398 *Bull. Korean Chem. Soc.* 1995, *Vol. 16, No. 5*

Ki-Won Jun et al.

Cyclohexane Oxidations by an Iron-Palladium Bicatalytic System; Soluble Catalysts and Polymer Supported Catalysts

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Selective oxidation of cyclohexane in acetone solution has been studied using iron catalysts with hydrogen peroxide *in-situ* produced by palladium catalyst. Iron tetraphenylporphyrin chloride shows the highest activity among the tested chlorides and porphyrin complexes of some metals of the first transiton series. Iron chloride and iron tetraphenylporphyrin chloride were supported on four kinds of 4-vinylpyridine copolymer with styrene or divinyl- benzene. Nitrogen 1s photoelectron spectra give the evidence that pyridyl nitrogens of the 4-vinyl pyridine copolymer act as ligands to bind iron species. The copolymer with styrene is the most efficient support for the binding because its solubility in catalyst preparation solvent (methylene chloride) gives the pyridyl group advantage to contact with the iron catalysts. However, better catalytic activity per iron atom could be obtained with a rigid crosslinked polymer due to active site isolation.

Introduction

It is well known that some biological systems and their mimetic systems are able to catalyze the oxidation of alkanes under mild conditions. The hydrocarbon oxidation system mimicking the monooxygenases demands the presence of a catalyst, an electron source and protons, oxygen, and a solvent. Many biomimetic catalysts utilize not only metalloporphyrins[1~4] but also various iron compounds.[5~8] The molecular oxygen with electron source and protons can be replaced by various single oxygen transfer reagents such as hydrogen peroxide or iodosobenzene.[3,4,8]

The development of heterogeneous biomimetic catalysts has recently received a lot of attention because it appears to provide a method of obtaining more practical catalysts as well as the ideal imitation of enzymes.[9~16] In addition, supporting a metalloporphyrin often makes the complex be more active through active site isolation that prevents dimerization leading to deactivation.[10,13,15]

We have been developing the heterogeneous catalytic systems which are active for the oxidation of cyclohexane under mild conditions.[17~19] A bicatalytic system, silica supported iron oxide and palladium, was previously shown to be efficient for the cyclohexane oxidation using acetone solvent.[17,18]

In the present study, various soluble metal compounds have been examined for the oxidation of cyclohexane by *in situ* generated hydrogen peroxide with a palladium catalyst, the insolubilization of iron catalysts has been accomplished by using vinylpyridine polymer (PVP). We now wish to report that PVP supported iron chloride and iron tetraphenylporphyrin chloride (Fe(TPP)Cl) catalyze the cyclohexane oxidation.

Experimental

Catalyst preparation. All metalloporphyrins such as Fe(TPP)Cl, Mn(TPP)Cl, Co(TPP), Ni(TPP), and Cu(TPP) were obtained from Aldrich.

Trinuclear iron comlex, $Fe^{II}Fe^{III}_2O(OAc)_6pyr_{3.5}$, was prepared by the isolation method from Gif reaction mixture according to a literature procedure.[7]

Four kinds of 4-vinylpyridine copolymer with styrene or divinylbenzene (DVB) were used as supports: they were PVP-s (styrene content 10%, Aldrich), PVP-d2 (DVB content 2%, Janssen), PVP-d6 (DVB content 6%, Koei), and PVP-d24 (DVB content 24%, Koei). Their BET suface area were 0.3, 0.4, 5.7, and 25.6 m^2/g, respectively.

The catalysts supported on PVP were prepared as follows: an iron compound, $FeCl_2 \cdot 4H_2O$ (1 g) or Fe(TPP)Cl (0.5 g), and a PVP (5 g) were added to methylene chloride (200 mL) and the mixture was refluxed under nitrogen atmosphere for 2 h. While evaporation of solvent and adequate washing with acetone were carried out in the preparation of PVP-s supported catalysts, filtration and washing with methylene chloride and acetone were carried out in the preparation of PVP-d supported catalysts. The catalysts finally dried *in vacuo*. The degree of anchoring was determined by atomic absorption analysis of the iron ions remained in the solution for the determination of iron content of $FeCl_2$/PVP catalysts.

Silica supported palladium catalyst containing 0.6 wt.% palladium was prepared by the impregnation of $PdCl_2$ onto silica gel (Kiesel gel 60, surface area=426 m^2/g). The catalyst was subsequently dried at 150 ℃ for 2 h and calcined at 400 ℃ for 3 h in an air stream.

Catalyst characterization. A Seiko SEA 2001 X-ray fluorescence (XRF) spectrophotometer with a rhodium target and a silicon semiconductor was used for the determination of iron content of Fe(TPP)Cl/PVP catalysts.

X-ray photoelectron spectroscopic (XPS) measurements were carried out on a VG ESCALAB MK II photoelectron spectrometer, which was equipped with an Al anode operated at 15 KV and 20 mA. Binding energies for N of $FeCl_2$/PVP catalysts were adjusted for charging by referring them to that for C 1s, taken to be 284.6 eV which is that of polyethylene. Binding energies for Pd of the palladium catalyst was referenced to the Si 2p of the silica support at 103.4 eV.

