

Research Letter

Catalytic Oxidative Cleavage of C=N Bond in the Presence of Zeolite H-NaX Supported $\text{Cu}(\text{NO}_3)_2$, as a Green Reagent

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Copper(II) nitrate supported on faujasite zeolites such as H-NaX is employed as solid acid catalysts for the clean and less hazardous catalytic oxidative cleavage of C=N bond under mild conditions. The reactions proceed very smoothly, and the yields are excellent.

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1. Introduction

Increasing awareness of environmental hazards forces chemists to look for “eco-friendly” reaction conditions. In this connection, the use of heterogeneous catalysts involving solid reagents supported on high surface area materials, obtained by introduction of the reagent onto or into an organic polymeric or an inorganic porous or layered support material meets the fundamental challenges in the protection of the environment. These supported reagents have advantages such as easy handling, good dispersion of active sites leading to improved reactivity, safer and milder reaction conditions and minimal pollution [1, 2]. Oximes, hydrazones, and semicarbazones are useful as preferred derivatives for the identification and characterization of carbonyl compounds [3]. Several reagents have been reported for the regeneration of the carbonyl groups from the mentioned derivatives [4–9]. Although some of the methods involve mild reaction conditions, most of them require strong acidic media, long reaction time, a strong oxidizing agent (which causes over oxidation), and expensive and not readily available reagents.

Anhydrous metallic nitrates with a bidentate covalent coordination and with the available lower intermediate oxidation state for the metal, find maximum reactivity, and wider applicability [10, 11]. Their use, however, in organic syntheses is limited by solubility problems.

Laszlo et al. have used the K10-montmorillonite clay-supported copper(II) nitrate (claycop) and iron(III)

nitrate (clayfen) for many of the organic reactions like oxidation of alcohols, oxidative coupling of thiols, hydrolytic cleavage of imine derivatives of carbonyl compounds, cleavage of tosylhydrazones, phenyl hydrazones, 2,4-dinitrophenylhydrazones and semicarbazones [12]. K10-montmorillonite supported Thallium nitrate is used for the oxidative rearrangement of alkyl aryl ketones into alkyl aryl carboxylates [13]. Pyridinium chlorochromate [14], potassium dichromate [15] and sodium metaperiodate [16] are some alumina-supported oxidants used for the chemoselective oxidation of alcohols and sulfides. In this paper we report a general method for the oxidative cleavage of C=N to their carbonyl derivatives in excellent yields without using any microwave or ultrasonic irradiation. To the best of our knowledge, this is the first report using a zeolite-supported cupric nitrate as the reagent for the regeneration of carbonyl group from oximes, hydrazones and semicarbazones. Moreover, copper-salts are inexpensive, easy to handle and environmentally friendly.

2. Experimental

2.1. Preparation of Zeolite H-NaX Supported Copper(II) Nitrate. To a solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.483 g, 2 mmol) in acetone (15 mL), activated zeolite H-NaX (1 g) (obtained by activating NH_4 -NaX form of zeolite which has been prepared by partial exchange of sodium with ammonium salt in commercially available NaX) was added

TABLE 1: Conversion of oximes, phenyl hydrazones, 2,4-dinitrophenylhydrazones and semicarbazones to corresponding carbonyl compounds.

