Electrocatalytic Reactivity of Zeolite-Encapsulated Co(salen) with Benzyl Chloride

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Zeolites are microporous aluminosilicate materials capable of restricting the size and shape of the molecules that enter, reside within, or exit the crystalline lattice.[1] The syntheses of zeolite-encapsulated transition metal complexes (designated as {M(L)}Z) have evoked interest in regard to the actual coordination of a supercage-confined transition metal complex, the effects of pore and supercage steric limitations on its reactivity, and the effect of site isolation on its stability.[2−9] We are interested in these effects due to our recent work on electrified microheterogeneous catalysis (EMC), a method in which voltages (>10 V$_{dc}$) are passed through aqueous suspensions of zeolite particles to decompose environmental toxins (e.g., polychlorinated biphenyls) or selectively produce industrially relevant oxidation products (propylene oxide from propene) in the absence of added oxidants.[10] This study was undertaken to explore the physicochemical effects of the zeolite on the electrocatalytic activity of {Co(salen)}NaY (salen = N,N'-bis-(salicylidene)ethylenediamine) as compared to the same complex in homogeneous solution.

The reaction of benzyl chloride with CO_2, catalyzed by electrogenerated [Co^I(salen)]$^-$, produces a mixture of phenylacetic acid, 1,2-diphenylethane, and toluene in homogeneous solution.[11] The oxidative addition−reductive elimination mechanism of this reaction has been thoroughly tested[11−13] and thus

provides a good starting point for electrocatalytic studies using {Co(salen)}NaY, where Co^{II}(salen) is synthetically encapsulated within the 13-Å supercages of zeolite Y through the "ship-in-the-bottle" method.[14−16] In this method, once the adsorbed, flexible ligand (salen) coordinates to the metal center (Co^{2+} is pre-exchanged for extraframework Na$^+$), the resultant complex is trapped by its own rigid structure and cannot pass readily through the 7.4-Å pore openings of the host.[17] {M(L)}Z is typically purified by multiple extractions to remove as much excess ligand and partially encapsulated complex as possible. {Co(salen)}NaY was previously characterized with results consistent with complex formation within the supercages of the zeolite.[14−16]

The electrochemical properties of {Co(salen)}NaY and related zeolite-encapsulated complexes have been much debated.[15,16,19−23] The most recent research[19] indicates that electron transfer for {M(L)}Z proceeds only for electroactive species at the external surface (boundary) of the zeolite. A boundary-associated process implies that M(L) is (1) adsorbed at or occluded in zeolite defect sites (such as truncated or partially broken zeolite supercages) or possibly (2) electroactive only in the outermost layer of the supercages.[19,24] Boundary siting is particularly consistent with voltammetric data which indicate that only ca. 0.5% of {Co(salen)}NaY is redox active.[16,19]

To avoid unencapsulating the zeolite-associated Co(salen) through the mechanical work often necessary to prepare a zeolite-modified electrode,[19,23,25−27] the electrocatalytic activity of {Co(salen)}NaY was studied as a microheterogeneous dispersion undergoing controlled potential electrolysis at a large surface area reticulated vitreous carbon (RVC) electrode. We previously showed that the physical collision of zeolite particles into the RVC transfers electrons to boundary-associated Co-(salen) and that no significant shifts in the Co(III/II) or Co(II/I) couples are observed for {Co(salen)}NaY as compared to homogeneous Co(salen).[19]

A comparison of reaction yields and product distributions between homogeneous [Co^I(salen)]$^-$ and {Co^I(salen)}NaY for the carboxylation of benzyl chloride under zero-order conditions (Table 1) demonstrates the importance of the zeolitic environ-

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(17) Rigorous size *exclusion* of a molecule or cation from an X or Y supercage with a 7.4-Å pore window requires a kinetic diameter >10 Å,[18] so presumably size *inclusion* within a faujasite supercage requires similar dimensions. Our previous studies have shown that Co(salen) and salen can be purged from a CH_2Cl_2-extracted sample of {Co(salen)}NaY by overnight stirring in polar solvents; such zeolites are voltammetrically[16,19] and electrocatalytically inactive. To prepare a rugged zeolite-encapsulated electrocatalyst, complexes with kinetic diameters >10 Å should be synthesized in the zeolite. Previous dispersion voltammetry determined that the electrochemistry of {Co(salen)}NaY is stable for $t < 3$ h with no voltammetrically detectable Co(salen) observed in the electrolyte when the zeolite particles were allowed to settle out.[19]
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Table 1. Product Yields and Selectivities for the Reaction of Benzyl Chloride and Carbon Dioxide Using Co^I(salen) Catalysts[a]

catalyst	total turnovers[b]	% phenylacetic acid	% 1,2-diphenyl-ethane	% toluene
Co(salen)[c]	6.2	81	3	16
Co(salen)[d]	34	88	8	4
{Co(salen)}NaY[d]	270[e]	95	2	3
	8×10^{4}[f]			

