# Catalyst H-ZSM 5 in Amines addition on Carbonyl Compounds α, β-unsaturated catalyzed by H-ZSM 5

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**Research Article**

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# Abstract

### Background

Zeolites are crystallized aluminum silicates. Their structure consists of an arrangement of TO4 tetrahedral (T = Si, Al ...), creating a regular nonporous system made up of channels with a diameter of less than 1 nm and cages (the channel intersections). These materials were discovered by the mineralogist in 1756. These porous materials are used in the paper industry, in jewelry, and in other fields. Certain applications require pure materials with specific properties, hence the need to develop their synthesis. Zeolites are obtained hydrothermally at temperatures below 200°C. The dimensions of the pores are of the order of a nanometer, close to the dimensions of certain organic molecules which make these zeolitic materials find applications in various fields, separation by molecular sieving, purification by adsorption, cation exchange and catalysis.

### Result

We are successful in the reaction of addition the series of amines to unsaturated alkenes, catalyzed by zeolite H-ZSM-5, the results show good products obtained with excellent yields, in short time, pure products can be obtained after filtering the catalyst and then removing the excess amines, the catalyst is recoverable, reactivated and reused several times for other addition reactions, the products were defined by 1 H NMR spectroscopy.

### Conclusion

According to the results obtained. It can be said that the addition of various aliphatic or aromatic amines reacted successfully with alkenes, in the presence of the catalyst H-ZSM-5, to give the corresponding adducts with excellent yields in time and in perfect conditions, solvent-free and room temperature, so our H-ZSM-5 catalyst is effective, can meet our goal of adding amines to unsaturated carbonyl components.

# 1. Introduction

Zeolites are natural (volcanic rock) or synthetic materials [1]. There are about fifty natural zeolites and more than 150 synthetic zeolites [2]. The activity and the selectivity of the catalyst are influenced by the characteristics of the catalyst when these characteristics depend on the method of preparation [3]. A method often used in the preparation of the catalyst is the impregnation method [4]. Zeolites are stable at high temperatures and have a broad porous structure [5], which opens new perspectives for the treatment of large molecules especially in the field [6] of petroleum refining and petrochemical catalysis processes [7].

The addition of a series of amines to α, β-unsaturated alkenes, [8] an interesting methodology for [9] for the efficient coupling of amines with a wide range of α, β-unsaturated carbonyl components [10], to obtain the excellent products show the role of a material like HMZ5 in reactions in organic chemistry [11].

With this addition we can synthesize similar products, where other reactions do not work

The use of this addition of amines to α, β-unsaturated alkenes in vast areas such as biology [12], medicine, agriculture.

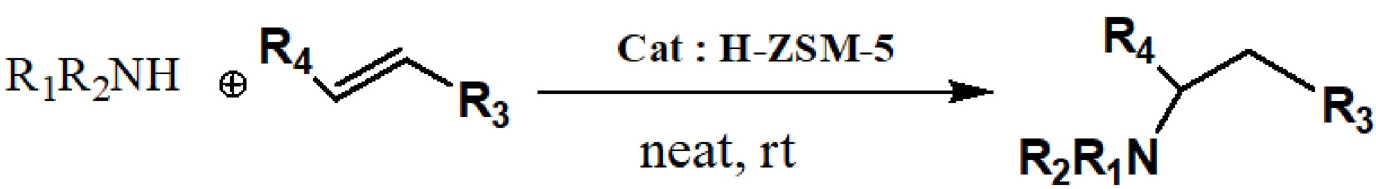
Following the addition Michael [13], there is a practical method has been developed for the addition of aliphatic or aromatic amines to alkenes [14], catalyzed by a heterogeneous catalyst [15], in this sense we can be carried out our addition amines on α, β-unsaturated alkenes [16].

