

Immobilized metal complexes in porous hosts: catalytic oxidation of substituted phenols in CO₂ media

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Development of processes that utilize heterogeneous catalysis in environmentally beneficial media is of fundamental and practical importance. The oxidation of 2,6-di-*tert*-butylphenol (DTBP) to 2,6-di-*tert*-butyl-1,4-benzoquinone (DTBQ) and 3,5,3',5'-tetra-*tert*-butyl-4,4'-diphenoquinone (TTBDQ) has been investigated to evaluate the factors necessary to achieve high product conversion and selectivity in various media. A series of porous materials with immobilized Co(II) complexes served as catalysts and their reactivities using O₂ as the terminal oxidant were screened in neat acetonitrile, supercritical carbon dioxide (*sc*CO₂), and CO₂-expanded acetonitrile. The highest conversions were found with the catalysts that had high affinity for dioxygen. Moreover, the greatest conversions (~60%) were obtained when reactions were done in *sc*CO₂, which is attributed to improved mass transfer of O₂ and substrates through the porous catalysts. Furthermore, the heterogeneous catalysts can be recycled with some loss of activity (~30%) after three cycles; nonetheless these results suggest that the polymer hosts efficiently protect the immobilized catalytic sites from destructive bimolecular routes.

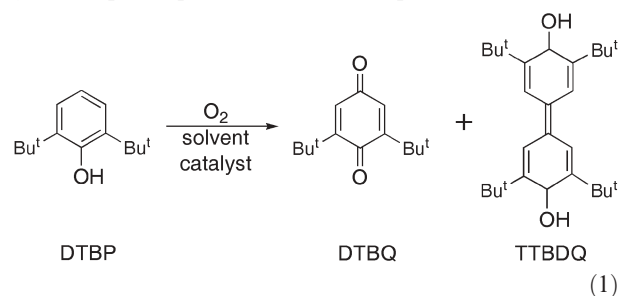
Introduction

Materials as heterogeneous catalysts have received considerable attention because of their possible use in a wide variety of reactions, convenient post-reaction separation, and reusability.^{1–3} This has led to methods for incorporating catalytic centers on solid supports, including those for immobilization of metal complexes into porous hosts. However, many of these methods produce heterogeneous catalysts that have limited function, in part, because the properties of the supported catalysts differ from those of their homogenous counterparts. It is therefore necessary to integrate catalyst preparation with specific reaction conditions in order to obtain optimal activity.

We have found that template copolymerization is an effective method for immobilizing metal complexes within porous organic host.^{4–6} Formation of the immobilized sites occurs during polymerization, using a substitutionally inert metal complex as the template—this allows each site to have similar structural properties that are related to those of the template compound. Materials produced with this methodology have high site accessibility and control of ligand positions around the immobilized metal centers. Moreover the immobilized sites are isolated from each other, producing functional materials for the reversible binding of CO, NO, and O₂. Four of these materials, P-1[Co^{II}], P-1[Co^{II}(py)], P-1-py[Co^{II}], and P-2[Co^{II}] are shown schematically in Scheme 1.

The high degree of dioxygen binding to the immobilized Co^{II} complexes in these porous materials (90% for P-1-py[Co^{II}])

suggested that they might function as heterogeneous oxidation catalysts. To evaluate this possibility, we have investigated the catalytic activity of P-1[Co^{II}], P-1[Co^{II}(py)], P-1-py[Co^{II}], and P-2[Co^{II}] to oxidize 2,6-di-*tert*-butylphenol (DTBP) to 2,6-di-*tert*-butyl-1,4-benzoquinone (DTBQ) and 3,5,3',5'-tetra-*tert*-butyl-4,4'-diphenoquinone (TTBDQ) (eqn 1).



This reaction has been thoroughly studied for homogenous catalysts using conventional organic solvents and dioxygen as the oxidant. We reasoned that conventional conditions might not be suitable for catalysis with our porous materials; in particular, catalysis may be limited by the solubility of dissolved dioxygen in organic solvents, which could hinder mass transfer to the catalytic sites.

