



Preparation and Characterization of Metals nanostructures supported on zeolitic and clay, application in the transformation of glycerol

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Abstract: The substituted or exchanged zeolites have large applications in petrochemical and hydrocarbons refining¹. The active sites versatility that may be present in these materials increases significantly their catalytic potential in the zeolite¹⁻⁴. Some authors associated with Shell International Petroleum, have studied the properties of zeolite catalysts exchanged or not by group VIII elements in the perspective of improving the fuel quality⁵.

The method that we have developed permits to obtain oxides (CoO and CeO) compounds under nanostructures amorphous forms supports on zeolite LTA, HY and the clay montmorillonite, the oxides arrivals comes from the decomposition of Murexide-metal complex in a slightly acid medium. The kinetically released cations form colloidal sols are more attractive by the electronegativity supports for this fact. The excess charges were characterized by laser zetametry.

The prepared catalysts powders were analyzed by X-ray diffraction (EXD) to determine their crystallinity degree in one hand and on the other determine the average dimensions of the nanostructures obtained materials. The carried out TGA and DSC analyzes for each sample at a temperatures variation (25-500 °C) to ensure the stability of the catalysts in practice mode. The Readings of Fourier transform infrared spectra were determined by the pyridine adsorption, this to determine the Bronsted and Lewis of catalyst surface acidity and the presence of elements (Co and Ce) under their most stable form in the cared structures. The catalytic tests were carried out on the glycerol transesterification at a temperature (T=75-80 ° C) and on the isomerization reaction of normal hexane (T =250-350° C).

1-Introduction

The main goal is to prepare oxides nanoparticles of transition metals (Co and Ce), this in three mineral matrixes, the montmorillonite, the synthetic zeolites (LTA) and HY. The used matrixes present the same qualitative composition practically but of different structures, it would permit to compare their characteristic and their properties physic-chemical.

The elements (Co and Ce), extensively used in petrochemical and raffling.

The gotten nanostructures are tested then in the transformation of the glycerol. Universally the glycerol is a secondary product, the too elevated quantities of this last are destined then to be a carburant valorized.

2 - Preparation of catalysts nanocomposites

2.1-Purification of the montmorillonite(MMT)

The treatment is subdivided in three stages: An acidic activation followed a washing and a decanting. The solutions are constituted steady colloidal, practically of montmorillonite particles and for the recuperation of this last centrifugation (4000 tour/min). The powder of the montmorillonite purified is gotten after having dried the montmorillonite wet to a temperature of 120°C during 18 hs.

2.2-Treatment of the zeolites

These zeolites (LTA) and HY were transformed to the NH₄-A and NH₄-Y respectively.

The composition of the mixture to 5% in mass of active matter of Co and Ce, this (Co (NO₃)₂·6H₂O and Ce (SO₄)₂·4H₂O) is added to the colloidal solutions of NH₄-A, NH₄-Y there and MMT (montmorillonite).

The pH is adjusted to 6,5 with the help of a solution of acetic acid or a solution of ammonium (according to the initial pH of the mixture, of the colloidal solution and the solution of the active matter). The value of the pH assures the existence of metals of transition in the solution to do exchange cationic (Co²⁺ and Ce⁴⁺), and also to assure the stability of the supports zeolites.

The quantity of murexide is added for every solution of the cation given before contact with the solution of the virgin matrix. This complex then decomposes itself in the pH of the middle while freeing them, in a controlled manner, so one avoids the agglomeration of the active phase on the support. After an intense agitation during 12(h), the solutions are let to decant and to wash several times with water distilled until the test negative of the detection (SO₄²⁻ and NO₃⁻). The parts is not decanted this destabilized by centrifugation (4000 tour/min during 10÷20min). The powders are dried to temperature 120°C during 18h. The temperature of calcination under static conditions with a constant fire-chamber 100°C/h, until 400°C.

3-Characterization of catalysts prepared

3.1 - Analysis by FTIR

The numbers of wave and the affectations of the main vibration fashions in the FTIR specters of the raw bentonite. For the raw bentonite and the activated one, the absorbance of strips 468,93 cm⁻¹, 572,35 cm⁻¹, 793,36 cm⁻¹ is owed to the vibration over respectively -OH, -O-Al and Al-OH and that appear more distinctly in the treated sample. A peak of strong intensity, 1027,12 cm⁻¹ caused by groups silanol, whereas the peaks localized to 3444,05 cm⁻¹ and 3670,72 cm⁻¹ result from the vibration of the groupings hydroxyls - OH respectively of HS - OH and of Al-OH^{6,7}.

