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Catalytic Performance of M-ZSM-5 Catalysts for Conversion of 5α-cholestanol and Cinnamic Alcohol

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ABSTRACT

Selective oxidation of 5α-cholestanol and cinnamic alcohol was studied on M-ZSM-5 catalysts, the physico-chemical characterization were investigated by nitrogen adsorption desorption at 77K, X-ray Diffraction (XRD), Thermogravimetric Analysis (TGA), UV-Visible and FTIR spectroscopies. The effect of operating conditions (concentration of metal nitrate and temperature on exchange rate) has been studied. Results show that the M-ZSM-5 catalyst was high stable when the concentration of the metal nitrate $C_{n\text{-}metal}=0.2$ *mol and temperature on exchange rate T=80°C, the characterization results of M-ZSM-5 reveals that Silanols on the catalyst surface play and substantial role in dispersing the MOx active species. Finally, the use of the MFI-type zeolites exchanged with transition metals such as Cr, Cu and Co in oxidation reactions of allylic and steroidal alcohols provides the corresponding products with very high yields and total conversions.*

Keywords: M-ZSM5, Zeolite, 5α-cholestanol, Cinnamic alcohol, Selective oxidation, Characterization, Catalyst

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INTRODUCTION

The oxidation of alcohols to ketones and aldehydes is probably one of the most common transformations [1,2]. There are many of homogeneous and heterogeneous catalysts to carry out this transformation; among the most widely used, we can mention the zeolites of the MFI type. These processes need the use solvents, relatively short reaction times and the presence of an oxidizing agent, the use heterogeneous catalysts is intended to improve the durations, selectivity and yields of the reactions. The latter are recyclable and capable of effecting controlled oxidation reactions of the alcohols in liquid phase under mild conditions of temperature and pressure. Thus, for their low costs, the use of zeolites in this type of reactions and more particularly in liquid medium encourages researchers to synthesize environmental products. The catalysts used in our reactions are zeolites of the ZSM-5 type exchanged at low Chromium (Cr), Cobalt (Co) and Copper (Cu) contents. This study is devoted to oxidation reactions in liquid medium, we synthesized ZSM-5 zeolites in an alkaline fluoride medium. We then characterized the materials obtained by different spectroscopic techniques to predict their structural and morphological properties. Finally, we have carried out the oxidation reactions of the allylic and steroidal alcohols (cinnamic alcohol, 5α-cholestanol) in liquid phase to prove the catalytic effect of these zeolite materials in this type of reactions.

MATERIALS AND METHODS

IM-ZSM5 synthesis procedure

Reagents used and stoichiometric range: Source of silica: sodium silicate of composition (63% SiO_2, 18% Na_2O, 18H_2O (Fluka). Aluminum source: aluminum sulphate hexadecahydrate (Prolabo). Hydrofluoric salts: potassium fluoride (KF), Prolabo. Source of structuring Tetrapropylammonium Bromide (TPABr), Aldrich. Solvent demineralized water.

Preparation of the reaction mixture

The reaction mixtures are prepared at room temperature under strong magnetic stirring in two solutions: *Solution A:* Sodium silicates are dissolved in deionized water with vigorous stirring and a solution of TPA-Br. *Solution B:* A slurry consisting of aluminum sulphate and potassium fluoride is prepared and dissolved in deionized water.

Solution B is added to solution A, stirring continues until a gelatinous and homogeneous mixture is obtained. The stirring time is 2 h. The pH of the reaction mixture is measured before and after crystallization with pH meter. It is generally of the order of 13. It is adjusted to 10.5 by the addition of a solution of 1 N sulfuric acid. The composition of the reaction mixture: 100 SiO_2, $Al_2 O_3$, 27 Na_2O, x KF, TPA-Br, 7000 H_2O. The gel is allowed to ripen for 24 h at room temperature and with magnetic stirring before bringing it to the crystallization temperature.

