minimize steric repulsions between the extra methyl group of the mesitylene fragment and the methylenic portion of the CTV molecule. The result, in any case, is loss of the cation disorder and propagation of the interaction along the predicted 1D stack (Figure 2b), rather than 2D format observed in **2**–**4**.

The host and guest seem to have little affinity in polar solvents. The visible absorption spectrum of the [CpFe(arene)][PF_6] salts in CH_3CN shows essentially no change upon the addition of up to a 50-fold excess of CTV. Furthermore, no chemical shift changes are observed for either CTV or the guest cation in the ^1H NMR spectrum upon the addition of up to a tenfold excess of [CpFe(ClC_6H_5)][PF_6].[14] This is not surprising considering that the association constant of various electron-rich arenes with [(mesitylene)$_2$Fe]$^{2+}$[15] are less than 2.5 M^{-1} in acetonitrile solution.[9]

The present work demonstrates a very significant extension of supramolecular chemistry involving the cavity of CTV. The formation of this type of inclusion species with electron-poor guests, in contrast to the well-known channel complexes, suggests possible applications in the engineering of crystalline materials with interesting physical properties, and in separation science. These areas are currently under investigation.[16]

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Solvent-Anchored Supported Liquid Phase Catalysis: Polyoxometalate-Catalyzed Oxidations**

Ronny Neumann* and Michal Cohen

An important desired refinement of homogeneous transition metal catalyzed reactions is the heterogenization of the catalysts to achieve facile recovery and recycling of the catalyst. Two basic approaches have been used. The first is immobilization by covalent binding or adsorption of catalysts on supports.[1] This generally leads to loss of activity and selectivity with respect to the original homogeneous analog. For catalytic oxidations the polar products and oxidants react with the binding units, resulting in leaching of the metal; recent reports describe improved supported catalysts.[2] Loss of catalytic species in oxidations has been prevented by confinement within zeolites[3] or dissolution in nonvolatile siloxanes.[4] The second approach is to carry out the reaction with two liquid phases; the catalyst is dissolved in one phase (water[5] or fluorinated hydrocarbon[6]), and the product is separated into the other. Rates of such reactions are often limited by slow mass transfer.

Supported liquid phase (SPL) or supported aqueous phase (SAP) catalysis[7] combines two-phase catalysis with the use of a solid support. This hybrid technique calls for dissolution of a catalyst in a hydrophilic phase (water, ethylene glycol, or polyethylene glycol), which is then adsorbed onto a support. Although the catalyst is immobilized on a solid surface, the reaction takes place at the liquid–liquid interface. Hydroformyl-

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ations,[8] Wacker-type oxidations,[9] and enantioselective hydrogenations[10] have been described.

Here we report on a new immobilization technique for homogeneous catalysts, solvent-anchored supported liquid phase catalysis. In the present application polyethers are covalently attached to silica surfaces. The bound polyether acts as a solvent and/or a complexing agent for the oxidation catalyst, in this case polyoxometalates (POM). Two different reaction modes have been described (Figure 1). In the first case the bound phase with polyether (polyethylene oxide (PEO)) catalyst is in contact with a single liquid phase containing substrate. As opposed to SPL and SPA catalysis, the liquid phase here is miscible with the bound polyether, and reaction takes place within the polyether phase, thus minimizing mass-transfer constraints. The mixture appears homogeneous upon stirring but separates upon settling. In the second case the bound polyether catalyst phase is in contact with two imiscible liquid phases; one contains the oxidant, and the other the organic substrate. The supported catalyst phase is at the interphase where both reactants are soluble and meet to react.