Some organic impurities have been detected in the raw bentonite. Indeed, the peaks: 535,52 cm⁻¹, 2851,86 cm⁻¹ and 2924,11 cm⁻¹ reflections the vibration of the link C-HS of an organic entity⁷, that has be burn in the phase of the calcination since these peaks don't present themselves in the specter of the bentonite activated.

3.2-Determination of the specific surface by BET

The isotherms of adsorption/desorption of the liquid N₂ (77K) for the two samples are represented in her (fig.1). The isotherms show that the adsorption capacity of the montmorillonite prepared (MMT) is a lot higher than the raw bentonite (RawMMT) one. According to Brunauer, these isotherms classification is of IV type, these shapes also indicate the presence of the mesoporous and the microporous. The overlap of the adsorption and desorption curves (P/P° < 0.58 for Raw MMT and P/P° < 0.42 MMT) indicates that the adsorption and desorption process happen in a reversible manner.

In a general manner, the mesoporous can have several shapes with different volumes; the capillary condensation begins in the narrow mesoporous first, while the capillary evaporation begins earlier with the biggest mesoporous. This difference is the main reason of the hysteresis between the adsorption and the desorption.

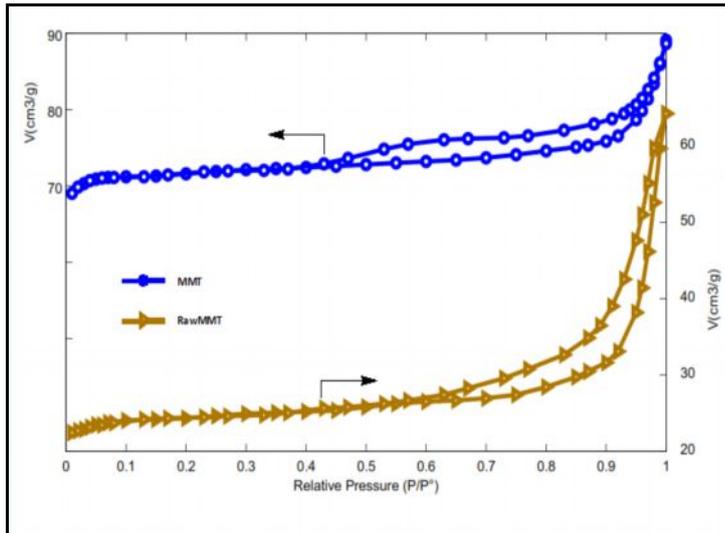


Fig.1- Isotherms adsorption/desorption of N₂ (77K) for the raw clay (RawMMT) and the activated one (MMT).

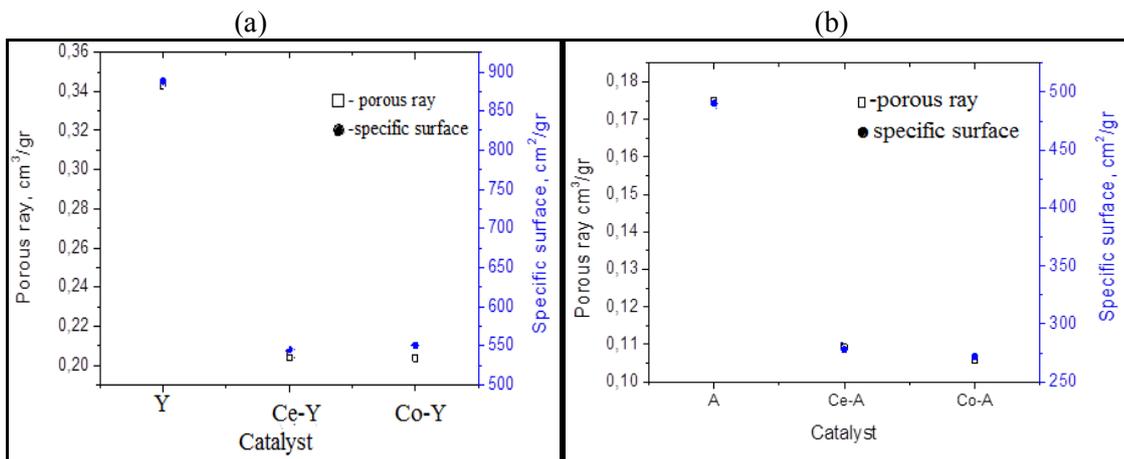


Fig (2 a)- Volumes of the micro porous and specific surfaces of zeolite Y and (b) The

