

Catalytic oxidation of aromatic oxygenates by the heterogeneous catalyst Co-ZIF-9

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ABSTRACT

The catalytic activity of Co-ZIF-9, a zeolitic imidazolate framework of sodalite topology, in the oxidation of small aromatic molecules including phthalan, vanillyl alcohol, guaiacol, syringol, veratryl alcohol, and cinnamyl alcohol by molecular oxygen has been investigated. Co-ZIF-9 selectively oxidized the substrates and thus represents a promising heterogeneous catalyst for the oxidation of small aromatic substrates. Phthalan was converted to three different products, i.e. phthalide, phthalaldehyde, and small amounts of phthalic acid. In addition to phthalan, the alcohol functionality of vanillyl alcohol, veratryl alcohol, and cinnamyl alcohol was also similarly oxidized to yield the corresponding aldehydes in high yields and excellent selectivity. The effect of solvent, temperature and NaOH addition on the Co-ZIF-9 catalytic system has been studied. The presence of NaOH in the solution greatly enhanced the oxidation activity. The structure and stability of the heterogeneous catalyst was probed by UV–vis diffuse reflection spectroscopy, confirming the coordination geometry of cobalt in the catalyst framework, thermal gravimetric analysis, establishing the thermal stability of the structure, and XRD to monitor crystallinity of the catalyst. The heterogeneous nature of the catalyst was established by a hot filtration experiment, ICP analysis of the liquid phase, and by UV–vis absorption spectroscopy on the hot filtered reaction mixture.

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1. Introduction

Catalytic oxidations are an important class of reactions for the production of fine aromatic chemicals. With the depletion of fossil fuels as chemical feedstock, the fraction of aromatic chemicals obtained from renewable resources, such as biomass, can be expected to increase in the foreseeable future; thus, the development of processes for the catalytic oxidation of biomass-derived feed is becoming increasingly important [1]. Lignin, one of the most abundant natural polymers, consists of methoxylated phenylpropane structures, and the depolymerization and subsequent valorization of these units represents a viable method to produce renewable aromatic compounds on which society depends [1].

One possible strategy to valorize lignin is to produce fine chemicals via the selective oxidation of monomeric lignin-derived aromatic molecules. Although many metals are used as oxidation catalysts, promising examples include those that use cobalt as a catalyst. Cobalt is known to readily activate molecular oxygen for substrate oxidation [2–5], which is attractive for both environmental reasons and associated lower chemical expenses relative to other stoichiometric oxidants. Recently, we demon-

strated that Co salts in the ionic liquid [EMIM][DEP] serve as excellent homogeneous catalysts for the oxidation of alcohol-containing aromatic compounds, achieving very high turnover frequencies [6,7]. Other examples include the oxidation of aromatic cyclic ethers directly with molecular oxygen, which has been successfully performed with cobalt salts and complexes [2,3]. The anhydrous cobalt(II) chloride catalyzed oxidation of phthalan, performed in 1,2-dimethoxyethane (DME) under an oxygen atmosphere, resulted in the highest reported catalytic activity with 82% phthalide yield [3]. Small quantities of phthalic anhydride were also formed [3]. The principle disadvantage of all these processes originates with the homogeneous nature of the catalyst, which necessitates efficient catalyst separation and recovery industrially. The development of a heterogeneous catalyst system capable of using molecular oxygen for the oxidation of lignin-derived aromatics to produce fine chemicals would thus be an attractive industrial alternative to these homogeneous systems as it would allow for facile separation and recovery of these catalysts.

Recently, a new class of crystalline porous materials known as metal organic frameworks, more particularly the family of zeolitic imidazolate frameworks (ZIFs), has been developed for use in various applications such as carbon dioxide capture [8,9]. The primary building unit of ZIFs [M(Im)₄], (M = transition metal center; Co²⁺, Zn²⁺, Fe²⁺, Cu²⁺, Im = imidazolate-type linker) are structurally similar to the TO₄ tetrahedra of aluminosilicate zeolites and allow for

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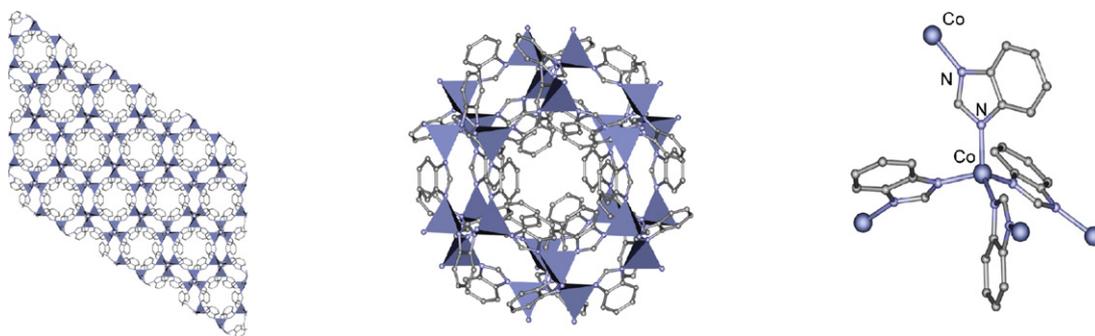


