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Aerobic Oxidations Catalyzed by Zeolite-Encapsulated Cobalt Salophen

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Abstract: Cobalt salophen was encapsulated in a series of zeolites with a wide variation of the silicon-to-aluminium atomic ratio and with different cations. The zeolite-cobalt salophen catalysts were prepared using the "ship-in-a-bottle technique" where the complex was synthesized in the super cage of the zeolite and therefore locked into the pocket. The encapsulated catalysts were then tested in the aerobic oxidation of hydroquinone to *p*-benzoquinone; the best encapsulated catalyst was shown to be an efficient electron-transfer mediator in a palladium-catalyzed aerobic oxidative carbocyclization.

Keywords: aerobic oxidation; cobalt salophen; nanostructures; zeolite

Introduction

Oxidation reactions are prevalent and important transformations in organic chemistry and are essential in the production of bulk feedstock chemicals and fine chemicals.[1,2] There is an increasing demand to develop new methods for oxidation that are highly selective, easy to use, economical, and environmentally friendly.[3] In this respect, molecular oxygen is an attractive oxidant; it is readily available, inexpensive, and gives water as the only by-product.[2,4–8] Several approaches can be employed to modulate the reactivity of molecular oxygen so that it can be used selectively and under mild reaction conditions. Previously our group has reported the use of molecular oxygen in coupled catalyst systems that include an oxygen-activating catalyst, an additional electron-transfer mediator (ETM), and a substrate-selective metal catalyst (Figure 1). These multi-catalytic systems have been used to carry out the aerobic oxidation of alcohols to aldehydes and ketones,[9] the oxidation of secondary amines to imines,[10] the oxidation of alkenes and conjugated dienes[11] and oxidative carbocyclizations.[12,13] In these oxidations, the redox couple hydroquinone (HQ)/*p*-benzoquinone (BQ) is used as an ETM, and because dioxygen is not able to directly reoxidize HQ[14] under non-alkaline conditions, an additional ETM as oxygen-activating catalyst is required.

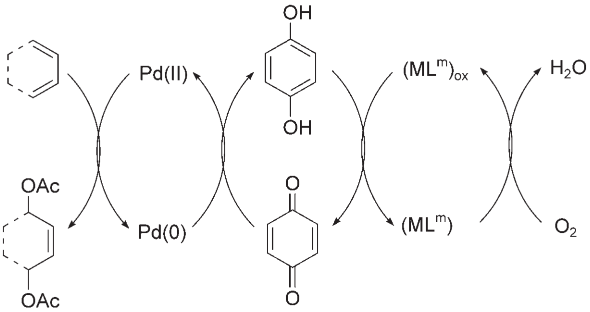


Figure 1. Example of a triple catalytic systems with cobalt salophen (ML^m) as oxygen activating catalyst, *p*-benzoquinone (BQ) as electron transfer mediator, and palladium(II) and substrate-selective catalyst, in this case for an oxidative addition to 1,3-cyclohexadiene.

In order to improve the cost-effectiveness and performance of catalysts and to facilitate the separation of catalysts from products, various methods have been developed for the immobilization of metal catalysts in and on solid supports.[8,15] The project described here makes use of zeolites as porous supports,[15] and one type of oxygen-activating catalyst, cobalt salophen [Co(Sal)], is synthesized inside the pores and trapped there irreversibly.[16–18] The hydroquinone (HQ) and molecular oxygen are able to diffuse through the pore channels and react with the catalyst and the *p*-benzoquinone (BQ) and H_2O formed can subsequently dif-

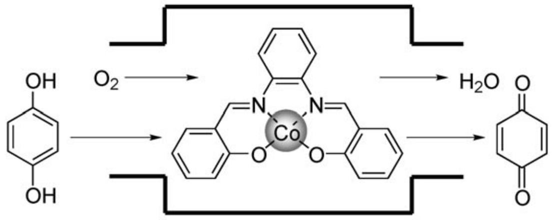


Figure 2. Zeolite-encapsulated cobalt salophen as an oxidation catalyst. Reagents O_2 and HQ can diffuse into the zeolite pores and react with the catalyst. After the reaction, the products BQ and water diffuse out.

fuse out (Figure 2). The properties of the zeolite can improve the performance of the catalyst and tune its selectivity towards reactants that are small enough to fit within the pores. Furthermore, the solid catalyst can be recovered and re-used by simple filtration. In the present project we have studied how the Si/Al ratio of the zeolite affects the efficiency and selectivity of the encapsulated Co(Sal). The zeolite-bound catalyst developed in this project can, in principle, be applied to all of the oxidations listed above. In the present work we have tested oxidative carbocyclization with good results.

Table 1. Tested zeolites and their Si/Al ratios.