A comparative study shows that the aza-Michael addition reaction [17] (Scheme1) leads to the formation of the C-C or C-heteroatom bond. From these results [18], we carried out a series of amine addition on a,b-unsaturated alkenes [19], active or not active in a dry medium catalyzed by zeolite H-ZSM-5 [20]. Table 1 shows the 1, 4 - addition of a series of amines on α,b-unsaturated alkenes, ate catalyzed by zeolite H-ZSM-5 [21], in dry medium and a temperature T= 25°C.

## 2. Materials And Methods

In an Erlenmeyer flask, we add (1eq) of alkenes, to the (3eq) of amines with stirring, we add a quantity of (0.1) mg of H-ZSM-5 catalyst at an ambient temperature T = 25 ° C, and without solvent.

The reaction is followed by C.C.M, the products obtained are recovered by filtration and washed with dichloromethane, and the excess of the starting reagents are removed using a rotary evaporator. The products obtained are analyzed by proton nuclear magnetic resonance, 1H N.M.R and represented in Figure 01 (N1-(3-bromopropyl) ethane-1, 2-diamine), Figure 02(3-(2-aminoethylamino)-3-phenylpropan-1-ol), Figure 03(-(3-chlorophenylamino)-3-phenylpropan-1-ol).




$$R_3 = ROH, CH_2Br \; ; \; R_4 = Ph, CH_2$$

**Scheme1: Aza-Michael addition**

## 3. Spectral Data

# N.M.R. Spectra of Product Entry 1 of table

RF= 0.80 (Hexane-EtoAc): 2/1

RMNH[1] ($CDCl_3$, 300 MHz) d: 1.91(m ,J=5 .2H $CH_2$-C$\underline{H}_2$- $CH_2$-Br ) 2.0 ( s, 3H, $NH_2$, NH) ; 2.55 (t , 2H, NH-C$\underline{H}_2$-$CH_2$– $CH_2$.Br) ; 2.77-2.81 (m, J=7.6HZ , 4H, $NH_2$-C$\underline{H}_2$- C$\underline{H}_2$ -NH) , 3.30 (t, 2H, $CH_2$- C$\underline{H}_2$-Br)

# N.M.R. Spectra of Product Entry 02 of table

RF= 0.82 (Hexane-EtoAc): 2/1

RMNH[1] ($CDCl_3$, 300 MHz) d:2.0 ( s, 4H, $NH_2$, NH, OH) ; 18-2.81 (m ,J=5 .4H $NH_2$-C$\underline{H}_2$- C$\underline{H}_2$ -NH) ; 2.77 (t, J=7.6HZ , 2H, OH- C$\underline{H}_2$ – $CH_2$) 2.90(t, 1H, $NH_2$-( C$\underline{H}$-PH)- $CH_2$) ; 7.08-7.21(m, 5H, PH)

# N.M.R. Spectra of Product Entry 03 of table

RF= 0.70 (Hexane-EtoAc): 2/1

RMNH[1] ($CDCl_3$, 300 MHz) d:1.5 ( m,7Hz, 6H, m, p ,$CH_2$- C$\underline{H}_2$- C$\underline{H}_2$- C$\underline{H}_2$- $CH_2$ $C_5\underline{H}_{10}N$) ; 2.4(t ,J=5 .6Hz , 4H,ortho, N-C$\underline{H}_2$- C$\underline{H}_2$ -N $C_5H_{10}N$) ; 2.5 (t, J=7.6HZ , 2H, $CH_2$- C$\underline{H}_2$ -$CO_2CH_3$) 2.6-2.7(t, J=7.2Hz, 2H, N- C$\underline{H}_2$-$CH_2$) ; 3.65(s, 3H, C$\underline{H}_3$).

## 4. Results And Discussion

We are successful in the reaction of addition the series of amines to unsaturated alkenes, catalyzed by zeolite H-ZSM-5, the results show good products obtained with excellent yields, in short time, pure products can be obtained after filtering the catalyst and then removing the excess amines, the catalyst is recoverable, reactivated and reused several times for other addition reactions, the products were defined by 1 H NMR spectroscopy.

