

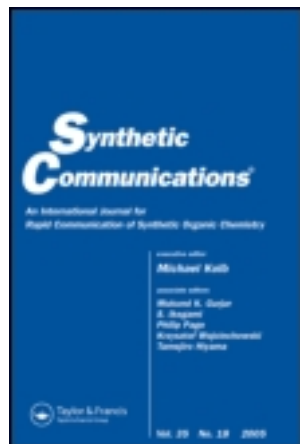
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Zeolite H-Y–Supported Copper(II) Nitrate: A Simple and Effective Solid-Supported Reagent for Nitration of Phenols and Their Derivatives

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Abstract: Highly regiospecific mononitration of phenols and substituted phenols is accomplished by employing copper(II) nitrate supported on a catalytic amount of zeolite H-Y in a solid state.

Keywords: Microwave, nitration, phenol, supported reagent, zeolite

The nitration of aromatic compounds is an immensely important industrial process, and many new methods and procedures have become available recently that address contemporary issues such as selectivity, safety, economy, waste, and the environment. Previously, traditional methods for the nitration of aromatic compounds have used mixtures of nitric acid and sulfuric acid, which have not always been selective and lead to problems associated with waste, disposal under environmentally friendly conditions. Also, such methods, when employed to phenols, generally give complex mixtures containing *o*- and *p*-nitro phenols, dinitrated phenols, and inextractible tars of phenolic oxidation products.^[1] This necessitates the need for new, novel, and simpler methods for nitration that can overcome the problems pointed out earlier.

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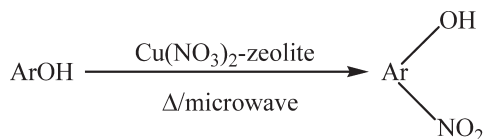
Heterogeneous catalysts based on aluminosilicates, which are environmentally friendly, are attractive alternatives for many conventional processes. Zeolites, with their well-defined cages and channels, find extensive applications in organic reactions, either as an active participant or as an inert support.^[2] Zeolite-based solid acid catalysts are potentially attractive because of the easy removability of substrate/product, catalyst recycling, and possible regioselectivities due to their constraining environment.^[3]

Over the past few decades, there has been a considerable interest in improving the *para*-selectivity of phenol nitration, and many attempts have been made using the catalysts supported on porous inorganic solids. Inorganic solids can offer significant benefits by providing both effective catalysis and, in some cases, enhanced selectivity.^[4] Such solids are easily removed from reaction mixtures and can often be recycled. Therefore, study of the use of inorganic solids as catalysts for electrophilic aromatic substitution reactions can make an important contribution to green chemistry. Recently, novel nitration systems composing of nitric acid, trifluoroacetic anhydride, and zeolite H- β have been reported^[5] for the nitration of deactivated aromatic compounds. Smith has shown that mordenite and zeolite H- β can play an important role in the selective mononitration of phenol, where high *para*-selectivity is achieved when acetyl/benzoyl nitrate are used along with HNO₃. The *para*-selective nitration of halogenobenzenes using a nitrogen dioxide–oxygen–zeolite H- β /HY system is also reported. Zeolite-assisted nitration of neat toluene and chlorobenzene with a nitrogen dioxide/molecular oxygen system is reported,^[5] and a remarkable enhancement of *para*-selectivity is observed. The same group also reports, in the Kyodai nitration of the same substrates over zeolites, a high preference for the 2,4-dinitro isomer at the second nitration stage.^[6]

Nitration of phenolic compounds using nitrate salts such as Bi(NO₃)₃ · 5H₂O, VO(NO₃)₃, Fe(NO₃)₃ · 9H₂O, (Me₄N)NO₃, Mg(NO₃)₂ · 6H₂O, and NaNO₃ as the nitrating reagents has been reported, and in some cases organic acids have been included in the reaction media.^[7] Gigante et al. have developed Claycop [Cu(NO₃)₂/montmorillonite-K10], which selectively nitrates phenol in acetic anhydride/CCl₄ with an isomer distribution of *ortho* 23, *meta* 1, and *para* 76%, where the actual nitrating species is claimed to be acetyl nitrate.^[8]

In this article, we report the results of our investigation on the nitration of more active phenolic compounds using Cu(NO₃)₂ · 3H₂O supported on zeolite H-Y as a nitrating reagent in the solid phase. Microwave irradiation leads to an excellent yield of nitro products compared to classical heating procedures.