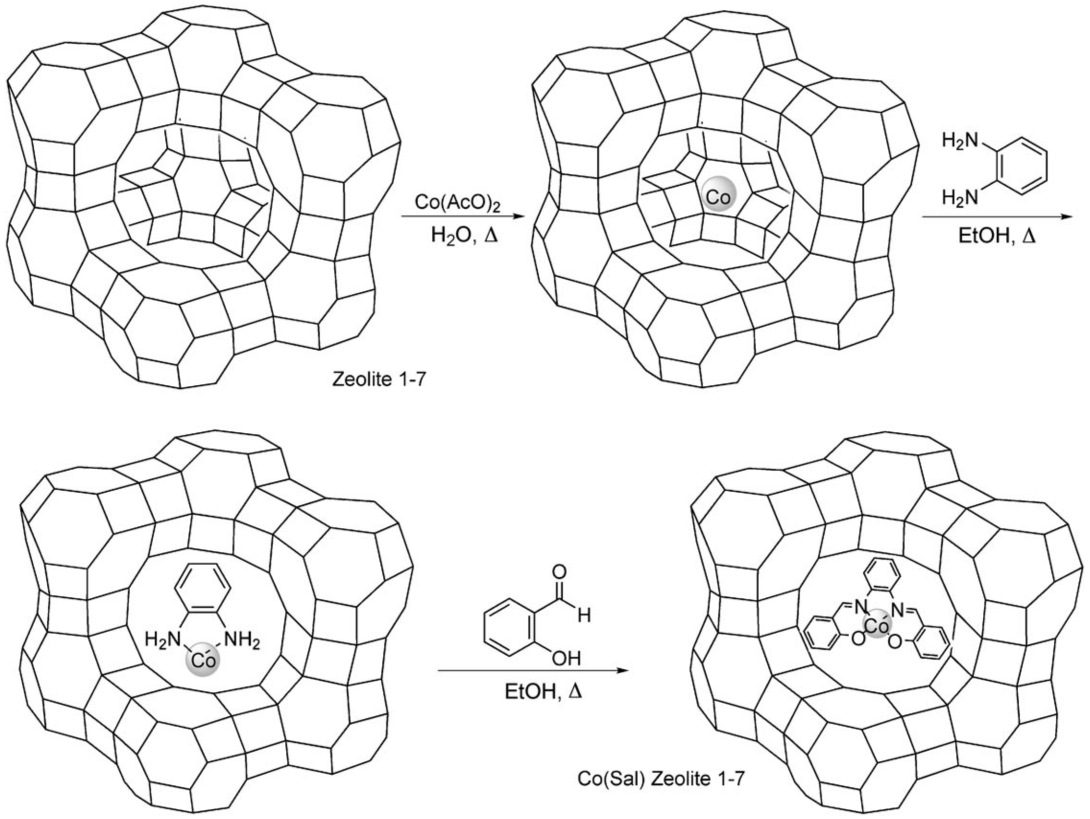
Entry	Zeolite	Si/Al ratio
1	Na/K-FAU[a]	1.0
2	Li-FAU	1.0
3	Na-FAU	1.0
4	H-FAU	1.25
5	Na-FAU	2.75
6	H-FAU	127
7	Na-EMT	7.43

[a] Mixture of cations Na/Al = 0.72 and K/Al 0.27

Results and Discussion

Catalyst Synthesis and Characterization

A series of zeolites was prepared with a range of Si/Al ratios (Table 1). These zeolites were used as the matrices for ship-in-a-bottle syntheses of the Co(Sal) catalysts (Scheme 1).[16,18] In the first step, the cations present in the zeolite are exchanged with cobalt(II) ions by heating the zeolite in a solution of cobalt acetate at reflux. The cobalt-exchanged zeolites are subsequently treated with phenylenediamine to form a cobalt phenylenediamine complex in the pores of the zeolite. Salicylaldehyde is then introduced, which



Scheme 1. The ship-in-a-bottle synthesis (Method A) of cobalt salophen within the cavities of zeolites **1**–**7** (Table 1).

leads to the formation of the cobalt salophen catalyst. A thorough extraction procedure with a Soxhlet apparatus is used to remove any cobalt salophen that is not trapped within the pores of the zeolite. Because of this operation, it is possible to compare solely those oxidation reactions that take place inside the pores of the zeolite. To find out how the Si/Al ratio affects the activity and re-use of the encapsulated catalyst, cobalt salophen was synthesized in the pores of seven different zeolites (Table 1).

The zeolites tested here are all of the FAU (Faujasite) type or the closely related EMT type[19] framework and cover a range of Si/Al ratios. In general, different Si/Al ratios of the framework lead to differences in the overall charge and in the distribution of the charge-balancing cations. The zeolite H-FAU 127, with a high Si/Al ratio, has a lower overall charge (SiO_2/AlO_2^- ratio high) and lower acidity. In the catalyst synthesis described above (method A) the cations of the zeolite are exchanged with cobalt cations in the first step. The catalyst loading in the zeolites is therefore dependent on the amount of negative charge in the zeolites. With method A, H-FAU 127 gave a zeolite catalyst with low activity because of the low loading of Co cations. Therefore a second method (method B) was investigated for this zeolite where the salophen without metal was synthesized in the cavity of the zeolite prior to the introduction of metal. Cobalt acetate was subsequently added, which leads to cobalt cation complexation with the salophen inside the cavity of the zeolite. Method B is not dependent on the zeolite charge.