Fig. 1. From left, single crystal X-ray structure of ZIF-9, a single sodalite cage, and the tetrahedral coordination of the benzimidazolate linkers to cobalt [11].

construction of open framework zeolite-like structures. Several of these materials, especially ZIF-8, -9, and -10, display considerable chemical and thermal stability [10]. Purple cubic crystals of Co-ZIF-9 incorporate nets of corner-sharing tetrahedral CoN_4 where the bond between the benzimidazolate anion and Co(II) is one of the most stable among N-donor ligands [11] (see Fig. 1). Co-ZIF-9 has an open-framework structure adopting sodalite topology with hexagonal symmetry, composed of bridging benzimidazolate (PhIm) anions and cobalt cations with the formula $\text{Co(PhIm)}_2 \cdot (\text{DMF}) \cdot (\text{H}_2\text{O})$. Tunable pore size along with unique diffusion pathways (e.g. sodalite cages interconnected by six-membered rings as in the case of ZIF-7, ZIF-8, ZIF-9, ZIF-90) make ZIFs attractive not only for membrane and gas storage applications [11–15], but also for use as heterogeneous catalytic systems [16,17]. Indeed, several metal-organic-framework (MOF) catalysts have been developed for alcohol oxidation [18] using air [19] or H_2O_2 [20]. The examples of ZIFs used as heterogeneous catalysts are much more limited, but Corma et al. showed that Co-ZIF-9, for instance, has excellent catalytic activity for the oxidation of tetralin [21].

Inspired by the high catalytic activity demonstrated by the homogeneous cobalt complexes and promising leads using Co-ZIF-9 as a heterogeneous oxidation catalyst, we hypothesized that catalytic oxidation of small, highly functionalized aromatic molecules was also attainable using Co-ZIF-9, which could thus potentially serve as a heterogeneous catalyst to replace the homogeneous systems described above. The objective of this work was therefore to investigate the ability of Co-ZIF-9 to serve as a catalyst for the oxidation of aromatic molecules containing benzylic alcohols, phenols, methoxy groups, and benzylic ethers, which could be expected from lignin depolymerization feeds. We analyze the performance of the catalyst in a wide range of solvents, test the stability of the catalyst, and ascertain the heterogeneous nature of the system.

2. Experimental

2.1. Catalyst preparation

Co-ZIF-9 was prepared as described previously by Park et al. [11]. Cobalt(II) nitrate hexahydrate (0.210 g, Sigma–Aldrich, 99%) and benzimidazole (0.060 g, Sigma–Aldrich, 98%) were dissolved separately in approximately 9 mL DMF. The solutions were then combined in a capped 20 mL glass scintillation vial. This vial was placed in a programmable oven, heated to 403 K from room temperature at 5 K min^{-1} and held at this temperature for 48 h. The vial was then cooled to room temperature at 0.4 K min^{-1} . The purple cubic crystals were separated from the mother liquor, washed thrice with 3 mL DMF, and allowed to dry in air. The dried catalysts were crushed using a mortar and pestle prior to reaction.

2.2. Catalyst characterization

The powder X-ray diffraction pattern of the as-synthesized Co-ZIF-9 was recorded with a Bruker AXS D8ADVANCE diffractometer using $\text{CoK}\alpha$ radiation. BET surface area and properties of the pore structure were measured by TriStar 3000 V6.04 A. Thermogravimetric analysis (TGA) was carried out on a Pyris TGA thermogravimetric analyzer from Perkin Elmer with the sample held in a ceramic pan in a continuous flow nitrogen atmosphere (10 mL min^{-1}). Samples were heated at a constant rate of 5 K min^{-1} . UV–visible diffuse reflectance spectra of powdered catalyst were recorded between 200 and 700 nm on a Varian Cary 500 Scan spectrophotometer equipped with an integration sphere.

2.3. Catalyst testing

Reactions were conducted in a 40 mL Parr stainless steel autoclave equipped with a thermocouple and a magnetic driver. Stirring was done with an impellor at 750 rpm. Into 5 g of toluene there was successively added: 0.13 mmol of powdered Co-ZIF-9 (0.05 g), 1 mmol NaOH (0.04 g, Aldrich, 97%) and 4.04 mmol of selected substrate consisting of either phthalan (Aldrich, 97%), veratryl alcohol (Aldrich, 96%), syringol (Aldrich, 96%), guaiacol (Aldrich, 98%), vanillyl alcohol (Acros Organics, 99%), or cinnamyl alcohol (Acros Organics, 98%). Some substrates were contaminated with oxidized product (i.e. cinnamyl aldehyde in the case of cinnamyl alcohol, veratraldehyde in the case of veratryl alcohol, etc.). The quantity of these contaminants was measured and calculations were adjusted accordingly. The sealed autoclave with the reaction mixture was first purged three times, charged with oxygen (0.5 MPa, Hoekloos, 99.5%) and then heated to the designated temperature. During the course of the reaction, samples of 0.35 g were collected every hour and for that purpose the autoclave was cooled to 343 K and vented. The autoclave was again purged and charged with 0.5 MPa O_2 and heated. Between reactions, the autoclave was cleaned with water and ethanol and then rinsed with acetone. The autoclave vessel was treated overnight with aqueous NaOH in order to remove contaminants left on the walls.

