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Immobilization of Co(III) using tethered cyclam ligand on SBA-15 mesoporous silica for aerial oxidation of ethylbenzene

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ABSTRACT

Cyclam type macrocyclic ligand was tethered onto mesoporous silica surface through N-functionalization of the cyclam. The mesoporous silica was synthesized directly with in-built chloropropyl functional group by applying microwave synthesis approach and the cyclam ligand was tethered via the surface substitution reaction of the chloro group. The tethered cyclam ligand was proven to facilely accommodate Co(III) cation into its cavity. This Co(III)cyclam-functionalized mesoporous silica showed good catalytic activity in the aerial oxidation of ethylbenzene to give acetophenone as the major product, which exceeded 60%. The presence of pyridine ligand which bounded to the axial sites of the tethered Co(III)cyclam complex enhanced the activity of the catalyst with sustaining the selectivity.

1. Introduction

Ordered mesoporous silicas have opened many applications in the field of heterogeneous catalysis, adsorption, and separation due to their large and well-defined pore sizes and high surface areas [1–3]. However, for the practical applications in catalysis, these materials have suffered from lack of active sites due to the inert nature of silica surface. In recent years, surface functionalization with metal complexes has been widely applied in order to generate active sites onto these mesoporous silica surfaces. The immobilization of catalytically active metal complexes onto the surfaces offered advantages of combination of high catalytic activity, selectivity and stability with easy separation of catalysts from the reaction media [2,4]. Among the variety of catalytically active metal complexes that have been functionalized onto mesoporous silica surfaces, the transition metal complexes which were active in oxidation of hydrocarbons and olefins have given rise to numerous studies [5]. Indeed, it is a particularly useful catalytic reaction since oxygenated hydrocarbons are important intermediates for many chemical and fine chemical products.

Herein, we report our investigation on the catalytic property of immobilized Co(III) cation which was accommodated into the cavity of tethered cyclam type macrocyclic ligand onto mesoporous silica material for the aerial oxidation of ethylbenzene to acetophenone as a major product. The Co(III) species has been found to be the catalytically active species in many oxidation reactions [5,6]. Das and Clark [6] and Park and coworkers [7] immobilized Co(III) onto carboxylic group tethered HMS and SBA-15 mesoporous silicas, respectively, and found that in these heterogeneous systems, the cobalt cation was weakly bound to the carboxylic group and the accommodation of Co(III) occurred only with the addition of pyridine. Even when pyridine was used to stabilize the Co(III) species, the catalyst was still easily deactivated during the catalytic reaction due to the loss of pyridine. To overcome this problem, the challenge is to find a ligand that can provide a stable environment and stabilize the high-valent metal centers. The cyclam is a well-known tetraazamacrocycle ligand that can form and stabilize various high-valent transition metal complexes due to the macrocyclic effect [8]. The cyclam also offers ease surface tethering with N-functionalization through substitution reaction with surface tethered alkylating agents such as chloropropyl group. Therefore, the mesoporous silica was synthesized directly with in-built chloropropyl functional group by applying microwave synthesis approach and the cyclam ligand was tethered via the surface substitution reactions of the chloro group. Pyridine bound to Co(III) species has been proven to accelerate the oxidation of Co(II) to Co(III) and stabilize the Co(III) state and hence improved the catalytic activity [5]. In this work, we also investigated the effect of axially bound pyridine to the tethered Co(III)cyclam complex on the catalytic activity in aerial oxidation of ethylbenzene.

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2. Experimental

2.1. Chemicals

Sodium metasilicate ($Na_2SiO_3{\cdot}9H_2O$; Sigma–Aldrich) and 3-chloropropyl triethoxysilane/CPTS ($Cl(CH_2)_3Si(OEt)_3$; Aldrich) were used as silica and chloropropyl group sources, respectively. A Pluronic P123 triblock copolymer (poly(ethyleneoxide)–poly(propyleneoxide)–poly(ethyleneoxide)/$EO_{20}PO_{70}EO_{20}$; MW5800; BASF) was used as a structure directing agent. $CoCl_2{\cdot}6H_2O$, ethylbenzene, and HPLC grade acetonitrile solvent were purchased from Aldrich. The tetraazamacrocycle (cyclam) was synthesized according to the reported procedure [9].