Phenol and different types of substituted phenols were subjected to nitration using H-Y-zeolite-supported copper(II) nitrate (Scheme 1). The nitration reactions were performed under mild and heterogeneous conditions



Scheme 1. Nitration of phenols with zeolite HY-supported copper(II) nitrate.

at optimum temperature and under microwave irradiation to give the products in moderate to excellent yields (Table 1).

The nitration reactions were carried out by gently grinding the catalyst and substrates, the catalyst-substrate; mixture is either irradiated under microwave or heated over an oil bath. The resulting mono nitro phenols were separated by extraction with solvent and evaporation of the solvent.

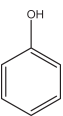
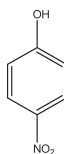
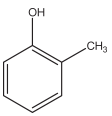
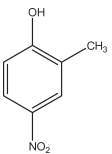
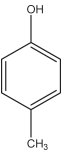
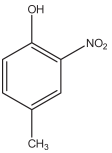
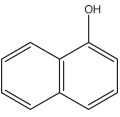
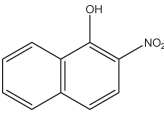
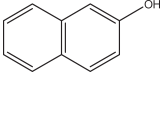
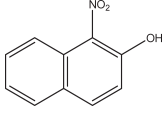
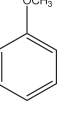
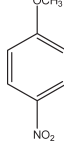
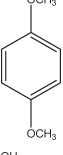
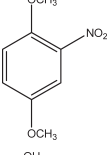
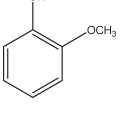
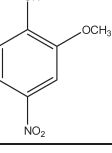
Although the nitration reaction also occurred with $\text{Cu(NO}_3)_2$ in the absence of zeolite H-Y, the reaction time was very long and needed several days for completion. Also, the resulting product looked like a charred mass and remained difficult to isolate. Therefore, it is clear that the zeolite acts as an effective reaction medium, providing a heterogeneous effective surface area. It also makes workup easy.

The nitration reactions of anisole and phenol, in contrast to most other methods, led to excellent yields of nitration products (Table 1). In the cases of phenol and anisole, trace amounts of 1,4-benzoquinone are also obtained as a result of oxidation.

Ali et al. reported that while treating phenol, substituted phenols, 1,4-dimethoxybenzene, and the substituted dimethoxybenzenes with ceric ammonium nitrate supported on silica gel, benzoquinone was the only product.^[9] But in the present study with $\text{Cu(NO}_3)_2/\text{zeolite}$, only for 1,4-benzenediol, the oxidation product, the benzoquinone was formed as sole product, whereas for substituted phenols, 1,4-dimethoxybenzene, and substituted methoxybenzene, nitration was observed as the only process.

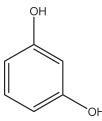
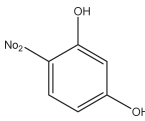
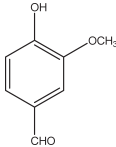
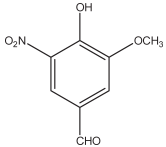
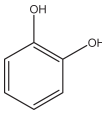
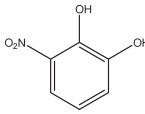
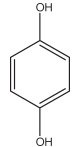
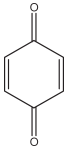
The nitration of phenol/anisole in copper nitrate-zeolite was carried out, which afforded 70% of *para*-nitro product. On the other hand, the nitration of *para*-cresol yielded 2-nitro-4-methylphenol and 3-nitro-4-methylphenol in 84% and 6% yield respectively. The nitration of 4-hydroxy-3-methoxybenzaldehyde (vanillin) gave 88% yield of 4-hydroxy-3-methoxy-5-nitrobenzaldehyde. Although the corresponding 4-nitro-1,3-benzenediol was obtained in around 40% yields by the nitration of resorcinol (Table 1, entry 9), in contrast to the observation that under the same reaction conditions, the reactions of 1,4-benzenediol and 4-methoxy phenol yielded 100% oxidized products. Under microwave irradiation, the duration of reaction was lower than the classical heating.

