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Zeolite Y encapsulated Cu (II) and Zn (II)-imidazole-salen catalysts for benzyl alcohol oxidation

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ABSTRACT

To mimic biological enzyme in catalysis, metal-imidazole-salen complexes were proposed (via DFT calculation) and synthesized *in situ* within the cavities of Y zeolite. Among the synthesized zeozymes, the Cu-salenIIY exhibited a prominent catalytic efficiency for the selective oxidation of benzyl alcohol. Specifically, the activity and selectivity of the encapsulated catalyst were comparable to those of the free Cu-salenII complex in solution. Furthermore, the high activity and selectivity were preserved during the repeated cycles. The similarity in the initial activity implies that the Cu-salenII complex just resides in the cavity of the zeolite Y, and its intrinsic properties responsible for the catalytic activity keep intact after encapsulation. The confinement of zeolite nanocavities effectively inhibited the dimerization or aggregation of the Cu-salenII complex and prevented the active species from escaping into reaction solution, thus resulting in a remarkably improved in the catalytic reusability and durability.

1. Introduction

The design and development of environmentally benign catalytic process is of perennial importance. Transition metal complexes have attracted enormous attention over the past few decades [1–3], due to their unique structural, physio-chemical properties and catalytic behaviors under mild reaction conditions. Of particular interest is metal-salen complex having unsaturated coordination sites in the axial direction, which has been employed as dioxygen activating catalysts mimicking catalase and superoxide dismutase [4–6]. However, the neat metal-salen complexes suffer from the inherent disadvantages associated with homogeneous catalysts and are prone to deactivation due to the occurrence of molecular dimerization in solution. These drawbacks hinder the large-scale industrial application despite of the high activity of metal-salen complexes [7–11]. To overcome the limitation, immobilization of the metal-salen complexes on a non-toxic and recyclable support is essential.

Inspired by the structure of enzyme, worldwide efforts have been made to encapsulate the metal complexes into porous materials [12–15], mimicking the characteristics of enzyme. Y zeolites have been considered as one of the most promising host matrices for encapsulation of Metal-salen complexes since the channels and cages in Y zeolites are similar to those created by the protein structure of natural enzyme [16–18]. In recent years, a series of zeolite Y-encapsulated metal-salen complexes have been successfully synthesized and employed as catalysts for many reactions [19–23]. In most cases, these encapsulated complexes with an enzyme-like structure showed intriguing catalytic behavior that can hardly be achieved by homogeneous system or conventional heterogeneous system, which motivates the development of zeozyme catalysts and catalytic innovation [24–26]. Intensive research in the area continues in two aspects: 1) the rational design and fabrication of transition metal complexes having suitable geometry and electronic properties via tailoring ligands [27–29], and 2) the development and optimization of encapsulation technologies [30,31].

As an effort in exploring the catalytic applications of zeozymes, metal-imidazole-salen complexes were designed by the aid of density functional theory (DFT) calculation. The complexes were synthesized and encapsulated in zeolite cages by a flexible ligand method, followed by the catalytic evaluation in the selective oxidation of benzyl alcohol. The influence of the intrinsic and extrinsic properties of immobilized active metal complexes on their catalytic behaviors were also discussed. The goal of this work is to develop a novel enzyme-like catalyst with high activity, selectivity and recyclability.