Preparation of ZSM-5 zeolites exchanged with transition metals

Cation exchange is an important operation since it makes it possible to modulate the adsorption and catalysis properties of the zeolites. Several studies concerning the thermodynamic and kinetic aspects as well as the parameters of the zeolite exchange process are published in the bibliography [3,4]. The passage from the sodium or proton form to the MZ forms, where M is a given cation (usually transition metals or hydrogen) and Z The ZSM-5 zeolite is generally carried out in various ways: Exchange in contact with an aqueous or non-aqueous saline solution (hydrothermal exchange), exchange in contact with a molten salt, exchange of the zeolite cations with anionic metal complexes, exchange in contact with a gaseous compound. In general, the majority of the works consider that the exchange process is ternary between the proton, the sodium and the cation to be exchanged.

In this work, we followed the protocol developed by Lounis et al. [5], as follows: The ZSM-5 synthesized previously with the following composition of the starting gel: 100 SiO_2, 1 $A1_2O_3$, 27 Na_2O, 20 KF, 40 TPA-Br, 7000 H_2O, is exchanged with sodium as follows: 2 g synthesized zeolite are contacted with 200 ml of 1 M NaCl solution for 24 h at room temperature under gentle agitation. The initial ion exchange is followed by the second, under the same conditions as above. Na-ZSM5 samples are later exchanged with metal ions by bringing 2 g of the solid material into contact with a 40 ml solution of metal salts. The salts used are nitrates of metals. This cation exchange is carried out at 80°C for 2 h. The pH control is monitored in all cation exchanges and adjusted to 6 by 40% aqueous methylamine solutions. Demineralized water is used for all synthesis and exchange procedures. The resulting M-ZSM-5 form is filtered and washed several times. The final product is dried at 80°C overnight before being analyzed by the various characterizations.

The used instrument of characterization

The exchanged products are identified and their crystallinity is determined by X-ray Diffraction (XRD) using copper Kα radiation (Philips PW-1130/00). The morphology and size of the crystals of the zeolites are determined by Scanning Electron Microscopy (SEM) (Philips model of XL30 FEG). The chemical composition is calculated by X-ray fluorescence (Philips of Magix). The A.T.G and A.T.D are carried out under an N_2 atmosphere using the apparatus (Seteram de Labsys) with a heating rate of 10°C/min (Flow rate of 10 centimeters per minute). The specific surface is calculated using the ASAP 2010 apparatus.

RESULTS AND DISCUSSION

Effect of the concentration on the exchange rate

The initial nitrate concentration of metals is an important parameter in cation exchange, because it affects the exchange rate as well as the crystal structure of the material used, we have observed a maximum exchange rate especially for the concentration of (0.2 M), because beyond this concentration the exchange rate is considerably reduced. This can be explained by the fact that, at a high concentration (0.3 M), the interactions between the cations become more and more important, which considerably reduces their mobilities and consequently their diffusions within the crystal lattice (Figure 1).

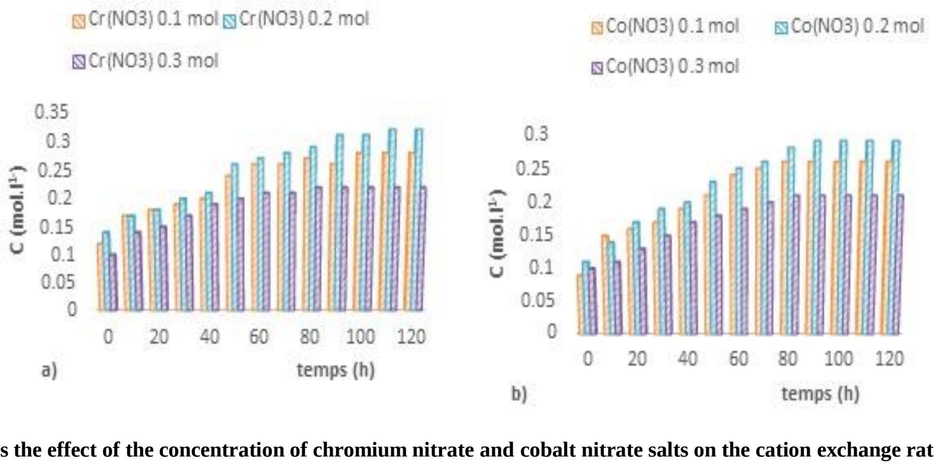


Figure 1: Histogram shows the effect of the concentration of chromium nitrate and cobalt nitrate salts on the cation exchange rate in ZSM-5 zeolite, (a): Cr, (b): Co.

