

## BIOMIMETIC SOLUBILIZATION OF BROWN COAL BY OXYGENASE MODEL WITH HYDROGEN PEROXIDE

Keiji Miki and Yoshiaki Sato  
Energy Resources Department  
National Institute for Resources and Environment  
16-3, Onogawa, Tsukuba, Ibaraki 305  
Japan

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### INTRODUCTION

As an alternative processing of coal conversion, biosolubilization has been intensively studied[1-4]. Most of the studies in 1980's involve the oxidative solubilization of preoxidized coal or lignite to render the coal water soluble. The products contain primarily polycarboxylic compounds and are suggested to be of lower quality than the materials derived from conventional thermochemical conversion[5]. Thus there has been arguments about the biological processes for the production of alternate fuels or chemicals from coal[6]. Current reductive solubilization of coal under anaerobic conditions could provide more desirable products[7,8]. On the other hand, these biological processes imply a potential route to liquefy coal catalytically under considerably mild conditions. The elucidation of mechanisms involved in the biosolubilization and the application of the catalyst systems in analogous to enzymes or microorganisms may offer an attractive processing for coal conversion.

During the past decade, numerous studies on oxidation reaction catalyzed by synthetic metalloporphyrin have been reported[9]. These catalysts have been synthesized as the models for cytochrome p450 and peroxidase, and some of them exhibit extremely high turn over number in the oxidations of alkenes and alkanes[10,11]. To date the mechanisms of oxidation reactions catalyzed by synthetic metalloporphyrins are fairly well understood and the utilization of the catalyst for the oxidations of various stable compounds is of great interest. Preliminary attempt using a simple iron porphyrin complex for coal conversion, however, did not show a significant effect on the solubilization. In addition, the contamination of catalyst and residual oxidant affected the evaluation of the products. Therefore as the first step, we developed a new supported biomimetic catalyst capable of using hydrogen peroxide as an oxidant. In this paper we describe the solubilization of coal by the oxygenase model, immobilized iron porphyrin catalyst.

### EXPERIMENTAL

#### Preparation of catalyst

A biomimetic model for monooxygenase enzyme was synthesized on a silica surface as the following 5 steps (Fig. 1), based on the detailed design considering the structures of bulky porphyrin and the silica surface[12]. 1) Amorphous silica powder, Aerosil 200, was dispersed in toluene to which 3-mercaptopropyltrimethoxysilane was added. Refluxing overnight and removal of solvent under vacuum yielded the support-anchored silica (a). 2) A was dispersed in pyridine, to which phthalocyaninatoiron (II) was added. The mixture was stirred overnight and the solid collected by filtration. Drying under vacuum gave phthalocyaninatoiron-loaded silica (b). 3) B was dispersed in CH<sub>2</sub>Cl<sub>2</sub>, to which excess dodecyltriethoxysilane was added. After refluxing 48 h with stirring, the container was evacuated, sealed and heated for 24 h at 150-160°C. It was cooled, opened and washed with CH<sub>2</sub>Cl<sub>2</sub> and acetone resulting hydrophobic silica (c). 4) C was subjected to Soxhlet extraction with pyridine for 72 h and yielded iron-free silica (d). 5) D was dispersed in benzene, to which iron tetraphenylporphyrin acetate was added under argon. After refluxing 48 h with stirring, the solid was collected by filtration and washed with CH<sub>2</sub>Cl<sub>2</sub> until the filtrate turn to colorless. The dark green solid obtained (E) had a loading of iron tetraphenylporphyrin complex of  $1.34 \times 10^{-2}$  mmol g<sup>-1</sup>.

#### Solubilization of brown coal

A brown coal (Australian Yallourn coal), ground to <149 μm, dried and stored in a glass ampoule, was used.

The catalyst (1.0-1.5 μmol) and the coal (300 mg) were dispersed in 10 ml of deionized water or acetate buffer (pH 5.0) to which imidazole (1 mmol) and H<sub>2</sub>O<sub>2</sub> (2 mmol) were added. The container was sealed with a septum and shaken at 150 stroke/min at 40°C using a Bio-shaker for 24 h. For anaerobic assays, manipulations were done in a glove box.

After reaction, the mixture was filtrated and extracted with tetrahydrofuran/H<sub>2</sub>O (v/v=4:1) until the filtrate turn to colorless. The filtrate and extract were combined, evaporated and dried at 110°C under vacuum.

## RESULTS AND DISCUSSION

### Catalytic activity of oxygenase model

As mentioned above, from the point of product quality, it is most desirable to mimic enzymes functioning reductive reactions under anaerobic conditions. But the studies on such enzymes involving electron transfer seem to be at an early stage. For that reason we attempted the synthesis of the model for cytochrome P450 monooxygenase.