Quantitative analysis of the products in solution was performed using a Shimadzu GC-2010A gas chromatography unit equipped with a WCOT fused silica CP-WAX 57CB column. Product identification was conducted using a Shimadzu GC/MS-QP2010 Mass Spectrometer and compared with pure samples when available.

2.4. Stability test of Co-ZIF-9

UV–visible spectroscopy was performed on the reaction mixture after 12 h reaction with Co-ZIF-9 using toluene as solvent. A part of the reaction mixture was hot filtered directly into a glass vial and subsequently measured using a Varian Cary 50 Conc UV–vis spectrometer equipped with an immersion probe. The immersion

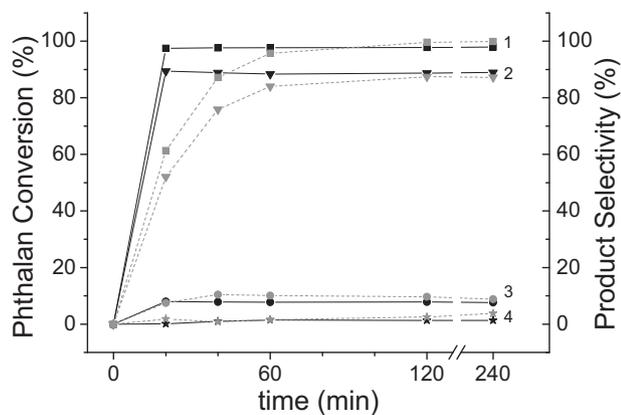


Fig. 2. Oxidation of phthalan by Co-ZIF-9 with molecular O_2 with 1.4 mmol NaOH (solid black) and without NaOH (dashed grey): phthalan (1), phthalide (2), phthalaldehyde (3), and phthalic acid (4). Reaction conditions: 7.00 g toluene, 0.07 g Co-ZIF-9 (0.13 mmol), 0.675 g phthalan (5.59 mmol), 0.5 MPa O_2 , 363 K.

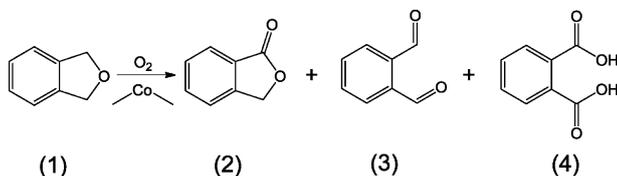
probe with a 1 mm path length was placed directly in the solution. The spectrum of toluene was collected as a background. The hot filtered solution was also submitted to the Mikroanalytisches Labor Kolbe (Mülheim, Germany) for ICP elemental cobalt analysis. The remaining solution was transferred into a clean autoclave, pressurized with O_2 , and heated again.

!Caution: The flash point of benzimidazole is 419 K and extra care must be taken to ensure that excess benzimidazole is removed from the catalyst prior to conducting oxidation reactions to prevent explosions at higher temperatures.

3. Results and discussion

3.1. Substrate oxidation

We begin our analysis of the Co-ZIF-9 system for the oxidation of aromatic substrates with phthalan, although, as indicated below, the Co-ZIF-9 system is capable of oxidizing a wide range of substrates. The selective catalytic oxidation of phthalan represents a potential route to obtain phthalide, which is an attractive industrial intermediate for pharmaceuticals and fine chemicals. Initially, with Co-ZIF-9 as catalyst, several solvents including water, acetonitrile, methanol, ethanol, dimethylformamide and toluene were tested. The best results were obtained using toluene, and this solvent was used for all subsequent reactions. Initial experiments were conducted at temperatures 363, 383, 403 and 423 K. Conversion was found to increase with increasing temperature, and the highest catalyst activity was achieved at 423 K (see below for analysis of the stability of the catalyst versus temperature). The results of the Co-ZIF-9 catalyzed oxidation of phthalan both with and without NaOH using toluene as the solvent are given in Fig. 2. In both cases, phthalan was readily oxidized to produce phthalide, phthalaldehyde and phthalic acid using molecular O_2 and Co-ZIF-9:



No reaction occurred in the absence of the catalyst. Although rapid phthalan oxidation occurred using just the Co-ZIF-9 (61% conversion after 20 min), the presence of NaOH further accelerated the oxidation rate, which resulted in nearly complete phthalan con-