Effect of temperature on exchange rate

We have studied the effect of temperature on the activation of the exchange, as well as on the cation exchange rate, five temperatures are chosen: 40°C, 50°C, 60°C, 70°C and 80°C. The nitrate concentration of metals under these conditions is set at 0.2 M. The exchange rate of the metal in the zeolite increases with temperature. This explains why thermal activation greatly affects the velocity of cations in solution and consequently accelerates the step of intra-network exchange [6]. The free energy of the exchange increases with the temperature according to the relation in Equation 1:

$$AG^0 = -\frac{RT}{Z_A Z_B}\ln K_a \qquad (1)$$

Where, R perfect gas constant, Ka equilibrium thermodynamic constant, Z_A and Z_B valence of cations A and B. In Figure 2 there is a rapid change in the exchange rate during the first half-hour, then it becomes slower and tends towards a limit value after approximately 2 h of exchange.

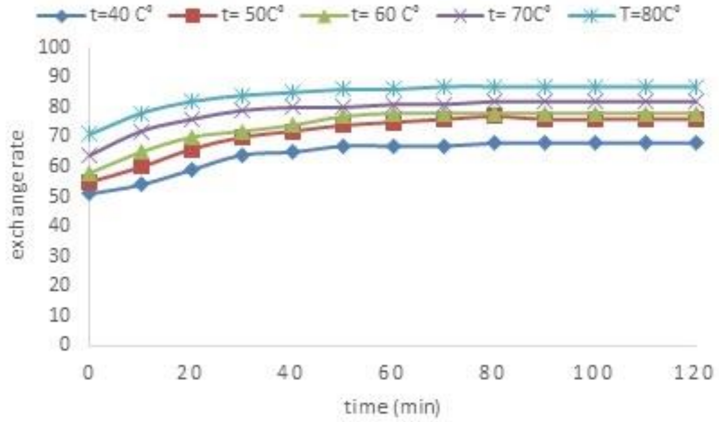


Figure 2: Effect of temperature on the exchange rate of chromium in ZSM-5

Characterizations of ZSM-5 exchanged with transition metals

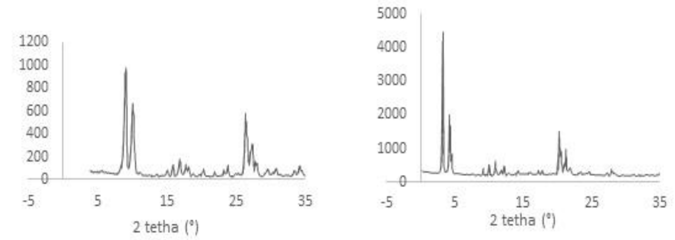
Characterization by XRD

XRD is an excellent method for detecting the structure of crystalline phases, this technique was used under ambient conditions of temperature and pressure to determine the structures of the frameworks of synthesized zeolites. The method involves sending an X-ray stream to the pulverulent sample and harvesting the diffracted rays. The diffractrograms obtained represent the intensity of the diffracted radiation as a function of the angle of incidence. XRD allows the identification of crystalline phases, the evaluation of the crystallinity of the samples and the calculation of the parameters of the crystal lattice. The analysis was carried out using a Philips X-ray diffractometer PW-1130/00, working on the monochromatic Kα1 radiation of copper (1.5406 Å). A counter (PM 8203) records a signal proportional to the intensity of the diffracted ray. Figure 3 shows the X-ray diffractrograms of the synthesized zeolites, was found that all the catalysts exhibited the crystalline phase and the characteristic structure of MFI zeolite. These peaks in the range 2θ=(6°-10°) and 2θ=(22°-24°).

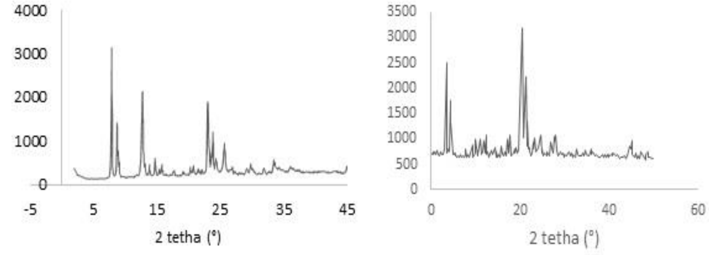
We computed the elemental mesh parameters of the zeolites by crystallographic data and found that these structures were orthorhombic (Table 1).

