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CHARACTERIZATION OF ZEOLITE-ENCAPSULATED IRON PHTHALOCYANINES AND BUTADIENE HYDROGENATION CATALYZED BY THEIR ELECTRON DONOR-ACCEPTOR COMPLEXES WITH SODIUM

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NaY zeolite-encapsulated iron phthalocyanine (FePc) was synthesized from $[HFe_3(CO)_{11}]^-$ in NaY. The structural properties of FePc in NaY were studied by EXAFS, Mössbauer, FT-IR, and diffuse reflectance UV-VIS. The spectroscopic results suggest that NaY-encapsulated FePc (FePc/NaY) is slightly distorted from the original planar structure of a phthalocyanine molecule due to the intrazeolitic constraint. Electron donor-acceptor (EDA) complex $(Na^+)_4(FePc^{4-})$/NaY was prepared from FePc/NaY by the reaction with sodium-naphthalene $(Na^+)(C_{10}H_8^-)$. They gave a higher trans/cis ratio of 2-butenes in butadiene hydrogenation compared with the EDA complex on the external surface of NaY.

1. Introduction

"Ship-in-a-bottle" synthesis of metal complexes inside zeolite cages has gained growing attention for the purpose of obtaining the catalytically active precursors surrounded with configurationally constrained circumstances [1,2]. The zeolite framework may impose shape selectivity in metal-catalyzed reactions due to the limitation of size against in-coming reactant molecules [3–10].

Metallophthalocyanine complexes [11] and their electron donor-acceptor complexes have been extensively studied as biological analogues such as chlorophylls and hemoglobins. They are applied to catalytic reactions such as sulfur oxidation, hydrocarbon oxidation, and hydrogenation of olefin, CO, and N_2 [12,13].

Recently, Romanovsky [14] reported the intrazeolitic preparation of Co phthalocyanines, and Herron et al. [5] have used Fe phthalocyanines in NaX as catalysts in the hydroxylation of alkanes.

We have synthesized iron phthalocyanine (FePc) inside NaY zeolite from the precursor of Fe carbonyl cluster, and characterized it by means of XANES, EXAFS, ^{57}Fe Mössbauer, FT-IR, and diffuse reflectance UV-VIS. In this communication, the distortion of an FePc molecule in NaY cage is discussed in terms of the intrazeolitic constraint. Additionally, electron donor-acceptor (EDA) complexes of FePc, $(Na^+)_4(FePc^{4-})$, were prepared and their catalytic behaviors in butadiene hydrogenation were investigated.

2. Experimental

$[HFe_3(CO)_{11}]^-$ in NaY (pale pink) was presynthesized from $Fe_2(CO)_9$ (0.25 mmol) and powdered NaY (Linde LZ-Y52, 1 g, dehydrated under vacuum at 593 K for 2 h) [15]. $[HFe_3(CO)_{11}]^-$ formed on the external surface of NaY was removed by washing with a tetraglyme solution of bulky alkyl ammonium halides such as $[N(n\text{-}C_6H_{13})_4]Br$ and $[NMe_3(CH_2Ph)]Cl$. A trace amount of $[HFe_3(CO)_{11}]^-$ salts was recovered in the extracted solution. $[HFe_3(CO)_{11}]^-$/NaY was subsequently oxidized in air at room temperature for 50 h, followed with the reduction in H_2 flow at 423 K for 12 h. The reduced sample was reacted with 1, 2-dicyanobenzene (2 mmol) in a sealed glass tube under vacuum at 573–583 K for 50 h [16], resulting in the formation of FePc in NaY. Unreacted 1,2-dicyanobenzene was removed by sublimation at 573–583 K. FePc formed on the external surface of NaY was also removed as phthalocyaninebis(pyridine)iron(II) by Soxhlet extraction with pyridine for 24 h. The crude product was washed with hot ether and acetone, and the intrazeolitic FePc in NaY (FePc/NaY, green-blue powder) was obtained after drying in vacuo. FePc on NaY external surface (FePc + NaY) was independently prepared by the impregnation of FePc on NaY from the pyridine solution of FePc (purchased from Tokyo Kasei Kogyo Co., Ltd., purified by sublimation at 673 K). Pyridine was eliminated by evacuation at 473 K for 2 h. The total loading of Fe in FePc/NaY and FePc + NaY was ca. 0.6 wt%.

