Catalytic Alkane Oxidation by Homogeneous and Silica-supported Cobalt(II) Complex Catalysts with a Triazolyl Group-containing Tetradentate Ligand

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Homogeneous and heterogeneous cobalt complex catalysts with bis(pyridylmethyl)(triazolylmethyl)amine ligand were prepared. Although simple cobalt salts catalyze cyclohexane oxidation with *m*CPBA, the cyclohexane selectivity increases upon coordination of tetradentate ligands. In the heterogeneous catalysis, the yield and selectivity of cyclohexanol are improved with an increase in the ligand density on the silica support due to the suppression of metal leaching.

Partial and selective oxidation of alkane remains a challenging reaction. To overcome this issue, the development and understanding of metal-based oxidants are considered important.¹⁻³ Accordingly, Itoh and co-workers have reported the catalytic oxidation of alkanes (e.g., cyclohexane) by metal complexes with a tpa (= tris(2-pyridylmethyl)amine) ligand and acetate coligands (Figure 1).^{4,5} Among the tpa complexes of divalent nickel, cobalt, iron, and manganese, the nickel(II) complex shows the highest conversion, with good selectivity of alcohol over ketone. The cobalt(II)-tpa complex exhibits the highest alcohol selectivity with moderate conversion, although a longer reaction time is needed. In terms of nickel(II)-tpa complexes, the roles of the tpa ligand and the acetate coligand have been investigated.^{6,7} Other nickel(II) complexes have also been reported as mCPBA-activating catalysts, and related nickel-oxygen complexes such as nickel(II)-acylperoxo and nickel(III)-oxygen species have been characterized by some research groups, including ourselves.⁸⁻¹⁰ In contrast, examples of mCPBA-activating cobalt complexes remain scarce, and the role of the ligands as well as the reaction mechanism of the cobalt catalysts remains to be clarified.^{11–17} Meanwhile, we have been investigating heterogenized metal complex catalysts.¹⁸⁻²² We have recently prepared triazolyl group-containing poly(pyridyl)amine ligands, N,N-bis(2-pyridylmethyl)-N-[(1-R-1H-1,2,3triazol-4-yl)methyl]amine, of which R is *tert*-butyl (= L^{t-Bu}) for a homogeneous complex catalyst, while it is a linker to silica gel (= SBA*-L-x, x denotes the content of a ligand tether in mol % of silicon atom) for a heterogenized complex catalyst.²³ The nickel catalysts with these ligands exhibit cyclohexane oxygenation activity with mCPBA, and the catalytic performances of the heterogenized catalysts depend on the loading density of L on the surface of the silica support. In this work, we have prepared homogeneous and heterogeneous cobalt(II) complex catalysts in order to clarify the role of L and the trend of catalyses depending on the central metal ion.

A homogeneous catalyst $[Co^{II}(OAc)L^{t-Bu}](BPh_4) (= L^{t-Bu}/Co)$ was prepared from $Co(OAc)_2 \cdot 4H_2O$ and L^{t-Bu} with the treatment of NaBPh₄ in methanol according to the reported



Figure 1. Cyclohexane oxidation with *m*CPBA catalyzed by cobalt(II) complex catalysts (a). Molecular structures of homogeneous and silica-immobilized complexes having tetradentate ligands (b).

procedure of $[Co(OAc)(tpa)](BPh_4) (= tpa/Co).^{4,24}$ The molecular structure of L^{t-Bu}/Co was revealed by X-ray crystallography (Figure 2).²⁵ In addition to the bidentate coordination of an acetate anion, the tetradentate coordination structure of L^{t-Bu} is similar to the reported tpa/Co complex.²⁶ In addition, the strongly coordinating acetate O1 atom (Co1–O1 2.001, Co1–O2 2.438 Å) is located in a trans position to the tertiary amine N3 (Co1–N3 2.292 Å), as observed in tpa/Co. We have previously reported the molecular structures of the related nickel(II) complexes, $[Ni^{II}(OAc)_2(L^{t-Bu})(H_2O)] (= L^{t-Bu}/Ni)$ and $[Ni(L^{t-Bu})_2](BF_4)_2 (= L^{t-Bu}_2/Ni).^{23}$ In both nickel complexes, the L^{t-Bu} ligand coordinates to the nickel centers not by the triazole nitrogen but by the three nitrogen donors of the bis(pyridylmethyl)amine unit at facial positions. This tridentate coordination induces the formation of L^{t-Bu}_2/Ni .

Heterogenized cobalt complex catalyst was prepared by the procedure for the corresponding nickel catalyst.^{23,24} The ligandimmobilized mesoporous silica gels, SBA*-L-x (x = 0.5 and 4 mol% of silicon atoms), were treated with a MeOH solution of Co(OAc)₂·4H₂O to obtain the SBA*-L-x/Co catalysts. Cobalt loadings on the catalysts were determined by atomic absorption



Figure 2. Molecular structure of $[Co(OAc)(L^{t-Bu})](BPh_4)$. Hydrogen atoms on the carbon backbone and BPh₄ anion are omitted for clarity. Thermal ellipsoids are drawn for a 30% probability level. Co1–O1 2.001(1), Co1–O2 2.438(2), Co1–N1 2.065(2), Co1–N2 2.079(2), Co1–N3 2.292(1), Co1–N4 2.051(2) Å.