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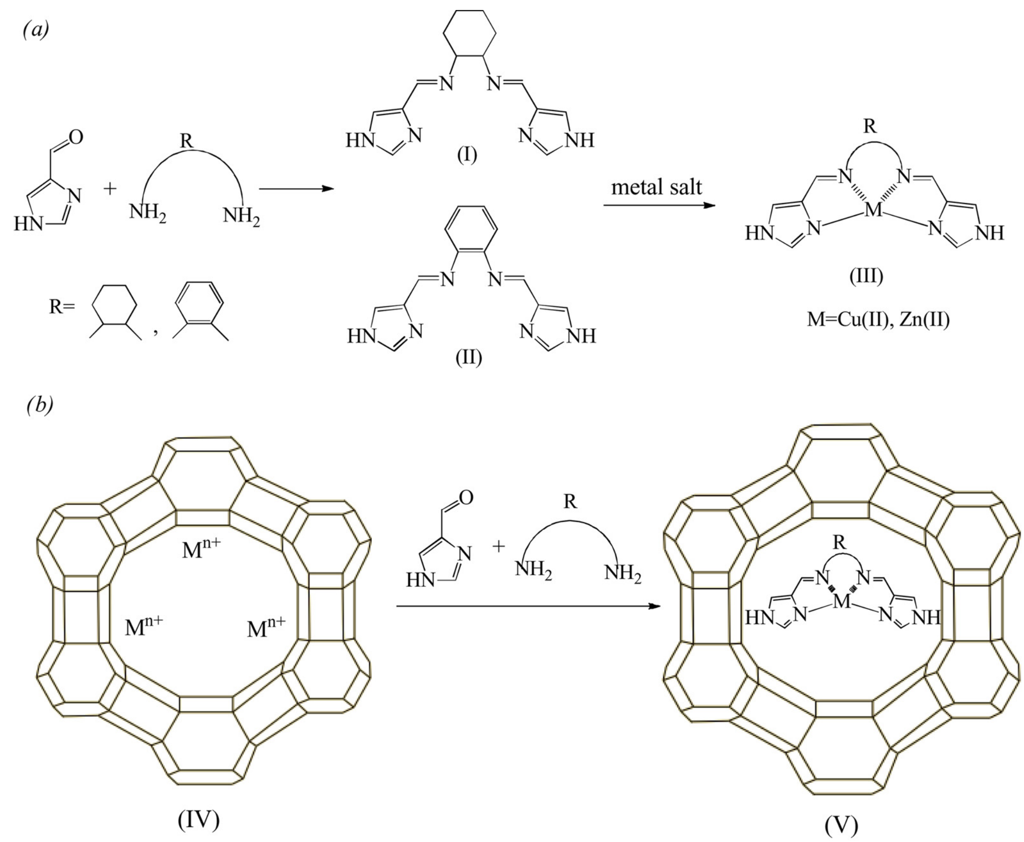

(I) salenI
(II) salenII
(III) Metal-salen complexes (Metal=Cu, Zn)
(IV) MY (metal-exchanged Y zeolite)
(V) M-salenY (Zeolite-encapsulated metal salen complexes)

Scheme 1. Schematic of zeolite encapsulated Metal-salen complexes.

2. Experiments

2.1. Density functional theory calculation

The geometry optimization was carried out using density functional theory (DFT) calculation with the B3LYP functional [32–35], as implemented in the Gaussian 09 suite of programs [36,37]. The effective core potentials (ECPs) of Hay and Wadt with a double-ζ valence basis set (LanL2DZ) were used in describing Cu and Zn [38–40], whereas the 6-31G* basis set was used for all other atoms. The electron distribution and transfer mechanism are determined using the Mulliken method [41] The spin of Cu-salen is double duo to single electron of *d* orbital of Cu^{2+}, while the spin of Zn-salen was single, because of the full-filled *d* orbital of Zn^{2+}.

2.2. Materials

NaY zeolite (Si/Al = 2.4, 200 mesh) was purchased form Nankai University (Tianjin, China), 1H-imidazole-4-carbaldehyde (98%) from Maya Reagent Co. 1,2-Diaminocyclohexane (98%) and *o*-phenylenediamine (98%) were supplied by Aladdin Reagent Co. Benzyl alcohol (99%), hydrogen peroxide (30%), $Cu(NO_3)_3{\cdot}3H_2O$ (99%) and $Zn(CH_3COO)_2$ (99%) were obtained from Adamas Reagent Co. All the chemicals were used without further treatment.

2.3. Characterization

IR spectra were recorded using a Thermo Nicolet Magna IR 750 Spectrometer with a 4 cm^{-1} resolution in the range of 400–4000 cm^{-1} after the samples were mixed with KBr and pressed into tablets. Powder X-ray diffraction (XRD) patterns were obtained on a Bruker D8 Advance diffractometer equipped with Cu-Kα radiation (λ = 0.15418 nm) in the 2θ angles range between 4°~40° (step size: 0.02°, step time: 1 s). Nitrogen adsorption–desorption isotherms were measured with a Micromeritics ASAP 2020 system at liquid N_2 temperature. Before measurement, the samples were outgassed at 130 °C for 6 h. BET specific surface areas were calculated using the Barrett–Emmett–Teller (BET) method. Metal content was measured on a Shimazu ICPE-9000 inductively coupled plasma atomic emission spectrometer (ICP-AES) after the sample was treated by concentrated hydrofluoric acid. Thermogravimetric analyses (TGA) were obtained on a Shimazu TGA-50H analyzer in N_2 atmosphere in the temperature range of 353–973 K with a heating rate of 10 K min^{-1}. The TGA curves were normalized by gravimetric method. Elemental analysis of C, H and N was performed with a Perkin-Elmer 2400 apparatus. UV–vis spectra were recorded on a Lambda 950 spectrophotometer. The UV–vis spectra of zeolite-based samples were recorded in diffuse reflectance mode (DR).

2.4. Synthesis of metal-salen complexes

Metal-imidazole-salen complexes were prepared by one pot method according to previous report [42]. In a typical procedure, 6 mmol 1,2-