

Valorization of agricultural waste corn cob for the preparation of a Cu- activated charcoal and its use as catalyst for the Biginelli reaction

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Abstract— The objective of this study is to evaluate an original biocatalyst which is the valorization of an activated carbon prepared from agricultural waste consisting of the corn cob, as well as the synthesis of 3,4-dihydropyrimidin-2 (1H) -one (DHPM) by the multi-component reaction of Biginelli. Thus, we have undertaken this study by modifying this catalyst in different ways. First, the activated charcoal was prepared from the cob corn and then we impregnated it with the copper by having fixed and accumulated the latter on its surface, after came the heat treatment. The chemical reactions were followed using thin layer chromatography (TLC) and the obtained products are characterized by infrared spectroscopy, in addition to the determination of the melting point. It has been shown that activated carbon is a good catalyst for achieving the selective reaction of Biginelli. On the other hand, activated carbon proved to be more effective when enriched with copper.

Keywords— Corn cob, Activated carbon, Catalyst, Biginelli reaction

I. INTRODUCTION

Nowadays, the pharmaceutical industry is confronted to both the increase in productivity and the dearness of the synthesis process of molecules. By investigating solutions that can reduce the costs of the synthesis of these molecules, the engineering of the chemical reaction is more linked than ever to this industry. Among the axes of the of the chemical reaction engineering, the heterogeneous catalysis is an alternative to the homogeneous catalysis since it has many advantages. Indeed, in addition to being very effective, the heterogeneous catalyst is recovered and reused several times, it can be less expensive and more environmentally friendly, solid catalysts can be prepared from agricultural waste as in

the present study [1-4]. The valorization of agricultural wastes without generating pollutants is a major challenge and is recommended for sustainable industrial development in order to preserve the environment. The solids having a large specific area are activated by increasing the active sites with the incorporation of chemical species on their surface [5,6].

The Biginelly reaction is one of the most important organic reactions in the pharmaceutical industry [7-8]. This multicomponent reaction synthesizes dihydropyrimidinones (DHPMs) from the condensation of alpha-beta keto esters, aldehyde and urea / thiourea in the presence of Lewis acids or mineral acids, these DHPMs find their application in a wide medical field as blockers of calcium, antihypertensives, antibacterials and anti-tuberculosis [9-11].

The reaction of Biginelli was carried out in the presence of homogeneous [12-18] and heterogeneous acid catalysts [19-23]. It should be noted that in the heterogeneous catalysis, efforts are steadily increasing to synthesize new materials at low cost, more efficient and without detrimental effect on the environment.

Based on these different considerations, we propose, in this work, to test the catalytic activity of novel catalysts prepared using an activated carbon, which we synthesize from a natural precursor, namely the corn cob; this represents a new and original way of replacing the various mineral solid catalysts. Activated carbon has a large specific area; it can also accommodate chemical species on this area, further increasing its reactivity. Copper is the subject of several studies on heterogeneous catalysis, especially in pharmaceutical chemistry. For this purpose, we have carried out the adsorption of copper on activated carbon and the reaction of biginelli has been conducted first on the activated carbon prepared from the corn cob, then on the activated carbon whose surface has adsorbed the copper and finally on the activated carbon having undergone a heat treatment to further increase the fixation of copper on its surface.

II. EXPERIMENTAL PART

A. Preparation of activated carbon

Activated charcoal was prepared from corn cobs; it was crushed, washed and then dried in an oven at 105 ° C for 24 hours. Two methods of activation were used successively, the chemical method using phosphoric acid as activating agent and the physical method carried out in a tubular furnace under a stream of water vapor at 700 ° C for 2 hours. The obtained activated carbon is then characterized by different methods; the Fourier transform infrared spectroscopy using a FTIR 8400 SCHIMADZU spectrometer, the scanning electron microscopy on a JEOL JSM-6010LV apparatus, while the specific area is determined by the BET method on a QUANTACHROME.

B. Copper Adsorption

The prepared carbon was mixed with a solution of copper nitrate having a concentration of 100 ppm. The mixture is stirred at room temperature with a speed of 500 rpm for a contact time of 2 hours. At the end of the adsorption, the solution is centrifuged to separate the solid and the solution, and then the concentration of the fixed copper is determined by atomic absorption. Afterwards, the copper activated carbon is recovered and a part thereof is subjected to a heat treatment in an oven at 300 ° C.