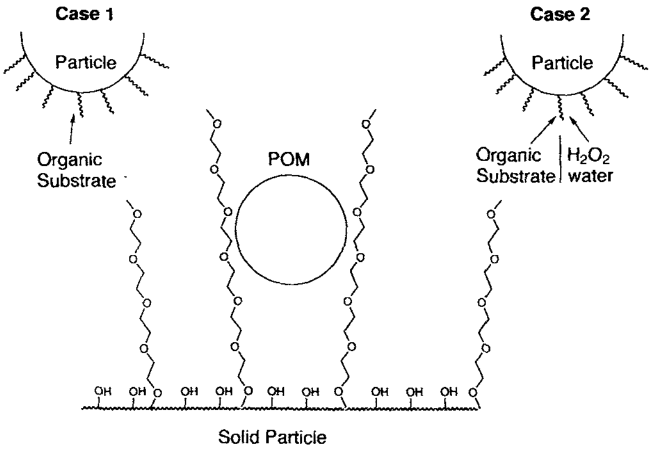
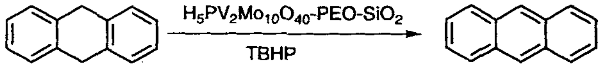


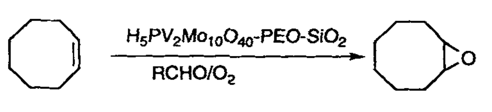
Figure 1. Illustration of the solvent-anchored supported liquid phase catalytic system. POM = polyoxometalate.

The catalyst particles were prepared in three stages. First $(CH_3O)_3SiPhCH_2Cl$ was allowed to react with polyethylene glycol monomethyl ether (PEGME, MW = 350) or polypropylene glycol monomethyl ether (PPGME, MW = 200) to form $(CH_3O)_3SiPhCH_2O(CH_2CHRO)_nCH_3$ (**1a**: R = H; **1b**: R = Me). Then the monomer **1** was copolymerized with $Si(OCH_2CH_3)_4$ by the sol-gel method with dibutyltin dilaurate as catalyst. Finally the xerogel obtained was impregnated with the polyoxometalate catalysts to form the final catalyst assembly.

Examples that demonstrate the first reaction mode are the dehydrogenation of 9,10-dihydroanthracene with $H_5PV_2Mo_{10}O_{40}$ as catalyst[11] and 70% *tert*-butylhydroperoxide (TBHP) as oxidant [Eq. (a)],[12] and the epoxidation of cyclooctene with the same catalyst and aldehyde/O_2 as oxidant [Eq. (b)].[13]



(a)



(b)

Dehydrogenation of dihydroanthracene was carried out by mixing dihydroanthracene (0.2 mmol) in toluene (0.1 mL), 70% TBHP (0.4 mmol), and catalyst (15 mg) containing 0.002 mmol of $H_5PV_2Mo_{10}O_{40}$ at room temperature for 24 h. The silica used was 25% PEO-SiO_2. Analysis of the reaction mixture showed that the reaction was quantitative, yielding 96% anthracene and 4% anthraquinone. The catalyst was recycled without loss of activity, and no catalyst leaching or decomposition was measured by UV/Vis spectroscopy or atomic absorption, respectively. This is perhaps not surprising considering that such acidic Keggin compounds are strongly complexed by diethyl ether.[14] Therefore, the $H_5PV_2Mo_{10}O_{40}$ polyoxometalate is most likely complexed rather than simply dissolved within the PEO phase. Nonsupported $H_5PV_2Mo_{10}O_{40}$ was less effective (87% conversion) and less selective (77% selectivity with respect to anthracene). Using simply unsupported or unattached $H_5PV_2Mo_{10}O_{40}$ tetraglyme as controls did not yield a true heterogeneous system, but rather a catalyst dissolved in the organic phase.