Table 1: The variation of the mesh parameters of the ZSM-5 and its exchanged forms

Samples	a (Å)	b (Å)	c (Å)	V (Å)^3
ZSM5	20.10	19.81	13.28	5287.84
Na-ZSM-5	19.99	19.72	13.16	5187.70
Cr-ZM-5	20.0851	19.9623	13.4656	5398.96
Cu-ZSM5	19.967	19.819	13.180	5215.66
Co-ZSM5	20.21	19.85	13.27	5323.50



(a) ZSM-5 (b) Cr-ZSM-5



(c) Co-ZSM-5 (d) Cu-ZSM-5

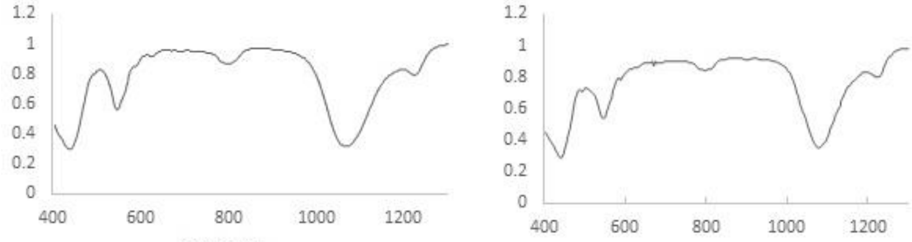
Figure 3: X-ray diffractrograms of zeolites (a) ZSM-5, (b) Cr-ZSM-5, (c) Co-ZSM-5 and (d) Cu-ZSM-5

IR spectroscopy analysis

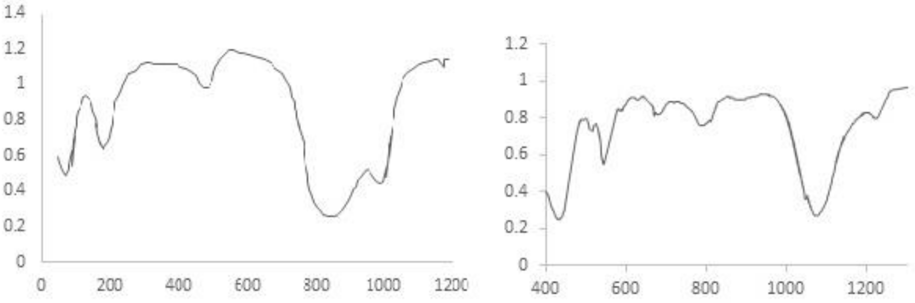
FTIR spectroscopy is based on the absorption of infrared radiation by the analyzed catalysts; it makes it possible to analyze the chemical functions present in the materials *via* the detection of the characteristic vibrations of the chemical bonds. For this purpose, we performed this technique using a Perkin-Elmer FT 1720 spectrometer over a range of 400-4000 cm^{-1} with a resolution of 2 cm^{-1}. The samples were packaged as dispersions in KBr pellets (Figure 4).

Examination of the infrared spectra reveals adsorption bands which are as follows:

- Vibration bands of valence of the OH groups between 940 and 3625 cm^{-1} [7]. These vibration bands also characterize the elongation of Al_2OH (interaction between OH and Al) [8].
- The bands recorded at 470 and 540 cm^{-1} are respectively assigned to the deformation vibration bands of the Si-O, Si-O-Si and Si-O-Al bonds [9].
- The vibrating band characteristic of the aluminosilicate is between 1010 and 1130 [10], this band also exhibits the valence vibration of the Si-O bond.
- Additional bands between 1380-1450 cm^{-1} can be attributed to the metal oxide in the zeolites.
- All infrared results confirm the presence of MFI structures.