Cyclohexane oxidation. The reaction was conducted in a round-bottomed flask equipped with gas bubbler and

Cyclohexane Oxidation by Bicatalytic System

Bull. Korean Chem. Soc. 1995, Vol. 16, No. 5 399

Table 1. Oxidation of cyclohexane with unsupported metal comounds[a]

Catalyst	Yield[b] (mole%)			Turnover number[c] (h^{-1})
	Cyclohexanol	Cyclohexanone	Total	
$MnCl_2 \cdot 4H_2O$	0.60	0	0.60	0.24
$FeCl_2 \cdot 4H_2O$	3.62	0.63	4.25	1.67
$CoCl_2 \cdot 6H_2O$	0.61	0	0.61	0.29
$NiCl_2 \cdot 6H_2O$	1.30	0.22	1.52	0.72
$CuCl_2 \cdot 2H_2O$	0	0	0	0
Mn(TPP)Cl	2.10	0.10	2.20	3.07
Fe(TPP)Cl	2.82	0.59	3.41	4.77
Co(TPP)	1.64	0.42	2.06	2.73
Ni(TPP)	1.18	0.25	1.43	1.90
Cu(TPP)	0.96	0.02	0.98	1.31
Gif complex[d]	0.55	0.18	0.73	0.04

[a] Condition: metal compound, 0.1 g; Pd catalyst, 2 g; cyclohexane, 5 g; acetone, 20 mL; H_2, 20 mL/min; O_2, 20 mL/min; temperature, 30 ℃; reaction time, 3 h. [b] Yields are based on cyclohexane. [c] Division of moles of oxidized products per an hour by moles of metal ion. [d] Trinuclear iron complex, $Fe^{II}Fe^{III}_2O(OAc)_6pyr_{3.5}$.

Table 2. Binding energies for Pd $3d_{5/2}$ electron in the Pd catalysts

Catalyst	Binding energy (eV)
Fresh Pd catalyst	337.5
Pd catalyst contacted with $H_2 + O_2$[a]	334.5
Pd catalyst contacted with H_2	334.8

[a] The catalyst was contacted with the gas(es) in the same system as the oxidation reaction but without the iron catalyst.

Table 3. Iron contents of supported iron catalysts

Catalyst	Iron content (wt.-%)	Anchoring degree[a]
$FeCl_2$/PVP-s	4.8	0.97
$FeCl_2$/PVP-d2	3.3	0.68
$FeCl_2$/PVP-d6	2.4	0.43
$FeCl_2$/PVP-d24	1.7	0.36
Fe(TPP)Cl/PVP-s	0.42	0.56
Fe(TPP)Cl/PVP-d2	0.048	0.061
Fe(TPP)Cl/PVP-d6	0.019	0.024
Fe(TPP)Cl/PVP-d24	0.014	0.018

[a] Division of moles of anchored iron by moles of added iron in the catalyst preparation.

refrigerated condenser (maintained at -20 ℃) as follows: a polymer supported catalyst and the palladium catalyst were added to a solution of cyclohexane in acetone and the gases of hydrogen and oxygen were bubbled through the stirred reaction mixture at 30 ℃ under atmospheric pressure.

The products were analyzed by gas chromatograph (Shimadzu GC-14A) equipped with a 5% OV-17 on chromosorb column with a flame ionization detector. The amounts of iron dissolved out of the catalyst during the reaction were measured by atomic absorption spectroscopy (Perkin-Elmer 2380).

Results and Discussion

Initially, some unsupported metal compounds were examined for the oxidation and the results are given in Table 1. Iron(II) chloride and iron porphyrin show the highest catalytic activity in each series of the compounds. It is also seen that the metalloporphyrins give much higher catalyst turnover number than metal chlorides. This fact can be interpreted by the fact that the easiness of forming high-valent metal-oxo complex due to TPP ligand favors the oxidation. The trinuclear iron complex, reported as an effective non-heme biomimetic catalyst,[7] was also examined, but it is almost ineffective for this reaction.

Table 2 shows the change of Pd $3d_{5/2}$ BE in the palladium catalyst. The fresh palladium catalyst gives the BE = 337.5 eV which corresponds to $PdCl_2$. The BE is decreased to 334.5-334.8 eV which are almost identical with metallic palladium, after contacting with the hydrogen or hydrogen-oxygen mixture. This indicates that the palladium(II) cation is readily reduced to Pd(0) by the hydrogen in the reaction system, and the resulted palladium could combine hydrogen and oxygen to generate hydrogen peroxide.

In this study, iron(II) chloride and Fe(TPP)Cl were immo-

bilized on different PVP samples. Table 3 represents the iron contents of prepared catalysts. Seeing the results with PVP supported iron chloride, it is evident that the PVP-s anchors iron chloride most effectively. It is most likely that solubility of PVP-s in catalyst preparation solvent gives the pyridyl group an advantage to contact with the iron catalysts. Furthermore, the iron content of the catalysts decreases as the crosslinking of PVP is increased, implying that the swellable property of lightly crosslinked polymers favors catalyst anchoring. On the other hand, Fe(TPP)Cl is able to be anchored effectively only on PVP-s being soluble in methylene chloride, indicating that iron porphyrin is too bulky to be diffused internally into crosslinked PVP.

