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Alkane oxidation reactivity of homogeneous and heterogeneous metal complex catalysts with mesoporous silica-immobilized (2-pyridylmethyl)amine type ligands

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ABSTRACT

Attachment of *N*,*N*-bis(2-pyridylmethyl)amine (**L1**) and *N*-(2-pyridylmethyl)glycine (**L2**) ligands on the azide-functionalized SBA-15 type mesoporous silica support and subsequent insertion of metal salts into the ligand-immobilized supports yielded heterogeneous metal complex catalysts, M(A)/SBA*-**Ln**-*x*, where M, A, *, *n*, and *x* indicate the metal ion (Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}), counter anion (Cl, OAc, OTf), trimethylsilyl end-capped silica, the numbering of the ligands, and the initial content of the azide tether group (tether/Si mol%) respectively. The cyclohexane oxidation activity of these immobilized catalysts and corresponding homogeneous complexes have been evaluated with the use of *m*-chloroperbenzoic acid as an oxidant. The activity of the immobilized catalysts is influenced by the ligand density on the support. Both the site-isolated immobilized catalysts and the related homogeneous catalysts of ligand **L1** show similar trends of their final TONs on the type of metal ions (Co ≈ Ni > Fe > Mn > Cu). These results suggest that all of the metal complex sites are successfully immobilized without structural changes under the site-isolated condition. The reactivity trends of the complexes with the **L2** ligand and their dependence on the ligand density were complicated. The observed results may be explained by the formation of cluster complexes via bridging carboxylate moieties of the ligand.

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1. Introduction

Owing to its high reactivity toward organic molecules, meta-chloroperbenzoic acid (*m*CPBA) has been widely applied as an oxidant for laboratory level syntheses [1]. This oxidant can react with inactive saturated hydrocarbon molecules such as cyclohexane by gentle heating over 60 °C. For this reaction, metal salts or metal complexes act as catalysts to accelerate the reaction rate and to change product selectivity via the coordination and activation of *m*CPBA on the metal center [2]. Significant research effort has been invested in the development of metal complex catalysts for selective oxidation reactions with the control of site selectivity (e.g. 1°–3° C—H, steric, and electronic) and over oxidation (e.g. alcohols to ketones/aldehydes to carboxylates/lactones) [3–5]. Furthermore, mechanistic studies of the activation of the oxidant

on the metal sites and subsequent C—H bond scissions have contributed toward our understanding of metalloenzymes in the field of bioinorganic chemistry [6,7].