We also note that the hysteresis phenomenon becomes more important with the acidic activation, since it begins at a relative pressure lower than the one for the raw bentonite. Indeed, the acidic activation can increase the number of mesoporous following a structural distortion, the samples specific surfaces have been obtained from the (BET) method while using the adsorption data of N₂ in 0,01 <P/P⁰ <0,14. The raw bentonite possesses a surface specific S = 91, 24 m²/g (with V_m = 20, 95 cm³ and C = 416, 95). The acidic activation permits to reach a higher specific surface, S = 387, 72 m²/g (with V_m = 89, 01 cm³ and C = 254.72). This big specific surface is due to the generation of a considerable number of mesoporous by the acidic activation.

The zeolites catalysts (Ce and Co) show isotherms of I type, characteristic of the microporous. The adsorption capacity by the specific surface (determined by the BET method) of the supported catalysts is distinctly lower to the one of the pure matrixes (Ce and Co) figure2 (a and b), it indicates that the formed nanoparticles is not only in external surface but also to the interior of the microporous. The figure.2, summarize the volume variation of the micropores calculated by the t-contact method. Indeed, it appears like a decreasing dependence in relation to the microporous volume of the virgin matrixes (Ce and Co) microporous and specific surfaces of catalysts (Ce and Co), determined by the t-contact method Fig.2 (a and b), corresponding volumes of the micro porous and specific surfaces of zeolite A, catalysts (Ce and Co), determined by the t-contact method.

The particularity of the MMT catalysts is the presence of mesoporous, it can be deduced from their shapes. In fact, all isotherms are of IV type with a buckle of hysteresis of H4 types⁸. The specific surfaces of this catalysts family of are also calculated by the BET method, (figure3)

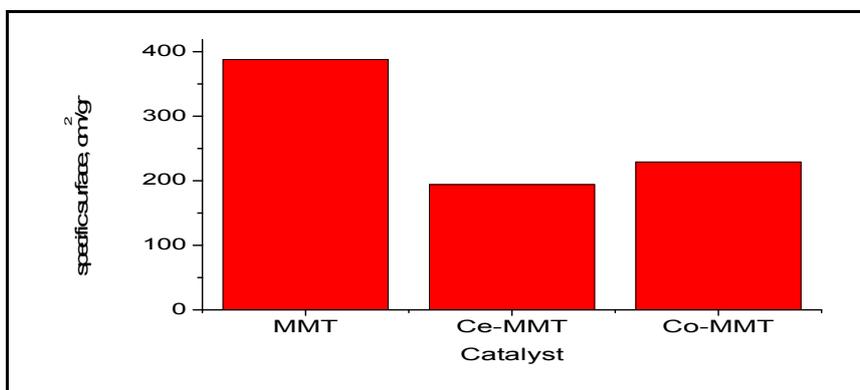


Fig.3. specific Surfaces of the catalysts to basis of MMT

3.3 - "Analysis by XRD

3.3.1- prepared montmorillonite Characterization

The raw montmorillonite interfoliaire space d-001 was of 10, 22 (Co). The strong basic reflection around $2\theta = 8,65^\circ$ are generally characteristic of the montmorillonite, This space d-001 of the montmorillonite activated is increased of 3 (Co) (13,24 - 10,22 = 3 (Co)), It can be assigned to the exchange of pressed them hydrated (Ca^{2+} and Na^+) by H^+ in the inset layer. The efficient diameter of H^+ (hydrated: 900 pm) is known to be bigger than the one of the cation of Ca^{2+} (no hydrated: 140 pm and hydrated: 600 pm)⁹.

