



Research paper

Effect of cesium ion on the synthesis and catalytic properties with FeCo Prussian blue analogue

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HIGHLIGHTS

- CsFeCoPBA has a smaller particle size and a larger specific surface area.
- The conversion rate of CsFeCoPBA is up to 96% in epoxidation of styrene.
- The thermodynamic data of synthesizing FeCoPBA and CsFeCoPBA are obtained by ITC.

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ABSTRACT

In this article, cesium ions were introduced into the FeCo Prussian blue analogues (PBA) catalyst to increase the styrene conversion and the selectivity in styrene oxide in the reaction of epoxidation of styrene. The conversion of styrene over CsFeCoPBA-1 on the optimal condition reach up to 96%, in comparison to 88% over FeCoPBA. The catalysts were characterized by fourier transform infrared spectroscopy, X-ray diffraction, transmission electron microscopy (TEM), X-ray energy dispersive spectroscopy (EDS), thermogravimetric analysis (TG) and N₂ adsorption/desorption, respectively. To further illustrate the phenonmen, the detailed kinetic studies on epoxidation of styrene were carried out. It is found that the rate equations is similar between the catalyst CsFeCoPBA-1 and FeCoPBA, while the reaction activation energy with CsFeCoPBA-1 catalyst is reduced obviously. Meanwhile, isothermal titration calorimetry (ITC) had also been employed to directly probe thermodynamic changes during the formation of the PBA with or without Cs ions. It is noteworthy that higher enthalpy change in the presence of cesium ions.

1. Introduction

Prussian blue analogues, represented as A_xM_y[M'(CN)₆] · nH₂O (A = alkali metal; M and M' = divalent and trivalent transition metal ions, respectively) [1,2], are nanoporous framework, with a face-centered cubic cell. Alkaline cations (A⁺) and a portion of the water molecules are accommodated in the nanopores, and the other portion of the water molecules (ligand waters) occupy the vacancies of the [M'(CN)₆] sites and coordinate to the M sites [3,4]. Recently, PBAs have gained considerable attention for their spectacular electrochemical [5,6], magnetic [7], photomagnetic [8], gas sorption [9,10] and novel catalytic properties.

Prussian blue analogues as heterogeneous catalysts are a class of

double metal cyanide (DMC) catalysts, DMCs have been reported to be useful for Prins condensation [11], transesterification [12], copolymerization of epoxides and CO₂ [13,14], synthesis of polyether-polyols [15,16], synthesis of β-amino alcohols [17] and β-alkoxy alcohols [18], synthesis of styrene oxide [19], production of biofuels and lubricants [20,21], and preparation of hyperbranched polymers [22,23]. On the one hand, the synthesis conditions of the DMCs catalysts have an effect on the catalytic performance, such as synthesizing DMC complexes by mechanochemistry [24,25], in different acidic solutions [26], or under ultrasonic conditions [27]. On the other hand, the type and amount of transition metal salt during the preparation of the catalysts also have great impact on the performance of the catalysts [28,29]. Furthermore, the introduction of a number of organic matters like alcohols [30],

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lactate esters [31] and inorganic compounds such as calcium chloride [32,33], silicon dioxide [34,35] can obviously improve the catalytic activity.

Alkali metal ions were used to improve the catalytic activity of catalysts, such as zeolites, [28,29] metals (silver [36,37], ruthenium [38]) and silica [39]. In 1985, Richard M. Lambert [40] investigated the epoxidation of ethylene by Cs-doped Ag (1 1 1), but the mechanism remained unclear. In 2010, Robert J. Madix [37] found that the dominant products in the oxidation of styrene was reversed from phenylacetaldehyde and phenylketene to styrene oxide, when low concentrations of Cs adsorbed on Ag (1 1 0). Cesium ions with low concentration indeed exerted a cooperative effect on the surface structure of Ag (1 1 0), reconstructing the entire surface into Ag (1 1 1) microfacets.

Numerous researches were reported about the electrochemical and magnetic properties of PBA with alkali metal ions [2,41,42]. However, the effects of alkali metal ions on the catalytic performance of PBA are rarely studied. In this article, we report that low concentrations of cesium ion in FeCoPBA could significantly improve the catalytic performance for the epoxidation of styrene. The effects of the concentration of cesium ions were investigated and the catalysts were characterized by various techniques. Herein, to extend our understanding, the kinetic studies were carried out. Also, for the first time, isothermal titration calorimetry (ITC) had been employed to investigate the difference on the thermodynamic changes during the formation of the PBA with and without cesium ions.

2. Experimental

2.1. Materials

$K_3Co(CN)_6$ ($\geq 90\%$) was procured from Alfa Aesar, and was used without further purification. Styrene was distilled under reduced pressure before use. $FeSO_4 \cdot 4H_2O$ ($\geq 99.5\%$), $CsCl$ ($\geq 99.5\%$), *tert*-butyl hydroperoxide (TBHP, 70%), acetonitrile and bromobenzene were all analytical grade reagents and were used without further purification.

