Efficient synthesis of imines by MCM-41-SO_3H nanocatalyst

Ali E., Naimi-Jamal M. R.*

Research Laboratory of Green Organic Synthesis, Department of Chemistry
Iran University of Science and Technology, Tehran 16846, Iran

E-mail: naimi@iust.ac.ir

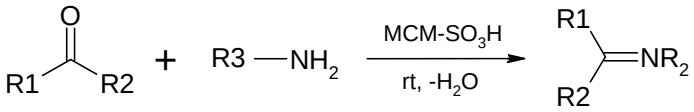
Abstract
In this study, MCM-41-SO_3H has been regarded as an efficient catalyst for the synthesis of aldimines and ketimines by the reaction of carbonyl compounds with primary amines at room temperature in excellent conversion yields.

Introduction
Imines have been discovered to have a wide spectrum of biological activities such as lipoxygenase inhibition, anti-inflammatory [1] and anti-cancer behavior [2]. Furthermore, they are used as versatile components in the formation of optically active α-alkyl aldehydes [3], in the preparation of secondary amines by hydrogenation [4], in nucleophilic addition with organometallic reagents [5] and in cycloaddition reactions [6].
On the other hand, ordered mesoporous materials are very attractive as heterogeneous solid catalysts for fine chemical synthesis. Mesoporous materials provide high surface areas with high concentration of active sites. A possibility to develop modified mesoporous materials is the modification of their surfaces by covalent anchoring of different organic moieties. For example, several types of mesoporous sulfonic acids have been created in recent years, while there are only a few reports about their applications as catalyst in chemical transformations [7].
Imines, also known as azomethines, have been usually prepared by a reversible condensation reaction between a primary amine and a carbonyl compound. Some recent methods for the preparation of imines are including polymer-supported [8], catalyzed by different Lewis acids, e.g. $ZnCl_2$ [9], Infrared Irradiation [10], P_2O_5/SiO_2 [11], or molecular sieves [12], $MgSO_4$–$Mg(ClO_4)_2$ [13], promoted by microwave irradiation [14], ultrasound irradiation[15], and or their combination. These methodologies often require complex procedures, long reaction times, large quantities of organic solvents, high reaction temperatures, huge amounts of costly dehydrating agents or catalysts, etc.
In this work, we present our preliminary results on a novel and efficient method for the synthesis of aldimines and ketimines in the presence of MCM-41-SO_3H nanocatalyst in ethanol with high yields.

Result and Discussion

In a model reaction, to a mixture of 4-chlorobenzaldehyde (0.140 g, 1 mmol) and aniline (0.093 g, 1 mmol) in 5ml ethanol in a round bottom flask, MCM-41-SO_3H (0.005 g) was added slowly, with stirring at room temperature. A prompt exothermic reaction was occurred. Thin layer chromatography (TLC) of the reaction mixture after 1 min showed the completion of the reaction. Then, the mixture reaction was filtered,

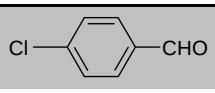
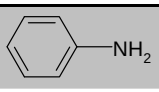
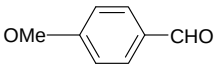
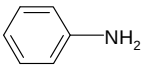
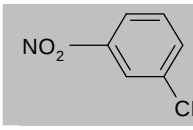
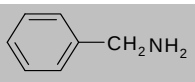
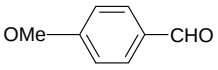
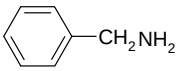
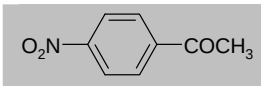
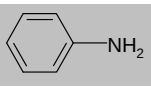
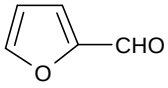
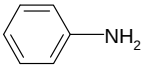
and the solid was washed with hot ethanol or ethyl acetate. The filtrate was then evaporated under reduced pressure to give the crude product. The pure product was crystallized from ethanol.



Scheme1: General method for the preparation of imines

A similar procedure was then used for different carbonyl compounds (Scheme 1, Table 1). Aromatic aldehydes afforded excellent yields in short reaction times, whereas ketones need longer time to complete and afforded lower yields. Heterocyclic aldehydes like furfural react also well with primary amines and produced corresponding imines in quantitative yields.
Other solvents such as dichloromethane and ethyl acetate have also been studied, but ethanol was found to be better, regarding higher yields of the products and its more greenness. Other carbonyl compounds are under further investigation.