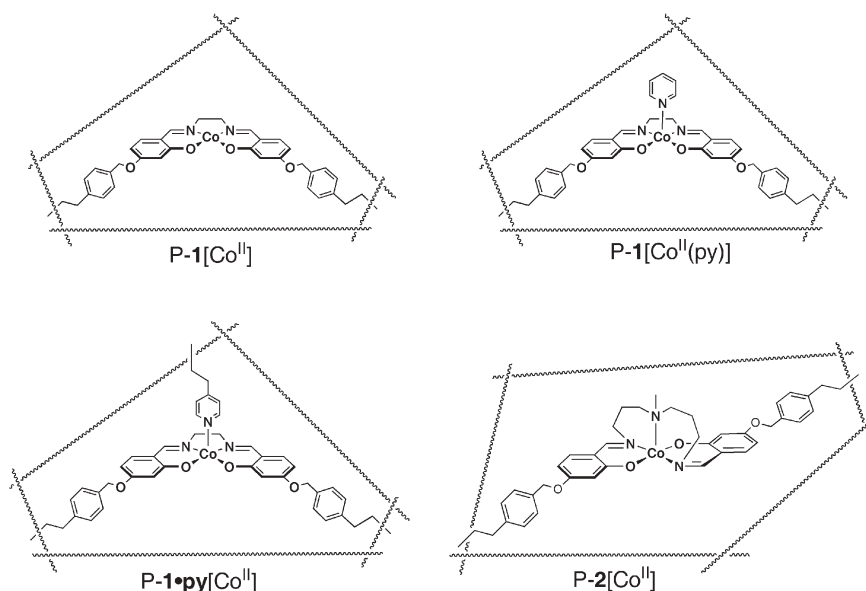
One way to circumvent this problem is to perform the reaction in CO₂-containing media. Supercritical carbon dioxide (*sc*CO₂)^{7,8} has several beneficial attributes for oxidative processes,⁹ including complete miscibility with O₂, resistance to oxidation, and tunable transport properties. Other potentially useful solvent systems are the CO₂-expanded liquids (CXLs), which can have a large portion (up to 80%) of a conventional organic solvent replaced by dense phase CO₂.^{10–15} CXLs are advantageous because they combine the beneficial properties of organic solvents (which solubilize catalysts and substrates easily) with those of dense CO₂ (better O₂ miscibility

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Scheme 1 Depictions of the immobilized metal sites in P-1[Co^{II}], P-1[Co^{II}(py)], P-1·py[Co^{II}], and P-2[Co^{II}].

compared to neat organic solvents). Taking advantage of these properties, recent studies showed that the homogenous oxidation of DTBP with Co(salen') catalysts [salen', *N,N'*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-ethylenediaminato(2-)] in CXLs significantly increased the rate of oxidation compared to reactions done in either conventional organic solvents or *sc*CO₂.¹⁰ We report herein results for the oxidation of DTBP with the heterogeneous catalysts P-1[Co^{II}], P-1[Co^{II}(py)], P-1·py[Co^{II}], and P-2[Co^{II}] in CH₃CN, CO₂-expanded CH₃CN, and *sc*CO₂. In contrast to the homogeneous case, our findings demonstrate that *sc*CO₂ as reaction medium provides better conversion compared to either the neat organic solvent or the CO₂-expanded organic solvent with the heterogenized Co complex. We attribute this behavior to a combination of complete O₂ miscibility and improved pore diffusion rates with *sc*CO₂ which cumulatively offset the tunable dielectric constant afforded by CO₂-based mixtures. Oxidation is also correlated to the dioxygen affinity of the materials and the fraction of CO₂ used as the reaction solvent.

Experimental

All chemicals and solvents used in the catalyst synthesis were purchased from either Aldrich or Fisher Scientific and used without further treatment. Coolant grade liquid CO₂, filled in cylinders with dip-tubes, and cylinders of ultrahigh purity oxygen (99.94%) were purchased from Airgas Inc.

Synthesis

The synthesis of the air-sensitive complexes and polymers were conducted in a Vacuum Atmospheres dry box under argon atmosphere. Standard Schlenk type glassware under N₂ was used to work up reactions outside the drybox. The compounds 2-hydroxy-4-(4-vinylbenzyl-methoxy)benzaldehyde¹⁶ and bis[2-hydroxy-4-(4-vinylbenzylmethoxy)benzaldehyde]ethylenediimine (H₂I)¹⁷ were synthesized following literature procedures. Detailed preparative routes to

P-1[Co^{II}], P-1[Co^{II}(py)], and P-2[Co^{II}] have been reported previously.^{4,18,19} Note that the polymer, P-1[Co^{II}(py)] was generated *in situ* by addition of pyridine to suspensions of P-1[Co^{II}].