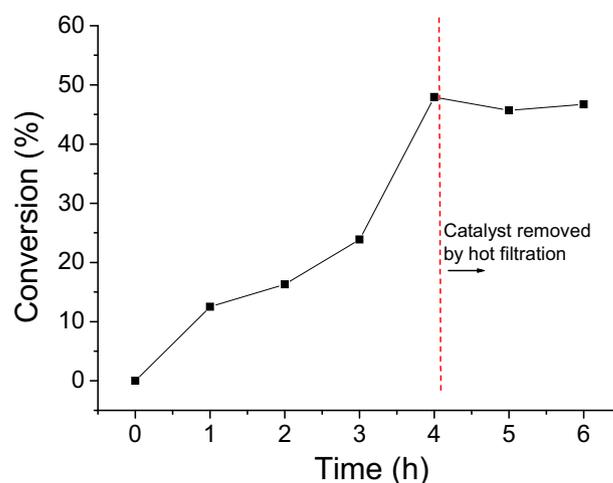


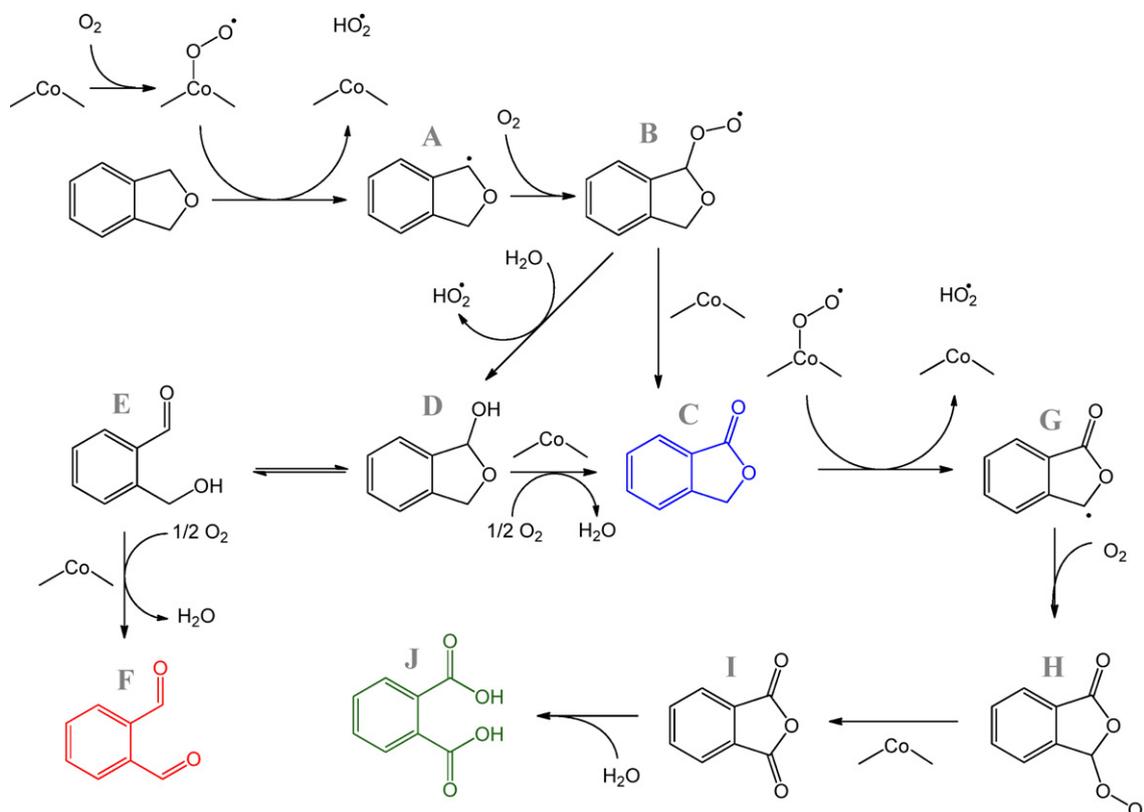
Fig. 3. Co-ZIF-9 catalyzed veratryl alcohol oxidation: veratryl alcohol conversion versus time. Reaction conditions: 5.00 g toluene, 0.05 g Co-ZIF-9 (0.13 mmol), 1 mmol NaOH (0.04 g), 4.04 mmol veratryl alcohol (0.68 g), 0.5 MPa O_2 , 423 K.

version in 20 min (see below for further discussion of NaOH in the reaction). Phthalide was the most abundant product, which was formed in 89% yield after one hour of reaction, followed by phthalaldehyde (8% yield). Phthalic acid yield increased slightly with increasing reaction time, whereas the quantity of the other products remained approximately constant.

As depicted in Scheme 1, the reaction may proceed mechanistically by the reaction of the phthalan with cobalt-activated molecular oxygen to form a radical intermediate (A) as previously observed with homogeneous cobalt catalysts [2,3]. This radical intermediate can then react with molecular oxygen to form radical intermediate (B), which either reacts with the Co-ZIF-9 catalyst to form phthalide (C) or with water to form 1-hydroxyphthalane (D). The phthalaldehyde was likely produced via ring opening of the hemiacetal 1-hydroxyphthalane to form species E, and the hydroxyl group is then subsequently oxidized by the Co-ZIF-9. Since species D was not detected at the conclusion of the reaction, this isomerization and subsequent oxidation likely occurs rapidly. According to the findings of Bovicelli et al. the oxidation of cyclic hemiacetals (species D) is faster than the cleavage of the phthalan C(1)–O(2) bond [22], which is necessary to form species E. In support of these observations, considerably higher yields of phthalide were obtained than phthalaldehyde. The formation of the phthalic acid likely occurs through the formation of radical intermediates (G) and (H) in analogy to the formation of species (A) and (B). Further reaction of radical intermediate H with Co-ZIF-9 results in phthalic anhydride formation (not detected), which hydrolyzes to form phthalic acid.