2.2. Synthesis of chloropropyl-functionalized SBA-15 (Clpr-SBA-15)

Chloropropyl-functionalized SBA-15 mesoporous silica was synthesized from synthesis gels with composition of $(1+x)SiO_2{:}x\mathrm{CPTS}{:}0.018\mathrm{P123}{:}11HCl{:}117{\cdot}1H_2O$, with $x = \mathrm{CPTS}/(\mathrm{CPTS} + SiO_2) = 5\%$. In a typical synthesis, 5.00 g P123 ($EO_{20}PO_{70}EO_{20}$; MW5800; BASF) was dissolved in 128.12 g of distilled water and followed by the addition of 0.05 mole sodium metasilicate ($Na_2SiO_3{\cdot}9H_2O$; Sigma–Aldrich). To the clear solution, 13.0 g of concentrated hydrochloric acid (37.6%; Fisher Scientific) was quickly added into the solution and stirred for 1–3 min at 40 °C. To this solution, 0.0025 mole 3-chloropropyl triethoxysilane/CPTS ($Cl(CH_2)_3Si(OEt)_3$; Aldrich) was added. The final mixture was further aged under stirring for 1 h to get the reactive gel before moving to the microwave digestion system (CEM Corporation, MARS-5). The microwave condition for crystallization was set under static conditions at 100 °C for 2 h at an operating power of 300 W (100%). The crystallized products were filtered, washed with warm distilled water, and dried at 80 °C. The surfactant was then selectively removed by Soxhlet extraction with ethanol for 24 h.

2.3. Preparation of Co(III)cyclam-SBA-15 and Co(III)(cyclam)py$_2$-SBA-15

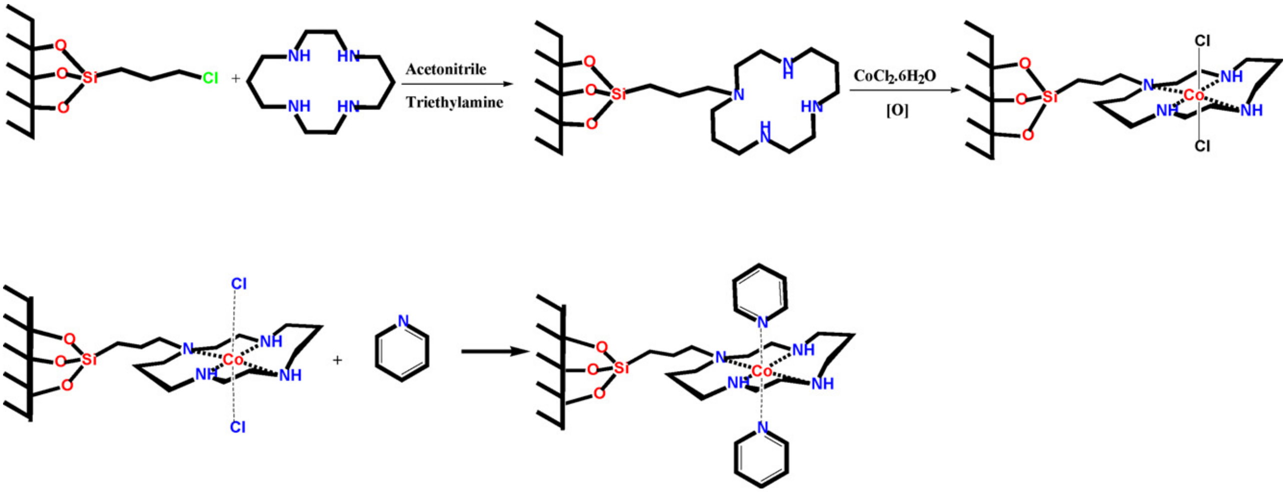
The cyclam-functionalized SBA-15 was prepared by substitution reaction of chlorine with the cyclam in acetonitrile with triethylamine as base. In the typical synthesis, a mixture of cyclam (0.5 g, 2.5 mmol), Clpr-SBA-15 (1.0 g) in 90 ml of acetonitrile, and triethylamine (1.1 g, 10.9 mmol) was refluxed at 90 °C under stirring for 2 days. The resulting white solid was quantitatively recovered by filtration and washed five times with hot chloroform and three times with hot ethanol. The excess cyclam was removed by Soxhlet extraction over ethanol for 24 h and finally dry under vacuum at 100 °C for 24 h. The Co(III)cyclam-SBA-15 catalyst was prepared as followed: cyclam-functionalized SBA-15 (cyclam-SBA-15) was dispersed into 90 ml of an ethanolic solution of 0.5 g $CoCl_2{\cdot}6H_2O$ and refluxed for 12 h. During this process, the reaction mixture was constantly bubbled with air to oxidize the Co(II)(cyclam) to Co(III)(cyclam) complex. The final Co(III)cyclam-SBA-15 was recovered by filtration and washed three times with ethanol, water, and diluted HCl solution and dry under vacuum at 100 °C for 24 h. For the preparation of Co(III)(cyclam)py$_2$-SBA-15, excess pyridine was added into the suspension of Co(III)cyclam-SBA-15 in methanol and the mixture was refluxed for 6 h. The final Co(III)(cyclam)py$_2$-SBA-15 was recovered by filtration and washed three times with ethanol and water and dried under vacuum at 100 °C for 24 h (Scheme 1).