C. Synthesis of 3,4-dihydropyrimidin-2 (1H) -one (DHPM)

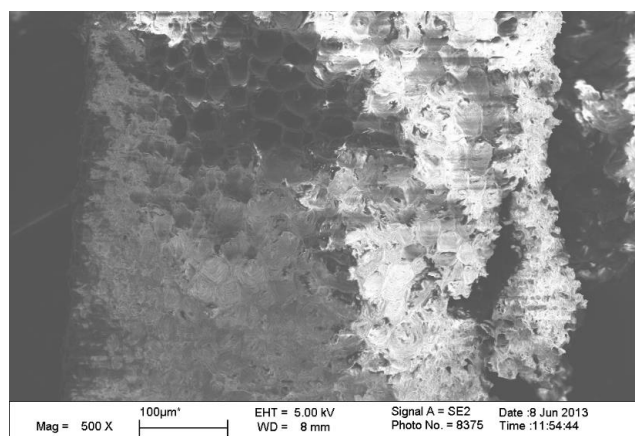
The required quantities of aldehyde, ethyl acetoacetate and urea as well as the catalyst are introduced into a 50 ml Bicol, equipped with a magnetic bar. The mixture is brought to reflux in ethanol as solvent, the reaction medium of interaction is taken every 30 minutes using the TLC plates, in order to control the progress of the reaction. The combined organic phases are washed with methanol to remove the impurities. The mixture is then filtered and the filtrate is collected. The methanol is then evaporated with rotavapor to obtain a white solid. The crude products were purified by recrystallization in ethanol to get the desired product. At the end of this reaction, we proceed by filtration to separate the final product which is dried in an oven for several hours and then weighed. The characterization is carried out by determining the melting temperature using a Koffler apparatus, the infrared spectra are determined using a Shimadzu apparatus. The reaction of Biginelli was carried out on the following products:

- The activated carbon CA.
- The activated carbon to the copper CAC.
- The activated carbon to the coated carbon subjected to a heat treatment CACT; the amount of catalyst was varied from 20% to 40% by the weight of aldehyde.
- Without catalyst; this case is taken as a benchmark

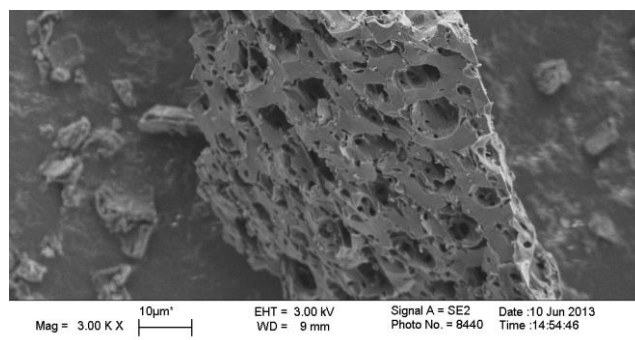
III. RESULTS AND DISCUSSIONS

A. Characterization of activated carbon

1) *SEM image*: We carried out SEM images on the precursor material which is the corn cob as well as on the activated carbon obtained by chemical treatment with acid followed by a physical treatment with steam at 700 ° C. The obtained images are shown in Fig.1, it is noted that the initial material has a nonporous structure; this porosity has developed enormously on the activated carbon in a homogeneous manner with pores of different Sizes this shows the effectiveness of the treatments performed on the precursor material.



a. corn cob



b. activated carbon
Fig.1 SEM Image

2) *Specific surface area*: The surface area results obtained by the BET method were similar to the SEM image, the starting material which had no porosity in the SEM image had a specific surface area of 13.9 m² / g , We note that the treatments carried out on this material to obtain an activated carbon made it possible to develop its surface up to a value of 460 m² / g, this is due to the creation of pores as shown by the SEM image, this value is a very good surface for the material to be used as a catalytic support.

3) *Infrared Spectroscopy*: The infrared spectrum of the activated carbon prepared is shown in Fig.2