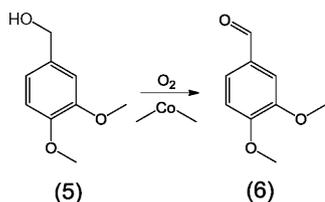
3.2. Other substrates

Based on the success of the Co-ZIF-9 catalyst in phthalan oxidation, we extended the system to other aromatic compounds, including veratryl alcohol, vanylyl alcohol, and cinnamyl alcohol. Veratryl alcohol (3,4-dimethoxybenzyl alcohol), synthesized *de novo* by the *P. chrysosporium* fungus during its lignolytic phase [23–25], is a representative non-phenolic model compound for lignin substructures and is widely used as a substrate in catalytic oxidation reactions [26]. The results are presented in Fig. 3. The Co-ZIF-9 catalyst selectively oxidized veratryl alcohol at the benzylic position affording veratraldehyde, which was the only observed



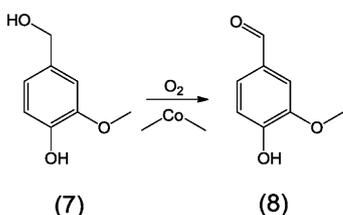
Scheme 1. Possible reaction path for the oxidation of phthalan.

product of the reaction:



After 4 h veratraldehyde was obtained in 46% yield, which corresponded to 1.9 mmol of veratryl alcohol consumed.

In contrast to veratryl alcohol, the reaction of vanillyl alcohol resulted in the consumption of 90% of the initial of substrate (3.99 mmol) after 4 h to form vanillin (4-hydroxy-3-methoxybenzaldehyde):



The results of the oxidation are given in Fig. 4. Note that the reaction rate tends to increase with time. This activity increase may be attributed to changes in the long range structure of the material, as discussed in further detail in Section 3.4 (XRD analysis). No products other than vanillin were observed. Over-oxidation of vanillin could give vanillic acid or quinones, which require cleavage of carbon-carbon bond *para* to the phenolic group, but these compounds were not detected. Successful oxidations with Co/O₂ complexes affording benzoquinones have been previously reported, mostly on phenolics lacking *para* substituents or phe-

nolics substituted with simple alkyl groups [27]. In order to test for this reactivity, syringol (2,6-dimethoxyphenol) and guaiacol (3-methoxyphenol) were used to study the performance of Co-ZIF-9 catalytic system for the oxidation. Both compounds were reactive under the applied reaction conditions, however, benzoquinones were not observed. Within 1 h of the reaction the guaiacol concentration decreased from 3.78 mmol to 0.72 mmol (81%) and syringol from 4.15 mmol to 0.49 mmol (88%). No monomeric products were observed by GC, suggesting possible oligomerization of the substrates, and a brown-colored solid formed on the bottom of the autoclave.

Cinnamyl alcohol contains both a C_γ-OH and a C-C double bond functionality and thus serves as an interesting compound to

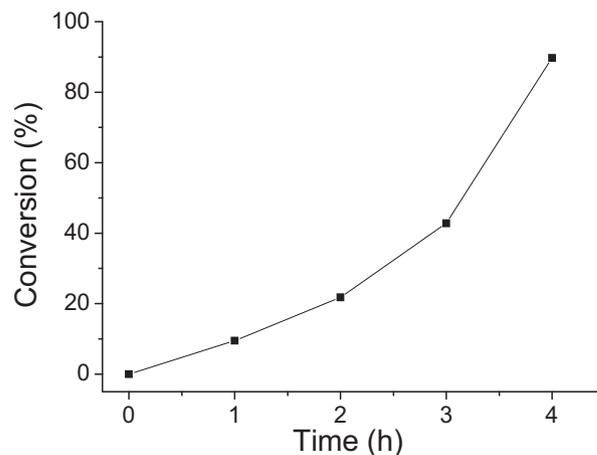


Fig. 4. Co-ZIF-9 catalyzed vanillyl alcohol oxidation: vanillyl alcohol conversion versus time. Reaction conditions: 5.00 g toluene, 0.05 g Co-ZIF-9 (0.13 mmol), 1 mmol NaOH (0.04 g), 3.99 mmol vanillyl alcohol (0.48 g), 0.5 MPa O₂, 423 K.

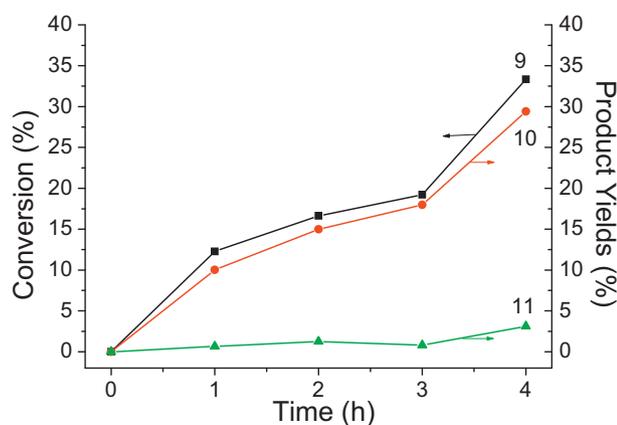
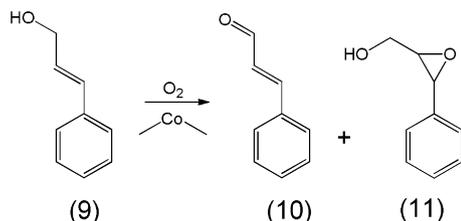