P-1·py[Co^{II}] was prepared as described previously¹⁸ with the following modifications: after copolymerization and reduction, P-1·py[Co^{II}(dmap)] (0.30 g) was placed into a 100 mL flask and treated with 20 mL of 0.10 M Na₂EDTA solution in deionized water. The mixture was refluxed for 24 h, after which it was allowed to cool to room temperature and the resulting polymer was collected on a medium porosity glass frit. The polymer was washed with five 5 mL portions of deionized water, three 3 mL portions of diethyl ether, and dried under vacuum for 6 h to yield 0.275 g of a polymer formulated as P-1_{sal}·py. Elemental analyses suggested that hydrolysis to salicylaldehydes moieties has occurred. Anal Calcd for P-1·py[Co^{III}(dmap)]: Co, 145 μmol Co per g of polymer and 998 μmol N per g of polymer; Anal Calcd for P-1_{sal}·py: Co, 50.1 μmol Co per g of polymer and N, 282 μmol of N per g of polymer.

The salen ligand was reformed by treating P-1_{sal}·py with ethylenediamine (5.5 μL, 4.97 mg, 0.81 mmol) in 10 mL of methanol. After 6 h of stirring, the polymer was collected on a medium porosity glass frit, washed twice with 3 mL portions each of methanol and diethyl ether, then dried under vacuum for 6 h to yield 0.250 g of P-1·py. This yellow polymeric material was mechanically crushed to particles with an average size of approximately 150 μm and then treated with Co(OAc)₂ in 10 mL of methanol to afford 0.23 g of P-1·py[Co^{II}], having 150 μmol Co per g of polymer.

Instruments

All proton nuclear magnetic spectra (¹H NMR) were collected on a Bruker DRX400 spectrometer equipped with an SGI INDY workstation to characterize the template complexes. EPR spectra were collected using a Bruker EMX spectrometer

equipped with an ER4102SR cavity. The instrument was previously calibrated using DPPH. The spectra for the Co^{II} samples were collected at the following settings: attenuation = 25 dB, microwave power = 0.64 mW, frequency = 9.34 GHz, sweep width = 5000 G, modulation amplitude = 10.02 Gpp, gain = 5.00×10^{-3} , conversion time = 81.92 ms, time constant = 655.36 ms, and resolution = 1024 points. Elemental analyses of the fresh and used catalyst were performed at Desert Analytics (Tucson, AZ). BET surface area and pore volume were measured with a Gemini 237011 surface area analyzer employing N₂ physisorption. A Hewlett-Packard gas chromatograph (HP 5890) with a FID detector was used for the routine analysis for compound identification. The instrument was equipped with a 30 m HP 5 MS column crosslinked 5% PH- methylsiloxane film.

Solvent expansion by CO₂

These studies were conducted in a 100 mL high-pressure Jurgeson view cell ($P_{\max} = 400$ bar, $T_{\max} = 100$ °C) described elsewhere.¹⁰ Volumetric expansion of acetonitrile by dense CO₂²⁰ and the solubility limits of [Co^{II}(salen)] complexes in CO₂-acetonitrile CXLs have previously been reported.¹⁰ The expansion ratio is defined as the ratio of the volume of the equilibrated CO₂-expanded liquid phase at pressure P and temperature T [$V(P,T)$] to the initial volume of the neat solvent at atmospheric pressure and temperature $T[V_0(P_0,T)]$. Complementary expansion data were obtained in this study at different temperatures ($T = 35$ – 80 °C). The results from these studies provided guidance for the choice of pressure and temperature used in the catalytic runs.