 Table 1. Ligand and metal loadings on the immobilized catalysts

Catalyst	L	Co	Co (recovered)	
	$/\rm{mmol}g^{-1}$	$/mmol g^{-1}$	$/mmol g^{-1 a}$	
SBA*-L-0.5/Co	0.080	0.080	0.034	
SBA*-L-4/Co	0.316	0.225	0.162	

^aAfter usage for the oxidation catalysis.

analysis of the KOH-digested solution (Table 1). The molar ratios of the ligand and cobalt on the two immobilized catalysts were different (L:Co ca. 1:1 in SBA*-L-0.5/Co and 1.6:1 in SBA*-L-4/Co), as was found in the nickel catalysts. Assuming that the coordination structure of the immobilized cobalt centers is the same as that of L^{rBu}/Co , some free ligand sites remain on the SBA*-L-4/Co.

The cyclohexane oxidation catalysis with mCPBA oxidant was initially examined on the homogeneous catalysts (Table 2 and Figure S8).²⁴ Generally, this type of cyclohexane oxidation yields cyclohexanol (A) with its overoxidation products, cyclohexanone (K) and caprolactone (L). The reactivity of catalysts for the oxidation was evaluated by the product formation turnover number (= TON) and the alcohol selectivity A/(K + L)at 35 °C. The oxidation did not proceed catalytically in the absence of a catalyst or the presence of nickel acetate. In the presence of L'-Bu/Ni catalyst, the reaction proceeded within 1 h to give a high TON (599) and selectivity (7.4) for A^{23} This result showed clear reactivity enhancement of the nickel center upon coordination of the L^{t-Bu} ligand. In the case of cobalt, simple cobalt(II) salts such as CoCl₂, Co(NO₃)₂, and Co(OAc)₂ catalyzed the oxidation with moderate TON and with an alcohol selectivity range of 2.3 to 4.5, as has been previously reported for catalysis with the use of Co(ClO₄)₂.²⁷ On the other hand, both cobalt complexes with the tetradentate ligands (Lt-Bu/Co and tpa/Co) showed higher TON and alcohol selectivity than simple cobalt salts. It is noteworthy that the catalysis with the

Table 2. Product TON in cyclohexane oxidation catalyzed by homogeneous and immobilized cobalt complex catalysts with $mCPBA^a$

Catalyst	t/h	TON				A/(V + I)
		Α	Κ	L	С	-A/(K+L)
None ^b	3	8	5	0	15	1.8
Ni(OAc) ₂	3	18	7	0	11	2.6
CoCl ₂	0.5	515	221	4	511	2.3
$Co(NO_3)_2$	0.5	331	66	8	255	4.5
Co(OAc) ₂	0.5	368	80	7	277	4.2
tpa/Co ^c	1 ^d	300	16	nd	nd	18.8
	3	ca. 600	nd	nd	nd	nd
L ^{t-Bu} /Co	2	604	98	14	459	5.4
SBA*-L-0.5/Co	3	577	138	6	377	4.0
SBA*-L-4/Co	3	745	80	25	582	7.1
SBA*-L-4/Co ^e	3	533	191	13	432	2.6

^aCatalyst 2 µmol, cyclohexane 15 mmol, *m*CPBA 2 mmol in CH₂Cl₂ (3 mL)/MeCN (1 mL) at 35 °C for 3 h under Ar. ^bValues based on 2 µmol of virtual catalyst. ^cFrom ref 4, at room temperature for 1 h. nd: no data. ^dThe reaction is in progress. ^eThe catalyst was removed at 15 min.

tetradentate ligands required a longer reaction time (2-3 h) than that with simple salts (within 30 min). A major difference in reactivity of \mathbf{L}^{t-Bu}/Co from tpa/Co is the reduction in alcohol selectivity. Based on the similar molecular structures of the two complexes, the reactivity difference may be caused by coordination properties of the triazole moiety. In the nickel(II) complexes, $[Ni^{II}(OAc)_2(\mathbf{L}^{t-Bu})(H_2O)]$ and $[Ni(\mathbf{L}^{t-Bu})_2]^{2+}$, the triazole group does not coordinate to the nickel(II) centers.²³ Thus, the coordinating triazolyl side arm on the cobalt center may be capable of replacement with *m*CPBA or *m*CBA (= *m*chlorobenzoic acid, by-product) molecules under the oxidation catalysis. A large quantity of chlorobenzene (*C*), which is a side product from *m*CPBA via homolytic cleavage of the peroxide O–O bond, was detected in all cases with homogeneous cobalt catalysts.