The active sites, iron tetraphenylporphyrin units, were immobilized by coordinative ligation to anchored mercaptopropyl groups in hydrophobic cavities formed by alkyl chains attached to silica surface. This is the characteristic structure distinguished from other efficient iron porphyrin catalysts (Table 1). When the oxidation reaction is performed in aqueous solution, lipophilic substrates are assumed to condense on the catalyst surface by hydrophobic interactions. Further it inhibits contact between the active center and H<sub>2</sub>O<sub>2</sub>. As the result, the catalytic reaction takes place even with a small amount of substrate without the decomposition of fragile porphyrin structure by H<sub>2</sub>O<sub>2</sub> attack.

The catalytic activity of the synthetic catalyst was clarified by the epoxidation of alkenes. In the presence of externally added imidazole, the substrates were efficiently epoxidized (Table 2). Although the iron center have an axial sulfur ligand in the same manner as native enzyme, the promotion of heterolytic cleavage of H<sub>2</sub>O<sub>2</sub> by general catalyst seems to be required. Thus the following coal solubilization reactions were carried out in the presence of imidazole.

### Solubilization of brown coal

It has been reported that coal reacts rapidly with H<sub>2</sub>O<sub>2</sub> in the study on the coal solubilizing activity of horseradish peroxidase[13]. H<sub>2</sub>O<sub>2</sub> is known to decompose at a higher pH, but a lower pH may favor hydrolysis reaction of coal. Further the aqueous buffers contaminate the residue in the concentrated solubles. Hence controls were always run and deionized water was mainly used in the coal solubilization experiments. As shown in Table 3, a considerable amount of soluble fraction was obtained after the treatment with H<sub>2</sub>O<sub>2</sub> or H<sub>2</sub>O<sub>2</sub>/imidazole in the absence of the catalyst. The yields seem to be strongly affected by the presence of oxygen and imidazole.

The results indicate clearly the effect of catalyst addition in every series of experiments. The presence of 1 μmol catalyst increased in conversion by 10-15% under aerobic conditions. Anaerobic assay required a slightly larger amount of catalyst to obtain the similar conversion. No appreciable effect on the solubilization was found in the absence of imidazole.

Elemental analyses showed high nitrogen contents in the products derived from imidazole-added runs. There was a difficulty in removing it completely even by prolonged vacuum drying at 110°C. Therefore the correction of elemental compositions was made for the evaluation of oxygen incorporation. The amount of imidazole in the product was calculated from the excess of nitrogen, assuming that the nitrogen content equals that in imidazole-free control. The results showed the remains corresponding to about a half of initially added imidazole. Recalculated elemental compositions from the data were shown in Table 4. The catalytic treatment caused a decrease in carbon content and an increase in oxygen content. The change is not so drastic as seen in the oxidative microbial conversion. As the result, the solubilization reaction does not involve the introduction of a high concentration of carboxylic acid. The assumption is also supported by FT-IR analysis which reveals the decrease in the relative intensity of carbonyl band to aromatic band by the catalyst addition compared with that from control. Further no aromatic acid derivative is detected in the catalytic oxidations of various model compounds.

At present further detailed studies are in progress to explore the function of biomimetic model in connection with the solubilization reaction of coal, including the capability of catalytic carbon-carbon bond scission.

## CONCLUSION

A biomimetic model for monooxygenase enzyme was synthesized and utilized for the solubilization of brown coal. In the presence of imidazole as a general catalyst and H<sub>2</sub>O<sub>2</sub> as an oxidant, it was suggested that the model catalyzed the solubilization reaction of coal. This is partly due to the characteristic nature of the model in addition to the catalytic activity.

#### REFERENCES

1. Cohen, M.S., and Gabriele, P.D., *Appl. Environ. Microbiol.*, **1982**, 44, 23-27
2. Couch, G.R., "Biotechnology and Coal", **1987**, IEA Coal Research, London
3. Cohen, M.S., Bowers, W.C., Aronson, H., and Gray, Jr., E.T., *Appl. Environ. Microbiol.*, **1987**, 53, 2840-2843
4. Pyne, Jr., J.W., Stewart, D.L., Fredrickson, J., and Wilson, B.W., *Appl. Environ. Microbiol.*, **1987**, 53, 2844-2848
5. Wilson, B.W., Bean, R.M., Franz, J.A., and Thomas, B.L., *Energy & Fuels*, **1987**, 1, 80-84
6. Narayan, R., and Ho, N.Y., *Am. Chem. Soc., Div. Fuel Chem. Prepr.*, **1988**, 33, 487-495
7. Jain, M. K., Burgdorf, D., and Narayan, R., *Fuel*, **1991**, 70, 573-576
8. Scott, C.D., Faison, B.D., Woodward, C.A., and Brunson, R.R., *1991 Second International Symposium on the Biological Processing of coal*, **1991**, EPRI, Palo Alto, CA, 4-5-4-22
9. Meunier, B., *Chem. Rev.*, **1992**, 92, 1411-1456
10. Traylor, P.S., Dolphin, D., and Traylor, T.G., *J. Chem. Soc., Chem. Commun.*, **1984**, 279-280
11. Traylor, T.G., Tsuchiya, S., Byun, Y-S., and Kim, C., *J. Am. Chem. Soc.*, **1993**, 115, 2775-2781
12. Miki, K., and Sato, Y., *Bull. Chem. Soc. Jpn.*, **1993**, 66, 2385-2390
13. Quigley, D.R., Breckenridge, C.R., Polman, J.K., and Dugan, P.R., *Fuel*, **1991**, 70, 581-583

