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Iron complex immobilized catalyst based on β-ketiminate ligand: Alkene oxygenation activity depending on the morphology of silica support and the structures of base additives

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ABSTRACT

Novel immobilized iron complex catalysts based on a β-ketiminate ligand have been developed. Dehydrative condensation between β-diketone and the ethylenediamine derivative of silane-coupling reagent yields the silanol ester of the ligand motif which can be anchored on the silica supports through covalent bond. The morphology of the silica supports affects the structures of active sites and catalytic activities on alkene oxygenation with H_2O_2. The ordered flat surface of SBA-15 allows to immobilize the ligand with highly-dispersion and to form the coordinatively unsaturated iron active site. Addition of small amount of pyrazoles improves the catalytic performance without leaching of iron.

1. Introduction

Development of heterogeneous catalysts which mediate the selective oxygenation of hydrocarbons with environmentally friendly oxidant such as O_2 and H_2O_2 under mild condition is an attractive and challenging subject from the viewpoint of green chemistry [1]. In nature, iron-containing enzymes catalyze selective hydrocarbon oxygenation under physiological mild condition. The iron centers of these enzymes are supported by organic ligands such as porphyrin in heme enzymes or amino acid residues in non-heme enzymes [2]. From biomimetic viewpoints, various iron complexes with organic supporting ligand (porphyrin, Schiff base, amine, heterocyclic compounds including pyridine and so on, amino acid derivatives, phenols, carboxylic acid derivatives, etc.) have been explored as homogeneous oxidation catalysts so far [3]. Some of these complexes catalyze the oxygenation of hydrocarbons with H_2O_2 at ambient temperature: In these systems, iron-peroxo and/or high-valent iron-oxo species seem to be an active intermediate(s) as well as enzymes [4]. In order to improve catalytic efficiencies, decomposition of the catalyst by leaching of iron, or/and transformation to inactive compounds such as dinuclear Fe(III)-μ-oxo species and coordinatively saturated complex must be avoided.

Immobilization of the non-heme iron complexes on an appropriate support would make possible to construct isolated catalytic active sites [5]. Such immobilized catalyst might hinder the transformation of the iron complex to inactive species and that result in the elongation of catalyst lifetime. In addition, the resulting heterogeneous catalyst would have an advantage for recovering the used catalyst. The most important requirement is no leaching of complex and metal ions. In this context, we have been designing novel immobilized metallocomplex catalysts based on anionic chelating ligands which are anchored to appropriate supports through covalent bond [6].

A family of β-diketonates is one of the well-defined anionic chelating ligands. Importantly, one of two carbonyl groups of the β-diketones (parent of β-diketonate ligands) can be replaced by an imino group giving the corresponding β-ketimine compounds, and their deprotonated form are recognized as β-ketiminate ligands [7]. Recently, metal complexes with *NNO*-chelating β-ketiminate ligands, which are obtained by dehydrative condensation between acetylacetone and ethylendiamine derivatives, are investigated as homogeneous catalysts for coupling reaction and polymerization [8–10]. Especially, the applicability of the *NNO* β-ketiminate complexes toward redox process containing reaction, i.e. the cross-coupling catalysis of the Fe(III) complex [8] and the atom-transfer radical polymerization catalysis of the Cu(II) complexes [9], motivate us to explore oxidation catalysis of the *NNO* β-ketiminate ligands complexes. Herein we report development of β-ketiminate ligand-based immobilized iron complex catalysts. Structures of

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the immobilized iron complex species and their catalytic activities toward oxygenation of cyclohexene with H_2O_2 depend on the morphology of silica support. In addition, base additives improve the catalytic activity.

2. Experimental

2.1. Instruments

Atomic absorption analysis was performed on a Shimadzu AA-6200. Elemental analysis was performed on a Perkin-Elmer CHNS/O Analyzer 2400II. ESI (electrospray ionization)-MS spectra were measured on a JEOL JMS-T100LC mass spectrometer. Gas chromatographic (GC) analyses were carried out on a Shimadzu GC-2010 (flame ionization detector) equipped with a RESTEK Rtx-5 capillary column (length = 30 m, i.d. = 0.25 mm, thickness = 0.25 μm). 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 liquid nitrogen temperature (77 K) using a Micromeritics TriStar 3000. Before the adsorption experiments, the samples were outgassed under reduced pressure for 3 h at 333 K.

2.2. Materials and methods

All solvents (THF, toluene, CH_2Cl_2, MeCN) were purified over a Glass Contour Solvent Dispending System under Ar atmosphere. The reagents of the highest grade commercially available were used without further purification. Merck Silica gel 60 (70–230 mesh; BET surface area = 714 $m^2\,g^{-1}$; pore volume: 1.13 $cm^3\,g^{-1}$) was employed as an unmodified amorphous silica support (═**SiO$_2$**). SBA-15 (BET surface area = 578 $m^2\,g^{-1}$; pore volume = 0.76 $cm^3\,g^{-1}$) was prepared according to the previously reported procedure [11].

2.3. Catalyst preparation

A linker-attached β-ketiminate ligand H**L** was synthesized as follows. *N*-(3-trimethoxysilylpropyl)ethylenediamine (1.08 g; 5.00 mmol) and one equivalent (0.500 g; 5.00 mmol) of acethylacetone were refluxed in toluene (100 mL) for 3.5 h. Pale yellow oil of H**L** was obtained by evaporation of volatiles under reduced pressure, and characterized by ^{1}H NMR. ^{1}H NMR ($CDCl_3$): δ 1.61 (m, 2H, CH_2), 3.58 (s, 3H, CH_3), 4.92 (s, 1H, C═CH).