Catalytic conversion studies

General operational procedures and details of experimental set-up can be found elsewhere.¹⁰ In brief, the oxidation studies of 2,6 di-*tert*-butylphenol (eqn 1) in neat organic solvent, CO₂ expanded solvent and *sc*CO₂ were carried out in a 15 mL stainless steel reactor ($p_{\max} = 400$ bar, $T_{\max} = 300$ °C; Thar Designs) equipped with two sapphire windows. A computer controlled data acquisition system (Camile TG) was used for monitoring the reaction temperature and pressure. To facilitate comparison, the reactor operating conditions for the heterogeneous catalysis studies were chosen to be similar to those employed in the homogeneous catalytic runs as follows: catalyst : substrate : O₂ molar ratio of 1 : 80 : 800, and a reaction time of 21 h at various temperatures (35–80 °C). Molecular oxygen was used as an oxidant in all the reactions. The catalysts were housed within a stainless steel cage (mesh per inch = 325 × 325) with a stirrer bar affixed to the bottom of the cage. This set-up confined the catalysts within the cage throughout the reactions, obviating post-reaction catalyst separation. Catalysts were prepared for reuse studies by simply washing the cage with acetonitrile and purging with N₂. The reactions with the organic solvents (acetonitrile and acetonitrile-pyridine) were initiated by addition of the dioxygen. In runs involving CXLs and *sc*CO₂, the O₂ was admitted following CO₂ addition to achieve either the desired expansion ratio or pressure, respectively. Following a batch run, the reactor was gradually depressurized over a period of 2 h and

the contents were led to a cold trap containing 5 mL of acetonitrile. Aliquots of diluted samples were analyzed for reaction products. Experiments were done at $T = 35$ °C, 50 °C and 80 °C in neat acetonitrile, CXLs ($V/V_0 = 1.4$ and 3), and *sc*CO₂.

The following experiments were performed to evaluate whether catalysis occurred from substances leached from the heterogeneous catalysts. Following the procedure described above, catalytic reactions were run for 4 h, following which an aliquot was removed and analyzed for products. The cage containing the catalysts was then removed from the reaction mixture by simple filtration, and the resulting homogeneous mixtures were further stirred for 17 h with aliquots removed and analyzed for products every 4 h. No additional products were detected after the removal of the catalyst cage.

Results and discussion

Expansion studies

The volumetric expansions of solvents (acetonitrile and pyridine) by addition of CO₂ were determined at various temperatures (25 °C,²⁰ 50 °C,²⁰ 80 °C) prior to the catalytic studies. Fig. 1 shows the isothermal volumetric expansion ratio (V/V_0) of acetonitrile with CO₂ mixtures at various temperatures. The volume of the CO₂-expanded liquid phase expands exponentially as the CO₂ critical pressure is approached. This is to be expected since CO₂ is highly compressible in the vicinity of its critical point (31.1 °C and 72.8 atm) causing the density (and therefore the miscibility with organic solvents) to increase sensitively with pressure. Note from Fig. 1 that at a given pressure, higher temperatures decrease the expansion ratio due to a reduction in CO₂ density. Hence, increased CO₂ pressures were needed to provide the same expansion ratio. For instance, at the expansion ratio of $V/V_0 = 1.4$ for acetonitrile, 23 bar of CO₂ is needed at 25 °C, compared to 58 bar of CO₂ at 80 °C. Clearly, the expansion data are essential for determining reaction operating conditions when employing CXLs as reaction media.

Properties of the catalysts

The materials used in this study contain immobilized cobalt complexes dispersed throughout the porous poly(methacrylate) hosts. The sites where the metal complexes are housed

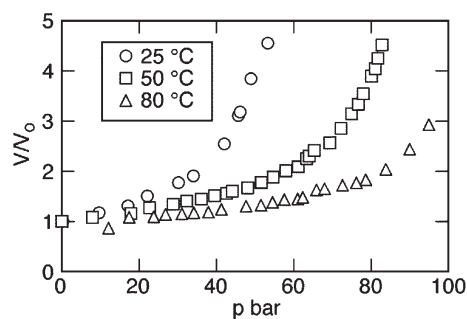


Fig. 1 Volumetric expansion ratio V/V_0 of pure acetonitrile vs. CO₂ expansion pressure at 25 °C, 50 °C, and 80 °C measured in the Jurgeson high pressure cell.

