

Experimental and theoretical studies on efficient regeneration of carbonyl compounds from oximes under green, mild and completely heterogeneous nanocatalysis

Gh.R. Najafi^{1,*}, M.Saffari², M. Masteri-Farahani³ and F.Mollaamin¹

¹ Department of Chemistry, Qom Branch, Islamic Azad University, Qom, Iran

² Department of Chemistry, Rasht Branch, Islamic Azad University, Rasht, Iran

³ Department of Chemistry, Tarbiat Moallem University, Tehran, Iran

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ABSTRACT

New type of heterogeneous nanocatalyst for deoxygenation based on Tungsten oxide supported on mesoporous molecular sieve MCM-41 was developed. This new system represents inexpensive and highly active heterogeneous nanocatalyst for deoxygenation under green and mild reaction conditions.

Keywords: Green deoxygenation; Hydrogen Peroxide; Nanocatalyst; Ab initio; Relative stability energies; Thermodynamic computation

INTRODUCTION

Oximes are used not only for isolation, purification and characterization but also for protection of carbonyl compounds. Since oximes can be prepared from non-carbonyl compounds, deoxygenation of such oximes provides an alternative method for the preparation of aldehydes and ketones [1]. Oxidation of organic substrates in aprotic solvents under mild and neutral conditions is important in modern organic synthesis. Therefore, the search for new oxidizing reagents is of interest to synthetic organic chemists.

Heterogeneous catalysis has always been an inherently nanoscopic phenomenon with important technological and societal consequences for energy conversion and the production of chemicals. In fact, catalysts have been reported to represent the oldest commercial application of nanotechnology. Nanocatalysts are generally defined as nanoscale materials that have at least on nanoscale dimension, or have been subjected to nanoscale structural modification in order to enhance their catalytic activity. They could be classified into four distinct types of catalysts: nanoparticulate, nanoporous, nanocrystalline, and supramolecular catalysts. Most catalysts have been

consisted of nanometer-sized particles dispersed on a high-surface-area support, but recent advances in synthetic methods are leading to increasingly precise control of the variables affecting catalyst activity and selectivity in the nanoporous catalyst. Widespread applications of nanoporous materials in the fields of catalysis, adsorption and separation have emphasized the need to search for new structures with new framework compositions.

The MCM-41 supported nanocatalysts are being increasingly used in many fields of chemical reactions. These reagents are examples in this field: cationic rhenium (I) complex was encapsulated into mesoporous Al-MCM-41 for oxidation of aromatic hydrocarbons [2], Au-Ag alloy nanocatalyst to CO oxidation [3, 9], ball-shaped palladium nanocatalysts to cleavage of benzyl ethers [4], gold nanoparticles were formed inside MCM-41 for CO oxidation [5], α -amylase immobilized in ordered MCM-41 to hydrolysis of starch [6], MoO₃ supported on MCM-41 to metathesis of 1-octene [7], MCM-41

*Corresponding author: q_najafi@yahoo.com

supported Ru and Pd nanoparticle to clean hydrogenation of naphthalene and cyclic polyenes [8], SnO₂ grafted MCM-41 sensor was prepared for CO detection [10], immobilized form of ammonium perruthenate on MCM-41 for oxidation of benzylic and allylic alcohols [11], supported binaphthyl- Schiff's based complex of Cr on MCM-41 to asymmetric epoxidation of alkenes [12].

EXPERIMENTAL AND COMPUTATIONAL SECTIONS

Preparation and characterization of Catalyst

Our nanocatalyst, the MCM-41 supported Schiff base complex of molybdenum was prepared and characterized with FT-IR, atomic absorption spectroscopy, XRD and BET nitrogen sorption method according to previous work [13].

General Procedure for Deoxygenation

Some of the reagents reported for deoxygenation are often hazardous or very toxic or expensive, they need to be freshly prepared or the reaction require drastic conditions, long reaction times and tedious workup. Thus a milder, green, selective, nonhazardous and inexpensive reagent is still in demand. H₂O₂ is known to bring about certain desirable chemical transformation without creating unwanted by products, thereby eliminating many problems and costs associated with environmental cleanup. This article describes the development of green, efficient H₂O₂-based deoxygenation system (Scheme 1, Table 1).

In the first step, we considered three thermal conditions, i. e. room, 60° and reflux temperatures. After several experiments, we found that 60°C is an appropriate temperature for this procedure. After that we carried out reactions without one of the three components, MCM-41, H₂O₂ and MoO₂. The results suggested

that in absence of one of these reagents no reaction occurred. Then to demonstrate the recyclability of the catalyst, it was reused at least three cycles for further deoxygenation without a significant decrease in yield (Table 2).