## 5. Conclusion

According to the results obtained. It can be said that the addition of various aliphatic or aromatic amines reacted successfully with alkenes, in the presence of the catalyst H-ZSM-5, to give the corresponding adducts with excellent yields in time and in perfect conditions, solvent-free and room temperature, so our H-ZSM-5 catalyst is effective, can meet our goal of adding amines to unsaturated carbonyl components.

## Declarations

# Ethics approval and consent to participate

We, the authors of the manuscript, acknowledge ethical approval and consent to share

# Consent for publication

Yes, we agree to publish

# Availability of data and materials

There is no data with the manuscript

# Competing interests

The work is very important in the biochemistry and synthetic he carried out to synthesize a product which destroys the fungus of date palm disease

All authors declare that there is no conflict of interest, or funding from any party for this work.

# Funding

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# Authors' contributions

## 1 Author

Implementation of the idea, and carrying out this work

## 2 Author

Work in the laboratory on the reactions

## 3 Author

Correct mistakes

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# References


1. Vinoth Kumar Chenniappan and Ronald J. Rahaim (2016). Titanium-Promoted Cross-Coupling for the Selective Synthesis of Polysubstituted, Conjugated Amides. Organic Letters . 18, 5090-5093. https://doi.org/10.1021/acs.orglett.6b02537
2. Reddy BM, Patil MK, Reddy BT, Park S-E, *Catal Commun.* 9, 950–954. https://doi.org/10.1007/s10562-008-9646-7
3. Jose L. Vicario, Dolores Badía, Luisa Carrillo, Juan Etxebarria (2005), Organic Preparations and Procedures International. 37, 513-538. https://doi.org/10.1080/00304940509354981.
4. Li-Wen Xu, Chun-Gu Xia (**2005**) . *European Journal of Organic Chemistry* , 633, 68-97. https://doi.org/10.1002%2Fejoc.200400619.
5. Mónica Rodríguez, Jose L. Vicario, Dolores Badía, Luisa Carrillo (2005). *Organic & Biomolecular Chemistry* , 2026, 38-40. https://doi.org/ 10.1039%2Fb502995c.
6. Cao-Cao Sun, Kun Xu, Cheng-Chu Zeng (2019). Transition Metal- and Base-Free Electrochemical aza-Michael Addition of Aromatic aza-Heterocycles or Ts-Protected Amines to α,β-Unsaturated Alkenes Mediated by NaI. *ACS Sustainable Chemistry &Engineering* . 7, 2255-2261. https://doi.org/10.1021/acssuschemeng.8b04934.
7. Seongil Kang, Subin Park, Kyung-su Kim, Changsik Song, and Yunmi Lee (2018). Copper-Catalyzed Aza-Michael Addition of 2-Aminobenzoate to β-Substituted α,β-Unsaturated Ketones: One-Pot Synthesis of 3-Carbonyl-2-Substituted Quinolin-4(1H)-ones. *The Journal of Organic Chemistry* . 83, 2694-2705. https://doi.org/10.1021/acs.joc.7b03162.
8. Adisak Chatupheeraphat, Hsuan-Hung Liao, Shao-Chi Lee, and Magnus Rueping (2017). Nickel-CatalyzedC–CNBond,Formation. *OrganicLetters*. 19, 4255-4258. https://doi.org/10.1021/acs.orglett.7b01905.
9. Beibei Guo , Douwe S Zijlstra , Johannes G de Vries , Edwin Otten (2018). Oxa-Michael Addition to α,β-Unsaturated Nitriles: An Expedient Route to γ-Amino Alcohols and Derivatives , *ChemCatChem*. 9, 10 , 2868-2872. https://doi.org/10.1002/cctc.201800509.
10. Katherine T. Best, Diana Li, and Eric D. Helms (2017) . Molecular Modeling of an Electrophilic Addition Reaction with “Unexpected” Regiochemistry. *Journal of Chemical Education* . 94, 936-940. https://doi.org/10.1021/acs.jchemed.6b00488
11. Sankar K. Guchhait, Neha Hura, and Archana P. Shah (2017) . Synthesis of Polysubstituted 2-Aminoimidazoles via Alkene-Diamination of Guanidine with Conjugated α-Bromoalkenones. *TheJournal of OrganicChemistry* . 82, 2745-2752. https://doi.org/10.1021/acs.joc.6b03021.
12. Maxim G. Vinogradov, Olga V. Turova, Sergei G. Zlotin (2019). Recent advances in the asymmetric synthesis of pharmacology-relevant nitrogen heterocycles via stereoselective aza-Michael reactions. *Organic & Biomolecular Chemistry*. 17, 3670-3708. https://doi.org/10.1039/C8OB03034K.
13. Changqing Miao, Liya Jiang, Lanhui Ren, Qingxia Xue, Fang Yan, Weiwei Shi, Xinjian Li, Jiwen Sheng, Shuangshuang Kai (2019). Iodine-catalyzed coupling of β-hydroxyketones with aromatic amines to