were formed during copolymerization from monomeric Co(III) template complexes and have approximately the same size and shape as the metal template. We have found that styryloxy groups, appended from the aromatic rings, serve as good linkers for covalent attachment of the metal complexes to the polymer backbone. All polymers¹⁸ were mesoporous with average pore diameters ranging from 25 to 50 Å. Our previous investigations found that each porous material binds dioxygen at atmospheric pressure, although with different affinities. P-1[Co^{II}] has a relatively low affinity for dioxygen with less than 10% of the immobilized site forming Co–O₂ adducts. Treating suspensions of P-1[Co^{II}] with excess pyridine forms P-1[Co(py)], a porous polymer with immobilized sites containing five-coordinate Co^{II} complexes. In solution, monomeric five-coordinate [Co^{II}salen(py)] complexes are known to have substantially greater thermodynamic affinity for dioxygen than their four-coordinate [Co^{II}salen] counterparts.²¹ We observed a similar trend in our porous polymers—nearly 60% of the cobalt sites bind dioxygen in P-1[Co(py)]. The two additional polymers, P-1·py[Co^{II}] and P-2[Co^{II}], have architectures that promote formation of five-coordinate Co(II) complexes and show the greatest affinity for dioxygen: 90% of the immobilized sites reversibly bind O₂ in P-1·py[Co^{II}] and P-2[Co^{II}]. It is important to note that the metal sites in all these porous materials are sufficiently isolated so that unwanted and detrimental intermolecular interactions between metal complexes are prevented.

P-1[Co^{II}] as an oxidation catalyst

Table 1 lists results for the oxidation of DTBP with P-1[Co^{II}] in various media. In neat acetonitrile at 35 °C, only 11% conversion to oxidized products was observed, with a large preference for the quinone, DTBQ ($S = 86\%$), over the coupled product TTBDQ ($S = 14\%$).²² Only small changes in conversion were found upon increasing the reaction temperature; for instance, a 20% conversion was found at 80 °C.

Reactions done in CO₂-expanded acetonitrile ($V/V_0 = 1.4$) at 35 and 50 °C had similar conversions as those done in acetonitrile. However, a significant difference was seen at 80 °C where the conversion to products increased to 43% with $S = 77\%$ for DTBQ. Larger conversions were found at all temperatures when reactions were done under supercritical conditions. For example, at 80 °C in *sc*CO₂, conversion to products reached 50% with a slight drop in selectivity for DTBQ to $S = 70\%$. Note that at all temperatures the selectivity

Table 1 Substrate conversion and selectivity results for catalyst P-1[Co^{II}] catalyst for 35 °C and 80 °C in various reaction media (error limits in parentheses)

Solvent	$x(\text{CO}_2)$	$T/^\circ\text{C}$	% X	% S	
				DTBQ	TTBDQ
Neat CH ₃ CN	0	35	11(1)	80	20
CXL	0.695	35	11(1)	77	23
<i>sc</i> CO ₂	0.979	35	17(2)	74	26
Neat CH ₃ CN	0	80	30(2)	81	19
CXL	0.695	80	43(2)	77	23
<i>sc</i> CO ₂	0.979	80	50(2)	70	30

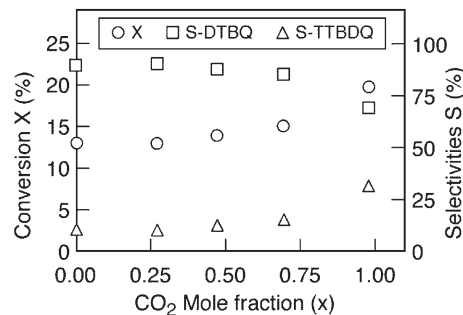


Fig. 2 Substrate conversion (X) of 2,6-di-*tert*-butyl phenol and selectivities (S) towards DTBQ and TTBDQ vs. mole fraction of CO₂ (x) with P-1[Co^{II}] catalyst at 50 °C. Reaction conditions: total pressure 1 bar in neat solvent, 125 bar in *sc*CO₂ and 50–80 bar in CO₂-expanded solvent, catalyst : substrate : oxygen ratio = 1 : 80 : 800, $t = 21$ h, $T = 50$ °C, $V = 15$ mL.

for DTBQ decrease as the amount of CO₂ in the media increases (Fig. 2), a trend that is not yet understood.