Table 1. Solid-state nitration of phenols with zeolite H-Y-supported copper(II) nitrate under classical heating and microwave irradiation^a

Entry	Substrate	Products	Microwave irradiation		Classical heating	
			Time (s)	Yield ^b (%)	Time (min)	Yield ^b (%)
1			90	64	30	60
2			60	84	30	78
3			60	88	30	84
4			90	80	45	76
5			90	82	45	77
6			120	77	60	73
7			30	90	30	92
8			50	80	45	76

(continued)

Table 1. Continued

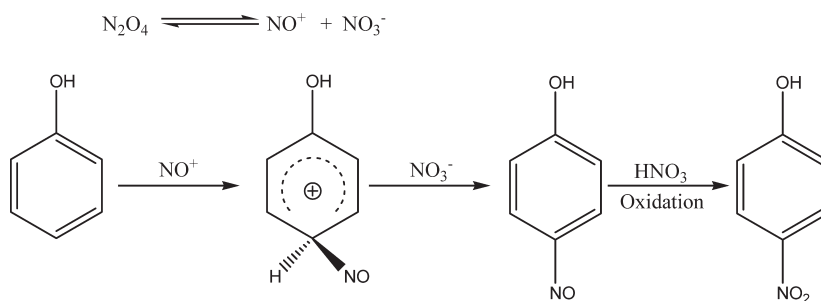
Entry	Substrate	Products	Microwave irradiation		Classical heating	
			Time (s)	Yield ^b (%)	Time (min)	Yield ^b (%)
9			150	40	120	32
10			45	89	30	81
11			150	50	120	65
12			30	100	15	100

^aThe reactions were carried with supported reagent–substrate (1 g: 1 mmol) ratio.

^bIsolated pure yields.

Regarding the mechanism of the nitration, it is proposed that the diffusion of the cupric ions into the zeolite H-Y surface lattices and the subsequent formation of N_2O_4 finally leads to the generation of NO_3^- and NO^+ ions. The presence of these ions have been confirmed by comparison of IR spectra of $Cu(NO_3)_2$ and $Cu(NO_3)_2$ -loaded zeolite, which shows strong peaks for NO_3^- and NO^+ ions. The nitrosonium ion may act as an electrophile, giving the nitroso phenols initially, which then are oxidized to nitro phenols (Scheme 2).

To check the reusability of the catalyst, experiments were performed with 1,4-dimethoxybenzene as a representative example. After extraction of the product, the H-Y-zeolite-supported copper(II) nitrate reagent was washed twice with chloroform and dried under vacuum before reuse. The percentage conversion was found to decrease in the subsequent reactions (about 50–60% of nitrated product was formed in the second time usage of the supported reagent), and the catalyst was deactivated after four times.



Scheme 2. Plausible mechanism of nitration of phenol using zeolite HY-supported copper(II) nitrate.

EXPERIMENTAL WORK

General

Chemicals were purchased from the Aldrich, Merck, Loba, and Rankem chemical companies. Yields refer to isolated pure products. The products were characterized by comparison of their spectral (IR, ^1H NMR, ^{13}C NMR), thin layer chromatographic, (TLC) and physical data with the authentic samples.

Preparation of Supported Reagents

To 0.483 g of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (2 mmol) dissolved in 15 ml of acetone, 1 g of activated zeolite H-Y (obtained by activating the $\text{NH}_4\text{-Y}$ form of zeolite in a muffle furnace at about 500°C for 12 h) was added at once with stirring over a magnetic stirrer for 2 h. Then the solvent was removed in a rotary evaporator. The blue powder formed was dried further at 130°C under reduced pressure. One gram of H-Y zeolite-supported copper(II) nitrate reagent contains about 0.326 g of $\text{Cu}(\text{NO}_3)_2$ (1.35 mmol). The reagent was stored in a vessel sealed with Para film.

Nitration of Phenol/Substituted Phenols with Copper(II) Nitrate-Loaded Zeolite under Classical Heating/Microwave Irradiation

Substrate (1 mmol) and 1 g of cupric nitrate (1.35 mmol) loaded on zeolite were mixed thoroughly in a mortar (the blue-colored reaction mixture turned yellowish green during the grinding process) and the mixture was taken in a 100-ml conical flask fitted with an air condenser and heated over an oil bath maintained of $70\text{--}80^\circ\text{C}$ for various time intervals. A deep

brown gas evolved. The progress of the reaction was monitored using TLC (4:6 ethyl acetate/hexane). The product mixture was extracted with chloroform and separated by column chromatography and analyzed using spectral methods. A similar method was adopted for the preparation of reaction mixture, and the mixture was irradiated using a microwave oven at 900 W for different time intervals. All of the isolated products are known compounds, and their spectra and physical data have been reported in the literature.^[1,10–15]

CONCLUSION

Phenols are selectively nitrated to *para*-nitro derivatives in high yields with copper nitrate–zeolite catalyst. The catalyst could be easily separated from the reaction mixture for recycling, and the workup procedure for isolation of reaction products is simpler as compared to the conventional process. The regioselective nitration of phenol using cupric nitrate over solid acid, catalyst without any use of acetic anhydride/acetyl nitrate, nitric acid, or sulfuric acid is a comparatively clean and environmentally friendly process.

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