[a] Electrocatalysis was performed under zero-order conditions such that <10% of the initial concentration of benzyl chloride was converted. [b] Total turnovers = moles of product per mole of catalyst added. [c] From ref 11. Conditions: 0.3 M LiClO$_4$ in 40% tetrahydrofuran/60% hexamethylphosphoramide, 0.5 M benzyl chloride, Co(salen) (0.25 mM), 1 atm of CO$_2$(g), Hg pool cathode, time not given. [d] Conditions: 0.2 M LiClO$_4$ in DMF, 0.3 M benzyl chloride and either Co(salen) (1.5 mmol) or {Co(salen)}NaY (48.5 mg in 40 mL of electrolyte), 1 atm of CO$_2$(g). Potential controlled at −1.35 V vs SSCE; reaction time 2 h. Physical contact between the zeolite and the RVC electrode (60 ppi, 1 cm × 1 cm × 2.5 cm [Electrosynthesis Co.]) was promoted by mechanically stirring the solution and bubbling CO$_2$(g) through the zeolite suspension. Products were identified by GC−MS and quantified by GC−FID. [e] Turnover is calculated on the basis of the estimated *total* moles of Co(salen) in {Co(salen)}NaY as derived from bulk analysis for Co^{2+} ions and assuming that each Co^{2+} leads to a Co(salen) complex and that each is electroactive on the time scale of the catalysis. This estimation accounts for neither incompletely synthesized Co(salen) species within the zeolite crystallite nor boundary-only redox reactivity. [f] True electrocatalytic turnover is calculated using the moles of electroactive Co(salen), as determined by integrating the voltammetric wave for the Co(II/I)-centered reduction in a microheterogeneous dispersion of {Co(salen)NaY} (in the absence of substrate) and converting to moles via Faraday's law.[19]

ment on the reactivity of transition metal complexes. First, it is significant that the product distribution for {Co(salen)}NaY parallels that obtained for homogeneous Co(salen). Comparable specificity indicates no change in catalytic mechanism and implies that the substrate samples only the less sterically hindered Co(salen) during the redox process, in agreement with the boundary-isomer redox mechanism for {M(L)}Z.[19] Second, voltammetry provides an exact number (by coulometry) of the number of moles of reacting electrocatalyst—and this is <0.1% of the total zeolite-associated Co-based species. The true electrocatalytic turnover number for {Co(salen)}NaY is thus not on the order of 10^2 in 2 h, but rather ~10^5, ca. 3000 times that of homogeneous Co(salen); see Table 1.

In the homogeneous mechanism, the Co^{II} center of Co(salen) is first reduced to Co^I at the electrode, followed immediately by an oxidative addition of both halide (here, Cl$^-$) and the organic fragment (here, benzyl) to opposite sides of the newly octahedral complex.[11−13] The benzyl group may then insert CO$_2$ to produce phenylacetic acid which reductively eliminates as the major product of the reaction. Possible effects of a zeolite lattice on catalysis include (1) framework oxygens acting as a Lewis base[28] (rather than Cl$^-$), (2) "docking" of the substrate into the supercage, as facilitated by weak van der Waals interactions—which are especially important when the size of the guest molecule matches that of the zeolite pore[29,30] (as is nearly the case for benzyl which has an estimated CPK size of 5−6 Å), and (3) an electronic confinement or "boxing effect" for a guest trapped in the cavity of a zeolite.[31] An additional

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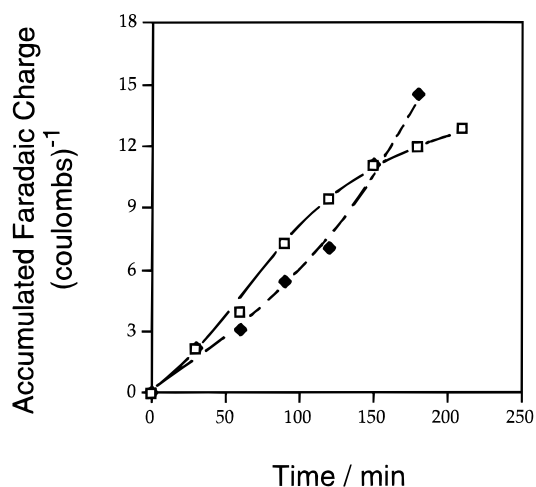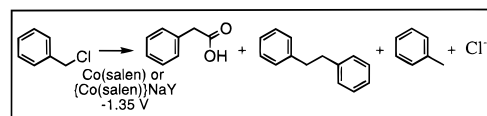
Figure 1. Time dependence of cathodic charge for the electrocatalytic reaction of benzyl chloride (0.18 M) and CO$_2$(g) (1 atm) with (a) homogeneous Co(salen) (2 mM) or (b) {Co(salen)}NaY (1.25 mg/mL) in 0.2 M LiClO$_4$/DMF. Potential was controlled at −1.35 V vs SSCE.

zeolitic influence is the electrostatic rejection of Cl$^-$ which should affect the energetics of the transition state. We cannot yet distinguish whether Lewis acid−base activity, confinement effects, or electrostatic exclusion of Cl$^-$ control the increased electrocatalytic activity of {Co(salen)}NaY relative to homogeneous Co(salen).

The effect of site isolation is observed in Figure 1 as a comparison between the rate of catalysis for Co(salen) and {Co(salen)}NaY. The accumulated faradaic charge (in coulombs) transferred to the homogeneous Co(salen) catalyst begins to plateau after ~120 min, indicating inactivation of the catalyst as a result of catalyst dimerization and/or irreversible CO$_2$ adduct formation.[11] The charge transferred to {Co(salen)}NaY increases throughout the time period studied, indicating that the zeolite-associated catalyst remains active. The durability of a zeolite-associated Co^I(salen) electrocatalyst is most likely the result of (1) supercage-minimized intermolecular Co^I(salen) interactions and/or (2) the steric constraints of the supercage which discourage irreversible CO$_2$ adduct formation.

While electrochemical techniques have not (yet) proved definitive in terms of identifying the actual coordination environment of zeolite-encapsulated transition metal complexes, electrocatalysis with {Co(salen)}NaY has shown that the physicochemical environment of the zeolite leads to 1000-fold increases in reactivity and that the effects of site isolation on the heterogeneous catalyst contribute to an increase in catalyst life of at least 200%.

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