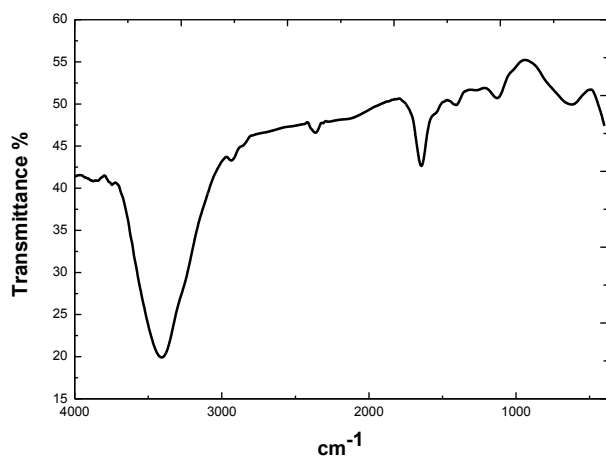


Fig. 2the spectrum FTIR of activated carbon

On this spectrum, an absorption band at 3422 cm^{-1} characteristic of the hydrogen elongation vibration of the hydroxyl groups is observed, absorption bands appear at 2918 and 2820 cm^{-1} resulting mainly from elongation vibrations of aliphatic C-H. The bands at 454 and 470 cm^{-1} are due to the deformation mode outside the C-H plane in aromatic rings. The band at 1650 cm^{-1} is usually attributed to the C = O elongation vibrations of the carboxylic acids. The spectrum also shows a band at 1470 cm^{-1} due to the vibrations of the C = C bonds in the aromatic rings. The spectrum also shows a small band in the spectral region between 1200 and 1072 cm^{-1} with a maximum at 1150 commonly described in the oxidized carbons, and it has been attributed to the C-O elongation of the carboxylic acids. The existence of all these links makes the activated carbon attractive for applications in surface phenomena such as adsorption and catalysis.

4) Quantity of adsorbed copper a: The results obtained after analysis by atomic absorption gave us an amount of 40.66 mg/g of the copper fixed on the activated carbon.

B. Chemical Reaction

1) *Effects of the different activated carbons:* The results of the Biginelli reaction as a function of both the reaction time and the type of the catalyst are shown in Table 1.

TABLE 1. REACTION TIME AND AMOUNT WITH AND WITHOUT CATALYST

Catalyst	CACT	CAC	CA	Without catalyst
Amount (%)	62	49	41	16
Time(h)	7h	7h	8h	13h

According to Table 1, the catalyst which gives the best amount is the activated carbon treated with copper and having undergone a heat treatment at $300\text{ }^{\circ}\text{C}$. (CACT). We can say that the activated carbon has been able to catalyze the reaction by its surface which has acidic active sites and

then the fixation of the copper on the surface of the carbon has improved the amount of the reaction in a very appreciable manner. In addition, the time of reaction was very short using CACT.

2) *Influence of the amount of catalyst:* Knowing that the CACT gives the higher reaction amount with the lower reaction time, we changed in this part the quantity of the catalyst, using twice the quantity already used for the CACT. The obtained results are shown in Table 2, they clearly show that the increase in the quantity of catalyst leads to an increase in the reaction amount accompanied with a reduction of the interaction time; this is related to the increase of the active sites on the surface of the catalyst. Note that the particularity of a solid catalyst is that catalysis is a surface phenomenon and in general, the activity of a solid increases with the surface to mass ratio.

TABLE 2. EFFECT OF THE CACT CATALYST MASS ON THE REACTION'S AMOUNT

Quantity of catalyst (%)	40	20
Amount (%)	83	62
Time(h)	6h	7h

C. Characterization of DHPM

1) *Melting point:* The melting point determined by the Kofler apparatus is a commonly used purity criterion. Furthermore, a pure product has a clearly defined melting point. In our case, all the products obtained in all cases had the same melting point equal to 206°C ., this temperature characterizes the pure DHPMs.

2) *Infrared spectra of DHPM:* The infrared spectra with Fourier transform are the same for all samples; FIG. 3 shows the infrared spectrum of the obtained product.

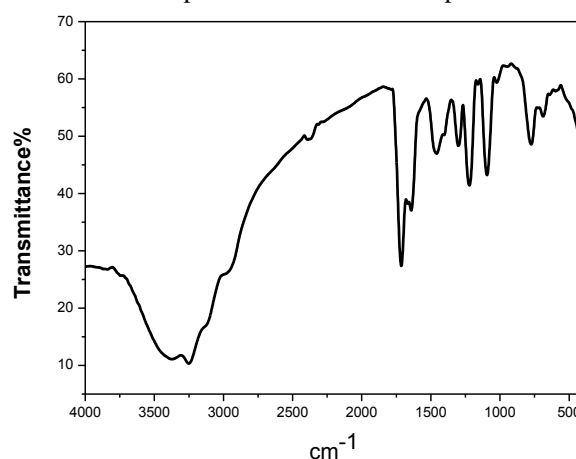


Fig.3 Product Infrared Spectrum of Biginelli

The presence in infrared spectroscopy of the characteristic absorptions of the DHPMS nucleus leaves no doubt about its formation. The IR spectra of Fig.3 are characterized by two successive bands corresponding to the elongation of the two N-H bonds of the dihydropyrimidin-2 (1H)-one nucleus