form β-aminoketones and Benzo[h]quinolones. *Tetrahedron*. 75, 2215-2228. https://doi.org/10.1016/j.tet.2019.02.041.

14. Aboubakr Hakiki, Riad Mustpha Kerbadou, Bouhadjar Boukoussa, Hadjira Habib Zahmani, Franck Launay, Alain Pailleret, Françoise Pillier, Salih Hacini, Abdelkader Bengueddach, Rachida Hamacha (2019). Catalytic behavior of copper–amine complex supported on mesoporous silica SBA-15 toward mono-Aza-Michael addition: role of amine groups*. Journal of Inorganic and Organometallic Polymers and Materials*. 53, 88-97. https://doi.org/10.1007/s10904-019-01139-7.
15. Subin Park, Seongil Kang, Yunmi Lee. . *Advanced Synthesis & Catalysis* , 361 (2019) 1071-1083. https://doi.org/10.1002/adsc.201801582.
16. Isak Rajjak Shaikh (2014). Organocatalysis: Key Trends in Green Synthetic Chemistry, Challenges, Scope towards Heterogenization, and Importance from Research and Industrial Point of view , *Journal of Catalysts.* 35, 402-860. http://dx.doi.org/10.1155/2014/402860
17. Efraim Reyes, Maitane Fernández, Uxue Uria, Jose L. Vicario, Dolores Badía and Luisa Carrillo (2012). Organocatalytic Enantioselective aza-Michael Reactions, *Current Organic Chemistry*. 16, 521-546. **https://doi.org/**10.2174/138527212799499804
18. Nancy Wu, Tomohiro Kubo, Kikelomo N. Sekoni, Ariana O. Hall, Sameer Phadke, Danielle M. Zurcher, Rachel L. Wallace, Devki B. Kothari, Anne J. McNeil (2019). Student-Designed Green Chemistry Experiment for a Large-Enrollment, Introductory Organic Laboratory Course. *Journal of Chemical Education.* 96, 2420-2425. https://doi.org/10.1021/acs.jchemed.9b00375
19. Kabita Boruah, Ruli Borah (2019). Design of Water Stable 1,3-Dialkyl- 2-Methyl Imidazolium Basic Ionic Liquids as Reusable Homogeneous Catalysts for Aza-Michael Reaction in Neat Condition, *ChemistrySelect* . 4, 3479- 3485. https://doi.org/10.1002/slct.201900187
20. A. Wagner, A.M. Kreuzer, L. Göpperl, L. Schranzhofer, C. Paulik (2019). Foamable acrylic based ink for the production of light weight parts by inkjet-based 3D printing. *European Polymer Journal* . 115, 325-334. https://doi.org/10.1016/j.eurpolymj.2019.03.031
21. Renzo Rossi, Gaetano Angelici, Gianluca Casotti, Chiara Manzini, Marco Lessi (2019). Catalytic Synthesis of 1,2,4,5-Tetrasubstituted 1 H -Imidazole Derivatives: State of the Art. *Advanced Synthesis & Catalysis*. 361, 2737-2803. https://doi.org/10.1002/adsc.201801381

# Table

Due to technical limitations, table 1 is only available as a download in the Supplemental Files section.

