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Preparation of Oxidation Catalysts by Immobilization and Isolation of Metal Complexes into Monolayer Matrix on Silica Surface

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Immobilization and isolation of cobalt-pyridine complexes in the fence of monolayer matrix on silica surface provided the active catalysts for oxidation of 1,2,3,4-tetrahydronaphthalene.

Isolation of active metal complexes in the polymer network to improve the catalysis is of essential feature of polymer-bound catalysts.[1)] However, there are drawbacks to use polymers as supports, involving the dimerization of active sites by the mobility of solvent-swollen polymer chain[2)] and the limitation of diffusional process inside a highly cross-linked particle.[3)] The active center and the local structure of sterically encumbered reaction sites should be distributed on the surface of rigid supports. An open space enclosed by monolayer matrix on silica surface (Fig. 1) is thought to provide such a reaction vessel.

In this letter, we report the result on a simple and easy preparation of silica-bound metal complexes fenced by long paraffinic chains. For the investigation of catalytic system, we have chosen the oxidation reaction of 1,2,3,4-tetrahydronaphthalene (THN) catalyzed by cobalt-pyridine complexes bound to colloidal polymer.[4)]

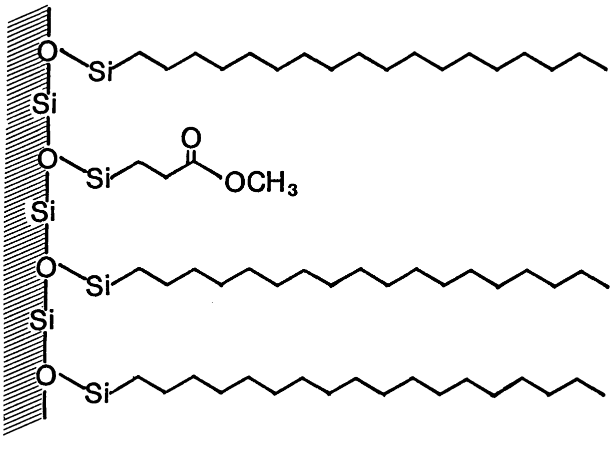

Fig. 1. Open space on modified silica.

Silica-bound cobalt-pyridine complexes as presented in Table 1 were prepared as follows: Nonporous silica "Aerosil" (average diameter of 12 nm, surface area of 200 m^2/g, 1.0-1.3 mmol SiOH/g) and a weighed amount of 2-(carbomethoxy)ethyltrichlorosilane were refluxed in toluene overnight under argon stream. The loading was controlled to cover less than 15% of free hydroxyl groups on the surface. Coverage of the remaining silanols was effected by keeping the modified silica smeared with octadecyltriethoxysilane (ODS) at 120 °C in a vacuumed and sealed bottle for 24 h, prior to boiling in toluene overnight. Attempt to increase the loading level of SC-2 was unsuccessful. This is presumably due to the fact that the initially anchored ester groups inhibit condensation reaction of ODS on the adjacent silanols by steric interference.

Hydrolysis of the resulting enclosed ester to potassium salt, characterized by its FT-IR data, was done with 5 times excess of t-BuOK to the ester in DMSO at room temperature for 15 min. Finally the salt was treated with cobalt(II) acetate and subsequently complexed with 6 mol of pyridine in water.

Catalytic oxidation of THN was carried out in water under oxygen atmosphere (Table 2). THN conversion of more than 70% is achieved in the presence of catalyst on which cobalt-pyridine complexes are isolated by ODS fence. The result exhibits a marked contrast to that found with SC-4. Further, in the case of SC-2, supercritical fluid chromatography using CO_2

Table 1. Surface modification mode of various catalysts

Catalyst	Anchored COOMe[a]	Immobilized Co[b]	ODS coverage[c]
	(mmol / g	of silica)	
SC-1	0.06	0.05	0.83
SC-2	0.14	0.13	0.58
SC-3[d]	0.14	0.07[e]	0.55
SC-4[f]	0.14	0.07[e]	0

a) By FT-IR analyses. b) By colorimetric methods. c) By elemental analyses. d) Octylsilyl group was used as the fence. e) Ester was hydrolyzed under the same condition as SC-1 and SC-2. Low conversion to Co salt is due to cleavage of Si-C bond.[5] f) Hydrolysis and complexation were done without monolayer coverage.

demonstrated the presence of a significant amount of 1-hydroperoxy-1,2,3,4-tetrahydronaphthalene (PTHN) in the ethyl acetate extracts of the reaction mixture. Thus the almost equivalent yields of 1-hydroxy- (HTHN) and 1-oxo-1,2,3,4-tetrahydronaphthalene (OTHN) were obtained after the reduction of PTHN by triphenylphosphine.