2.4. Aerial oxidation of ethylbenzene

The aerial oxidation of ethylbenzene was carried out at atmospheric pressure with 50 ml of substrate and 50 mg of the catalyst with air flow at 140 ml/min with constant stirring. The reaction was done in a two-neck round flask vessel which was connected to a chilled water condenser and a twin Dean–Stark separator to remove water from the reaction mixture. Small amount of reaction mixture was frequently removed from the reaction vessel and subsequently the reaction products were analyzed by using gas chromatograph.

3. Results and discussion

Highly ordered chloropropyl-functionalized mesoporous silica having hexagonal *p*6*mm* mesostructure phase of SBA-15 was successfully synthesized from the direct synthesis under microwave irradiation. Due to the intrinsic nature of microwave heating like the rapid and homogenous heating, the co-condensation of sodium metasilica and chloropropyltriethoxysilane (CPTES) was facilitated to enable the direct synthesis of the Clpr-SBA-15 in one step [10,11]. The SAXRD patterns of the samples exhibited very intense main diffraction peak at 0.99° of 2θ indicating (1 0 0) reflection and two or more additional peaks at higher degrees at 1.64° and 1.88° of 2θs reflecting (1 1 0) and (2 0 0) reflections,



Scheme 1. Schematic illustration for the preparation of Co(III)cyclam-SBA-15 and Co(III)(cyclam)py$_2$-SBA-15.

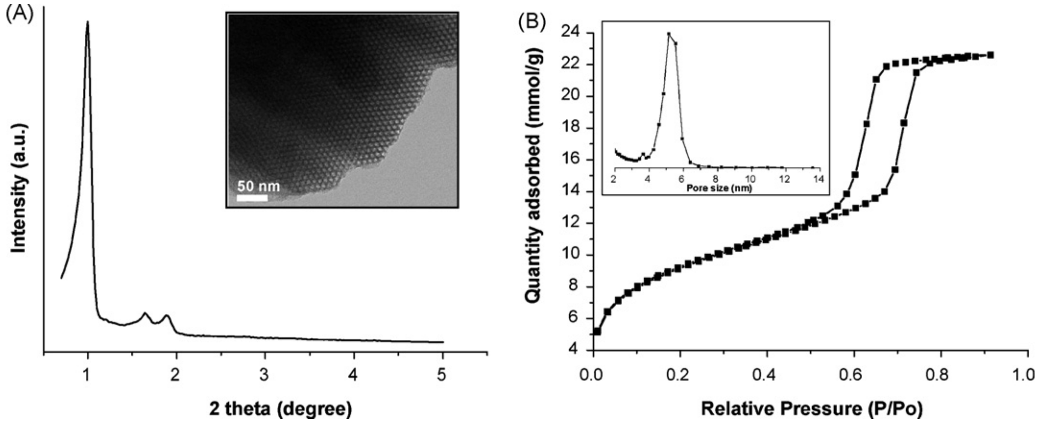


Fig. 1. (A) XRD pattern and TEM image (inset) of Clpr-SBA-15 synthesized by using direct synthesis under microwave irradiation. (B) N_2 adsorption–desorption full isotherm and pore-size distribution calculated by BJH method from desorption branch (inset) of Clpr-SBA-15.