The diffractogrammes of the prepared catalysts showed the presence of oxides characteristic peaks of transition metals. This indicates the formation on the montmorillonite (MMT). Also, the variation analysis of the space to interleave (d001) proves the birth of nanoparticles between the sheets of the clay support. Indeed, after the acidic activation, the space to interleave d001 of the montmorillonite was of 13,24 Å, increased then until the 14,02 Å (to $2\theta = 6,30^\circ$) for the Ni-MMT system, the same behavior has been noticed with the Co-MMT where the d001 = 14,09 Å, whereas it arrives until 15,61 Å for the Ce-MMT. This dilation is caused by the formation of oxides nanoparticles: CoO and CeO₂ respectively in Co-MMT and Ce-MMT after the fraction calcination (Co^{2+} and Ce^{3+}) exchanged with the montmorillonite.

3.3.2-Determination of the size of nanoparticles from the diffraction of the X. rays

Are the middle sizes of the area and the volume done ponder of nanoparticles gotten from the analysis of the lines of diffraction of the X-rays.

The Electronic Microscope in Transmittance (EMT) is the direct and most the preferable method for the determination of the dimension the nanoparticles. However, it presents some particularities and limitations¹⁰. Several methods have been developed to remedy these inconveniences, they present whatever based approaches on the exploitation of the diffractogrammes of XRD¹¹⁻¹³. The use of these methods is validated by several works^{10,14-15}.

The determination of the measurements dispersed of nanoparticles on different supports is done with the help of the software X powder. Every characteristic peak of a phase is used to calculate the middle diameter of the particles that causes it while using the formula of Scherrer, X powder, with a correction of this last formula. The tracing of Williamson-Hall (Fig.4) requires the treatment of two peaks to the minimum to end to find the middle diameter of the nanoparticles corrected of the distortion.

Whereas the method of Warren-Averbach is based then on the calculation of some coefficients for every peak one deducts the middle diameter also corrected of the distortion. the results calculated Williamson and Scherre, are carried on the (Fig.5)

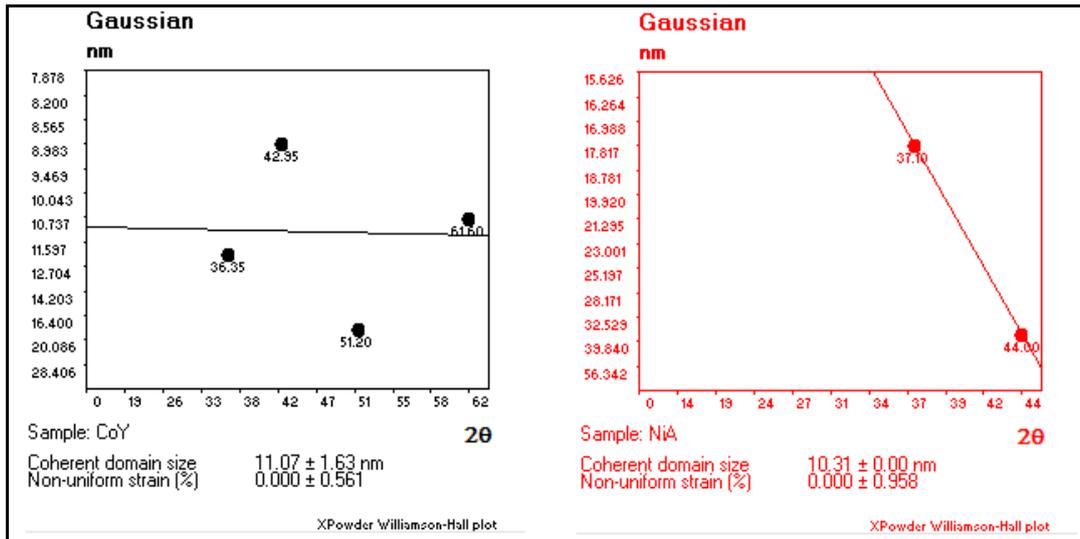


Fig.4-The Williamson-Hall tracing of CoY and of Denied.