FT-IR (KBr disc method) was used to characterize the Co(Sal) trapped within each of the zeolites (Figure 3 and Supporting Information). The IR spectra of the pure zeolites generally show bands at 3500–3100, 1650–1620, and 1300–950 cm^{-1} and several peaks in the fingerprint area. The Co(Sal) immobilized in zeolite Na-FAU 2.75 has characteristic peaks in the region 1612–1320 cm^{-1}. By comparing the IR spectra of Na-FAU 2.75 zeolites and Co(Sal) encapsulated in the same zeolite, bands characteristic of cobalt salophen are clearly visible for zeolite-encapsulated Co(Sal). Also, zeolite-encapsulated Co(Sal) from Na-FAU 1.0 and H-FAU 1.25 showed characteristic peaks in the region 1612–1320 cm^{-1} (see Supporting Information). No signals corresponding to cobalt salophen were seen in the spectrum of a sample prepared using H-FAU 127 and method A, but when method B was applied to the same zeolite, the cobalt salophen bands were present in the spectrum (see Supporting Information). In the catalyst testing (*vide infra*), it was found that there is a strong correlation between the appearance of cobalt salophen bands in

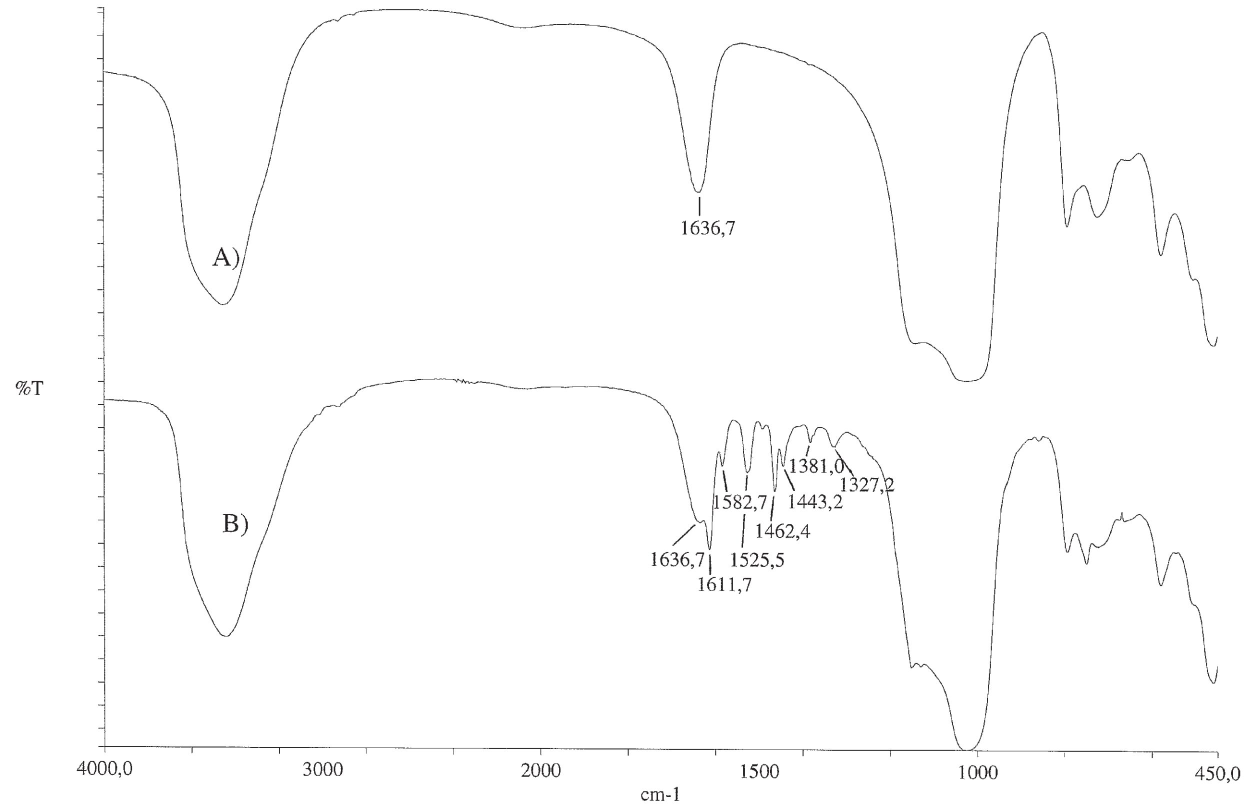


Figure 3. Characterization of zeolite-encapsulated cobalt salophens by FT-IR. The spectra of (**A**) Na-FAU 2.75 zeolite and (**B**) the spectrum of cobalt salophen synthesized within the cavities of zeolite Na-FAU 2.75 contains the signals of both.

the IR spectrum and the catalytic activity in aerobic hydroquinone oxidation. The catalyst with the sharpest, most intense salophen signals, the Na-FAU 2.75-encapsulated cobalt salophen, had the highest catalytic activity (Figure 3). The IR spectra provide a clear diagnostic for the presence of active catalyst in the zeolite cavities.