Table 1: Preparation of imines catalyzed by MCM-SO_3H

Carbonyl Compound	Amine	Time (min)	conversion %
		30	**>95**
		15	**>95**
		45	**>95**
		45	**>95**
		120	**>70**
		30	**>90**

Conclusion

To sum up, different kinds of imines have been prepared through these methods. MCM-41-SO_3H is a strong and effective nanocatalyst for the synthesis of aldimines and ketimines.
Among the merits of the method we can mention: (i) this process is simple to execute; (ii) by means of this catalyst, the imines have been produced by high yields; (iii) and it is considered to be a relatively inexpensive method.

Experimental

Typical experimental procedure for the preparation of MCM-41-SO_3H [8]***:***

MCM-41(1g) was poured into a 100 mL round bottom flask equipped with a gas inlet tube and a dropping funnel containing chlorosulfonic acid (2 ml) and dichloromethane (15ml). Then chlorosulfonic acid was added dropwise over a period of 30 min at room temperature. HCl gas evolved from the reaction mixture was conducted via the gas inlet tube over a NaOH solution. After the completion of the reaction, solvent was evaporated under reduced pressure and the white solid (MCM-41-SO_3H) was collected.

Typical experimental procedure for the preparation of imines:

To a mixture of an aldehyde or ketone (1 mmol) and amine (1 mmol) in 5ml ethanol in a round bottom flask, MCM-41-SO_3H (0.005 g) was added slowly and the resulting mixture was stirred at room temperature for the time given in Table 1. The progress of the reaction was monitored by thin layer choromatography (TLC). Then, the mixture reaction was filtered, and the solid was washed with hot ethanol or ethyl acetate. The filtrate was then evaporated under reduced pressure to give the crude product. The pure product was crystallized from ethanol.

Acknowledgment
We acknowledge Iran University of Science and Technology (IUST) for partial support of this work..

References

1. Hadjipavlou-litina, D. J. and Geronikaki, A. A.; *Drug Design Discov.* **1996,** *15*, 199.
2. Vicini, P.; Geronikaki, A.; Incerti, M.; Busonera, B.; Poni, G.; Cabras, C. A. and Colla, P. L. *Bioorg. Med. Chem.* **2003**, *11*, 4785.
3. Bergbreiter, D. E.; M. Newcombe, M.; *Asymmetric Synthesis*, *Vol. 2A*, J. D. Morrison (Ed.), p. 243. Academic Press, Orlando, FL (1983).
4. Schellenberg, K. A.; *J. Org. Chem.* **1963**, ***28***, 3259.
5. Kuznetsov, V. V.; Pal'ma, A. R.; Aliev, A. E.; Varlamov, A. V and Prostakov, S*.; Zh. Org. Khim.* **1991**, *127*, 1579.
6. Tsuge, O and Kanemasa, R. *Adv. Heterocycl. Chem.**1989**, 45*, 231.
7. Rostamizadeh, Shahnaz; Mohammad Amani, Ali; Mahdavinia, Gholam Hossein; Amiri, Gelareh; Sepehrian, Hamid *Ultrasonics Sonochemistry* **2010**, *17*, 306–309.
8. Annunziata, R.; Benaglia, M.; Cinquini, M.; Cozzi, F. Eur. *J. Org. Chem*. **2002**, 1184.
9. Billman, J. H.; Tai, K. *M. J. Org. Chem*. **1958**, *23*, 535–539.
10. Miguel A ´ Va´zquez, Miguel Landa, Leonor Reyes, Rene´ Miranda, Joaquı´n Tamariz, and Delgado, Francisco. *Synthetic communications* **2004**, *34*, 2705-2718.

11. Naeimi, Hossein; Sharghi, Hashem; Salimi, Fariba and Khadijeh, Rabiei *Heteroatom Chemistry* **2008**, *19*, 44-47.
12. Taguchi, K.; Westheimer, F. H. *J. Org. Chem*. **1971**, *36*, 1570-1572.
13. Chakraborti, Asit K.; Bhagat, Srikant and Rudrawar, Santosh. *Tetrahedron Letters* **2004**, *45*, 7641–7644.
14. Gopalakrishnan, M.; Sureshkumar, P. ; Kanagarajan, V. and Thanusu, J. *Res. Chem. Intermed.* **2007**, *33*, 541–548.
15. Karla P. Guzen, Alexandre S. Guarezemini, Aline T. G. rf O, Rodrigo Cella, Claudio M. P. Pereira and H lio A. Stefani, *Tetrahedron Letters*.**2007**, *48*,1845–1848.