In 2006, Itoh and co-workers found that a nickel(II) tpa complex (tpa = tris(2-pyridylmethyl)amine ligand) showed high catalytic activity for the oxidation of cyclohexane at ambient temperature [8]. In their report, these authors described a series of metal complexes of divalent metal ions (M = Mn, Fe, Co, Ni) and tpa ligand: [(tpa)Mn-(μ_2-1,3-*O*Ac)_2-Mn(tpa)](BPh_4)_2, [(tpa)Fe-(μ-1,3-*O*Ac)_2-Fe(tpa)](BPh_4)_2, [Co(κ^2-OAc)(tpa)](BPh_4)_2, and [Ni(κ^1-OAc)(H_2O)(tpa)](BPh_4). The metal complexes described in this article are denoted according to the scheme 'metal and (anions) in source/ligand'. Therefore, the above mentioned complexes can be written in the abbreviated form as Mn^{II}(OAc,BPh_4)/tpa, Fe^{II}(OAc,BPh_4)/tpa, Co^{II}(OAc,BPh_4)/tpa, and Ni^{II}(OAc,BPh_4)/tpa. Among these catalysts, the difference in the metal ion caused a change in the reactivity, which is evaluated by the catalyst turnover number (TON, Ni^{II} > Fe^{II} > Co^{II} > Mn^{II}) and the product selectivity for alcohol over ketone (*A/K* selectivity, Co^{II} > Ni^{II} > Fe^{II} ≫ Mn^{II}). The catalyst Ni^{II}(OAc,BPh_4)/tpa has inspired further investigations by other research groups into nickel complexes for reactiv-
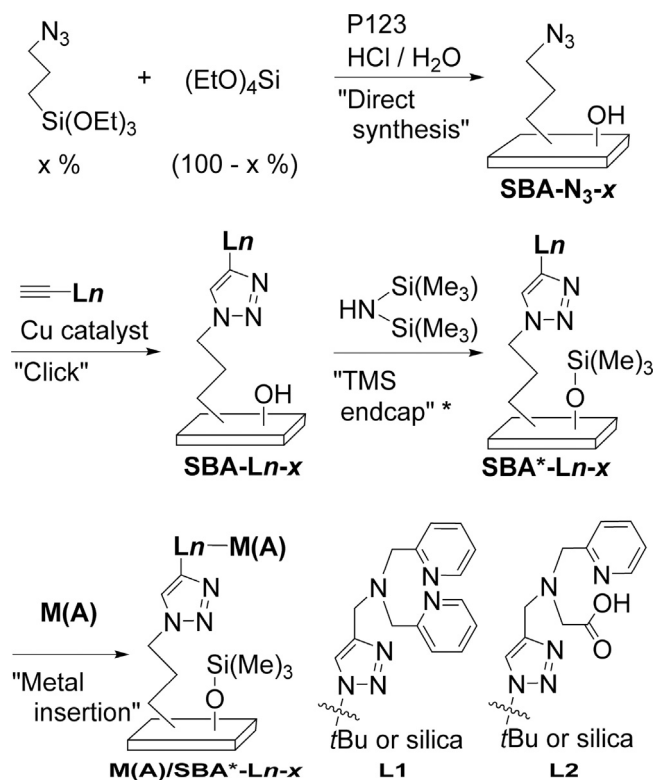
Scheme 1. Preparation of the immobilized metal complex catalyst M(A)/SBA*-L*n*-*x* on a mesoporous silica support, where *x* denotes the azide content of the silica, **L*n*** indicates the numbering of the ligands, * denotes the TMS end-capped support, and M(A) is the general description of metals and anions of the applied metal source.

ity enhancement, characterization of reaction intermediates, and understanding the reaction mechanism [9–16].

Consequently, several groups, including ours, have investigated the immobilization of these complexes on silica supports to develop further catalytic applications and to obtain any information on the reaction mechanism [17–21]. To date, several preparations, characterization, and reactivity studies of mesoporous silica supported metal complex catalysts with tpa and the *N,N*-bis(2-pyridylmethyl)-*N*-{(1*H*-1,2,3-triazol-4-yl)methyl}amine (**L1**) ligand (Scheme 1) have been reported [22–25]. Mesoporous materials have attracted much attention due to their potential for various applications including catalyst support [26–28]. The mesoporous silica support [29], SBA-15, allows an easy access of the reagents to the reaction sites in its mesoscale channels and minimizes the inter-site interactions because of its large surface area ($\sim$700 m^2 g^{-1}) and pore diameter ($\sim$5 nm). Usage of **L1** ligand simplifies the catalyst preparation with a tpa-type ligand [30,31]. We investigated the reactivities of homogeneous as well as immobilized nickel(II) and cobalt(II) complex catalysts with **L1** ligand (metal/SBA*-**L1**-*x*, where * indicated the trimethylsilyl treatment of the support surface and *x* = tether/Si mol%) for the catalytic oxidation of cyclohexane by *m*CPBA [24,25].