The $H_5PV_2Mo_{10}O_{40}$/PEO-SiO_2 catalyst assembly was further tested with the reaction shown in Equation (b). In typical reaction cyclooctene (5 mmol) was allowed to react with isobutyraldehyde (IBA, 10 mmol) in 1,2-dichloroethane (4 mL); the reaction was catalyzed by $H_5PV_2Mo_{10}O_{40}$/25% PEO-SiO_2 (150 mg) containing 0.0075 mmol of the POM at 23 °C under O_2 (1 atm). Figure 2 gives the reaction profile for the supported catalyst and the control experiment with the nonsupported catalyst. The advantage of using the supported catalyst is clear. Furthermore, loading of $H_5PV_2Mo_{10}O_{40}$ on the catalyst particle (constant weight) has little effect on the reaction profile. Use of other aldehydes showed the following relative reactivity normalized to IBA: $(CH_3)_3CCHO$ (2.2) > $(CH_3)_2CHCHO$ (1) > $CH_3(CH_2)_3CHO$ (0.2) ≈ $CH_3CH{=}CHCHO$ (0.015) > C_6H_5CHO (≈0). As in the previous case, the catalyst was recycled without loss of activity, and no catalyst leaching or decomposition was measurable.

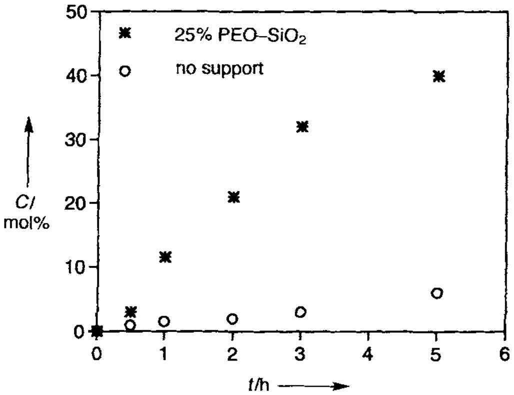
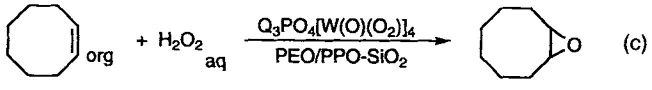


Figure 2. Oxidation of cyclooctene with isobutyraldehyde (IBA)/O_2 with supported $H_5PV_2Mo_{10}O_{40}$. Reaction conditions: cyclooctene (5 mmol), IBA (10 mmol), $H_5PV_2Mo_{10}O_{40}$/25% PEO-SiO_2 (150 mg) containing 0.0075 mmol of the POM in 1,2-dichloroethane (4 mL) at 23 °C and under O_2 (1 atm). Cyclooctene oxide was the sole product. C = conversion.

The utility of solvent-anchored supported liquid phase catalysis in the second reaction mode was demonstrated by the epoxidation of cyclooctene with aqueous hydrogen peroxide with $Q_3PO_4[W(O)(O_2)]_4$ as the catalyst [Q = tetrahexylammonium; Eq. (c)].[15] In a typical reaction cyclooctene (1 mmol) and 30% H_2O_2 (2 mmol) were mixed with the catalyst (100 mg) at room temperature. The latter consisted of $Q_3PO_4[W(O)(O_2)]_4$ (0.005 mmol) on 20% PEO/PPO-SiO_2. This reaction was per-



(c)

formed without an organic solvent, an important ecological advantage. In this case the functionalization of the silica with the correct balance of polyethers is critical (Figure 3). Use of hydrophilic PEO yielded only low rates and conversions. Nonsupported $Q_3PO_4[W(O)(O_2)]_4$, that is, solid POM that is slightly dissolved in cyclooctene, was also inactive. On the other hand, a mixture of 10% PEO and 10% PPO–SiO_2 gave the optimal catalyst particle. The hydrophilic–hydrophobic balance of the catalyst particle must be adjusted to optimize the solubility of both cyclooctene and hydrogen peroxide in the polyether-bound phase. The catalyst 20% PPO-SiO_2 was almost as effective, but further increases in PPO content reduced the activity. The catalyst particle was recycled five times without loss of catalytic activity. Use of a reaction filtrate showed no catalytic species and no catalytic activity.