NaY-encapsulated EDA complex $(Na^+)_4(FePc^{4-})$/NaY (blue-green) was stoichiometrically prepared by the reaction of FePc/NaY with an excess amount of sodium-naphthalene $(Na^+)(C_{10}H_8^-)$ [17] in 1, 2-dimethoxyethane (DME) at room temperature [13] under N_2. After removal of DME and residual naphthalene by evacuation, the resulting sample was transferred in a U-type glass reactor under N_2.

XANES and EXAFS were conducted at BL-10B in the Photon Factory of the National Laboratory for High Energy Physics (KEK-PF). ^{57}Fe Mössbauer spectra were recorded with a Shimadzu MEG-2 spectrometer. Isomer shifts were given relative to α-Fe. Infrared spectra were recorded by a Shimadzu Fourier-transform infrared spectrometer (FTIR-4100) with a resolution of 2 cm^{-1}. Diffuse reflectance UV-VIS spectra were obtained on a Hitachi 330 spectrophotometer.

Hydrogenation of butadiene was carried out over the EDA complexes of FePc/NaY (0.75 g) at 373 K and 250 Torr ($C_4H_6/H_2 = 1$) in a closed circulating

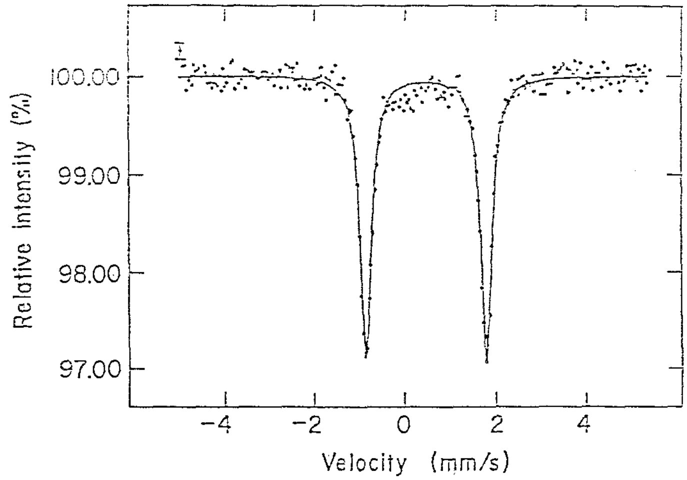


Fig. 1. ^{51}Fe Mössbauer spectrum of FePc/NaY at 78 K.

system (250 ml). Reaction gases were analyzed by TCD-GC using a Sebaconitrile column (10 m, 273 K).

3. Results and discussion

Figure 1 shows the Mössbauer spectrum of NaY-encapsulated FePc/NaY at 78 K, and the Mössbauer parameters for FePc/NaY, external FePc + NaY, and FePc crystalline are summarized in table 1. The Fe precursor in NaY reacted with 1, 2-dicyanobenzene to be converted into iron phthalocyanine without any other residual species of iron. No appreciable difference was observed for *I.S.* and *Q.S.* values between the internal and external FePc, indicating that the electronic states of Fe in FePc/NaY are basically the same as those in FePc + NaY and FePc crystalline. Interestingly, the temperature dependence of recoil-free fraction of FePc/NaY suggests that FePc is uniformly dispersed in NaY [18].

XANES data for FePc/NaY also support the formation of FePc; a sharp peak appeared at 7110 eV due to 1S–4pπ^* transition characteristic of FePc.