Fig. 5. Co-ZIF-9-catalyzed cinnamyl alcohol oxidation: conversion of cinnamyl alcohol (1) to cinnamaldehyde (2) and epoxide (3). Reaction conditions: 5.00 g toluene, 0.05 g Co-ZIF-9 (0.13 mmol), 1 mmol NaOH (0.04 g), 3.99 mmol cinnamyl alcohol (0.53 g), 0.5 MPa O₂, 423 K.

assess the activity of the catalyst towards these functional groups [28–32]. The products resulting from its oxidation most often include cinnamaldehyde, formed after oxidation of the C_γ-OH alcohol functionality, along with other products derived from reaction of the C–C double bond, depending on the reaction conditions and metal catalyst used [28,33]. As shown in Fig. 5, cinnamyl alcohol was the least reactive with oxygen in the presence of cobalt ZIF-9 compared to the previously discussed non-phenolic and phenolic aromatic compounds.



Both functional groups of the molecule included in the propyl side chain, C_γ-OH and the carbon–carbon double bond, were susceptible to oxidation, but the formation of cinnamaldehyde was distinctly favored. In addition to cinnamylaldehyde, a small quantity of the epoxide species was detected.

3.3. NaOH

As indicated above, the presence of ⁻OH is important for the rapid oxidation of the substrates. The results of the oxidation of phthalan, discussed above, and veratryl alcohol, given in Fig. 6, both in the presence and in the absence of NaOH, exemplify this importance. In the absence of NaOH, phthalan and veratryl alcohol oxidation occurred, but at a significantly lower rates than in the presence of NaOH. In the case of veratryl alcohol and the other substrates mentioned above, the yield of product exceeded the stoichiometric quantity of NaOH present in the system, which indicates that the ⁻OH may serve to activate the catalyst or it is regenerated as a result of the oxidation. Similar results were demonstrated for several homogeneous cobalt oxidation catalysts. In particular, the reaction of veratryl alcohol with molecular oxygen in the presence of Co(salen) complexes was thoroughly enhanced by the presence of NaOH either in aqueous medium or ionic liquids and different reaction conditions were revealed to be crucial for increasing the extent of veratryl alcohol oxidation [6,34]. The role of sodium hydroxide was quite different depending on the reaction medium used. In aqueous solutions, ⁻OH acted as a donor ligand which when

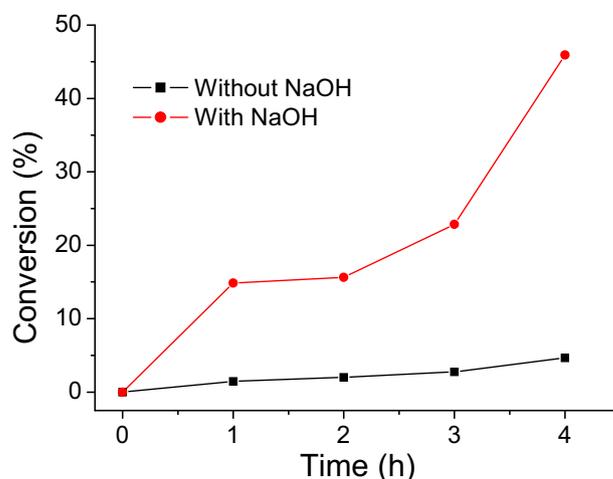


Fig. 6. Conversion of veratryl alcohol to veratraldehyde performed in the presence of NaOH (0.04 g) and absence of NaOH. Reaction conditions: toluene (5.00 g), 0.05 g Co-ZIF-9 (0.13 mmol), 4.04 mmol veratryl alcohol (0.68 g), 0.5 MPa O₂, 423 K.

present in the axial position of the complex stabilizes the Co–O₂ bond [35], while in [EMIM][DEP] solution it accelerated the formation of the active catalytic complex by aiding in deprotonation and coordination of the substrate [6], and similar activating effects may be occurring in the Co-ZIF-9 material depending on the substrate. In the case of phthalan, where substrate deprotonation is not a relevant mechanistic step, the increase in rate is possibly attributed to ⁻OH enhanced O₂ activation on the Co. In contrast, veratryl, vanillyl, and cinnamyl alcohols may first require ⁻OH aided deprotonation and catalyst coordination for rapid oxidation to occur.

3.4. Catalyst characterization and stability under reaction conditions

In order to confirm the structure and assess the stability of the synthesized Co-ZIF-9 materials used for the oxidation of the compounds listed above, XRD patterns of the catalyst were recorded. The results obtained for the fresh catalyst are depicted in Fig. 7. The recorded pattern corresponds well with the XRD pattern for the isostructural Zn-ZIF-7 reported by Park et al. [11]. In addition, the structure and the coordination geometry of cobalt were further confirmed by UV–vis diffuse reflection spectroscopy (see Fig. 8). Taken together, the results confirm the successful synthesis of Co-ZIF-9. The Co-ZIF-9 material exhibited bands in the region