Catalytic Aerobic Oxidation of Hydroquinone

All of the coupled oxidation reactions mentioned above employ a HQ/BQ redox couple as an electron transfer mediator, and it is the reduced form of this redox couple, HQ, that is oxidized by O_2. To test directly the efficiency of the zeolite-encapsulated salophens, each catalyst was examined for its ability to catalyze the aerobic oxidation of hydroquinone, the reaction progress being monitored by following the rate of oxygen consumption at atmospheric pressure using a gas burette (Table 2, Figure 4 and Figure 5). The oxidations were carried out in acetic acid. Recovery of the zeolite-encapsulated catalysts is readily performed by filtration though a glass frit with >90% recovery on small test-scale reactions. The zeolite can also be recovered by centrifugation; in this process the supernatant was removed followed by washing and collection of the precipitate. The recovered catalyst is active and was used again for catalytic oxidation of HQ under the same reaction conditions (*vide infra*). Moreover, the product BQ was separated from the catalyst and the conversion could be confirmed by ^{1}H NMR.

Table 2. Reaction rate for the oxidation of HQ with different Co(Sal) zeolite catalysts, based on oxygen consumption.[a]

Entry	Zeolite [Co-(Sal)][b]	Si/Al ratio	Rate constant [h^{-1}]	Conversion [%][c]
1	Na/K-FAU[d]	1.0	0.13	99
2	Li-FAU	1.0	0.10	99
3	Na-FAU	1.0	0.27	99
4	H-FAU	1.25	0.19	99
5	Na-FAU	2.75	0.50	99
6	H-FAU	127	0.01	-[e]
7	H-FAU[f]	127	0.17	99
8	Na-EMT	7.43	0.18	99

[a] The reactions were carried out with 1.2 mmol HQ with 75 mg Co(Sal) Zeolite catalyst and 1.2 mL solvent.
[b] Unless otherwise note method A was used, see Experimental Section.
[c] Determined by NMR after 24 h.
[d] Mixture of cations Na/Al = 0.72 and K/Al = 0.27.
[e] Not determined.
[f] Prepared with method B, see Experimental Section.

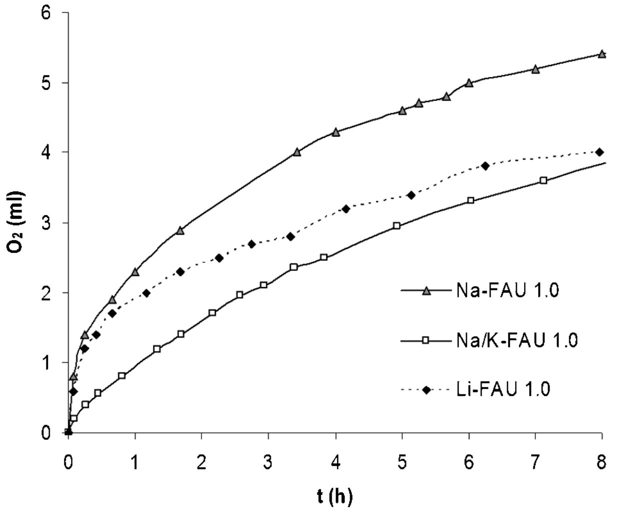


Figure 4. Reaction progress as measured by oxygen consumption for the catalytic aerobic oxidation of hydroquinone to benzoquinone with Co-salophen complex immobilized in FAU 1.0 zeolites with different cations.