# Figures


**Figure 1**

N1-(3-bromopropyl) ethane-1, 2-diamine

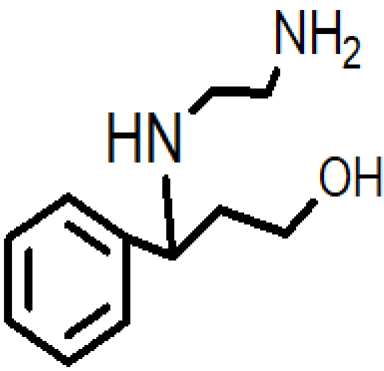


**Figure 2**

3-(2-aminoethylamino)-3-phenylpropan-1-ol

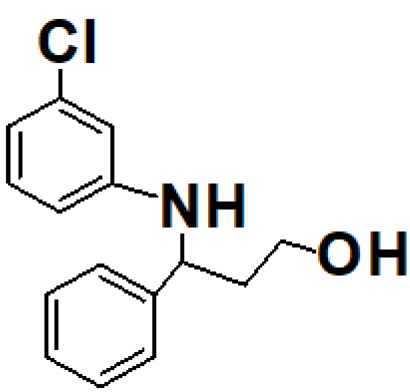


**Figure 3**

3-(3-chlorophenylamino)-3-phenylpropan-1-ol

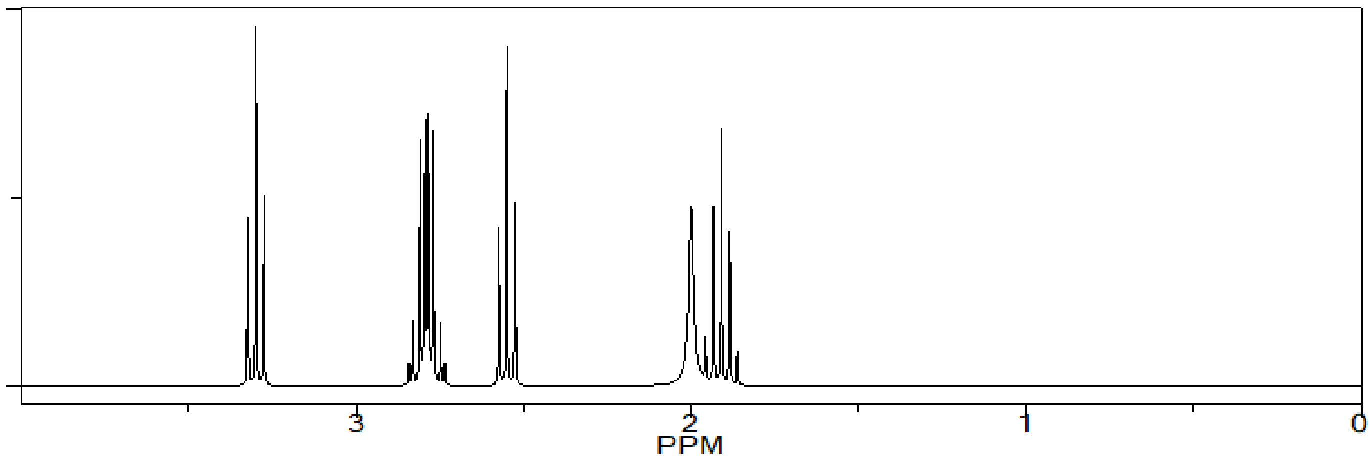