which appear respectively towards 3270 cm^{-1} and 3192 cm^{-1} . In addition, we observe a weak band characteristic of the elongation vibration of the C-H bond at 2940 cm^{-1} . Also a band exists at 1720 cm^{-1} and is characteristic of the C = O group of the ester function followed by the band of the C = O group of the amide function of the dihydropyrimidin-2 (1H) –one ring recorded at about 1650 cm^{-1} . We can easily identify on this spectrum an absorption band attributable to the (C-N) group, characterized by an absorption domain located at 1233 cm^{-1} . Other bands characterizing the C = C double bonds of the aromatic ring emerge at 1470 cm^{-1} . The bands corresponding to the peaks indicate that we are in the presence of the desired 3, 4-dihydropyrimidinone.

D. Conclusions

The condensation of Biginelli under the action of the activated carbon prepared from the corn cob as a catalyst in the presence of ethanol as a solvent allows obtaining, after 6 to 8 hours DHPM, with appreciable amount. Note that the best amount is reached with copper-treated and heated activated carbon; this shows the positive action of copper on the reactio. It is also observed that by increasing the quantity of the catalyst CACT the results are more effective, this can be explained by the fact that with an increased quantity, the active sites increase, as well as the amount.

Following these results, we have been able to show that the use of activated carbon as catalyst support is of interest for the biginelli reaction. This is justified by the importance of the exchange surface developed by this material.

We can also say that we have developed a new effective catalyst obtained from corn cobs which is an agricultural waste and whose valorization allows applying the principles of green chemistry.