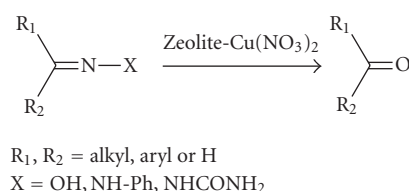
Entry	Substrate	Product	Time (h)	Yield %
1	Benzaldehyde oxime	Benzaldehyde	0.5	92
2	2-chlorobenzaldehyde oxime	2-chlorobenzaldehyde	0.25	78
3	4-chlorobenzaldehyde oxime	4-chlorobenzaldehyde	0.25	89
4	4-nitrobenzaldehyde oxime	4-nitrobenzaldehyde	0.25	88
5	Furfural oxime	Furfural	0.5	88
6	2-hydroxy 4-methoxy benzaldehyde oxime	2-hydroxy 4-methoxy benzaldehyde	0.5	87
7	Acetophenone oxime	Acetophenone	1	89
8	Benzophenone oxime	Benzophenone	1	89
9	4-hydroxyacetophenone oxime	4-hydroxyacetophenone	1	79
10	Cyclohexanone oxime	Cyclohexanone	0.5	90
11	Benzaldehyde phenylhydrazone	Benzaldehyde	1	66
12	Acetophenone phenylhydrazone	Acetophenone	2	79
13	Benzophenone phenylhydrazone	Benzophenone	2	69
14	Benzaldehydes 2,4-dinitrophenylhydrazone	Benzaldehyde	1	65
15	Acetophenone 2,4-dinitrophenylhydrazone	Acetophenone	3	86
16	Benzophenone 2,4-dinitrophenylhydrazone	Benzophenone	3	79
17	Furfural 2,4-dinitrophenylhydrazone	Furfural	1.5	75
18	Cyclohexanone 2,4-dinitrophenylhydrazone	Cyclohexanone	2	87
19	4-chlorobenzaldehyde 2,4-dinitrophenylhydrazone	4-chlorobenzaldehyde	3	66
20	2-chlorobenzaldehyde 2,4-dinitrophenylhydrazone	2-chlorobenzaldehyde	2	78
21	2-hydroxy -4-methoxy benzaldehyde 2,4-dinitrophenylhydrazone	2-hydroxy -4-methoxy benzaldehyde	0.5	69
22	2-hydroxy -4-methoxy benzaldehyde semicarbazone	2-hydroxy -4-methoxy benzaldehyde	1	78
23	Benzaldehyde semicarbazone	Benzaldehyde	2	91
24	Acetophenone semicarbazone	Acetophenone	2	78
25	Benzophenone semicarbazone	Benzophenone	2	76

at once with stirring over a magnetic stirrer for 2 hours. Then the solvent was removed in a rotary evaporator. The blue powder formed was dried further at 130°C under reduced pressure. 1 g of H-NaX zeolite supported copper(II) nitrate reagent contains about 0.326 g of $\text{Cu}(\text{NO}_3)_2$ (1.35 mmol).

2.2. General Procedure for the Oxidative Cleavage of C=N. 0.05 g of substrate was ground with 0.25 g of activated supported reagent using mortar and pestle and refluxed using 10 mL of dichloromethane as solvent for specified time. The reaction mass was cooled to room temperature, filtered the catalyst and washed with dichloromethane twice. The filtrate was washed with distilled water thrice. After drying over anhydrous sodium sulphate, the solvent was evaporated to give the product. Percentage conversion of deprotection was checked by GC analysis.

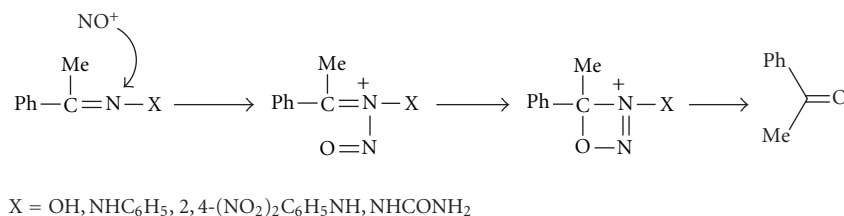
3. Results and Discussions

The results illustrated in Table 1 indicate that the reaction is successful for a variety of aliphatic and aromatic oximes, phenylhydrazones, p-nitrophenylhydrazones and semicarbazones (Scheme 1). All these carbonyl derivatives were converted back to their corresponding aldehydes and ketones in dichloromethane as the optimal solvent, among the

SCHEME 1: Catalytic oxidative cleavage of C=N bond in the presence of Zeolite H-NaX supported $\text{Cu}(\text{NO}_3)_2$.

tested solvents including: methanol, ethanol, and acetonitrile taking benzaldehyde oxime as a representative example where the yields are found to be 79%, 81%, 72%, respectively. The reaction is found to be general with compounds having variety of functional groups like chloro, nitro, phenolic hydroxyl, and methoxy groups.