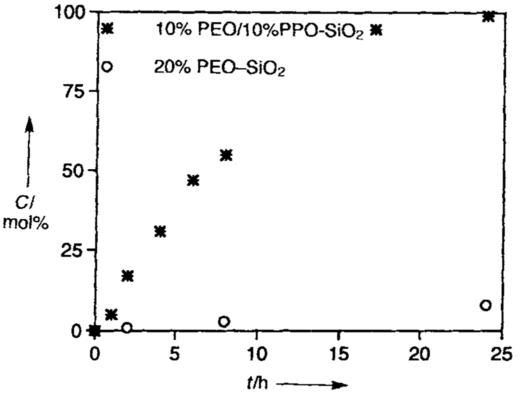


Figure 3. Oxidation of cyclooctene with 30% H_2O_2 catalyzed by supported $Q_3PO_4[W(O)(O_2)]_4$. Reaction conditions: cyclooctene (1 mmol), 30% H_2O_2 (2 mmol), $Q_3PO_4[W(O)(O_2)]_4$/20% PEO/PPO–SiO_2 (100 mg) containing 0.005 mmol of the POM at 23 °C. Cyclooctene oxide was the sole product. C = conversion.

The new concept of solvent-anchored supported liquid phase catalysis has been introduced and demonstrated for oxidation reactions catalyzed by polyoxometalates. These new catalytic systems are more active and selective than analogous nonsupported systems, and catalytic activity is retained after recycling. Use of this technique will be expanded to other reactions and catalysts.

Experimental Section

Monomers 1 were prepared by allowing $(CH_3O)_3SiPhCH_2Cl$ (25 mmol) to react with $CH_3(OCH_2CH_2)OH$ (MW = 350; 25 mmol) or $CH_3(OCH(CH_3)CH_2)OH$ (MW = 200; 25 mmol) in acetone (100 mL) in the presence of solid K_2CO_3 (125 mmol) at reflux for 18 h. The solid salts were removed by centrifugation, and the solvent removed under vacuum. No further purification was carried out at this point. The functionalized xerogels were prepared by dissolving appropriate amounts of 1 and $Si(OEt)_4$ (in total 5 mmol) in acetone (20 mL). Water (10 equiv) and dibutyltin dilaurate (0.01 equiv) were added to initiate polymerization. The reaction mixture was held at 60 °C for three hours and left to concentrate by evaporation of solvent for two days at room temperature. The functionalized silica particles were carefully washed twice with water and ethanol and dried under vacuum. Final catalytic assembles were prepared by impregnating the polyoxometalates onto the silicates as follows: For the reaction in Equation (a) $H_5PV_2Mo_{10}O_{40} \cdot xH_2O$ (440 mg, 0.2 mmol) was dissolved in acetone (10 mL) and added to 20% PEO-SiO_2 (1.5 g), and the solvent removed. The silicate was then dried overnight under vacuum at room temperature. The procedure was identical for the reaction in Equation (b) except that $H_5PV_2Mo_{10}O_{40} \cdot xH_2O$ (165 mg, 0.075 mmol) was used. For the reaction in Equation (c) $[(C_6H_{13})_4N]_3PO_4[W(O)(O_2)]_4$ (1.04 g, 0.5 mmol) was dissolved in $CHCl_3$ (20 mL) and added to 20% PEO/PPO–SiO_2. The mixture was then treated as above.

Typical oxidations were carried out in 5-mL, magnetically stirred vials. Material quantities and reaction conditions are given in the text. The reaction mixtures were analyzed by GLC (HP 5890) with a RTX-1 column (30 m, 0.32 mm ID, 0.25 µm methylsilicone coating). The catalyst was recovered by filtration followed by washing to remove reaction remnants and drying.

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Palladium-Catalyzed Regioselective Mono- and Diarylation Reactions of 2-Phenylphenols and Naphthols with Aryl Halides**

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The palladium-catalyzed substitution reactions of aryl halides and their synthetic equivalents such as aryl triflates are highly useful for the preparation of substituted aromatic compounds. In these reactions arylpalladium(II) complexes occur as common intermediates which react with various reagents including alkenes, alkynes, and a number of organometallic species to give the corresponding products.[1] While aryl halides may also react

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