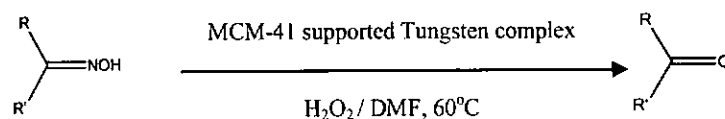
To a solution of 5 mmol oxime in 10 mL DMF, 150 mg catalyst was added. The reaction mixture was stirred at 60°C and about 2.5 mL H₂O₂ were added dropwise by the time indicated in table 1. The reaction progress was monitored by TLC.

The reaction mixture was cooled to room temperature and then filtered to recover the catalyst. The filtrate was extracted with toluene/H₂O (15 mL : 15 mL) the organic layer was dried over CaCl₂ and the solvent was then evaporated and the product purified by chromatography over silica gel (eluent in table 1). The procedure was same as our previous works [14].

AB Initio Calculations

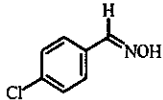
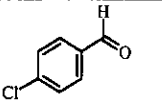
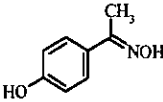
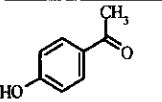
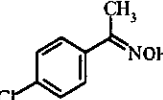
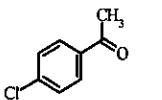
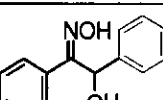
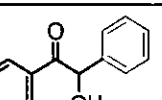
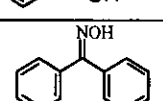
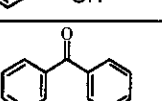
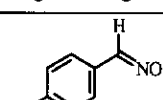
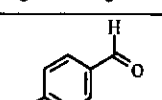
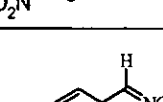
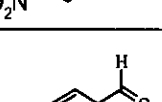
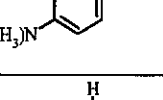
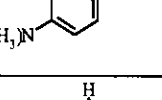
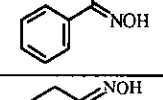
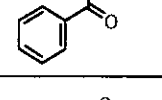
QM calculations were carried out at the HF/6-31G level of theory using the Gaussian 98 package, and the resulting of optimized relative stability energies and thermodynamic functions have obtained. Appropriate symmetry constraints were used in geometry optimizations. Harmonic vibrational frequency analyses were performed for all stationary points. Zero-point vibrational energies (ZPE) and thermodynamic properties at 25°C (room), 60°C and 153°C (reflux temperature) have calculated. 10 reagents were optimized using the opt keyword, and then their connectivities to the appropriate minima were investigated with the IR calculations by freq keyword from checkpoint files.

The application of these methods to systems of molecular interest has advanced tremendously in recent years to encompass models that describe local and global structural effects with great precision.



Scheme 1

Table 1. Deoximation using H₂O₂ catalyzed by MCM-41 supported Tungsten complex nanocatalyst

Entry	Substrate ^a	Product ^b	Eluent (TLC & Col. Chorm.)	Time (h)	Yield ^c (%)
1			Chloroform	7	97
2			Chloroform	6	90
3			Chloroform	6	98
4			Chloroform	8	90
5			<i>n</i> -Hexane : Ethyl acetate (7:3)	6	-
6			Chloroform	5	95
7			<i>n</i> -Hexane : Ethyl acetate (7:3)	6	85
8			Chloroform	6	92
9			Chloroform	5.5	70

a) All substrates were synthesized by known literature procedures.

b) All products were characterized by comparison of their m.p as well as their IR and ¹H NMR spectra[15] with those of authentic samples.

c) Yields refer to isolated products.