As evident from the results, aldehyde derivatives were generally deprotected relatively faster than keto derivatives. It was also interesting to note that by controlling the amounts of the reagent, it was possible to avoid further oxidation of the liberated aldehydes to the corresponding carboxylic acids (entries 1–6), while we have demonstrated a facile aromatic nitration reaction with cupric nitrate in the presence of solid support [17], we did not observe any nitration of



SCHEME 2: Proposed mechanistic pathway.

TABLE 2: The effect of various solid supports on the oxidative cleavage of benzaldehyde semicarbazone (a mixture of benzaldehyde semicarbazide (0.05 g) and supported reagent (0.25 g) was refluxed in dichloromethane for 2 hour).

Run	Solid acid support	Yield of Benzaldehyde %
1	H-NaX	91
2	NaX	20
3	NaY	24
4	ZSM-5	34
5	MCM-41	12
6	SiO ₂	14
7	None	—

aromatic substrates during the cleavage reaction when we used optimum ratio of substrates and oxidants. Prolonged reaction time as well as excess of supported reagent in the case of aldehydes leads to further oxidation to the respective acids. The reaction failed to produce the ketones without cupric nitrate or H-NaX zeolite.

The superiority of H-NaX supported cupric nitrate as catalyst has been proved by the inefficiency in the regeneration of carbonyl groups from benzaldehyde semicarbazones by simple NaX supported Cu(NO₃)₂ or with unsupported Cu(NO₃)₂, revealing the involvement of acidic sites present in the solid support. The optimum ratio of substrate to oxidant (1 : 5) was determined for complete conversion of oximes, semicarbazones and phenyl hydrazones to the corresponding carbonyl compounds. The recovered catalyst was verified for three times to catalyze the deprotection of benzaldehyde oxime. The efficiency of catalyst decreases considerably during the successive reusability tests.

Regarding the mechanism of the deprotection, it is proposed that the diffusion of the cupric ions into the zeolite H-NaX surface lattices and the subsequent formation of N₂O₄ finally lead to the generation of NO³⁻ and NO⁺ ions. The presence of these ions has been confirmed by comparison of IR spectra of Cu(NO₃)₂ and Cu(NO₃)₂-loaded zeolite, which shows strong peaks around 1030–1070 cm⁻¹ due to symmetric stretching of nitrate ion, 1374 cm⁻¹ due to asymmetric stretching of nitrate ion, 810 cm⁻¹ due to in-plane deformation of nitrate ion and 710 cm⁻¹ due to out-of-plane deformation of nitrate ion, and peak around 2332–2415 cm⁻¹ due to NO⁺. The nitrosonium ion may act as an electrophile, giving the corresponding carbonyl compounds. Based on the observations, the proposed mechanism for

cleavage of the carbon–nitrogen double bond in oximes is presented in Scheme 2.

4. Conclusions

In conclusion, from commercially available NaX zeolite, a facile heterogeneous catalytic method, involving the more acidic form, namely, H-NaX with cupric nitrate has been employed for oxidative cleavage of C=N for the regeneration of carbonyl compound. It will be obvious that advantages of heterogeneous catalysis in terms of easy separation; and consistent yields are noteworthy. The operational simplicity, selectivity and cheapness, and good yields in very short times make this procedure a useful, attractive alternative to previously available methods.

