1 incorporated with transition metals (VS-1 and CrS-1) synthesized from tetrapropylammonium hydroxide (TPOH) as a structuring agent showed that 57%, 49.38% of vanadium and chromium species were incorporated, respectively.

III.1.2 X-Ray Diffraction (XRD)

The diffractogram (Fig. 1.a) shows that the sample is well crystallized with an MFI topology [25], [26], [27]. The diffraction analysis of this material presents values in the 2θ domain is from 28.31 to 28.61°. The presence of the peak at $2\theta = 23.3^\circ$ generally indicates orthorhombic symmetry [28]. The crystallinity is calculated from a diffractogram considering the most intense peaks [29].

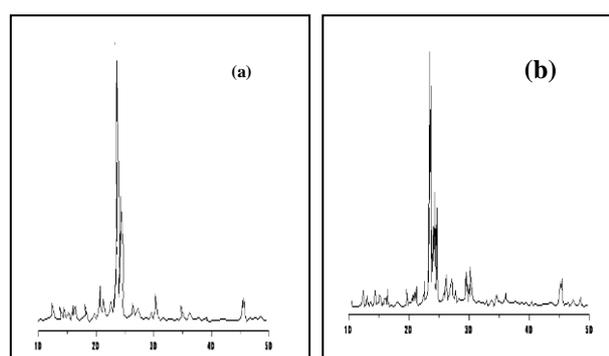


Figure1: XRD patterns of VS-1 and CrS-1.

The X-ray powder diffraction pattern of the Cr-containing sample exhibits a crystallized MFI structure is shown in (Fig. 1.b). The recovered sample has an orthorhombic structure. We observe the peaks at $2\theta = 8.0, 8.9, 23.1, 23.3, \text{ and } 24.0^\circ$ [37],[38],[39].

III.1.3IR spectroscopy

The FT-IR spectra of the synthesized materials are presented in figure 2, the spectrum (Fig. 2.a) shows adsorption bands

which are found at 550 and 960 cm^{-1} . These bands indicate the existence of the five-membered ring of the MFI-like zeolite structure and the incorporation of vanadium atoms into the zeolite structure, respectively [30].

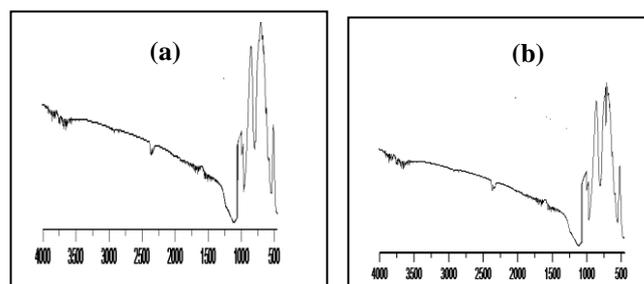


Figure 2: IR spectrum (transmission) of VS-1 and CrS-1.

The FTIR spectrum (Fig. 2.b) of Cr-containing materials with obtained MFI structure is shown in pure silicalite-1 at FTIR bands at 1230, 1100, 800, 550 and 450 cm^{-1} , which assigned to different vibrations of the tetrahedral and framework atoms of the MFI zeolite [33]. The band at 550 cm^{-1} confirms the presence of the MFI structure, whereas at 450, 800, 1100 and 1230 cm^{-1} are mainly affected by asymmetric elongation and symmetrical elongation [34]. Two absorption bands are present at 585 and 630 cm^{-1} which are assigned to the vibration of Cr=O and Cr-O bonds [35]. These cases prove that the crystallinity of CrS-1 increases with increasing crystallization temperatures or crystallization times.

III.1.4 UV-Vis. Spectroscopy

UV-Vis spectroscopy is a useful technique for obtaining information about the coordination environment and oxidation states of metal ions. The UV-Vis spectra of VS-1 and CrS-1 are given in Fig.3. The synthesized vanadium-incorporated material exhibits strong charge transfer (CT) bands below 500 nm. The spectrum of VS-1 (Fig. 3.a) was dominated by four characteristic TC bands from oxygen to metal. According to the literature, the CT band centered at about 230-240 nm has been attributed to the tetrahedral structure of $(\text{SiO})_3\text{V}^{\text{V}}=\text{O}$ located in the silica framework [31],[32].

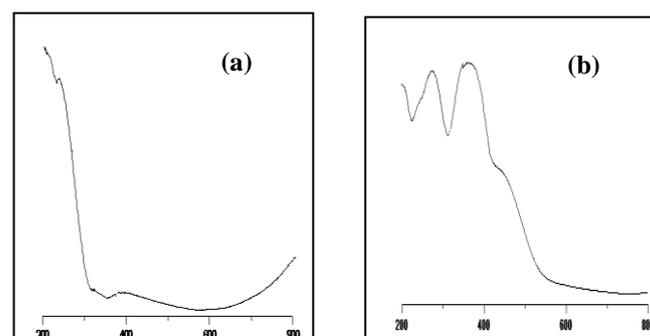
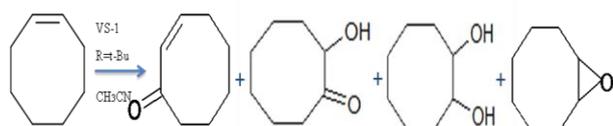


Figure 3: Diffuse reflectance UV-Vis. spectrum of VS-1 and CrS-1.