P-1[Co^{II}(py)] as an oxidation catalyst

The above results suggested that increased dioxygen concentrations within the reaction medium leads to higher conversion of products. Further improvements in catalysis could occur by increasing the dioxygen affinity of the catalyst. We thus explored the reactivity of the P-1[Co^{II}(py)] generated *in situ* by addition of excess pyridine to the reaction mixture. Formation of P-1[Co^{II}(py)] is achieved by treating acetonitrile suspensions of P-1[Co^{II}] with 20 equivalents of pyridine (relative to the Co(II) sites within the suspended polymer). Comparisons between the performance of P-1[Co^{II}(py)] and P-1[Co^{II}] shows small enhancements in conversions when using P-1[Co^{II}(py)]. In neat acetonitrile and CO₂-expanded acetonitrile–pyridine mixture a nearly 5% increase was observed. Unfortunately, the need to have pyridine present in the reaction medium prevents further studies of this polymer in *sc*CO₂.

P-1·py[Co^{II}] and P-2[Co^{II}] as oxidation catalysts

The use of pyridine to generate high affinity O₂-binding sites needed for catalysis was circumvented by employing P-1·py[Co^{II}] and P-2[Co^{II}] as catalysts. These polymers have immobilized sites containing the requisite five endogenous donors around the Co(II) ions required for O₂ binding.²³ Similar catalytic results were obtained for each polymer (Table 2) and will be discussed using P-1·py[Co^{II}]. In all cases, higher conversions were observed for P-1·py[Co^{II}] and P-2[Co^{II}] as catalysts compared to those that used P-1[Co^{II}]. For instance, an 8% increase in conversion was observed using P-1[Co^{II}] at 80 °C in neat acetonitrile. At all temperatures, maximum conversion was observed for reactions done in *sc*CO₂. Fig. 3 shows plots of conversions vs. temperature for reactions using P-1·py[Co^{II}] as the oxidation catalyst. Only modest improvement in catalytic performance was found in CO₂-expanded acetonitrile, while at all temperatures, maximum conversion was observed for reactions in *sc*CO₂. Moreover, in *sc*CO₂ at 80 °C, 60% phenol conversion was

Table 2 Substrate conversion and selectivity results for catalysts P-1·py[Co^{II}] and P-2[Co^{II}] at 35 °C, 50 °C, and 80 °C in various reaction media (error limits in parentheses)

Solvent	Catalyst	$x(\text{CO}_2)$	$T/^\circ\text{C}$	%X	%S	
					DTBQ	TTBDQ
Neat CH ₃ CN	P-1·py[Co ^{II}]	0	35	17(2)	79	21
<i>sc</i> CO ₂	P-1·py[Co ^{II}]	0.979	35	23(3)	74	26
Neat CH ₃ CN	P-1·py[Co ^{II}]	0	50	19(1)	75	26
CXL	P-1·py[Co ^{II}]	0.695	50	18(1)	82	18
<i>sc</i> CO ₂	P-1·py[Co ^{II}]	0.979	50	31(2)	69	31
Neat CH ₃ CN	P-1·py[Co ^{II}]	0	80	28(1)	78	22
<i>sc</i> CO ₂	P-1·py[Co ^{II}]	0.979	80	60(2)	70	30
Neat CH ₃ CN	P-2[Co ^{II}]	0	50	26(1)	80	20
CXL	P-2[Co ^{II}]	0.695	50	33(1)	82	18
<i>sc</i> CO ₂	P-2[Co ^{II}]	0.979	50	49(2)	67	23
Neat CH ₃ CN	P-2[Co ^{II}]	0	80	29(2)	79	21
CXL	P-2[Co ^{II}]	0.695	80	39(2)	70	30
<i>sc</i> CO ₂	P-2[Co ^{II}]	0.979	80	65(3)	63	37

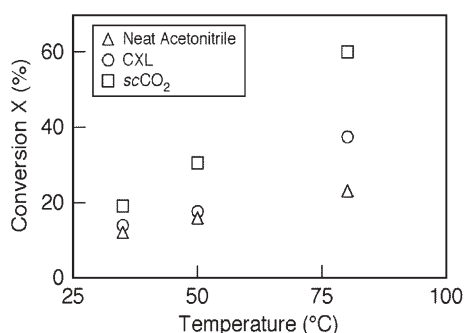


Fig. 3 Substrate conversion of 2,6-di-*tert*-butyl phenol as a function of temperature with P-1·py[Co^{II}] as catalyst in various reaction media: neat acetonitrile, CXL and *sc*CO₂.