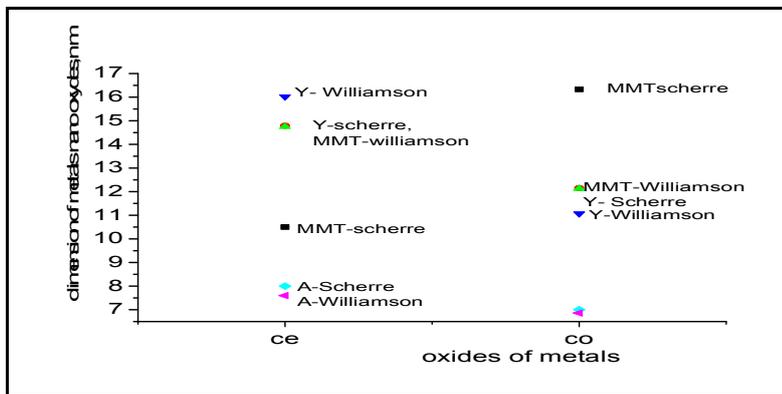


Fig.5- Measurements of the nanoparticles

A first analysis of the results indicates a consistency between the three calculation methods as it is foreseen well seen in other works^{16,17}. The nanoparticles average in relation to the three of calculation methods is (7÷17 nm).

3.4-Acidity and basicity:

The acidic sites can be classified like: of the acidic sites of Lewis and the Bronsted. Several techniques can be used. However, the discrimination between the acidic sites of Lewis and Bronsted is again a problem that cannot be solved by the use of the vibrational spectroscopies¹⁸.

3.3.1-Determination the catalysts acidity by Spectroscopy IR-pyridine Adsorption

The acidity has been determined by FTIR, based on the pyridine adsorption.

The Lewis and Brönstedsites concentrations can be calculated by the following formulas (1).

$$C_L = \frac{A_l S}{\epsilon_l \omega} 1000 C_B = \frac{A_b S}{\epsilon_b \omega} 1000 \quad \text{-----} \quad (1)$$

Where: Al: represent the surface centered to 1450 cm⁻¹, Ab: represent the surface of the peak centered to 1545 cm⁻¹, S: the surface of the tablet in cm², of to mass mgr. The coefficient of extinction (cm.μmol⁻¹), determined from^{19,20}. The peaks to them ~ (1455 and 1545) cm⁻¹ is owed interaction of the pyridine

respectively with the centers of Lewis and Brönsted, a third pic à $\sim 1492 \text{ cm}^{-1}$ products by the two acidic centers^{21,22}, to see (table 1).

Table 1- Acidity of the different catalysts prepared nanocomposites:

Catalyseur	Cites Lewis (L/10) ($\mu\text{mol/g}$)	Cites Brönsted (B/10) ($\mu\text{mol/g}$)	L/B	(L+B)/10 ($\mu\text{mol/g}$)
Y	3,65	0,53	6,88	4,18
CeY	11,05	6,62	1,70	17,67
CoY	116,83	36,43	3,20	153,26
A	4,52	1,13	4,00	5,65
CeA	1,04	0,56	1,86	1,60
CoA	1,56	0,68	2,30	2,24
MMT	4,23	2,12	2,00	6,35
CeMMT	2,42	1,26	1,90	3,68
CoMMT	4,58	1,26	3,60	5,84

Table 2- Volumes free and occupied of the three zeolites matrixes: MMT, A and Y, calculated from the data descended²³⁻²⁶.

Matrice	Free volume(Å^3)	occupied Volume(Å^3)
MMT	199,77	497,97
A	852,82	840,42
Y	6325,51	8817,04

Pressed them acting as acceptor of electrons provided by the molecules adsorbed, it is well the case with the catalysts CoY zeolite, and a few more months the CeY. Indeed, to see (Tab. 2),

However it is not the case with the cavities of the zeolite Co and the leaves of the MMT montmorillonite whose acidity decreased. The strengths of interaction between a cation and a support given will be bigger in the supports having a small free volume (Tab. 2), from where an interaction weakened with the pyridine. A second reason for which the acidity will be reduced and the compensation of the load of a cation oxidized, by the elements the more electronegative of the matrix.

4 - The analysis thermo gravimetric DSC

The peaks exothermiques (325 and 425) °C are caused by the interaction of H₂O with the electrostatic field of the different pressed and the generation of Co(OH)⁺, and Ce(OH)₂²⁷.

For all analyzed catalysts, one notes the presence of the peaks exothermic between (38 and 70) °C accompanied or of an increase or a stabilization of the variation of mass of the catalyst.