Table 1
^{57}Fe Mössbauer parameters for FePc/NaY, FePc+NaY, and FePc. [a]

Sample	*I.S.* [b] (mm/sec)	*Q.S.* [c] (mm/sec)
FePc/NaY	0.48	2.65
FePc+NaY	0.49	2.65
FePc	0.49	2.67

[a] Temperature 78 K.

[b] Isomer shift relative to α-Fe.

[c] Quadrupole splitting.

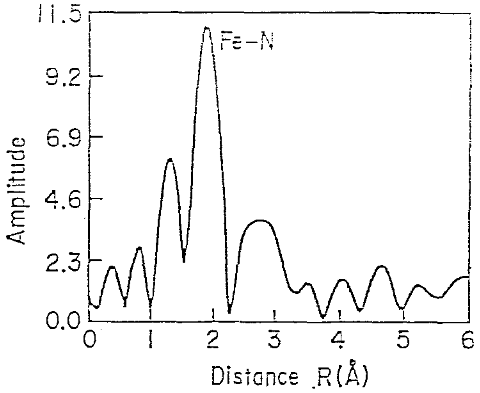


Fig. 2. Fourier transform of $k^3\chi(k)$ for FePc/NaY.

Figure 2 shows the Fourier transform of k^3-weighted EXAFS $\chi(k)$ for FePc/NaY with a phase shift correction [19]. The main peak at 1.8 Å is attributed to the first neighbor Fe-N interaction by the curve-fitting analysis. As shown in table 2, FePc/NaY gave a smaller coordination number (*C.N.*) and a longer interatomic distance (R) for the Fe-N bonding compared with those for FePc + NaY and FePc crystalline. The results suggest that an iron atom in FePc/NaY is slightly out of the phthalocyanine ring. This is reflected in the difference of Debye-Waller type factor ($\Delta\sigma^2$) for FePc/NaY, which was larger than for FePc + NaY, possibly due to the distortion of a phthalocyanine ring caused by the encapsulation of an FePc molecule (13 Å diameter) inside a NaY supercage (13 Å diameter).

The diffuse-reflectance UV-VIS spectrum of FePc/NaY shows large shifts of B-band (320 and 380 nm) and Q-band (560 and 620 nm) based on a π–π^* transition [20], compared with those for FePc + NaY and FePc. In addition, the absorbance of the Q-bands for the FePc/NaY considerably suppressed. The results also support a steric hindrance around the FePc ring induced by the intrazeolitic constraint.

Table 2
The results of curve-fitting analysis for the first neighbor Fe-N of FePc/NaY, FePc+NaY, and FePc.

Sample	*C.N.* [a]	R [b] (Å)	$\Delta\sigma^2$
FePc/NaY	3.6	1.84	-1.20×10^{-3}
FePc+NaY	4.0	1.83	-0.47×10^{-3}
FePc	4.0	1.83	0.00

[a] *C.N.*: coordination number
[b] R: interatomic distance,
$\Delta\sigma$: Debye-Waller type factor.

Table 3
Catalytic butadiene hydrogenation by NaY-encapsulated FePc-EDA complexes. [a]

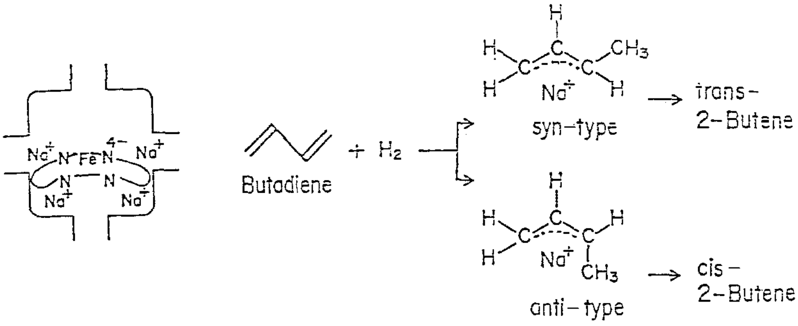
Catalyst	C_4H_6 conv. (%)	Product selectivity (%)				trans/cis ratio of $2\text{-}C_4H_8$
		C_4H_{10}	$1\text{-}C_4H_8$	trans-2-C_4H_8	cis-2-C_4H_8	
$(Na^+)_4(FePc^{4-})$/NaY	6	11	53	20	16	1.3
$(Na^+)_4(FePc^{4-})$+NaY	5	4	21	26	49	0.5

[a] Reaction temperature 373 K, initial pressure 250 Torr (C_4H_6:H_2 = 1:1) at room temperature, catalyst 750 mg, reaction time 10 h.