observed, a value comparable to that found for homogeneous Co(II) catalysts.¹⁰

The increased conversions in *sc*CO₂ relative to CXL is in contrast to the behavior observed using related homogeneous catalysts under similar reaction conditions. With a homogeneous [Co^{II}salen] catalyst, higher phenol conversions were reported in CO₂-expanded acetonitrile mixtures, which provides complete catalyst solubility (due to the presence of the organic solvent) and significantly better O₂ solubility (relative to the organic solvent at atmospheric pressure). For the heterogeneous catalysts, P-1·py[Co^{II}] and P-2[Co^{II}], the O₂ miscibility in the reaction medium and pore diffusion rates to the immobilized catalytic sites dictate the overall rate. In *sc*CO₂, the dioxygen miscibility is complete and the pore diffusion rates at certain pressures can be tuned to be significantly better than with either the organic medium or CO₂-expanded liquids. Thus, in the case of the heterogeneous catalysts, *sc*CO₂ provides the maximum conversion of substrate to products, as well as having the greatest environmental benefit.

The reusability of the catalyst P-1·py[Co^{II}] was also evaluated in neat acetonitrile, CXLs, and *sc*CO₂. All three media gave similar results, which are illustrated in Fig. 4 for reactions done in CXL ($V/V_0 = 3$) and *sc*CO₂ at $T = 50$ °C. There is a small drop in conversions between the first and

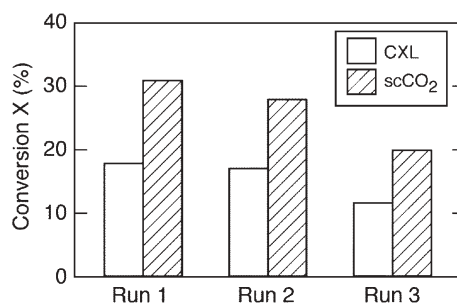


Fig. 4 Recycling experiments using P-1·py[Co^{II}] in CXL ($V/V_0 = 3$ in acetonitrile, unfilled rectangles) and *sc*CO₂ (filled rectangles).

second cycles, whereas an approximately 30% decrease in conversion occurred between the first and third experiments. ICP analyses indicate that the catalyst used over three cycles showed a decrease in the cobalt content (115 μmol Co per g of polymer) compared to the freshly prepared polymer (150 μmol Co per g of polymer). Between the initial and final cycles, the selectivity decreased to approximately 60% for DTBQ and increased to approximately 40% for TTBDQ, a trend which is not currently understood. Nevertheless, these reusability studies indicate that P-1·py[Co^{II}] retains a majority of its activity over several cycles.

Conclusions

We have demonstrated that immobilized [Co(salen)] complexes within porous polymers are effective catalysts for the oxidation of substituted phenols. The best conversions were obtained with reactions done in *sc*CO₂, findings that contrast with those reported for analogous homogenous systems where reactions done in CXLs gave the best results. The higher conversions obtained in CXLs for homogenous reactions have been partially credited to the presence of organic solvent that increases catalyst solubility and greater O₂ concentrations compared to neat organic solvent. For the heterogeneous catalysts described here, the complete miscibility of dioxygen in *sc*CO₂ yields substantially larger amounts O₂ in the reaction medium while improved mass transport through the pores to the immobilized catalytic sites is achieved. Thus, *sc*CO₂ can be the optimum solvent for heterogeneous oxidation catalysis where dioxygen is the terminal oxidant. Furthermore, our studies underscore the need to “match” reaction conditions with the type of catalyst to obtained maximum activity.

The maximum conversions of $X \approx 60\%$ were found with catalysts P-1·py[Co^{II}] and P-2[Co^{II}], polymers that have relatively high affinities for dioxygen—these conversion values approach those reported for related homogenous catalysts. Moreover, substantial activity for the P-1·py[Co^{II}] is maintained over several reactions, indicating improved catalyst lifetime is achieved. We attributed this enhanced activity to prevention, by the polymer host, of destructive bimolecular pathways that often are prevalent in metal ion mediated oxidative transformations. The ability to modulate the architecture of the immobilized catalytic sites in polymers prepared by template copolymerization methods provides an effective means to tune reactivity. Taken together, our results

clearly illustrate the potential of this approach in preparing heterogenized oxidation catalysts and the benefits of coupling their function with *sc*CO₂ reaction media.