Table 2. Reuse of the nanocatalyst to deoximation of 4-nitrobenzaldehyde

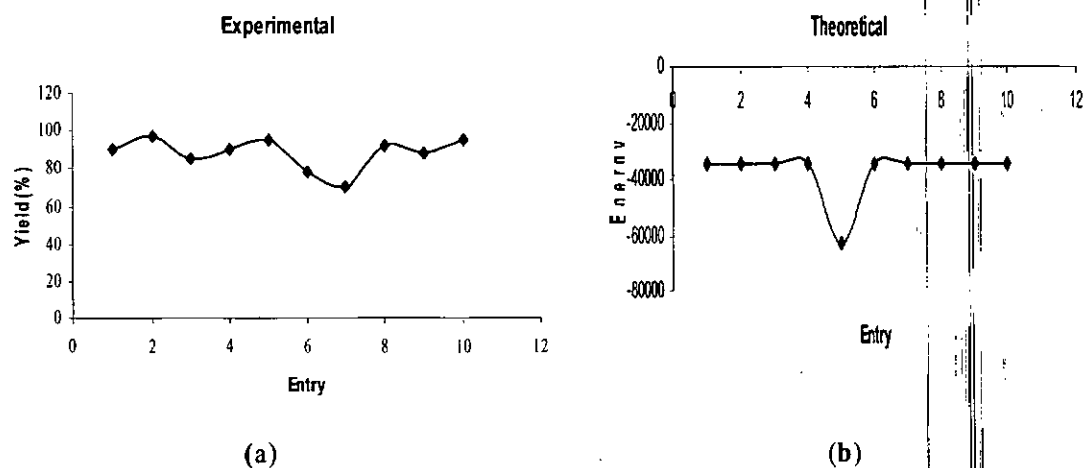
Run	Yield (%)
1	95
2	95
3	94

In the second step, we optimized the geometries of 10 substrates and products in table 1 at HF/6-

31G level in 25°C, 60°C and 153°C, and relative stability energies have been showed in table 3, then obtained results have been compared with experimental yields (Fig.1). In this investigation, Optimized geometries of 10 samples (including substrates and products) indicate limit of differences between the calculated and experimental observed values.

Table3. Optimized parameters at HF/6-31G theory level of relative stability energies (ΔE) and thermal enthalpy (ΔH), thermal entropy (ΔS) and Gibbs free-energy (ΔG) profiles (25^oC 60^oC and 153^oC) for the oxidative reactions by organic reagents

Entry	ΔE (kcal.mol ⁻¹)	Temperature (°C)	ΔH (kcal.mol ⁻¹)	ΔS (cal.K ⁻¹ .mol ⁻¹)	ΔG (kcal.mol ⁻¹)
1	-34479.6139	25	-34467.76077	6.582	-34469.72297
		60	-34457.57942	7.157	-34469.96267
		153	-34467.03413	8.596	-34470.6956
2	-34475.67896	25	-34464.33587	0.443	-34464.46827
		60	-34464.22606	0.789	-34464.48961
		153	-34463.87403	1.719	-34464.60632
3	-34473.0779	25	-34461.81645	1.318	-34429.96762
		60	-34461.70225	1.681	-34462.26135
		153	-34461.33767	2.642	-34462.4634
4	-34474.26689	25	-34462.956	0.971	-34463.2459
		60	-34462.8443	1.326	-34463.28606
		153	-34462.48474	2.273	-34463.4536
5	-62696.79397	25	-62684.89717	5.135	-62686.42827
		60	-62684.70515	5.743	-62686.61778
		153	-62684.13413	7.253	-62687.22332
6	-34474.24286	25	-34462.91897	0.996	-34463.21578
		60	-34462.80728	1.352	-34496.02595
		153	-34462.44834	2.297	-34463.42725
7	-34478.0998	25	-34466.27046	6.855	-34468.31423
		60	-34466.08597	7.441	-34468.56335
		153	-34465.53314	8.9	-34469.32451
8	-34476.41094	25	-34464.50467	5.305	-34466.08597
		60	-34464.32583	5.87	-34466.2805
		153	-34463.78994	7.286	-34466.89356
9	-34469.09829	25	-34457.65674	-6.178	-34455.81503
		60	-34457.55258	-5.847	-34455.60544
		153	-34457.21122	-4.95	-34455.10344
10	-34478.67032	25	-34466.70782	6.009	-34468.49934
		60	-34466.52899	6.575	-34468.71834
		153	-34465.99059	7.996	-34469.39667

**Fig.1.** Investigation of a) experimental yields in table 1 and b) Calculated (HF/6-31G) Relative stability Energies (kcal/mol) for Species Found on Potential Energy Surfaces in table 3.

The standard enthalpies (ΔE) and thermal enthalpy (ΔH), thermal entropy (ΔS) and Gibbs free-energy (ΔG) for these compounds have obtained by theoretical methods in program package of Gaussian 98 at 25°C, 60°C and 153°C as thermodynamic computations (Table 3). The best results in different reagents have given in HF/6-31G level.

Ab initio calculations for aromatic and aliphatic ketoximes and aldoximes support the proposed mechanism.

The shape of the ΔH , ΔS and ΔG surfaces in figure 2(a, b, c) is a consequence of environment of the calculated reactions. Since both reaction pathways involve organic reagents, computational errors should be minimized, and a meaningful comparison of pairs of individual reactions can be made.