**Figure 4**

N.M.R. Spectra of Product Entry 1

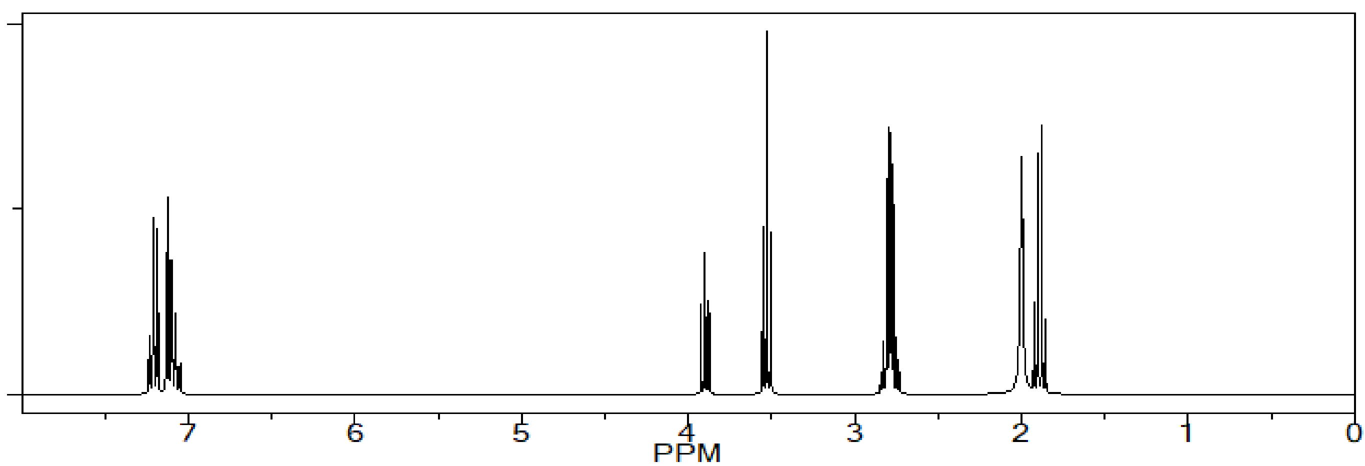


**Figure 5**

N.M.R. Spectra of Product 02

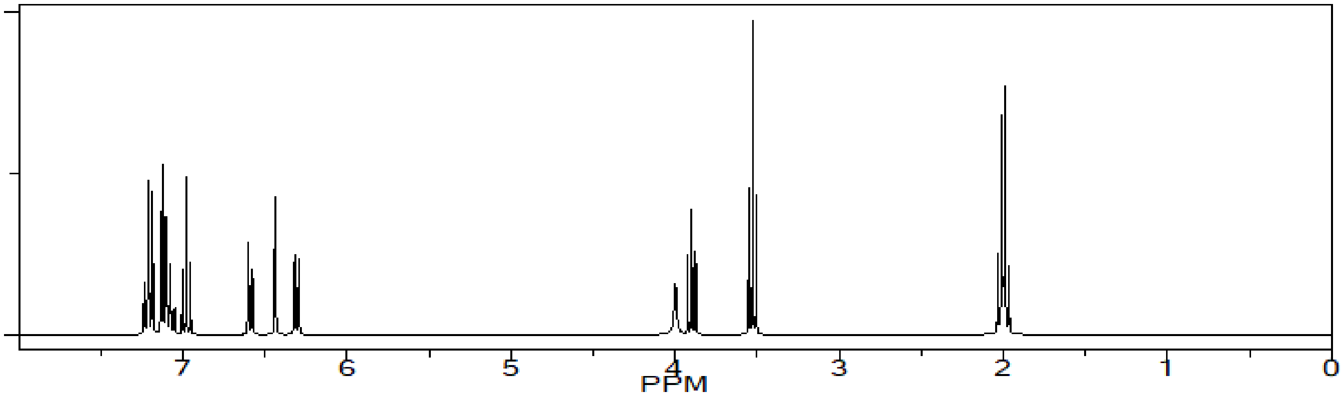


**Figure 6**

N.M.R. Spectra of Product 03

# Supplementary Files

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