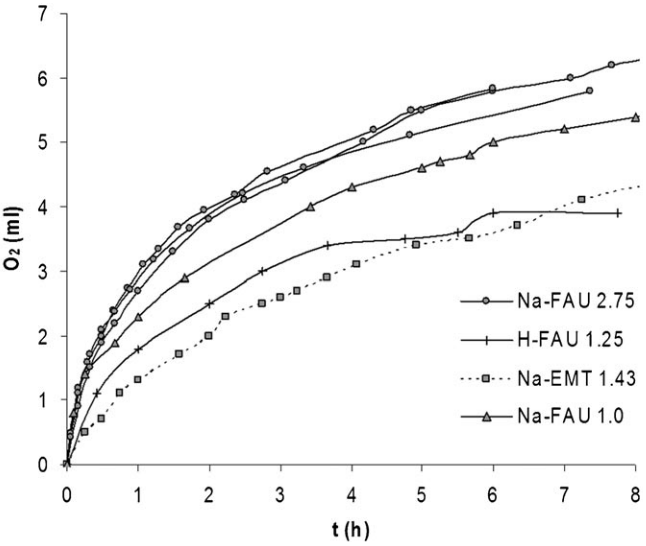


Figure 5. Reaction progress as measured by oxygen consumption for the catalytic aerobic oxidation of hydroquinone (HQ) to *p*-benzoquinone (BQ) with Co(Sal) complex immobilized in zeolites.

The catalyst encapsulated in zeolite Na-FAU 2.75 gave the best results with respect to rate, having a first order rate constant $k = 0.50$ h^{-1} (Table 2, entry 5). In general, zeolites with a Si/Al ratio close to one performed reasonably well and showed first order rate constants between 0.10 h^{-1} and 0.27 h^{-1} (entries 1–4). For the low silica FAU 1.0 zeolites synthesized with different cations (Table 2, entries 1–3), the Na-FAU 1.0 zeolite-encapsulated cobalt salophen catalysts preformed better than those derived from the Na- and K-FAU 1.0 zeolites. The hexagonal faujasite zeolite Na-EMT 7.43-encapsulated catalyst gave a slightly lower rate constant (entry 8) than the H-FAU 1.25-encapsulated catalyst (entry 4). The H-FAU 127 zeolite-encapsulated catalyst, synthesized with method A and having a high Si/Al ratio, performed poorly, giving the lowest rate for this oxidation (entry 6). When synthetic method B was applied to the H-FAU 127 zeolite, the result was an encapsulated catalyst with a 20-fold increase in activity with respect that catalyst derived from method A (entries 6 and 7 and Figure 6).

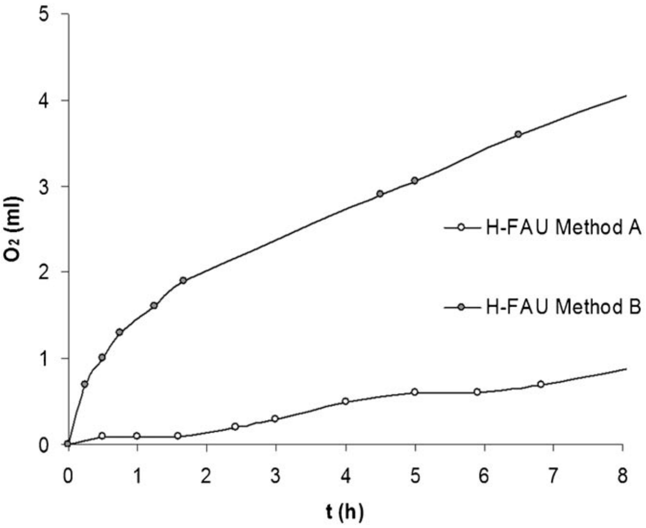


Figure 6. Catalytic aerobic oxidation of HQ to BQ with Co-(Sal) Zeolite H-FAU 127, where the immobilized catalysts were prepared with different methods (methods A and B).

The H-FAU 127-encapsulated cobalt salophen showed nearly the same catalytic activity as those zeolite-encapsulated cobalt salophens with low Si/Al ratio prepared by method A. The structure of the zeolite, as determined by cation choice and the Si/Al ratio, clearly plays a significant role for the activity of the encapsulated cobalt salophen.

Different solvents were tested in the oxidation reaction with Na-FAU 2.75-encapsulated cobalt salophen (Table 3). A change of solvent from acetic acid to toluene decreased the reaction rate, probably because of the low solubility of the HQ. When THF was used as solvent, the reaction rate increased substantially, giving complete oxidation of HQ in 3 h. Under these conditions, somewhat more than the theoretical amount of oxygen was consumed, which must be attributable to side reactions, although there was no evidence for further oxidation of the product BQ. When the oxidation reaction was followed by NMR with 1,2-dimethoxybenzene as an internal standard, it was observed that HQ was converted completely to BQ. No additional oxidation products were detected.

Catalyst Recycling

The recovery and reuse of zeolite-encapsulated cobalt salophens was investigated. After completion of an HQ oxidation reaction, the catalyst was recovered by centrifugation, and then was washed with the same kind of solvent as used in the reaction. After drying, the catalyst was reused directly in another HQ oxidation. In these small-scale test reactions, 90% catalyst recovery by weight was typical. The effects of solvent, additive, and agitation method were examined for their influence on the retention of catalyst activity (Table 4).