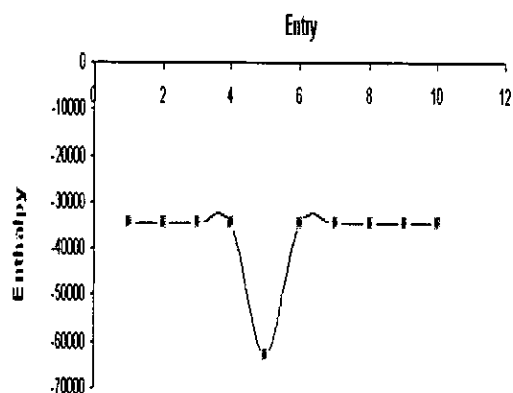
Then, changes of Gibbs free energy in the 10 organic agents in three temperatures by three have plotted in fig.2c. It turns out that the (HF) optimization is in good agreement with the experimental data. Also it is obvious that with decreasing of temperature the stability increases in theoretical level (Fig.2).

Intermolecular reactions of these compounds provide one of the most versatile ways to construct relative substances.

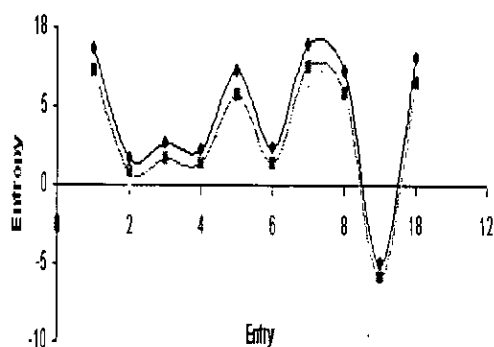
CONCLUSION

Remarkable structure which can be described as intramolecular reactants adduct for experimental yields. Also, this view is consistent with ab initio calculations. The formation of the expected products has been attributed to the more favorable yields in the reactions and comparison to ab initio data shows good agreement with experimental results. thermochemical computations presented here will allow their importance, or lack thereof, to be demonstrated significant differences in the predicted equilibrium composition. This will allow identification of the most important reactions, as well as the most important species, for indicated compounds.

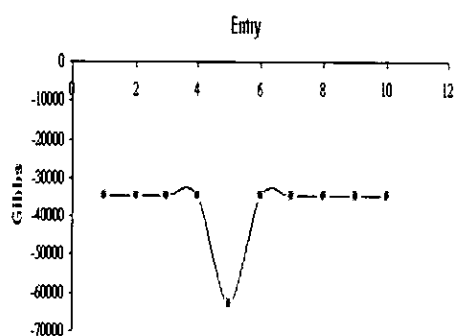
This study demonstrated that the MCM-41 supported Schiff base complex of molybdenum can be employed as a nanocatalyst to convert many oximes to corresponding carbonyl compounds. This method has many advantages such as mild reaction condition, high yields, reusable catalyst using H_2O_2 as a green oxidant and second elimination of hazardous solvent.



(a)



(b)



(c)

Fig. 2. HF/6-31G thermal enthalpy (ΔH), entropy (ΔS) and Gibbs free-energy (ΔG) profiles (25°C, 60°C and 153°C) for the oxidative reactions by organic reagents.

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Remarkable structure which can be described as intramolecular reactants adduct for experimental yields. Also, this view is consistent with ab initio calculations. The formation of the expected products has been attributed to the more favorable yields in the reactions and comparison to ab initio data shows good agreement with experimental results. Thermochemical computations presented here will allow their importance, or lack thereof, to be demonstrated. Significant differences in the predicted equilibrium composition. This will allow identification of the most important reactions, as well as the most important species, for indicated compounds.

This study demonstrated that the MCM-41 supported Schiff base complex of molybdenum can be employed as a nanocatalyst to convert many oximes to corresponding carbonyl compounds. This method has many advantages such as mild reaction condition, high yields, reusable catalyst using H₂O₂ as a green oxidant and second elimination of hazardous solvent.

ACKNOWLEDGMENTS

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- [15] ¹H NMR (300 MHz, DMSO) for selected compounds: Benzaldehyde: 9.8 (s, 1H), 7.4–7.8 (m, 5H), 4-Nitrobenzaldehyde: 10.1 (s, 1H), 8.1–8.4 (4H), 4-Chlorobenzaldehyde: 10 (1H), 7.6–7.9 (4H) Cyclohexanone: 1.5–3.2 (5H).
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