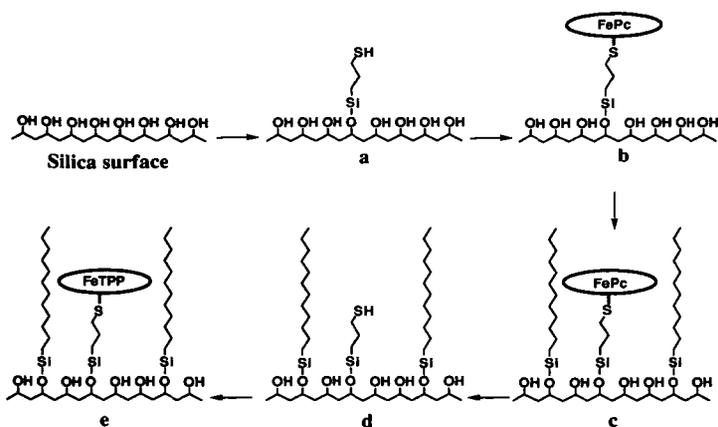


Fig. 1 Synthetic pathway of oxygenase model

Table 1. Structure and reaction system of oxygenase model and efficient iron porphyrin catalyst

active center	reaction site	axial ligand	oxidant	medium	reference
<u>oxygenase model</u>					
FeTPPOAc <sup>a)</sup>	highly hydrophobic	immobilized alkyl thiol	H <sub>2</sub> O <sub>2</sub>	H <sub>2</sub> O	this work
<u>efficient iron porphyrin catalyst</u>					
FeTDCPPCI <sup>b)</sup>	—	imidazole	H <sub>2</sub> O <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub> /CH <sub>3</sub> CN	9
FeTDCPPCI	—	—	C <sub>6</sub> H <sub>5</sub> IO C <sub>6</sub> F <sub>5</sub> IO	CH <sub>2</sub> Cl <sub>2</sub> /MeOH	10
FeTPFPCCI <sup>c)</sup>	—	—	H <sub>2</sub> O <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub> /MeOH	11

a) Iron tetraphenylporphyrin acetate. b) Iron tetrakis(2,6-dichlorophenyl)porphyrin chloride. c) Iron tetrakis(pentafluorophenyl)porphyrin chloride.

Table 2. Oxidation of alkene with immobilized iron porphyrin and hydrogen peroxide<sup>a)</sup>

run	atmosphere	substrate	product <sup>b)</sup>	
			oxide	aldehyde
1	aerobic	<i>trans</i> - $\beta$ -methylstyrene	125	154
2	anaerobic	<i>trans</i> - $\beta$ -methylstyrene	98	45
3	aerobic	<i>cis</i> -stilbene	30	7
4	anaerobic	<i>cis</i> -stilbene	31	5
5	aerobic	<i>cis</i> -cyclooctene	49	-
6	anaerobic	<i>cis</i> -cyclooctene	42	-

a) Alkene / H<sub>2</sub>O<sub>2</sub> / imidazole / catalyst = 0.4 mmol / 0.4 mmol / 0.2 mmol / 4mmol in 2ml H<sub>2</sub>O at 40° C for 17h. b) Yield based on equivalents of catalyst used.

Table 3. Solubilization of Yallourn coal with immobilized iron porphyrin and hydrogen peroxide<sup>a)</sup>

run	catalyst ( $\mu\text{mol}$ )	imidazole (mmol)	H <sub>2</sub> O <sub>2</sub> (mmol)	conversion (%)
1-1	0	0	2	51
1-2	0	1	2	23
1-3	1.0	1	2	66
2 <sup>b)</sup> -1	0	0	2	26
2-2	0	1	2	41
2-3	1.0	1	2	44
2-4	1.5	1	2	53
3 <sup>c)</sup> -1	0	0	2	44
3-2	0	1	2	46
3-3	1.0	1	2	56

a) Yallourn coal (300mg) was treated in deionized water (10ml) at 40°C for 24 h. b) Under argon. c) In 200 mM acetate buffer at pH 5.0.

Table 4. Elemental analysis of solubilization product<sup>a)</sup>

run	elemental analysis					
	C	H	N	O+S	H/C	O/C
original coal	64.2	4.9	0.7	30.2	0.91	0.35
1-1 <sup>b)</sup>	59.7	4.9	1.1	34.4	0.97	0.43
1-2	59.4	4.6	1.1	35.0	0.93	0.44
1-3	60.0	4.5	1.1	34.4	0.90	0.43
2-1	59.9	5.0	1.2	34.0	1.00	0.43
2-2	60.0	4.7	1.2	34.2	0.93	0.43
2-3	60.2	4.6	1.2	34.2	0.91	0.43
2-4	60.3	4.6	1.2	34.0	0.92	0.42

a) Corrected data (Refer to text). b) Run number is the same in Table 2.