Recycling with acetic acid as solvent and using a magnetic stirrer gave very poor results (Table 4, entry 1), which were partly attributable to the stir bar grinding the zeolite to a very fine powder during the course of the reaction. When stirring was changed to shaking slightly better results were obtained. A change of solvent to toluene improved the results significantly and now reasonable activity was maintained for four runs (Table 4, entry 3). When THF was used as the solvent, the activity slowly decreased over three runs. For the second reaction run the oxygen uptake and conversion are still good but for the third run, they are down to 22% conversion (entry 4).

Table 3. The influence of solvent on the reaction rate of aerobic oxidation of HQ with the Na-FAU 2.75 Co(Sal) zeolite catalyst.[a]

Entry	Zeolite [Co(Sal)]	Si/Al ratio	Solvent	Rate constant [h^{-1}]	Reaction time [h]	Conversion [%][b]
1	Na-FAU	2.75	THF	6.07[c]	3	99
2	Na-FAU	2.75	THF	2.80[d]	3	99
3	Na-FAU	2.75	Acetic acid	0.50[e]	8	99
4	Na-FAU	2.75	Toluene	0.10[e]	24	99

[a] The reactions were carried out with 1.2 mmol HQ with 75 mg Co(Sal) Zeolite catalyst and 1.2 mL solvent.
[b] Determined by NMR.
[c] Calculated from O_2 consumption up to 100% conversion of 1 equiv. HQ.
[d] Calculated from NMR conversion of HQ to BQ.
[e] Calculated from the O_2 consumption.

Table 4. Recycling of Co(Sal) zeolite Na-FAU 2.75 in HQ oxidation.[a]

Entry	Reaction conditions	Run 1	Run 2	Run 3	Run 4
1	Co(Sal), Zeolite Na-FAU 2.75, AcOH, sirring	100 (100)	12 (–)	-	-
2	Co(Sal), Zeolite Na-FAU 2.75, AcOH, saking	100 (100)	68 (18)	81 (19)	-
3	Co(Sal), Zeolite Na-FAU 2.75, PhMe, saking	84 (96)	100 (98)	39 (51)	40 (47)
4	Co(Sal), Zeolite Na-FAU 2.75, THF, saking	>100 (100)	>100 (67)	56 (22)	-
5	Co(Sal), Zeolite Na-FAU 2.75, THF, TEAA, sirring	>100 (100)	68 (83)	>100 (100)	44 (32)
6	Co(Sal), Zeolite Na-FAU 2.75, THF, LiOAc, sirring	>100 (100)	>100 (77)	97 (53)	46 (26)
7	Co(Sal), Zeolite Na-FAU 127, AcOH, stirring	94 (100)	98 (52)	77 (16)	-

[a] The reactions were carried out with 1.2 mmol HQ with 75 mg Co(Sal) Zeolite catalyst and 1.2 mL solvent. For recycling runs 2–4 the zeolite catalyst was centrifuged, solvent and HQ were added to the zeolite. O_2 uptake (%) and NMR conversion (%).

In recycling experiments, the zeolite H-FAU 127 catalyst gave a better result than the Na-FAU 2.75 zeolite. These results indicate that the zeolite charge and acidity is of importance for the stability of the cobalt salophen complex.[20] The imine functionality of the salophen is sensitive to acid in the presence of water. The recycling results with zeolite H-FAU 127 catalyst inspired us to test whether buffering the acidity of the zeolites could increase the catalyst stability when recycling. Two oxidation experiments with zeolite Na-FAU 2.75 catalyst in the presence of a base, either 20 mol% lithium acetate (LiOAc) or 20 mol% tetraethylammonium acetate (TEAA), were tested. The results showed that the activity is retained for several reuses (entries 5 and 6). This is to be compared with the oxidation reactions of zeolite Na-FAU 2.75 catalyst without the presence of base (entry 4), where most of the catalytic activity was lost in the recycling experiment. In general, it was possible to recycle the Co(Sal) zeolite catalysts for three runs with good retention of activity. With more recycling, the activity was reduced.

Pd-Catalyzed Ene-Allene Carbocyclization

Because it gave the best results, the zeolite Na-FAU 2.75 Co(Sal) catalyst was chosen for investigation of the compatibility in the triple catalytic carbocyclization of allene-substituted olefins catalyzed by palladium(II). Our group has previously reported the oxidative cyclization of ene-allenes catalyzed by Pd(II) and with BQ as stoichiometic oxidant.[21] More recently, this work has been extended by employing a triple catalytic system enabling the use of O_2 as terminal oxidant and with an iron(II) phthalocyanine as oxygen activating catalyst and a catalytic amount of BQ.[12] The bicyclic product was formed in high yield when the reaction was carried out in toluene at 95 °C. We tested whether the oxygen-activating catalyst could be replaced with Na-FAU 2.75-encapsulated cobalt salophen (Figure 7).

