

Oxidation of Benzene with Hydrogen Peroxide over Iron-Bipyridine Complexes Encapsulated in Metal Cation-Exchanged Zeolite

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Direct hydroxylation of hydrocarbons is one of very difficult oxidations. We have reported that the selective hydroxylation of cyclohexene with H_2O_2 in water solvent was successfully achieved using $[\text{Fe}(\text{bpy})_3]^{2+}$ complexes encapsulated into Y-type zeolite ($[\text{Fe}(\text{bpy})_3]^{2+}@\text{Na-Y}$) [1, 2]. This catalyst also exhibited the catalytic activity for oxidation of benzene to phenol as a main product [3]. In this study, iron complexes encapsulated in zeolite with different counter cation ($[\text{Fe}(\text{bpy})_3]^{2+}@\text{M-Y}$, $\text{M} = \text{Na}^+$, K^+ , Cs^+ , Mg^{2+} , or Ca^{2+}) were prepared and their catalytic activities for oxidation of benzene with hydrogen peroxide in H_2O solvent were investigated.

$[\text{Fe}(\text{bpy})_3]^{2+}@\text{M-Y}$ catalysts were prepared by using the corresponding metal nitrate, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, and bipyridine. The obtained compound was characterized by ICP, CHN elemental analysis, TG-DTA, XRD, UV-vis and FT-IR. As a model reaction for evaluating the catalytic activity, the partial oxidation of benzene was carried out. Each catalyst (7.9 μmol Fe atoms in catalyst), benzene (7.9 mmol), 30% H_2O_2 (7.9 mmol), and water (10 mL) were stirred at 50 °C under Ar. The product yield was determined periodically by GC analysis.

The formation of $[\text{Fe}(\text{bpy})_3]^{2+}$ complexes into supercages of zeolite Y was confirmed by the following experimental results; (1) XRD and FT-IR results suggested that structure of zeolite Y was maintained, (2) UV-vis, FT-IR, ICP, and CHN results suggested that $[\text{Fe}(\text{bpy})_3]^{2+}$ ($\text{Fe} : \text{bpy} = 1 : 3$) complexes were formed and approximately one $[\text{Fe}(\text{bpy})_3]^{2+}$

complex per two supercages in zeolite was containing in $[\text{Fe}(\text{bpy})_3]^{2+}@\text{Y}$, and (3) XRD, TG-DTA, and UV-vis results suggested that $[\text{Fe}(\text{bpy})_3]^{2+}$ complex ions were located within the supercages in Y-type zeolite frameworks [1, 2].

Figure 1 shows the catalytic activities for oxidation of benzene over $[\text{Fe}(\text{bpy})_3]^{2+}@\text{M-Y}$ catalysts. Phenol was obtained as the major product in the case of any catalysts. Catalytic activity of $[\text{Fe}(\text{bpy})_3]^{2+}@\text{M-Y}$ catalyst with monovalent metal cation (M^+) increased in the following order: $[\text{Fe}(\text{bpy})_3]^{2+}@\text{Na-Y} < [\text{Fe}(\text{bpy})_3]^{2+}@\text{K-Y} < [\text{Fe}(\text{bpy})_3]^{2+}@\text{Cs-Y}$. For the catalysts with divalent metal cation (M^{2+}), the catalytic activity of $[\text{Fe}(\text{bpy})_3]^{2+}@\text{Ca-Y}$ was higher than that of $[\text{Fe}(\text{bpy})_3]^{2+}@\text{Mg-Y}$. The hydrated ionic radii of monovalent and divalent metal cations increased in the following orders: $\text{Cs}^+ < \text{K}^+ < \text{Na}^+$ and $\text{Ca}^{2+} < \text{Mg}^{2+}$, respectively. Thus, it was found that the catalytic activity of $[\text{Fe}(\text{bpy})_3]^{2+}@\text{M-Y}$ increases with decreasing hydrated ionic radius of corresponding metal cations.

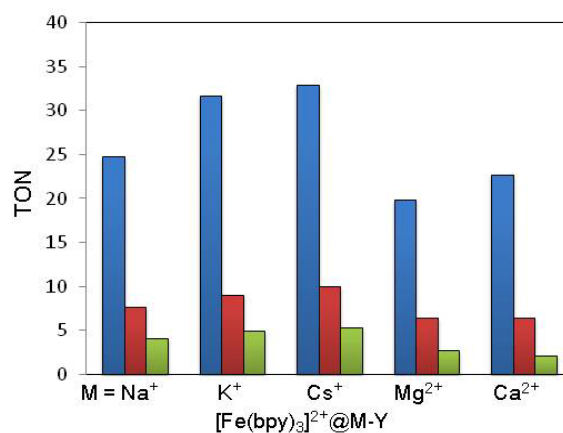


Fig.1 Oxidation of benzene with H_2O_2 over $[\text{Fe}(\text{bpy})_3]^{2+}@\text{M-Y}$ ($\text{M} = \text{Na}^+$, K^+ , Cs^+ , Mg^{2+} , and Ca^{2+}). Blue: phenol, red: catechol, and green: hydroquinone.

Reaction condition: catalyst ($\text{Fe} = 7.9 \mu\text{mol}$), benzene (7.9 mmol), 30% H_2O_2 (7.9 mmol), water (10 mL), 50 °C, 24 h, and in Ar.

REFERENCES

- [1] S. Yamaguchi, T. Fukura, C. Fujita, H. Yahiro, Chem. Lett., 41 (2012) 713.
- [2] S. Yamaguchi, T. Fukura, K. Takiguchi, C. Fujita, M. Nishibori, Y. Teraoka, H. Yahiro, Catal. Today, 242 (2015) 261.
- [3] S. Yamaguchi, T. Ohnishi, Y. Miyake, H. Yahiro, Chem. Lett., 44 (2015) 1287.