In our previous research on immobilized nickel and cobalt catalysts with SBA*-**L1**-*x* supports, we found that the "surface ligand density" on the supports effected the catalytic activity even though the trend of reactivity was opposite for the two metals. In the case of the Ni catalyst, the reactivity decreased with increasing surface ligand density (*x* = 0.5 to 4 mol%). Based on the spectroscopic comparison with the homogeneous model complexes, we concluded that the loss in activity of the immobilized catalyst originated from the [Ni(**L1**)(X)$_n$] site (X: labile coordinating solvent or ligand) with increase in the coordinatively saturated and catalytically inert [Ni(**L1**)$_2$] site under "ligand dense" conditions on the

support. Although the "ligand isolated" immobilized nickel complex catalyst (Ni^{II}/SBA*-**L1**-0.5) was highly reactive, this catalyst showed metal leaching into the reaction solution during catalysis. In the case of the cobalt(II) complex with the **L1** ligand, the "ligand dense" catalyst (Co^{II}/SBA*-**L1**-4) showed improved product selectivity for alcohol over ketone (*A/K*) ratio than that for free cobalt ions. Due to the free cobalt ions, faster catalysis was observed with low *A/K* values and the suppression of metal leaching at the "ligand dense" sites increased the reactivity of the Co^{II}/**L1** site.

In this article, we have explored three factors, namely, (1) type of metal source, (2) type of ligand, and (3) immobilization of the metal complexes with regulated site density, in order to understand the general features of homogeneous and immobilized complexes as well as to develop efficient catalysts (Scheme 1). We first synthesized complexes of metal ions such as Mn^{II}, Fe^{II}, Fe^{III}, and Cu^{II} ions in addition to previously reported Ni^{II} and Co^{II} ions for the heterogeneous SBA*-**L1**-*x* support. Second, we synthesized complexes with the new ligand, *N*-(2-pyridylmethyl)glycine (**L2**), which has a carboxylate side arm. The anionic *O*-donor in the side arm of this ligand shows enhanced affinity especially toward high valent Mn and Fe ions compared to **L1** and helps prevent metal leaching during catalysis. Third, we investigated the influence of the surface ligand density of the immobilized complex on the catalytic activity. In addition, we were also interested in the development of immobilized catalysts of the **L2** ligand from the viewpoint of the biomimetic chemistry of nonheme iron enzymes in which the iron centers are supported by imidazole and carboxylate donors from residues of their protein backbone [32–35].

2. Experimental

2.1. Materials and physico-chemical characterization techniques

Atomic absorption analysis was performed on a Shimadzu AA-6200 instrument. Elemental analysis was performed on a Perkin-Elmer CHNS/O analyzer 2400II. ESI- and CSI-MS spectra were measured on a JEOL JMS-T100LC mass spectrometer. GC analysis was performed on a Shimadzu GC-2010 gas chromatograph with a flame ionization detector (FID) and an Rtx-5 column (Restek, 30 m length, 0.25 mm i.d., and 0.25 μm thickness). IR spectra were recorded on a JASCO FT/IR 4200 spectrometer. NMR spectra were recorded on a JEOL ECA-500 spectrometer. UV–vis spectra were measured on a JASCO V650 spectrometer with a PIN-757 integrating sphere attachment for solid reflectance. Nitrogen sorption studies were performed at the liquid nitrogen temperature of 77 K using Micromeritics TriStar 3000. Before the adsorption experiments, the samples were outgassed under reduced pressure for 3 h at 333 K. Single crystal X-ray diffraction data was collected using a Rigaku Saturn 70 CDD area detector system with graphite-monochromated Mo-Kα radiation. Crystal information files (CIF) of the complexes reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC1536605 [Fe^{III}Cl$_3$(**L1**)], CCDC1536612 [Fe^{III}Cl$_2$(**L1**)](BPh$_4$), and CCDC1536613 [Cu^{II}(OAc)(**L1**)](BF$_4$)·(Et$_2$O)$_{0.5}$. This data can be obtained online free of charge from the Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif.

All commercial reagents and solvents were used as received without further purification unless otherwise noted. meta-Chloroperbenzoic acid (*m*CPBA) was washed with KH$_2$PO$_4$-Na$_2$HPO$_4$ buffer solution (pH 7.4) and water in order to remove meta-chlorobenzoic acid (*m*CBA). Azidopropyl-functionalized mesoporous silica SBA-N$_3$-*x* (*x* = N$_3$/Si mol%) was prepared according to our previously reported method [23–25]. The ligand immobilized and trimethylsilyl end-capped mesoporous silicas