The carbocyclization reaction of allene **9** (Scheme 2) was carried out in a sealed round-bottom flask under an oxygen atmosphere at 25 °C. The flask was charged with 1 mmol of allene **9**, the three cata-

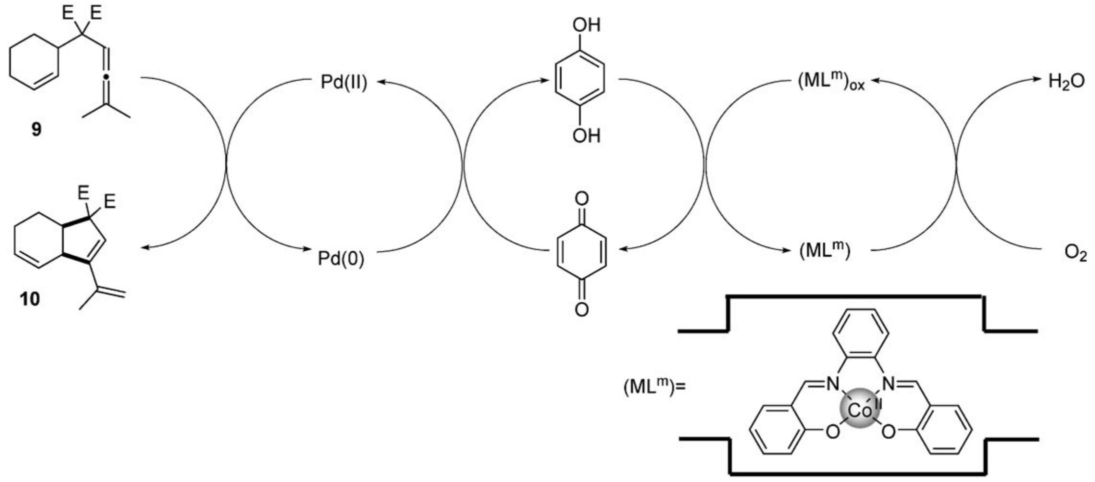
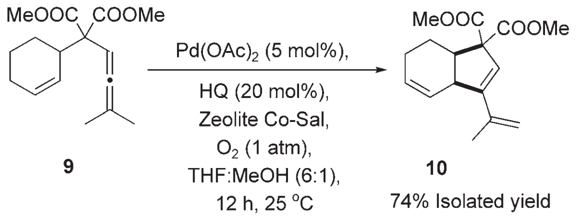


Figure 7. Triple catalytic system for palladium (II)-catalyzed aerobic carbocyclization with the cobalt salophen zeolite Na-FAU 2.75 complex as oxygen activating catalyst and catalytic amount of HQ as ETM.



Scheme 2. Palladium(II)-catalyzed aerobic allylic oxidative carbocyclization of allene-substituted olefin with the cobalt salophen zeolite Na-FAU 2.75 complex.

lysts, and the solvent. The reaction mixture was stirred for 12 h. The progress of the reaction was followed by ^{1}H NMR and by measuring the oxygen uptake. The result showed that all starting material was converted to product **10** after 12 h. The mixture was then filtered, the zeolite catalyst could be recovered and the product was isolated in 74% yield after purification.

In the original system, the aerobic reaction was run at 95 °C.[12] When using the zeolite Co(Sal) catalyst for molecular oxygen activation, the catalytic system performed very well at room temperature. In comparison to the previously reported procedure,[12] this is a significant improvement of the triple catalytic system for aerobic oxidative carbocyclization.

Conclusions

FAU- and EMT-type zeolites with a wide variation of the Si/Al ratios were evaluated for their ability to act as solid supports for a cobalt salophen catalyst. The cobalt salophen was synthesized in the zeolite cavity, using the ship-in-a-bottle method, and the resulting catalysts were trapped in the zeolites. The Co(Sal) zeolite catalysts showed good reactivity in the aerobic oxidation of HQ and the catalyst could be recovered and reused after simple filtration or centrifugation. The Co(Sal) zeolite catalysts were also effective in a triple catalytic systems, as was demonstrated by the palladium(II)-catalyzed carbocyclization of an allene-substituted olefin. The next step would be to find ligands that allow for the immobilization of the palladium catalyst in a second zeolite, so that both transition metal catalysts can be recovered simultaneously.

Experimental Section

NMR spectra were recorded with a Bruker 400 spectrometer. All NMR spectra were recorded in $CDCl_3$ solutions with tetramethylsilane as the internal standard for ^{1}H NMR and $CDCl_3$ for ^{13}C NMR. The IR spectra were recorded with a Perkin–Elmer 1600 Series FT-IR spectrometer. The oxygen uptake was measured by a gas burette.