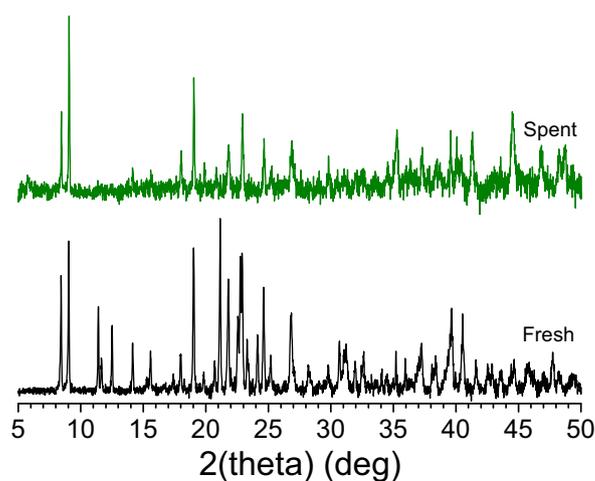


Fig. 7. X-ray diffraction patterns of the Co-ZIF-9 catalyst before and after reaction.

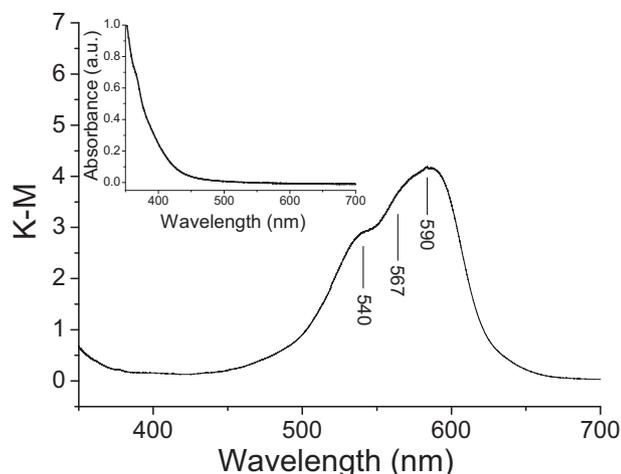


Fig. 8. UV-vis diffuse reflectance spectrum of Co-ZIF-9 sample and UV-vis of reaction solution after 12 h at 423 K following hot filtration (inset).

between 450 and 650 nm with two distinct maxima at 540 and 590 nm along with a shoulder at 567 nm. In their study of Co-containing aluminophosphate-based molecular sieves (Co-APO), Lourenco et al. observed three bands with maxima near 542, 583 and 623 nm in the UV-vis diffuse reflection spectrum, which is characteristic of cobalt in tetrahedral coordination and taken as an indication of isomorphous substitution [36]. In the case of Co-ZIF-9, bonding between the corner sharing nets formed between the imidazole, which is among the most stable for N-donor ligands, and Co(II) causes the shift in absorbance energy in UV-vis spectrum relative to the oxygen-sharing Co-APO structures.

Fig. 9 gives the results of thermal gravimetric analysis of the Co-ZIF-9 catalyst. Four weight loss steps were observed between 320 and 880 K. The first weight loss of 14.6%, the onset of which occurred at approximately 400 K, corresponds to the removal of a portion of the DMF and H₂O contained in the framework Co-ZIF-9 (1 DMF and 1 H₂O; calcd. 19.9% and 4.9%, respectively). Most likely, DMF is leaving the restricted porous system slower than H₂O based on its lower volatility and size relative to H₂O. The second weight loss of 22.3% between 560 and 680 K along with two small weight-loss steps of 3% and 3.5% (680–880 K) result because of decomposition of the ZIF framework. It can be concluded that Co-ZIF-9 is stable under reaction conditions, but temperatures exceeding 560 K have a deleterious effect on the framework resulting in its decomposition.

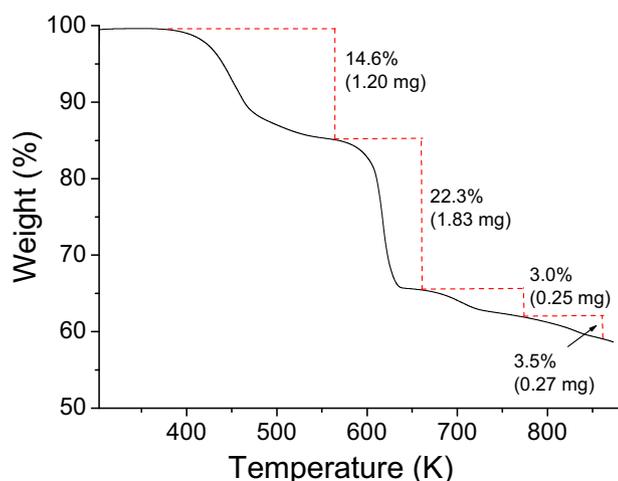


Fig. 9. Thermal gravimetric analysis of Co-ZIF-9.

