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

Ki-Won Jun, Eun-Kyung Shim, Sang-Eon Park, and Kyu-Wan Lee*

Catalysis Research Division, Korea Research Institute of Chemical Technology, F.O. Box 107, Yusung, Taejon 305-600, Korea
Received July 25, 1994

Selective oxidation of cyclohexane in acetonitrile 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 transition series. Iron chloride and iron tetrakis[4-vinylpyridine] porphyrin chloride were supported on four kinds of 4-vinylpyridine copolymer with styrene or divinylbenzene. 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 monoxygenases demands the presence of a catalyst, an electron source and protons, oxygen, and a solvent. Many biomimetic catalysts utilize not only metalloporphyrins but also various iron compounds. The molecular oxygen with electron source and protons can be replaced by various single oxygen transfer reagents such as hydrogen peroxide or iodosobenzene.

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. In addition, supporting a metalloporphyrin often makes the complex be more active through active site isolation that prevents dimerization leading to deactivation.

We have been developing the heterogeneous catalytic systems which are active for the oxidation of cyclohexane under mild conditions. A bimetallic system, silica supported iron oxide and palladium, was previously shown to be efficient for the cyclohexane oxidation using acetone solvent. 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 tetrakis[4-vinylpyridine] porphyrin 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 complex, Fe_{3}^{III}Br,O(OAc)_{3}pyt$_{32}$, was prepared by the isolation method from Gif reaction mixture according to a literature procedure.

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 surface area were 0.3, 0.4, 5.7, and 25.8 m$^2$/g, respectively.

The catalysts supported on PVP were prepared as follows: an iron compound, FeCl$_{3}$$\cdot$4H$_{2}$O (1 g) or Fe(TPP)Cl (0.5 g), and a PVP (5 g) were added to methylene chloride (200 mL) and the mixture was refluxed under nitrogen atmosphere for 2 h. While evaporation of solvent and adequate washing with acetone were carried out in the preparation of PVP-s supported catalysts, filtration and washing with methylene chloride and acetone were carried out in the preparation of PVP-d supported catalysts. The catalysts finally dried in vacuo. The degree of anchoring was determined by atomic absorption analysis of the iron ions remained in the solution for the determination of iron content of FeCl$_{3}$/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 °C for 2 h and calcined at 400 °C for 3 h in an air stream.

Catalyst characterization. A Seiko SEA 2001 X-ray fluorescence (XRF) spectrometer 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$_{3}$/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 a gas bubbler and...
Cyclohexane Oxidation by Bicatalytic System

Table 1. Oxidation of cyclohexane with unsupported metal compounds

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Yield (mole%)</th>
<th>Turnover number (h⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cyclohexanol</td>
<td>Cyclohexane Total</td>
</tr>
<tr>
<td>MnCl₂·4H₂O</td>
<td>0.60</td>
<td>0.60</td>
</tr>
<tr>
<td>FeCl₂·4H₂O</td>
<td>3.62</td>
<td>0.63</td>
</tr>
<tr>
<td>CoCl₂·6H₂O</td>
<td>0.61</td>
<td>0.61</td>
</tr>
<tr>
<td>NiCl₂·6H₂O</td>
<td>1.20</td>
<td>0.22</td>
</tr>
<tr>
<td>CuCl₂·2H₂O</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Mn(TPP)Cl</td>
<td>2.10</td>
<td>0.10</td>
</tr>
<tr>
<td>Fe(TPP)Cl</td>
<td>2.82</td>
<td>0.59</td>
</tr>
<tr>
<td>Co(TPP)</td>
<td>1.64</td>
<td>0.42</td>
</tr>
<tr>
<td>Ni(TPP)</td>
<td>1.18</td>
<td>0.25</td>
</tr>
<tr>
<td>Cu(TPP)</td>
<td>0.96</td>
<td>0.02</td>
</tr>
<tr>
<td>Gif complex</td>
<td>0.55</td>
<td>0.18</td>
</tr>
</tbody>
</table>

*Condition: metal compound, 0.1 g; Pd catalyst, 2 g; cyclohexane, 5 g; acetone, 20 mL; H₂, 20 mL/min; O₂, 20 mL/min; temperature, 30 °C; reaction time, 3 h. *Yields are based on cyclohexane.

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, was also examined, but it is almost ineffective for this reaction.

Table 2 shows the change of Pd 3d₅/₂ BE in the palladium catalyst. The fresh palladium catalyst gives the BE = 337.5 eV which corresponds to PdCl₂. 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 immobilized 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 solvable 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 FeCl₂/PVP catalysts. The pure PVP samples exhibit 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 ls photoelectron spectra of (a) PVP-s, (b) FeCl₂/PVP-d2, (c) PVP-d2, (d) FeCl₂/PVP-d2, (e) PVP-d6, (f) FeCl₂/PVP-d6.

Table 4. Oxidation of cyclohexane with supported iron catalysts

| Catalyst             | Yield (mole%) | Turnover number^
|----------------------|---------------|------------------
|                      | Cyclohexanol  | Cylohexanone     | Total            |
| FeCl₂/PVP-s         | 4.74          | 0.28             | 5.02             | 1.16 |
| FeCl₂/PVP-d2        | 2.81          | 0.77             | 3.58             | 1.20 |
| FeCl₂/PVP-d6        | 2.32          | 0.77             | 3.09             | 1.42 |
| FeCl₂/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                | 0    |
| Fe(TPP)Cl/PVP-d6    | trace         | 0                | 0                | 0    |
| Fe(TPP)Cl/PVP-d24   | 0.26          | 0                | 0.26             | 20.6 |

^
Condition: iron catalyst, 1 g; Pd catalyst, 2 g; cyclohexane, 5 g; acetone, 20 mL; H₂, 20 mL/min; O₂, 20 mL/min; temperature, 30 °C; reaction time, 3 h. Yields are based on cyclohexane. Division of moles of oxidized products per hour by moles of metal ion.

1. 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-

Acknowledgment. We wish to thank Prof. Y. Kurusu for providing PVP-d6 and PVP-d24 polymer samples, Ms. Moonhee Lee Kim for the X-ray photoelectron spectroscopy experiments.

References