(a) ZSM-5 (b) Cr-ZSM-5



(c) Co-ZSM-5 (d) Cu-ZSM-5

Figure 4: Infrared analysis of zeolites (a) ZSM-5, (b) Cr-ZSM-5, (c) Co-ZSM-5 and (d) Cu-ZSM-5

Analysis by ultraviolet spectroscopy

UV spectrophotometric analysis, based on the study of the change in light absorption by a medium, makes it possible to calculate the concentration of a constituent; this is calculated by measuring the relative absorption of light with respect to that of a substance of known concentration. This method of analysis allows working on small quantities of substances and can be applied to solid, liquid or gaseous samples. The spectrophotometer we used is a Thermo Electron corporation UV Nicolet evolution e100, has a spectral range of 200-900 nm. The accuracy is minus 1 nm at room temperature. The light sources used are two: à halogen tungsten visible lamp and a deuterium UV lamp. The scanning speed was set. The visible UV spectra of the catalysts: ZSM-5, Cr-ZSM-5, Cu-ZSM-5 and Co-ZSM-5 are shown in Figure 5.

Examination of the ultraviolet spectra reveals adsorption bands which are as follows:

- Two adsorption bands appear at 213 and 252 nm on the Cr-ZSM-5 catalyst and confirm the presence of the isolated molecules of Cr^{3+} and Cr_2O_3. As we noticed two bands at 375 and 600 nm correspond to the CrOx chromium oxides.
- We obtained three vibration bands in the case of Cu-ZSM-5, the first in the region 410 at 610 nm, linked to the transition T1 and attributed to the Al-O units and the metal ions, the second is between 350 and 400 nm bound to the charge transfer transition from ligand to metal [11]. A third between 356 and 495 nm attributed to Cu_2O_3 [12].
- An absorption band at 240 nm on the Co-ZSM5 spectrometer confirms the presence of the cobalt oxides CoOx and two bands at 340 and 410 nm due to the octahedral cobalt ions which constitute small Co-oxo oligomers.
- A band at 256 nm has been assigned to the Cu^{2+} species bound with the oxygen atom [13] and between 610 and 800 nm to the Cu^{2+} cations [14].

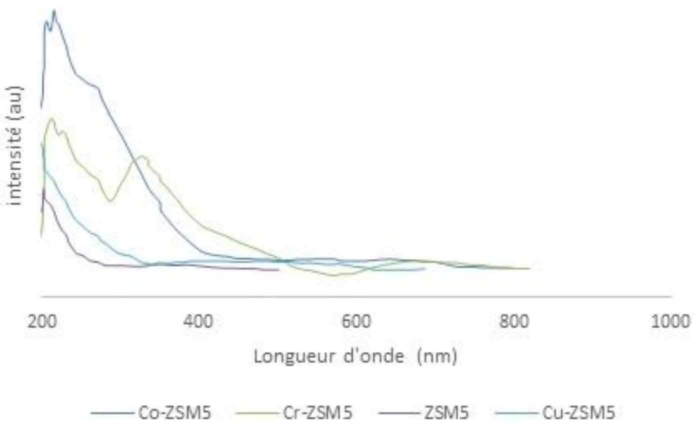


Figure 5: UV-Visible spectrometer for catalysts ZSM-5 and M-ZSM-5 (M=Co, Cu, Cr,)

Gravimetric thermal analyzes

The gravimetric thermal analysis makes it possible to measure the mass losses M of a sample as a function of the temperature (°C). This technique makes it possible to quantify the contents of physisorbed water, and of organic matter for a raw sample or in silanols for a calcined sample such as our catalysts. We used the Setaram thermo analyzer, and we filled alumina crucibles with 20 mg samples. The sample undergoes a temperature rise of 30-850°C, with a heating rate of 5°C/min.

The results of the gravimetric analysis (Figure 6) show the losses in weight over two intervals:

- The first in the temperature range between 50 and 330°C, which corresponds to the evaporation of water molecules.
- The second at a temperature higher than 300°C and which relates to the thermal decomposition of organic matter (structuring agent).
- Thermograms confirm good thermal stability of MFI zeolites.

