Selective Hydroxylation of Cyclohexene in Water Solvent with Hydrogen Peroxide Using Fe-Bipyridine Complexes Encapsulated in Y-Type Zeolite

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Encapsulation of transition metal complexes into zeolites has been attracted much interest for the development of the catalysts combining the advantages of homogeneous and heterogeneous catalysts. Fe(bpy)$_3^{2+}$ complexes encapsulated into Na-Y ([Fe(bpy)$_3^{2+}$]@Y) have been reported as a heterogeneous oxidation catalyst [1,2]. However there is less information about the activity of [Fe(bpy)$_3^{2+}$]@Y catalyst for selective oxidation with hydrogen peroxide as a oxidant. In this report, [Fe(bpy)$_3^{2+}$]@Y was characterized by several methods and its catalytic activity for oxidation of cyclohexene with hydrogen peroxide and solvent effects for that oxidation were investigated.

Fe ion-exchanged Y-type zeolite (Fe-Y) was prepared from Na-Y with FeSO$_4$ solution. [Fe(bpy)$_3^{2+}$]@Y was obtained by the reaction of Fe-Y with bipyridine (bpy). This compound was characterized by several methods. As a model reaction for evaluating the catalytic activity, the partial oxidation of cyclohexene was carried out. Each catalyst (7.9 µmol Fe atoms in catalyst), cyclohexene (7.9 mmol), 30% H$_2$O$_2$ (65 µL, 0.8 mmol), and solvent (acetonitrile (10-x mL) and water (x mL)) were stirred at 50 °C under Ar. The yield was determined periodically by GC analysis.

Figure 1 shows the effect of water addition to CH$_3$CN with [Fe(bpy)$_3^{2+}$]@Y and [Fe(bpy)$_3$](ClO$_4$)$_2$ catalysts. In the case of CH$_3$CN as solvent (x = 0 mL, Fig. 1), the selectivity to 2-cyclohexene 1-ol for [Fe(bpy)$_3^{2+}$]@Y-catalyzed oxidation of cyclohexene was found to be ca. 90%, which was much higher than that for [Fe(bpy)$_3$](ClO$_4$)$_2$ catalyst. The catalytic activity of [Fe(bpy)$_3$](ClO$_4$)$_2$ gradually decreased with increasing the amount of water added (Fig. 1b), while the catalytic activity of [Fe(bpy)$_3^{2+}$]@Y hardly decreased (Fig. 1a). It should be noted that TON of 2-cyclohexene 1-ol over [Fe(bpy)$_3^{2+}$]@Y in water solvent (x = 10 mL) was about five times larger than that over [Fe(bpy)$_3$](ClO$_4$)$_2$. This result demonstrated that [Fe(bpy)$_3^{2+}$]@Y catalyst exhibited both higher activity and higher selectivity to 2-cyclohexene 1-ol in water solvent than another our tested Fe catalysts. This result is very important from the viewpoint of green chemistry because H$_2$O is an environment-friendly solvent.

REFERENCES


Fig. 1 Effect of water addition into solvent for catalytic activity of (a) [Fe(bpy)$_3^{2+}$]@Y and (b) [Fe(bpy)$_3$](ClO$_4$)$_2$. (■): 2-cyclohexene 1-ol, (○): cyclohexene oxide, (▲): cyclohexene 1-ol, (●): cyclohexene oxide. TON = (product [mol]) / (Fe atoms in catalyst [mol]).