2.2. Catalyst preparation

mM of $K_3Co(CN)_6$ and 5 mM solutions of $CsCl$ were prepared in 25 mL of double-distilled water (solution 1). In a separate beaker, solution 2 was prepared with 10 mM of $FeSO_4$ in 25 mL

double-distilled water. Solution 1 was added dropwise into solution 2 under magnetic stirring at room temperature. The resulting precipitate was allowed to anneal in the mother liquor for 48 h, then filtered, and washed several times with distilled water. The precipitate was then dried in air to give $CsFeCoPBA-1$. To study the effect of different concentration of $CsCl$ on the catalytic activity, catalysts $CsFeCoPBA-2$ and $CsFeCoPBA-3$ were prepared using similar method as $CsFeCoPBA-1$, but with 10 mM, and 15 mM solutions of $CsCl$, respectively. For comparison, $FeCoPBA$ catalyst was prepared by similar procedures without $CsCl$ during the whole process.

2.3. Catalyst characterization

X-ray energy dispersive spectroscopy (EDS) data were collected using EDS Instrument on JSM-5600LV. Infrared spectra (IR) were recorded in a TENSOR27. FT-IR spectrophotometer using the KBr pressed disk technique. X-ray powder diffraction (XRD) measurements were performed on a Rigaku D/MAX-2400 X-ray diffractometer with graphite-monochromatized $Cu K_\alpha$ radiation ($\lambda = 0.15406$ nm) from 10° to 90° . Scanning electron microscopy (SEM) measurements were performed with a JEOLJSM-6701F. N_2 -adsorption/desorption isotherms were studied with a Quadachrome Adsorption Instrument. Thermogravimetric Analysis (TG) experiments were obtained on STA PT1600.

2.4. Catalytic reactions

The PBA catalysts were used for the catalytic studies without further activation. In a typical reaction, 3 mg of catalyst, 0.5 mmol of styrene, 0.75 mmol of *tert*-butyl hydroperoxide were added to a 10 mL round-bottomed flask in 2 mL of acetonitrile. The flask was equipped with a water condenser and was maintained in an oil bath at 345 K under agitation. After 6 h of reaction, the catalyst was separated by centrifugation. Then the products were identified by analyzing the reaction mixture with a gas chromatograph-mass spectrometer (GC-MS, Shimadzu GC-MS-QP-2010SE) having a programmed oven (temperature range 323–573 K). The conversion and product selectivity were monitored by gas chromatographic analysis with bromobenzene as internal standard. We used a gas chromatograph (Varian CP-3380) equipped with a flame ionisation detector and a KF1701 capillary column (15 m-long, 0.2 mm-wide, and with a $0.5 \mu\text{m}$ -thick coated film), a programmed oven (temperature range 323–533 K), and N_2 as the carrier gas.

2.5. Isothermal titration calorimetry

The Isothermal Titration Calorimetry measurement were carried out at 25°C with the TAM2277-201 microcalorimetric system (Thermometric AB, Sweden), which has 4 mL sample and reference cells. 2.3 mL of 5 mM $FeSO_4$ was placed in the sample ampoule, at the meantime, 2.3 mL distilled water was placed in the reference ampoule. The 1000 μL calorimeter syringe was filled with 80 mM $K_3Co(CN)_6$ and placed in a Lund pump. And the stirring speed in the sample ampoule was set at 60 rpm. At the beginning of the experiment, the sample ampoule was left for about 2 h to equilibrate thermally. Once the thermal signal was stable in a certain range the experiment was initiated. A titration run consisted of consecutive injections of 7 μL lasting 14 s, with an interval of 35 min. Similarly, the sample ampoule filled with 2.3 mL of 5 mM $FeSO_4$ and $CsCl$ mixed solution was studied in the same method.

3. Results and discussion

3.1. Application of catalytic reaction

The catalytic activities of $FeCoPBA$ and $FeCoPBA$ with cesium ion in the epoxidation of styrene are presented in Table 1. It is interesting that the $CsFeCoPBA$ catalysts all demonstrated better performances than the $FeCoPBA$ catalyst. The optimum concentration of Cs^+ was 5 mM. Compared to $FeCoPBA$, the styrene conversion and the styrene oxide selectivity increased by 8% and 10% with $CsFeCoPBA-1$, respectively.

3.2. Characterization of materials

Peak indexing of the powder XRD patterns (Fig. 1) showed sharp

Table 1
Effect of cesium ion on the catalytic epoxidation of styrene with $FeCoPBA$.

Catalysts	Composition	Styrene conversion (mol%)	Selectivity of styrene oxide (mol%)
$FeCoPBA$	$K_{0.14}Fe_{3.02}[Co(CN)_6]_2$	88	35
$CsFeCoPBA-1$	$Cs_{2.71}Fe_{2.66}[Co(CN)_6]_2$	96	45
$CsFeCoPBA-2$	$Cs_{3.32}Fe_{2.48}[Co(CN)_6]_2$	95	45
$CsFeCoPBA-3$	$Cs_{3.42}Fe_{2.50}[Co(CN)_6]_2$	95	44

Reaction conditions: catalyst: catalyst 3 mg, styrene: 0.5 mmol, TBHP (70%) 0.75 mmol, solvent: acetonitrile (2 mL), reaction temperature: 345 K, reaction time: 6 h, conversion and selectivity were determined by GC analysis.

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