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References

- 1 P. T. Anastas, M. M. Kirchhoff and T. C. Williamson, *Appl. Catal., A*, 2001, **221**, 3.
- 2 J. H. Golden, H. Deng, F. J. DiSalvo, J. M. J. Fréchet and P. M. Thompson, *Science*, 1995, **268**, 1463.
- 3 (a) S. J. Shuttleworth, S. M. Allin and P. K. Sharma, *Synthesis*, 1997, 1217; (b) A. Choplin and F. Quignard, *Coord. Chem. Rev.*, 1998, **178–180**, 1679.
- 4 K. M. Padden, J. F. Krebs, C. E. MacBeth, R. C. Scarrow and A. S. Borovik, *J. Am. Chem. Soc.*, 2001, **123**, 1072.
- 5 P. K. Dhal and F. H. Arnold, *Macromolecules*, 1992, **25**, 7051.
- 6 J. F. Krebs and A. S. Borovik, *J. Am. Chem. Soc.*, 1995, **117**, 10593.
- 7 G. T. Musie, M. Wei, B. Subramaniam and D. H. Busch, *Coord. Chem. Rev.*, 2001, **789**, 219.
- 8 Y. Arai, T. Sako and Y. Takebayashi, *Supercritical Fluids. Molecular Interactions, Physical Properties, and New Applications*, Springer-Verlag, Berlin, 2002.
- 9 G. T. Musie, M. Wei, B. Subramaniam and D. H. Busch, *Inorg. Chem.*, 2001, **40**, 3336.
- 10 M. Wei, G. T. Musie, D. H. Busch and B. Subramaniam, *J. Am. Chem. Soc.*, 2002, **124**, 2513.
- 11 (a) C. A. Eckert, D. Bush, J. S. Brown and C. L. Liotta, *Ind. Eng. Chem. Res.*, 2000, **39**, 4615; (b) C. A. Eckert, C. L. Liotta, D. Bush, J. S. Brown and J. P. Hallett, *J. Phys. Chem. B*, 2004, **108**, 18108; (c) D. Xu, R. G. Carbonell, D. J. Kiserow and G. W. Roberts, *Ind. Eng. Chem. Res.*, 2005, **44**, 6164.
- 12 M. Wei, G. T. Musie, D. H. Busch and B. Subramaniam, *Green Chem.*, 2004, **8**, 387.
- 13 K. K. Kapellen, C. D. Mistele and J. M. DeSimone, *Macromolecules*, 1996, **29**, 495.
- 14 B. Rajagopalan, M. Wei, G. T. Musie, B. Subramaniam and D. H. Busch, *Ind. Eng. Chem. Res.*, 2003, **42**, 6505.
- 15 J. C. De la Fuente Badilla, C. J. Peters and J. de Swaan Arons, *J. Supercrit. Fluids*, 2000, **17**, 13.
- 16 (a) J. Daly, L. Horner and B. Witkop, *J. Am. Chem. Soc.*, 1961, **83**, 4787.
- 17 J. F. Krebs and A. S. Borovik, *Chem. Commun.*, 1998, 553.
- 18 A. C. Sharma and A. S. Borovik, *J. Am. Chem. Soc.*, 2000, **122**, 8946.
- 19 J. F. Krebs, PhD Thesis, Kansas State University, 1998.
- 20 B. Kerler, R. E. Robinson, A. S. Borovik and B. Subramaniam, *Appl. Catal., B*, 2004, **49**, 91.
- 21 (a) R. D. Jones, D. A. Summerville and F. Basolo, *Chem. Rev.*, 1979, **79**, 139 and references therein; (b) E. C. Niederhoffer, J. H. Timmons and A. E. Martell, *Chem. Rev.*, 1984, **84**, 137.
- 22 Percent conversion: $X = (\text{moles of quinone products}/\text{moles of substrate}) \times 100$ and percent selectivity: $S = (\text{moles of quinone product (either DTBQ or TTBDQ)}/\text{total moles of products}) \times 100$.
- 23 J. A. Norman, G. P. Pez and D. A. Roberts, in *Oxygen Complexes and Oxygen Activation by Transition Metal Metals*, ed. A. E. Martell and D. T. Sawyer, Plenum Press, New York, 1988, pp. 107–127.