Figure 1 shows the N 1s photoelectron spectra of PVP samples and $FeCl_2$/PVP catalysts. The pure PVP samples exhibits narrow bands at BE = 398.7 eV which is associated with the pyridyl nitrogen. As the PVP supports iron chloride, the narrow and simple bands is replaced by broad and complicated bands. Bands at higher BE (ca. 400-402 eV) reflect that pyridyl nitrogens of PVP act as ligands to bind iron species. Broadening and complicating suggest that pyridyl nitrogens are complicated by complexing with iron ions. It is likely that the ligation is distorted partly because nitrogens of the rigid polymeric matrix can not afford homogeneous ligation.

The oxidation results with the PVP supported iron catalysts are shown in Table 4. During the oxidation, the solubility of the iron compounds on PVP was found to be negligible, reflecting heterogeneity of the catalysts. In the PVP supported iron chloride catalysts, the selective oxidation turnover number, which is based on metal ion, increases with the crosslinking degree. It is most likely that the highly crosslinked PVP has effective porous structure through which
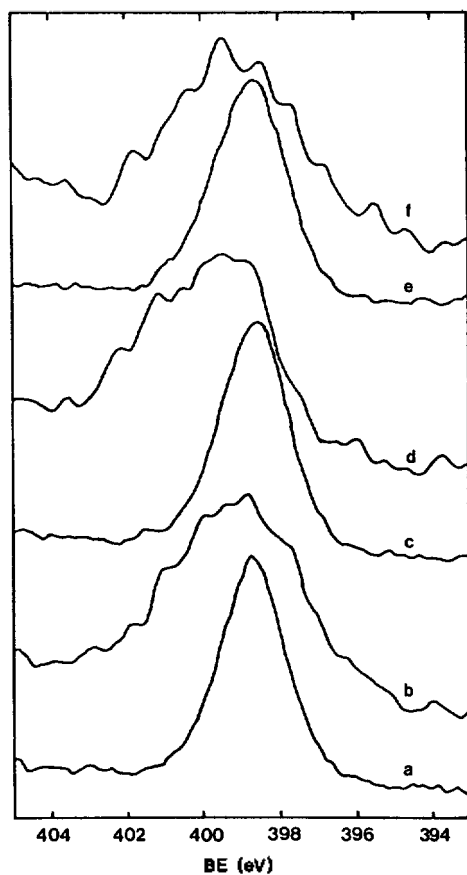
Figure 1. Nitrogen 1s photoelectron spectra of (a) PVP-s, (b) FeCl$_2$/PVP-s, (c) PVP-d2, (d) FeCl$_2$/PVP-d2, (e) PVP-d6, (f) FeCl$_2$/PVP-d6.

Table 4. Oxidation of cyclohexane with supported iron catalysts[a]

Catalyst	Yield (mole%)[b]			Turnover number[c] (h^{-1})
	Cyclohexanol	Cyclohexanone	Total	
FeCl$_2$/PVP-s	4.74	0.28	5.02	1.16
FeCl$_2$/PVP-d2	2.81	0.77	3.58	1.20
FeCl$_2$/PVP-d6	2.32	0.77	3.09	1.42
FeCl$_2$/PVP-d24	3.03	0.83	3.86	2.51
Fe(TPP)Cl/PVP-s	1.17	0.58	1.75	4.60
Fe(TPP)Cl/PVP-d2	0	0	0	
Fe(TPP)Cl/PVP-d6	trace			
Fe(TPP)Cl/PVP-d24	0.26	0	0.26	20.6

[a] Condition: iron catalyst, 1 g; Pd catalyst, 2 g; cyclohexane, 5 g; acetone, 20 mL; H$_2$, 20 mL/min; O$_2$, 20 mL/min; temperature, 30 ℃; reaction time, 3 h. [b] Yields are based on cyclohexane. [c] Division of moles of oxidized products per an hour by moles of metal ion.

the reactant can reach to iron active sites.

From the data of supported Fe(TPP)Cl samples, it is seen that Fe(TPP)Cl/PVP-d2 and Fe(TPP)Cl/PVP-d6 are almost inactive for the oxidation. This can be explained in terms of effective active site concentration: not only the iron con-

tents of Fe(TPP)Cl/PVP-d2 and Fe(TPP)Cl/PVP-d6 are too low, but acetone, being a weak solvent in contrast with methylene chloride, could not swell even the lightly crosslinked PVP. Therefore, the effective iron concentration of those samples that can be reached by the reactant are too low to give the oxidation reaction. However, PVP-24 seems to have the enough porous structure to provide diffusion of the reactants in acetone medium. It is worth noting that each of FeCl$_2$ and Fe(TPP)Cl supported on PVP-d24 gives high turnover number when compared with unsupported one. It is not likely that PVP-s creates site isolation of the active center, because of matrix flexibility in acetone. The higher catalytic activities with FeCl$_2$/PVP-d24 and Fe(TPP)Cl/PVP-d24 are possibly results of site isolation on rigid matrix.

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