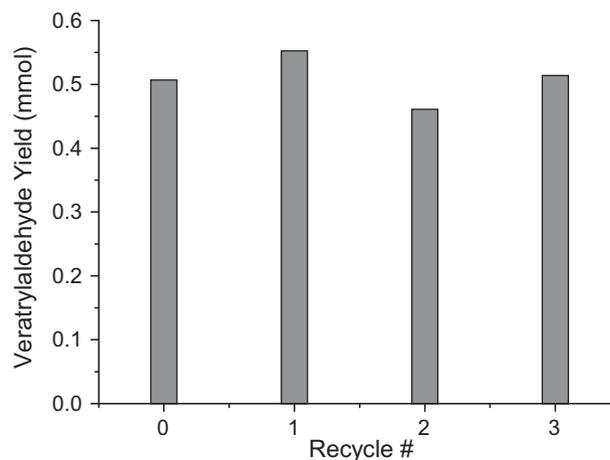


Fig. 10. Veratrylaldehyde yield versus number of recycle steps. Reaction conditions: 0.05 g Co-ZIF-9 (0.13 mmol), 0.04 mmol NaOH (1 mmol), 0.5 MPa O₂, 423 K, *t* = 1 h. Solutions: toluene (5.00 g), 4.04 mmol veratryl alcohol (0.68 g). Catalyst isolated by centrifugation and rinsed with toluene between reactions.

In addition to the XRD of the fresh catalyst, Fig. 6 includes the XRD of the recovered spent catalyst, recorded after use in the veratryl alcohol oxidation reaction. Comparison of the fresh and spent catalyst indicates that the Co-ZIF-9 catalyst maintains its crystallinity and overall structure as evident by similarities between the fresh and spent samples; however, the long range order of the material was altered as evident by the disappearance of peaks between 10 and 15° and at 21°. The decrease in the number of peaks is indicative of increased order in the catalyst. In order to test if DMF or H₂O was expelled from the pore system under reaction conditions led to this structural change, we heated the Co-ZIF-9 catalyst solely in the presence of toluene. No differences were observed between this sample and the fresh catalyst, which indicates that the differences in the spent catalyst do not occur from loss of spectator molecules but rather as a result of the substrate oxidation.

In order to further investigate the homogeneous or heterogeneous nature of the reactions, we performed UV-vis absorption spectroscopy on the hot filtered reaction mixture. The spectrum for this slightly yellow solution (see Fig. 8 inset depicted above) does not exhibit absorption bands in the region between 500 and 700 nm, which, if present, would confirm the presence of cobalt ions dissolved in the reaction mixture. When the hot-filtered solution was returned to a clean autoclave and reheated, no additional catalytic oxidation activity was observed (see Fig. 3 above). Additionally, ICP elemental Co analysis of the solution revealed Co concentrations of less than 1 ppm, which is the detection limit of the method used. Taken together, these results support the heterogeneous nature of the catalyst, and the increase in activity with reaction time observed with many of the substrates can be attributed to a solid–solid restructuring of the framework, indicated by XRD, rather than the slow dissolution of the cobalt ions. The reactions likely take place on coordinatively unsaturated cobalt defects that are possibly formed during the restructuring on the external surface of the ZIF-9 framework. Framework cobalt is coordinatively saturated, and although this saturation confers strength and stability to the Co-ZIF-9 material, it also prevents sites for oxygen or substrate coordination and activation. In addition, the small pore size of the ZIF-9 relative to the size of the substrates severely limits substrate diffusion into the ZIF-9, further supporting the occurrence of the reaction on the exterior surface.

The recyclability of the catalyst was tested by repeatedly conducting the oxidation of veratryl alcohol, isolating and rinsing the catalyst with toluene, and continuing the oxidation with fresh solutions of veratryl alcohol. The results, given as a percent of the initial

veratryl alcohol conversion, are given in Fig. 10. Despite a discoloration of the catalyst possibly attributable to the formation of coke-like species, the Co-ZIF-9 catalyst showed no apparent deactivation even after the 3rd recycle.

After 12 h of reaction in the presence of Co-ZIF-9 (with added NaOH), the colorless toluene turned slightly yellow. This coloration can be attributed to toluene itself being slightly reactive towards the catalytic system under reaction conditions, and two products of its oxidation, benzyl alcohol and benzaldehyde, were found in trace quantities (< 0.1%) after 4 h. The formation of the aldehyde likely occurs from oxidation of the benzyl alcohol [37]. No benzoic acid was detected.

4. Conclusions

Co-ZIF-9 can be effectively used as a heterogeneous catalyst for the oxidation of several small aromatic molecules in the presence of molecular oxygen. After 20 min under reaction conditions, nearly complete phthalan conversion was obtained to yield three products, consisting of phthalide, phthalaldehyde, and small amounts of phthalic acid. In addition to phthalan, the alcohol functionality of vanillyl alcohol, veratryl alcohol, and cinnamyl alcohol was also similarly oxidized to yield the corresponding aldehydes in high yields and excellent selectivity. UV–vis absorption spectroscopy and ICP analysis performed on the hot filtered reaction mixture confirmed the heterogeneous nature of the Co-ZIF-9 material. The catalyst was stable under the reaction conditions employed, as supported by TGA analysis; however, temperatures in excess of 560 K lead to the decomposition of the catalyst framework. Although the principle framework structure remained intact during reactions, long-range reordering of the catalyst occurred as determined by XRD analysis. The reaction rates were significantly enhanced in the presence of NaOH, which was not ultimately consumed during the course of the reaction. Co-ZIF-9 materials thus represent an attractive alternative to homogeneous catalysts for similar oxidations.

Acknowledgements

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