IR spectra for FePc/NaY had the absorption bands associated with C=N and C=C stretchings of Pc ring, and they are shifted to lower frequencies for the intrazeolitic FePc/NaY (1509ms and 1493w cm^{-1}) relative to the external FePc + NaY (1516ms and 1495w cm^{-1}) [21]. Romanovsky suggested that cobalt phthalocyanine in NaX was protonated by strong acids on the wall of supercages to give band shifts in UV-VIS [14]. However, we could not observe the bands of protonated FePc in the IR spectra. Consequently, the band shifts and intensity changes in UV-VIS and IR are not explained by a simple protonation of FePc in NaY, but by the intrazeolitic constraint of the phthalocyanine ring. According to these spectroscopic data, it is likely that FePc is highly dispersed and encapsulated inside a zeolite cage, and that the phthalocyanine ring is distorted.

EDA complexes $(Na^+)_n(FePc^{n-})$ (n = 1–4) in DME solutions were studied by UV-VIS with the characteristic colors; red (n = 1), blue-violet (n = 2), violet (n = 3), blue-green (n = 4), similarly as reported [22]. The NaY-encapsulated EDA complex prepared in this work was blue-green, suggesting the formation of $(Na^+)_4(FePc^{4-})$ in NaY.

Hydrogenation of butadiene was performed over the EDA complexes of FePc/NaY and FePc + NaY, and the results are summarized in table 3. The precursors FePc/NaY and FePc + NaY themselves exhibited no activity in this reaction. Interestingly, $(Na^+)_4(FePc^{4-})$/NaY showed a higher trans/cis ratio of 2-butene at the 6% conversion of butadiene. The external $(Na^+)_4(FePc^{4-})$ + NaY gave cis-2-butene as a major product (trans/cis = 0.5). At the lower conversion of butadiene, the trans/cis ratio was larger over the intrazeolitic EDA complex of FePc (trans/cis = 2.3). In the hydrogenation of butadiene over EDA complexes of sodium and anthracene $(Na^+)_2$ (anthracene^{2-}), equal amounts of trans- and cis-2-butene were produced [23]. It is proposed that H_2 is heterolytically dissociated and butadiene hydrogenation occurs at the aromatic polyanion with a sodium cation. 1, 4-addition of H^- and H^+ to butadiene is suggested via a π-allyl intermediate on the EDA complexes (scheme 1), similarly on the typical basic oxide catalysts such as ZnO and MgO. Generally, an anti-type of π-allyl intermediates is favorable on the basic catalysts to give high selectivity for cis-2-butene [13]. In contrast, the intrazeolitic $(Na^+)_4(FePc^{4-})$ complex catalyzes



Scheme 1.

high trans-2-butene formation in the hydrogenation of butadiene. This could be explained by the configurational circumstance which are considerably crowded with the distorted phthalocyanine ring and Na cations inside NaY cages. The isomerization of butenes proceeded at a negligible rate on $(Na^+)_4(FePc^{4-})$ under the reaction conditions. Consequently, trans-2-butene is produced through a syn-type of π-allyl intermediates having a smaller cross section.

$(Na^+)_4(FePc^{4-})$/NaY was oxidized by exposure to the air. The resulting sample showed no activity in the butadiene hydrogenation. This fact and the no activity on FePc/NaY indicate that the catalytic reactions were proceeded over the EDA complexes, and that the acidity and basicity of zeolite has little influence on this reaction under the reaction conditions.

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