The prepared H**L** (0.200 g) and SBA-15 (2.00 g) were suspended in toluene and refluxed for 2 h. Filtration of solid and wash with toluene then CH_2Cl_2 yielded pale yellow solid. Elemental analysis data (C, 1.34%; H, 0.40%; N, 0.21%) indicate the loading amount of H**L** was 0.08 mmol g^{-1}. Remaining silanols on silica were end-capped by trimethylsilyl group. A suspension of the obtained pale yellow solid (1.92 g) and hexamethyldisilazane (10 mL, 42.5 mmol) in toluene (30 mL) was stirred at 50 °C for 1 h. The resulting solid was collected by filtration then washed with toluene and CH_2Cl_2. Dryness under evacuation yielded 1.89 g of H**L**-anchored SBA-15 (**SBA$^{\mathrm{L}}$**). Elemental analysis data (C, 7.75%; H, 1.07%; N, 0.21%) suggest the retention of **L** on the support.

The pale yellow colored **SBA$^{\mathrm{L}}$** (1.00 g) was suspended in 20 mL of THF under Ar. A hexane solution of *n*-buthyllithium (0.12 mL; 0.16 mmol) was added slowly to this THF suspension at 0 °C and stirred at room temperature. After 1 h, methanol solution (20 mL) of $FeCl_3$ (0.02 g; 0.16 mmol) was added and stirred for 1 h. The resulting pale brown solid was collected by filtration and then washed with MeOH. Dryness by evacuation yielded the desired iron catalyst **Fe/SBA$^{\mathrm{L}}$**.

When amorphous silica (abbreviated as **SiO$_2$** in this paper) was employed as the support, the corresponding catalysts were prepared by same procedure. The loading amounts of **L** on **SiO$_2^{\mathrm{L}}$** were controlled by applied amount of H**L** upon immobilization. A lower ligand loading **SiO$_2^{\mathrm{L}}$** was prepared by the reaction of 5.0 g of SiO_2 and 0.50 mmol of H**L** in refluxing toluene (20 mL). Whereas a higher ligand loading **SiO$_2^{\mathrm{L}}$** was obtained by the reaction of 5.0 g of SiO_2 and 3.0 mmol of H**L** in refluxing toluene (120 mL).

2.4. Synthesis of model compounds [Fe(*L*′)]$^{2+}$ and [Fe(*L*)$_2$]$^+$

A ligand for model compounds, 4-[2-(ethylamino)ethylamino]-pent-3-en-2-one (H**L**′), was synthesized via similar procedure for H**L**. 30 mmol of *N*-ethylethylenediamine and equimolar of acetylacetone were refluxed in toluene (50 mL) for 1 h. Pale yellow oil of H**L**′ was obtained by evaporation, and characterized by ^{1}H NMR. ^{1}H NMR ($CDCl_3$): δ 1.03 (m, 3H, CH_3), 2.63 (t, 2H, CH_2), 2.85 (t, 2H, CH_2), 4.87 (s, 1H, CH). Metalation of **L**′ was achieved by reaction of sodium salt of **L**′, which was obtained by treatment of H**L**′ with sodium hydride in THF, with an appropriate ratio of $FeCl_3$.

2.5. Catalytic reaction

Typical reaction procedure is as follows: In Schlenk tube, 60 mg of catalyst (**Fe/SBA$^{\mathrm{L}}$**) was suspended in 5 mL of MeCN. Cyclohexene (0.25 mL, 2.5 mmol) and nitrobenzene (10 μL, 0.10 mmol; as internal standard) was added to this suspension. All reactions were carried under Ar and the products were analyzed by GC with an internal standard.

3. Results and discussion

3.1. Preparation of catalysts

There are two possible procedures for anchoring the *NNO* β-ketiminate ligand on silica supports. One is namely "in situ ligand formation" by reaction of an amine-modified silica gel with β-diketone [12]. Another is "grafting of pre-synthesized ligand" which is connected to a linker unit [13]. The analogous metallocomplex immobilized catalysts with a bidentate *NO* β-ketiminate ligand motif have been prepared by both procedures so far. We employed the later procedure [13] in order to construct the desired *NNO* β-ketiminate ligand certainly. A silanol ester derivative of the *NNO* β-ketiminate ligand (═**L**) was synthesized by dehydrative condensation of *N*-(3-trimethoxysilylpropyl)ethylenediamine with acetylacetone in refluxing toluene. The synthesized linker-attached ligand H**L** was anchored on pre-dried silica gels (amorphous silica with surface area = 714 $m^2\,g^{-1}$ or SBA-15 with surface area = 578 $m^2\,g^{-1}$), and remaining surface silanol moieties were end-capped by trimethylsilyl group in order to prevent the immobilization of extra metal ions on the surface of the silica (Scheme 1). Upon amorphous silica (═**SiO$_2$**) was employed as the support, amounts of anchored **L** were varied by changing the amount of applied **L** to **SiO$_2$**. The amounts and densities of anchored **L** on the supports are summarized in Table 1. **L** might be densely located on

Table 1
Properties of ligand-immobilized support **SBA$^{\mathrm{L}}$** and **SiO$_2^{\mathrm{L}}$**.

Ligand-immobilized support	**SBA$^{\mathrm{L}}$**	**SiO$_2^{\mathrm{L}}$**[a]	**SiO$_2^{\mathrm{L}}$**[b]
BET surface area of support/$m^2\,g^{-1}$	578	714	714
Loading of **L**/mmol g^{-1}	0.08	0.11	0.63
Density of **L**/molecule nm^{-2}	0.08	0.09	0.53
Loading of Fe/mmol g^{-1}	0.08	0.05	0.31
Ratio of **L**/Fe	1.0	2.2	2.0

[a] Lower ligand loading **SiO$_2^{\mathrm{L}}$**.
[b] Higher ligand loading **SiO$_2^{\mathrm{L}}$**.