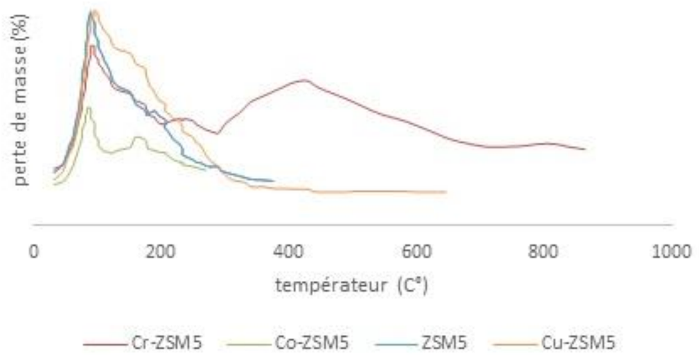


Figure 6: ATG thermograms for ZSM5 and M-ZSM5 (Cu, Cr, and Co)

Characterization by nitrogen adsorption-desorption at 77 K

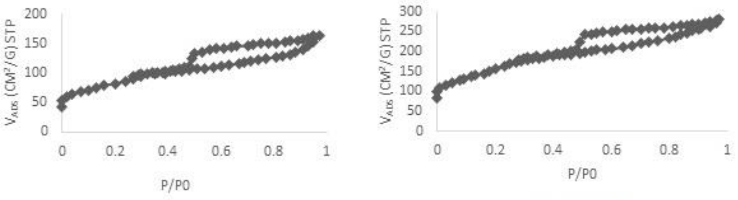
Measurement of the specific surface area by nitrogen adsorption is the most frequently used method for the characterization of materials. Brunauer, Emmet and Teller (BET) designed a multilayer adsorption model of nitrogen molecules (Equation 2); the adsorption-desorption isotherms of nitrogen at 77 K make it possible to characterize the textural properties of the microporous materials, that is to say the pore size, the specific surface area and the pore volume. The graphs shown in Figure 7 show that:

- Nitrogen desorption adsorption curves confirm the characteristics and structures of zeolites.
- The adsorption of nitrogen in the synthesized materials is characterized by a type IV adsorption isotherm according to the IUPAC classification.
- Generally, the M-ZSM-5 catalysts have a large surface area, this can be explained by the size of the metal ions which have swollen the pores and the walls of the zeolites.

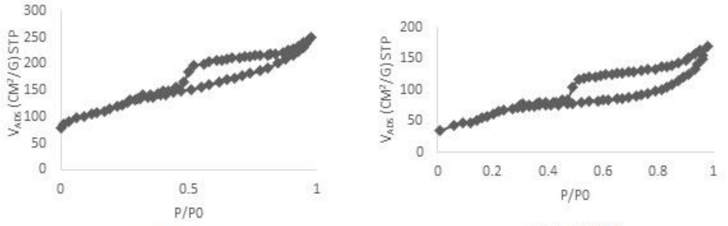
The theory formulated by BET in 1938 formalizes the phenomena of multilayer adsorption on the surface of the zeolites. This results in the BET Equation 2:

$$(p/p_0)/V_{ads}\,(1-p/p_0) = 1/V_m C_{BET} + \frac{C_{BET}-1}{V_m C_{BET}}.p/p_0 \qquad (2)$$

Where, V_{ads} is the adsorbed volume, V_m is the volume needed to cover the material of a monolayer and C_{BET} is the BET constant.



(a) Co-ZSM-5 **(b) Cr-ZSM-5**



(c) ZSM-5 **(d) Cu-ZSM-5**

Figure 7: Adsorption isotherms at 77 K of zeolites (a) Co-ZSM-5, (b) Cr-ZSM-5, (c) ZSM-5 and (d) Cu-ZSM-5

Oxidation of allylic and steroidal alcohols by M-ZSM5

The oxidation of the alcohols to their corresponding carbonyl compounds is an important reaction in chemistry [15]. In addition, the oxidations of allylic and steroidal alcohols are reactions of fundamental importance in organic chemistry with applications in fields ranging from pharmaceutical products to agricultural products [16]. For many years the oxidation of allylic and steroidal alcohols is a particularly important subject and has aroused interest in useful synthetic conversions. Several types of catalysts succeed in controlling the process of selective oxidation of this type of alcohols, the transition metal complexes of which are the best known and have been successfully applied [17]. Review of the literature also showed that other types of oxidants with a variety of catalytic methods were used for the oxidation of allylic alcohols [18,19]. In this thesis we are interested in heterogeneous catalysts of type MFI.