Co(salophen) (1)

For the preparation and spectroscopic data see ref.[11]

Zeolites (Table 1, 1–7)

In the present study, zeolite pure powders with different Si/Al ratios and cations were synthesized by using standard reported methods.[18,22]

Cobalt-Exchanged Zeolite (Co zeolite), Method A

Zeolites (Table 1, **1–7**) were dried at 100 °C for at least 12 h. The dried zeolite (1.0 g) was stirred and refluxed for 72 h with an aqueous solution of $Co(OAc)_2 \cdot 4H_2O$ (0.1 M, 25 mL). The pink solid was filtered off and dried under vacuum (110 °C, 0.05 mbar) (7 h).

Cobalt-Salophen [Co(Sal)] Zeolites, Method A

Co zeolite (1.0 g) from above was dried under high vacuum for 2 h at 100 °C. Dry ethanol (10 mL) and *o*-phenylenediamine (0.5 g) were added. The reaction mixture was stirred for 1 h under reflux. Salicylaldehyde (1.1 g) was added and the reflux was continued for another 2 h. The mixture was filtered and the solid residue was extracted in a Soxhlet extractor until the eluate became colorless (24 h). Non-complexed cobalt ions were replaced by sodium ions by gentle reflux with saturated NaOAc (75 mL). The solid catalyst was filtered off, washed with water (50 mL) and dried at 110 °C under high vacuum (0.05 mbar) for 7 h.

Co-salophen zeolite H-FAU 127 Method B

Zeolite H-FAU 127 was dried at 100 °C for at least 12 h. The dried zeolite (1.0 g) was mixed with dry ethanol (10 mL) and 3,5-di-*tert*-butylsalicylaldehyde (1.079 g) were added. The reaction mixture was stirred for 2 h under reflux. *o*-Phenylenediamine (235 mg) was added and the reflux was continued for another 3 h. The mixture was filtered and the brown solid residue was washed with ethanol and ether. The dried zeolite was stirred and refluxed for 24 h with an aqueous solution of $Co(OAc)_2 \cdot 4H_2O$ (0.1 M, 25 mL). The mixture was filtered and the solid residue was extracted in a Soxhlet extractor until the eluate became colorless (24 h). Non-complexed cobalt ions were replaced by sodium ions by gentle reflux with saturated NaOAc (75 mL). The solid catalyst was filtered off, washed with water, ethanol, and ether and dried at 110 °C under high vacuum (0.05 mbar) for 7 h.

General Procedure for the Catalytic Aerobic Oxidation of Hydroquinone to *p*-Benzoquinone with Different Cobalt Salophen Zeolites (Table 1, 1–7)

Hydroquinone (62.5 mg, 0.57 mmol) and the Co(Sal) zeolite **1–7** (75 mg) were added to the appropriate solvent (1.25 mL). The reaction mixture was stirred at room temperature under 1 atm oxygen for 12 h. The oxygen uptake was measured by a gas burette.

General Procedure for the Catalytic Aerobic Oxidation of Hydroquinone to Benzoquinone with Cobalt Salophen Zeolites for Recycling of the Catalyst

Hydroquinone (62.5 mg, 0.57 mmol) and the Co(Sal) zeolite Na-FAU 2.75 (75 mg) were added to the appropriate solvent (1.25 mL). The reaction mixture was stirred at room temperature under 1 atm O_2 for 24 h. The oxygen uptake and the ^{1}H NMR conversion of the formed *p*-benzoquinone were measured.

Recovery and Reuse of Co-Salophen Zeolites

The zeolite catalyst from the above experiment was collected by centrifugation and washed with AcOH and EtOH or only THF when it was used in the reaction. The zeolite was dried under vacuum which afforded the recovered zeolite catalyst. This catalyst was reused in a second aerobic oxidation of hydroquinone according to the procedure described above. The oxygen uptake was measured by a gas burette and conversion was measured by ^{1}H NMR. The same procedure for the recovery and reuse of the zeolite catalyst was used in a third reaction for aerobic oxidation of hydroquinone.

General Procedure for Palladium(II)-Catalyzed Aerobic Allylic Oxidative Carbocyclization of Allene-Substituted Olefin with the Cobalt Salophen Zeolite Na-FAU 2.75 [Zeolite Na-FAU 2.75 Co(Sal)]

The zeolite Na-FAU 2.75 Co(Sal) catalyst (75 mg), Pd-$(OAc)_2$ (5.6 mg, 5 mol%), and hydroquinone (10.8 mg, 20 mol%) were mixed in THF:MeOH (6:1, 2 mL), and the ene-allene **9** (139 mg) was added. The resulting slurry was stirred at room temperature and the oxygen uptake was measured under 1 atm of oxygen. After 12 h the reaction mixture was centrifuged and washed with THF, the solvent of combined solutions was removed under vacuum to afford the product in 99% conversion (NMR). The crude product was purified by silica chromatography with the eluent system pentane/diethyl ether (4:1) affording **10**; yield: 106 mg (74%). The ^{1}H NMR and ^{13}C NMR spectra of the product were in agreement with those previously reported.[21]

Acknowledgements

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