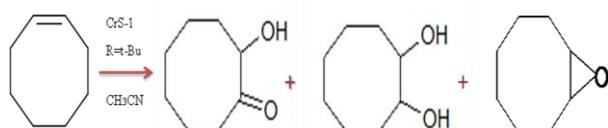
As shown in Fig.(3.b), the UV-vis spectrum of CrS-1 shows bands, which indicate the incorporation of the metal atoms into the framework of silicalite-1. Two distinct absorption bands at 280 and 370 nm that can be assigned to charge transfer from O²⁻ to Cr⁶⁺ [36].

III.2 Catalytic reaction

We present the evaluated catalytic performance of VS-1 and CrS-1 through epoxidation tests (scheme 1 and 2) performed using tert-butyl hydroperoxide (TBHP) as the oxidant. First, the flask was charged with 100 mg of synthesized materials (VS-1 or CrS-1), then 10 mL of CH₃CN, 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 to 70°C.



Scheme 1: Cyclooctene oxidation in the presence of VS-1 as a catalyst.



Scheme 2: Cyclooctene oxidation in the presence of CrS-1 as a catalyst.

Using VS-1 as catalyst, the reaction performed at 70°C resulted in a mixture of compounds (Fig. 4). Among the various products, the cyclooctene oxide that was formed, trans-1,2 cyclooctanediol, 2-hydroxy-cyclooctanone, and 2-cyclo-octene-1-one. In the table below, we give the products detected by GC-MS.

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

The products obtained	RT (min)	A _i /A _{is} *
<i>cis</i> cyclooctene	4.35	1.35
cyclooctene oxide	10.23	0.10
2-cyclooctene-1-one	11.46	0.04
2-OH-cyclooctanone	16.46	0.01
<i>trans</i>		
1,2-cyclooctanediol	18.55	0.006

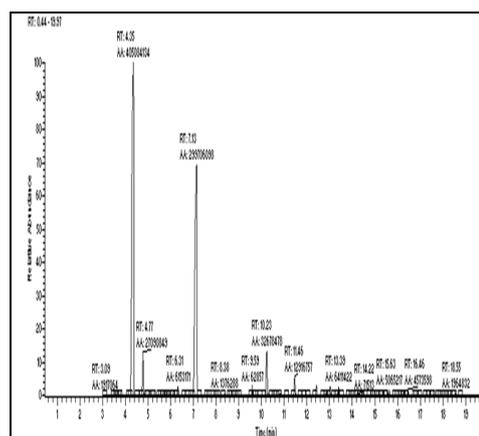


Figure 4: GC-MS of the cyclooctene epoxidation reaction using VS-1 as catalyst (24 hours) and TBHP as oxidant.

During the epoxidation of cyclooctene, in the presence of silicalite-1 incorporated with chromium as a catalyst (Fig. 5), the reaction gave as products: cyclooctene oxide, trans-1,2 cyclooctanediol and 2-hydroxy-cyclooctanone (see Table 2).

Table 2: Relative areas of compounds detected by GC-MS for TBHP/CrS-1 vs.time

The products obtained	RT (min)	A _i /A _{is} *
<i>cis</i> cyclooctene	4.29	4.93
cyclooctene oxide	10.38	1.48
2-OH-cyclooctanone	16.46	0.19
<i>trans</i>		
1,2-cyclooctanediol	18.55	0.09

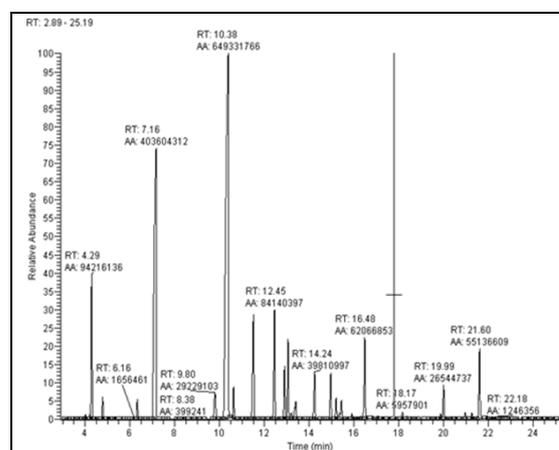


Figure 5: GC-MS of cyclooctene epoxidation reaction using CrS-1 as catalyst (24 hours) and TBHP as oxidant.

IV. CONCLUSION

In this work, we explored the catalytic performance of purely silicic zeolites incorporated with transition metals (V,Cr) in the epoxidation reaction of cyclooctene. Silicalite VS-1 of V/Si = 0.0025 and CrS-1 of Cr/Si =0.0020 (from X-ray fluorescence analysis) were prepared from vanadium oxide sulfate and nitrates of chromium under hydro-thermal conditions and characterized as an orthorhombic structure (XRD) with vanadium and chromium ions in tetrahedral coordination (UV-Vis data). The possibility of use as a

catalyst was demonstrated in the catalytic test of the epoxidation of cyclooctene, in the presence of TBHP in acetonitrile as oxidant.

The oxidation reaction in the presence of VS-1 gave a mixture consisting of epoxyde with a low percentage 6.71%. The products obtained are cyclooctene oxide, trans-1,2 cyclooctanediol, 2-hydroxy-cyclooctanone, and 2-cyclo-octene-1-one.

On the other hand, the oxidation reaction in the presence of CrS-1 gave a mixture with a very high epoxide yield of 100%. The products obtained are cyclooctene oxide, trans-1,2 cyclooctanediol and 2-hydroxy-cyclooctanone.

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