For the enhancement of THN conversion, it was important to increase the loading level of octadecylsilyl groups. In the study of surface geometry of silica, the maximum coverage of trimethylsilyl groups is estimated to be 0.61 for the dominant surface model.[6] The total coverage of 0.59 for SC-1 suggests the formation of closely packed surface, and the density of 0.48 for SC-2 implies moderate crowding of ODS. We also found

Table 2. Oxidation of THN using fenced cobalt-pyridine complex on silica[a)]

Run	Initial composition Catalyst	 Cobalt (mmol)	 THN (mmol)	Products[b)] HTHN	 OTHN	(Yield/ %) PTHN[c)]	 Others[d)]	THN conversion
1	SC-1	0.020	1.96	18	41	1	11	71
2	SC-1	0.025	2.42	17	42	1	10	70
3	SC-2	0.018	1.81	15	34	19	10	78
4	SC-2	0.025	2.51	16	33	17	6	72
5[e)]	SC-2	0.020	2.09	16	35	16	9	76
6	SC-3	0.025	2.64	15	27	10	6	58
7[e)]	SC-4	0.025	2.42	2	3	1	0	6
8[f)]	Co/AcOH	0.026	2.54	5	9	2	3	19
9[g)]	Co/Py	0.020	1.83	24	46	-[h)]	4	77

a) Reactions were carried out in 30 ml of water at 50 °C for 24 h under 770 mmHg of O_2 pressure using a platform shaker of 180 strokes/min. b) Determined by GC. c) Yields were calculated based on the increment of GC intensity of HTHN after reduction of hydroperoxide to alcohol by triphenylphosphine. d) 1,4-Dihydroxy-1,2,3,4-tetrahydronaphthalene and 1-hydroxy-4-oxo-1,2,3,4-tetrahydronaphthalene were identified by isolation and nmr analyses. e) Complexation of silica bound Co salt with 6 mol of pyridine was done prior to oxidation reaction and used without isolation. f) Cobalt(II) acetate in acetic acid. g) Ref. 4. h) Not reported.

the deterioration of THN conversion when C_8 silanes were loaded (SC-3) even at high coverage of 0.46 as the fence of the catalyst instead of C_{18}. Isolation of cobalt-pyridine complexes into the internal cavity of monolayer matrix resembling the local structures of "Pocket porphyrins"7) and "Octopus cyclophanes"8) seems to account for the stabilization of catalysts in terms of the protection of active center from solvation. In addition, as seen in Table 2, unexpectedly high yield of PTHN was obtained with SC-2 in contrast to the oxidation with SC-1 and in the homogeneous system.9) The finding that the product selectivity is also effected by the modification mode of silica surface indicates another advantage of the catalyst.

In conclusion, immobilization of metal complexes in the monolayer matrix on silica surface offers a useful system to improve the catalysis. Further study to understand the origin of site isolation effects is now under way.

References

1) W. T. Ford, CHEMTECH, 1987, 246.
2) J. P. Collman and C. A. Reed., J. Am. Chem. Soc., 95, 2048 (1973).
3) A. Guyot, Pure Appl. Chem., 60, 365 (1988).
4) R. S. Chandran and W. T. Ford, J. Chem. Soc., Chem. Commun., 1988, 104.
5) C. C. Price and J. R. Sowa, J. Org. Chem., 32, 4126 (1967).
6) D. W. Sindorf and G. E. Maciel, J. Phys. Chem., 86, 5208 (1982).
7) J. P. Collman, J. I. Brauman, B. L. Iverson, J. L. Sessler, R.M. Morris, and Q. H. Gibson, J. Am. Chem. Soc., 105, 3052 (1983).
8) Y. Murakami, Y. Hisaeda, J. Kikuchi, T. Ohno, M. Suzuki, and Y. Matsuda, Chem. Lett., 1986, 727.
9) M. Martan, J. Manassen, and D. Vofsi, Tetrahedron, 26, 3815 (1970).

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