REFERENCES

- [1] [1] V.S. Gerard, F. Notheisz, *Heterogeneous Catalysis in Organic Chemistry*, San Diego, USA, Elsevier, 2000
- [2] K. Wilson, J.H. Clark, Solid acids and their use as environmentally friendly catalysts in organic synthesis, *Pure Appl. Chem.*, vol.72, pp 1313-1319, 2000
- [3] N. Seifi, M.H. Zahedi-Niaki, M.R. Barzegari, A. Davoodnia, R. Zhiani, A.A. Kaju, Synthesis of 8-aryl-1H-pyrazolo[4,3-e][1,2,4]triazolo[4,3-a] pyrimidine-4(5H)-imine by using the Preyssler's anion $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$ as a green and eco-friendly catalyst, *J. Mol. Catal. A Chem.*, vol. 260, pp 77-81, 2006
- [4] M. Zeinali-Dastmalbaf, A. Davoodnia, M.M. Heravi, N. Tavakoli-Hoseini, A. Khojastehnezhad, H.A. Zamani, Silica Gel-Supported Polyphosphoric Acid (PPA-SiO₂) Catalyzed One-Pot Multi-Component Synthesis of 3,4-Dihydropyrimidin-2(1H)-ones and -thiones: An Efficient Method for the Biginelli Reaction, *Bull. Korean Chem. Soc.*, vol. 32, pp 656-658, 2011
- [5] S. Paul and J. H. Clark, "A Highly Active and Reusable Heterogeneous Catalyst for the Suzuki Reaction: Synthesis of Biaryls and Polyaryls," *Green Chemistry*, vol. 5, No. 5, pp. 635-638, 2003
- [6] M. Lagasi and P. Moggi, "Anchoring of Pd on Silica Functionalized with Nitrogen Containing Chelating Groups and Applications in Catalysis," *Journal of Molecular Catalysis A: Chemical*, vol. 182-183, pp. 61-72, 2002
- [7] L. Ismaili, A. Nadaradjane, L. Nicod, C. Guyon, A. Xicluna, J.F. Robert, B.Refouvelet, Synthesis and antioxidant activity evaluation of new hexahydropyrimido[5,4-c]quinoline-2,5-diones and 2-thioxohexahydropyrimido[5,4-c]quinoline-5-ones obtained by Biginelli reaction in two steps, *Eur. J. Med. Chem.*, vol 43, pp 1270–1275, 2008
- [8] J.T. Starceovich, T.J. Laughlin, R.S. Mohan, Iron(III) tosylate catalyzed synthesis of 3,4-dihydropyrimidin-2(1H)-ones/thiones via the Biginelli reaction, *Tetrahedron Lett.*, vol. 54, pp 983–985, 2013.
- [9] I.S. Zorkun, S. Sarac, S. Celebi, K. Erol, Synthesis of 4-aryl-3,4-dihydropyrimidin-2(1H)-thione derivatives as potential calcium channel blockers, *Bioorg. Med. Chem.*, vol. 14, pp 8582–8589, 2006
- [10] B. Schnell, U.T. Strauss, P. Verdino, K. Faber, C.O. Kappe, Synthesis of enantiomerically pure 4-aryl-3,4-dihydro-pyrimidin-2(1H)-ones via enzymatic resolution:preparation of the antihypertensive agent (R)-SQ 32926, *Tetrahedron: Asymmetry*, vol. 11, pp 1449–1453, 2000.
- [11] D.S. Bose, M. Sudharshan, S.W. Chavhan, New protocol for Biginelli reaction-a practical synthesis of Monastrol, *Arkivoc*, vol. iii, pp 228–236, 2005.
- [12] L.M. Ramos, B.C. Guido, C.C. Nobrega, R.C. Jose, R.G. Silva, H.C.B. de Oliveira, A.F. Gomes, F.C. Gozzo, B.A.D. Neto, The Biginelli Reaction with an Imidazolium-Tagged Recyclable Iron Catalyst: Kinetics, Mechanism, and Antitumoral Activity, *Chem Eur J*, vol.19, pp 4156-4168, 2013
- [13] J. Peng, Y. Deng Ionic liquids catalyzed Biginelli reaction under solvent-free conditions, *Tetrahedron Lett.*, vol. 42, pp 5917-5919, 2001
- [14] P. Karthikeyan, S.A. Aswar, P.N. Muskawar, P.M. Bhagat, S.S. Kumar, Development and efficient 1-glycyl-3-methyl imidazolium chloride–copper(II) complex catalyzed highly enantioselective synthesis of 3, 4-dihydropyrimidin-2(1H)-ones, *J Organomet Chem*, vol.723, pp 154-162, 2013
- [15] K. Ramalinga, P. Vijayalakshmi, T.N.B. Kaimal, L. Ramalinga, Bismuth(III)-catalyzed synthesis of dihydropyrimidinones: improved protocol conditions for the Biginelli reaction, *Synlett*, vol.6, pp 863-865, 2001
- [16] Z. Hassani, M.R. Islami, M. Kalantari, An efficient one-pot synthesis of octahydroquinazolinone derivatives using catalytic amount of H₂SO₄ in water, *Bioorg Med Chem Lett*, vol.16, pp 4479-4482, 2006
- [17] Ranu BC, Hajra A, Jana U, Indium(III) Chloride-Catalyzed One-Pot Synthesis of Dihydropyrimidinones by a Three-Component Coupling of 1,3-Dicarbonyl Compounds, Aldehydes, and Urea: An Improved Procedure for the Biginelli Reaction, *J Org Chem*, vol. 65, pp 6270-6272, 2000
- [18] D Russowsky, FA Lopes, VSS Da Silva, KFS Canto, MG Montes D'oca, M.N. Godoi, Multicomponent Biginelli's Synthesis of 3,4-Dihydropyrimidin-2(1H)-ones Promoted by SnCl₂.2H₂O, *J. Braz. Chem. Soc.*, vol. 15, pp 165169, 2004
- [19] Fazaeli R, Tangestaninejad S, Aliyan H, Moghadam M, One-pot synthesis of dihydropyrimidinones using facile and reusable polyoxometalate catalysts for the Biginelli reaction, *Appl. Catal. A*, vol. 309, pp 44-51, 2006
- [20] A. Hasaninejad, A. Zare, F. Jafari, A.R. Moosavi-Zare, P₂O₅/SiO₂ as an Efficient, Green and Heterogeneous Catalytic System for the Solvent-Free Synthesis of 3,4-Dihydropyrimidin-2-(1H)-ones (and -Thiones), *E-J. of Chem.*, vol. 6, pp 459-465, 2009
- [21] J. Mond, T. Senb, A. Bhaumik, Fe₃O₄ a mesoporous SBA-15: a robust and magnetically recoverable catalyst for one-pot synthesis of 3,4-dihydropyrimidin-2(1H)-ones via the Biginelli reaction, *Dalton Trans.*, vol. 41, pp 6173-6181, 2012
- [22] M. Nasr-Esfahani, J. Hoseini, F. Mohammadi, Fe₃O₄ Nanoparticles as an Efficient and Magnetically Recoverable Catalyst for the Synthesis of 3,4-Dihydropyrimidin-2(1H)-ones under Solvent-Free Conditions, *Chin. J. Catal.*, vol 32, pp 1484-1489,2011
- [23] R. Hekmatshoar, S. Majedi, Kh Bakhtiari, Sodium selenate catalyzed simple and efficient synthesis of tetrahydro benzo[b]pyran derivatives, *Catal. Commun.*, vol. 9, pp 307-310, 2008