Cyclohexane oxidation with heterogeneous cobalt complex catalysts was carried out (Table 2 and Figure 3). The liganddense catalyst, SBA*-L-4/Co, showed a higher product TON and alcohol selectivity than did SBA*-L-0.5/Co catalyst. This reactivity trend of the cobalt system was opposite to that of the related nickel system.²³ The lowest loading Ni catalyst, SBA*-L-0.5/Ni, showed high reactivity (TON = 534, and selectivity = 10.5 for A after 3 h), similar to that for the related homogeneous catalyst L^{t-Bu}/Ni. An increase in the loading of SBA*-L-x/Ni catalysts resulted in a decrease in TON while maintaining the high selectivity for alcohol. This tendency of the nickel systems may be due to the coordination of an excess ligand to form an inert L^{t-Bu} /Ni species that has no coordination site for the oxidant. After catalysis, cobalt loadings on both recovered catalysts were analyzed (Table 2). More than half the amount of cobalt ion was leached from SBA*-L-0.5/Co during the catalysis or workup process, and the leached amount was much higher than that from SBA*-L-4/Co. To investigate this leaching process, a filtration test was applied for the heterogeneous catalysis with SBA*-L-4/Co. 15 min after initiation of the catalysis, the catalyst was removed by filtration (Advantech



Figure 3. Time course of cyclohexanol (filled circle), cyclohexanone (open circle), and ε -caprolactone (cross) formations in cyclohexane oxidation reaction with *m*CPBA catalyzed by SBA*-L-0.5/Co (a), SBA*-L-4/Co (b), and catalyst removal of SBA*-L-4/Co at 15 min (c). Reaction conditions: Catalyst 2µmol, cyclohexane 15 mmol, *m*CPBA 2 mmol in CH₂Cl₂ (3 mL)/MeCN (1 mL) at 35 °C under Ar.

PTFE syringe filter), and the product formation in this solution was then monitored for 3 h. The reaction was found to remain in progress for 2 h after the filtration, although with a reduction in the alcohol selectivity. This result indicates that the eluted cobalt ion shows similar reactivity to that of the homogeneous simple cobalt salts. Due to the higher local ligand density and the existence of some free ligand sites on the silica surface, SBA*-L-4/Co retains its cobalt ion more tightly, resulting in the highest yield of cyclohexanol among the catalysts we prepared. It remains unclear, however, whether the leaching mechanism involves oxidation, protonation, or an exchange of L by the excess quantity of *m*CPBA oxidant during the reaction.

In conclusion, we prepared homogeneous and heterogeneous cobalt complex catalysts with a tpa-type ligand, which contains a triazole group. Coordination of the ligand improved the yield and selectivity of cyclohexanol in the cyclohexane oxidation with *m*CPBA. The ligand-dense environment on the silica surface prevented metal elution, thus improving the catalytic reactivity. Finally, the reactivity trend of the immobilized cobalt system, depending on the ligand density, was the reverse of that of the related nickel system. These results demonstrate the importance of site density control appropriate to the type of metal ion utilized in the development of immobilized complex catalysts.

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- 23 Alkane oxidation reactivity of related homogeneous and heterogeneous nickel complexes with L^{*L*Bu} and SBA*-L-*x*: J. Nakazawa, T. Hori, T. D. P. Stack, S. Hikichi, *Chem.*—*Asian J.* 2013, 8, 1191.
- 24 See Supporting Information. Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/ journals/chem-lett/index.html.
- 25 Crystal data for [Co(OAc)(L^{*r*Bu})](BPh₄): C₄₅H₅₁BCoN₆O₂, $fw = 773.63 \text{ g mol}^{-1}$, triclinic $P\overline{1}$ (No. 2), a = 11.120(3), b = 13.206(3), c = 14.592(4)Å, $\alpha = 91.811(1)$, $\beta = 102.361(4)$, $\gamma = 109.947(4)^{\circ}$, V = 1954.9(9)Å³, Z = 2, T = 113 K, $\mu = 0.487 \text{ mm}^{-1}$, $D_{calcd} = 1.314 \text{ g cm}^{-3}$. Number of unique reflections = 8905, number of reflections included in the refinement = 8031 ($I > 2\sigma(I)$), R = 5.48 (all data), 5.01 ($I > 2\sigma(I)$), $R_{w} = 10.70$ (all data), 10.14 ($I > 2\sigma(I)$). GOF = 1.138. Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-898169. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, U.K.; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).
- 26 Selected bond lengths in [Co(tpa)(OAc)](BPh₄) from ref 4: Co–N1 (4° amine) 2.234(2), Co–O1 (C–O, trans to 4° amine) 2.043(2), Co–O2 (C=O, trans to Py N3) 2.376(2), Co–N2 (Py, trans to Py N4) 2.086(2), Co–N3 (Py)2.081(2), Co–N4 (Py) 2.096(2) Å.
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