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References

- [1] P. Lazslo, *Preparative Chemistry Using Supported Reagents*, Academic Press, San Diego, Calif, USA, 1987.
- [2] J. H. Clark, A. P. Kybett, and D. J. Macquarrie, *Supported Reagents: Preparation, Analysis and Applications*, VCH, New York, NY, USA, 1992.
- [3] N. D. Cheronis and J. B. Entrikin, *Identification of Organic Compounds*, Interscience, New York, NY, USA, 1963.
- [4] M. M. Heravi, L. Ranjbar, F. Derikvand, H. A. Oskooie, and F. F. Bamoharram, "Catalytic oxidative cleavage of C=N bond in the presence of mixed-addenda vanadomolybdophosphate, H₆PMo₉V₃O₄₀ as a green and reusable catalyst," *Journal of Molecular Catalysis A*, vol. 265, no. 1-2, pp. 186–188, 2007.
- [5] S. B. Shim, K. Kim, and Y. H. Kim, "Direct conversion of oximes and hydrazones into their ketones with dinitrogen tetroxide," *Tetrahedron Letters*, vol. 28, no. 6, pp. 645–648, 1987.
- [6] B. P. Bandgar, L. B. Kunde, and J. L. Thote, "Deoximation with N-haloamides," *Synthetic Communications*, vol. 27, no. 7, pp. 1149–1152, 1997.
- [7] M. Giurg and J. Młochowski, "Regeneration of carbonyl compounds from azines with cerium(IV) ammonium nitrate," *Synthetic Communications*, vol. 29, no. 24, pp. 4307–4313, 1999.
- [8] M. M. Heravi, D. Ajami, M. Tajbakhsh, and M. Ghassemzadeh, "Clay supported bis-(trimethylsilyl)-chromate: an efficient

- reagent for oxidative deoximation," *Monatshefte für Chemie*, vol. 131, no. 10, pp. 1109–1113, 2000.
- [9] M. M. Heravi, D. Ajami, and M. M. Mojtahedi, "Regeneration of carbonyl compounds from oximes on clayfen under conventional heating and microwave irradiation," *Journal of Chemical Research*, vol. 2000, no. 3, pp. 126–127, 2000.
- [10] C. C. Addison, N. Logan, S. C. Wallwork, and C. D. Garner, "Structural aspects of co-ordinated nitrate groups," *Quarterly Reviews, Chemical Society*, vol. 25, no. 2, pp. 289–322, 1971.
- [11] C. C. Addison, "The relation between chemical reactivity of ligands and the nature of the metal-ligand bond: nitrate-complexes," *Coordination Chemistry Reviews*, vol. 1, no. 1-2, pp. 58–65, 1966.
- [12] A. Cornelis and P. Laszlo, "Clay-supported copper(II) and iron(III) nitrates: novel multi-purpose reagents for organic synthesis," *Synthesis*, vol. 10, p. 909, 1985.
- [13] E. C. Taylor, C.-S. Chiang, A. McKillop, and J. F. White, "Oxidative rearrangements via oxythallation with thallium(III) nitrate supported on clay," *Journal of the American Chemical Society*, vol. 98, no. 21, pp. 6750–6752, 1976.
- [14] D. Savoia, C. Trombini, and A. Umani-Ronchi, "Synthesis of 2-(6-carboxyhexyl)cyclopent-2-en-1-one, an intermediate in prostaglandin synthesis," *Journal of Organic Chemistry*, vol. 47, no. 3, pp. 564–566, 1982.
- [15] J. H. Clark, A. P. Kybett, P. Landon, D. J. Macquarrie, and K. Martin, "Catalytic Oxidation of Organic Substrates using Alumina Supported Chromium and Manganese," *Journal of Chemical Society, Chemical Communication*, p. 1355, 1989.
- [16] G. W. Kabalka and M. Richard, "Organic reactions on alumina," *Tetrahedron*, vol. 53, pp. 7999–8065, 1997.
- [17] A. Lalitha and K. Sivakumar, "Zeolite H-Y-supported copper(II) nitrate: a simple and effective solid-supported reagent for nitration of phenols and their derivatives," *Synthetic Communications*, vol. 38, no. 11, pp. 1745–1752, 2008.