Procedure for the oxidation of allylic and steroidal alcohols

ZSM-5 (3 mg, 0.002 mmol Cr), 5 ml of toluene, oxidizing agent (t-BuOOH 70% aqueous 0.54 ml, 4 mmol) are introduced successively into a 25 ml flask equipped with a refrigerant, or (4 mmol of 35% aqueous H_2O_2). After stirring for 10 min, the substrate (1 mmol) is then added. The reaction mixture is brought to a temperature of 80°C in an oil bath, with magnetic stirring. The evolution of the reaction is carried out every half hour by analysis on CCM plates. Developer: UV lamp (546 nm) and a developer based on phosphomolybdic acid diluted in ethanol [20].

At the end of the reaction, the solution is filtered through a small column of alumina eluted with ether to reduce the remaining oxidant. The solvents are removed in a rotary evaporator. The concentrated filtrate is purified by flash chromatography or by preparative plates. The eluent used for both types of chromatography is petroleum ether/ethyl acetate (90/10) [21].

Gas Chromatographic (GC) analyzes coupled with mass spectrometry were carried out on a Schimadzu GC-14 B chromatogram equipped with an Apiezon L column and an Flame Ionization Detector (FID). The results of oxidation reactions of 5α-cholestanol and cinnamyl alcohol in the presence of Cr-ZSM-5 and H_2O_2, t-BOOH were tabulated in Table 2.

Table 2: Results of oxidation reactions of 5α-cholesterol and cinnamic alcohol in the presence of Cr-ZSM-5 and H_2O_2, t-BOOH

Sample	Substrate	Oxidants		Time (h)	Product form	Yield (%)		
		H_2O_2	t-BOOH			Cr	Cu	Co
1	5 α-cholestanol	*		8	5α-cholestanone	50	42	38
2	5 α-cholestanol		*	8	5α-cholestanone	81	61	50
3	Cinnamic alcohol	*		8	Cinnamaldehyde	30	27	18
					Cinnamic acid	7	5	6
					benzaldehyde	32	30	30
4	Cinnamic alcohol		*	8	Cinnamaldehyde	40	38	28
					Cinnamic acid	10	8	9
					benzaldehyde	40	37	35

CONCLUSION

The main objective of our work was to determine the structural specificities and the reaction mechanisms between the MFI catalysts that we have synthesized and characterized and the substrates (Oxidants, allylic alcohols and steroids) in order to measure the catalytic performances of these products and determine the optimum conditions for achieving the best model systems in terms of reactivity and catalytic activity. For this purpose, in the first part of this work we carried out some catalytic tests by M-ZSM-5 and different oxidants on the oxidation reactions of allylic and steroidal alcohols in liquid phase with ZSM-5 zeolites exchanged at low levels in some transition metals.

The physicochemical analysis techniques were carried out after the syntheses of the MFI zeolites and on the catalytic tests in order to understand the efficacy of these catalysts. XRD a verified the crystallinity and purity of the zeolitic materials obtained. This technique shows that the characteristic peaks of the synthesized products located in the region 2θ=(22-24°) present higher intensities with respect to the region 2θ=(6-10°). This may be due to the fact that the organic structuring agent is occluded in this region at higher inter-lattice distances, Nitrogen adsorption/desorption manometry confirmed the presence of crystal agglomerates constituting the layers of the catalysts and the absence of the amorphous phases. The analysis of the optimized zeolites, allowed us to calculate the values of the specific surface area. It is of the order of 450 m^2/g. Analysis by infrared spectroscopy of the solid allowed us to observe two bands of vibrations in the vicinity of 550 cm^{-1} and 1225 cm^{-1}, confirm the structure of the ZSM-5 zeolites.

Analysis of the results obtained shows that the oxidation of allylic and steroidal alcohols provides the corresponding products with very high yields and total conversions especially with the use of Cr-ZSM-5 zeolite. Finally, the use of the MFI type zeolites exchanged with transition metals such as Cu, Cr and Co in oxidation reactions of allylic and steroidal alcohols provides the corresponding products with very high yields and total conversions.

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