Indeed, the oxidization is absent in CeY. Contrary to the other samples, an endothermic peak to 76°C and a loss of mass (water adsorbed) are noticed, what confirms that the oxidization of a fraction important of Ce³⁺ cation. This difference is assigned to the faculty of the matrix to consolidate pressed them Ce³⁺. Indeed, the three supports (MMT, Co and Ce) arrive with different degrees to consolidate pressed them Co²⁺ in the conditions of the calcination done, the complete oxidization of the 5% Co²⁺ cannot be reached that to a temperature neighboring of 550°C (6, 49% of mass gain correspond to the total oxidization of 5, 1% of calculated Co²⁺ from the equation of the reaction.

5- Catalytic Test: Synthesis of the acetines by transesterification of the glycerol:

Among all methods of transformation of the glycerol, the transesterification seems to be a promising and economically viable alternative because not only it valorizes the glycerol, but it also increases the selectivity in biofuels in the global process of biodiesel production²⁸⁻²⁹.

The products gotten by transesterification of the glycerol are esters of glycerol, named also: acetines, that is mono -, di -, and substituted sorting. The mono acetines and the di acetines have large applications in the industries. The sorting acetine occupies 10% of the consumption of the glycerol all over the world, it is used like additive Antiknock for the improvement of the quality of gases (improvement of the octane indication), reducing agent of viscosity that also improves the point of out-flow of diesels. He/it can also be used as additive in the cosmetic products, in food, and as solvent, among the other numerous uses²⁸⁻²⁹.

The catalytic test is destined to catalyst the reaction of transesterification du glycerol with acetate of ethylin a reactor batch. These conditions operators' have been fixed in basing on the works of Pereira²⁸, Reddy and all [30], Khayoon and Hameed[31,32], and the catalytic tests have been achieved in the following conditions:

- The proportions of the reagents are: glycerol/acetate of ethyl = (1/30) flight,
- The mass of the catalyst $m = 0,2$ g, the temperature is 94°C coins air pressure,
- The time of t reaction = 4 hs, with intense agitation.

The mixture (glycerol+products) has been analyzed by CPG, with a capillary column (ID = 0,25 mm, L = 30 m), (polydimethylsiloxane), a gas vector N₂ (20ml/min, T = 250°C). The chromatographic separation is done according to the mentioned conditions in [28,33] with some modifications.

The results of the catalytic test consist in seeing the effect of the catalyst on the progress of the reaction from the calculation of two parameters: the x conversion and the selectivity I_f to see (Tab 3).

Table 3-Catalytic Performances of the catalysts to support there Conversion of the glycerol and selectivity's toward the three acetines

Catalyseur	Conversion $x\%$	Sélectivité $S_i\%$		
		MonoA	DiA	TriA
Y	83,25	66,30	30,96	2,73
CeY	96,98	38,45	56,44	5,11
CoY	100,00	31,85	50,92	17,23
A	89,68	67,32	29,49	3,18
CeA	77,89	47,25	47,54	5,21
CoA	79,73	47,95	50,45	1,60
MMT	94,93	63,90	32,61	3,49
CeMMT	80,29	45,00	50,19	4,80
CoMMT	87,74	38,65	58,51	2,83

Conclusion:

The goal of our work was to synthesize some catalysts nanocomposites to basis of three supports of mineral nature: the montmorillonite, thezeolite A and Y, whose role is to assure stability for the nanoparticles of oxides of metals formed.

The based semi-empiric methods on the XRD showed the existence of nanoparticles of CeO₂ and CoO, with a middle diameter understood between 7 and 17 nm. The same method with the infrared (FTIR), also prove that the structures of the three supports didn't undergo any damage at the time of the procedures of synthesis.

The analyses thermal DSC-Tgs put in evidence that the calcination in static fashion doesn't manage to oxidize the whole quantity of Co²⁺ in the three matrixes.

The analysis of the results watch that the conversion of the glycerol for the three families of catalysts used in this test varies of (77-100)%. This variation is function of the acidity of the catalysts. The catalyst zeolite most acidic CoY assures a complete conversion in the conditions of the reaction. Besides the catalysts to

basis of zeolite Co showed some conversions lower to those noticed for the catalysts to basis of montmorillonite.

The selectivity is also affected by the acidity, besides one notes a maximal value of 17, 23% toward the triacetate by CoY. The pluparts of the other catalysts supported orient the reaction toward the maximization of the diacetines, a very good selectivity is noted while using CoMMT (respectively 58, 51% and 57, 07%). whereas the three virgin matrixes accelerate the reaction toward the production of the monoacetines.

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