respectively (Fig. 1A) [12]. TEM analysis clearly showed that the material had an array of highly ordered 2D hexagonal structure which was similar to those of typical SBA-15 material (Fig. 1A). The N_2 adsorption–desorption isotherms of the sample exhibited well-defined type IV isotherm with H1-type hysteresis loops which was the characteristic for mesoporous materials having cylindrical type mesostructures that facilitate the condensation of N_2 (Fig. 1B). The clear evidence for the successful incorporation of the chloropropyl moieties through the direct synthesis was provided by ^{13}C solid NMR, NIR and FTIR spectra. The TGA and elemental analysis revealed that the chloropropyl groups were quantitatively incorporated from the initial gel mixture [13].

Chloropropyl group tethered mesoporous material has been widely used as an intermediate for the further functionalization of mesoporous materials with a wide range of ligands and metal complexes because the chloro groups can be chemically modified by nucleophilic substitution [14–16]. In this work, the chloropropyl group was modified with cyclam type macrocyclic compound through the substitution reaction between the secondary amine of cyclam with the chloro group. The success of chemical modification into cyclam tethered SBA-15 was traced with NIR and FTIR spectra [13]. The N_2 adsorption–desorption analysis exhibited that the well-defined type IV isotherms with H1-type hysterisis loops were intact implying that the materials kept possessing the large mesopores with narrow pore-size distribution. The Clpr-SBA-15 had large mean pore size of 5.1 nm which could be accessible and substituted by cyclam. The resulted cyclam-SBA-15 had mean pore sizes of 4.8 nm. The BET surface area of Clpr-SBA-15 was found to be 702 m^2/g and was significantly reduced to 364 m^2/g due to the accommodation of the bulky cyclam inside the mesopores.

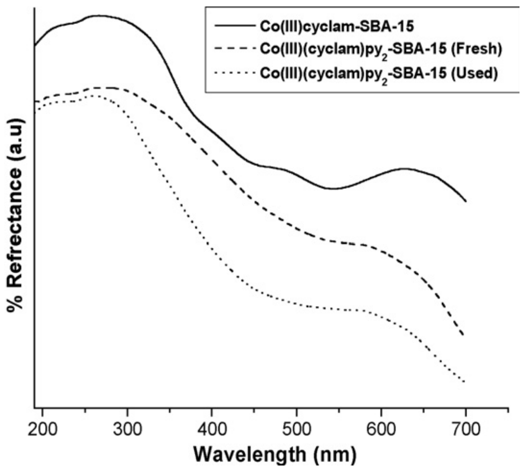
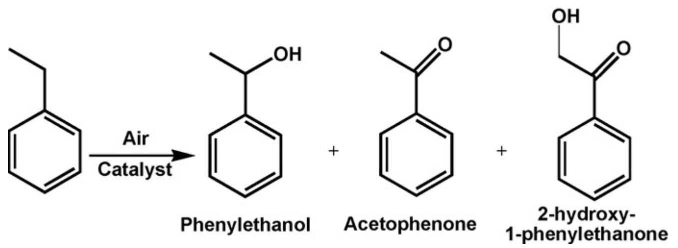


Fig. 2. UV–vis spectra of Co(III)cyclam-SBA-15 and Co(III)(cyclam)py$_2$-SBA-15.

The tethered cyclam showed high affinity to Co(II) cation to form tethered Co(II)cyclam complex on the surface. This Co(II)-cyclam could also be easily oxidized into Co(III)cyclam complex by simply air bubbling during the complexation reaction. Atomic adsorption spectroscopy analysis showed that 0.4 mmol Co(III) could be accommodated per 1 g cylam-SBA-15. Fig. 2 shows that the Co(III)cyclam-SBA-15 catalyst exhibited three absorption peaks at UV–vis region 659, 485 and 260 nm for $^1T_{1g} \leftarrow {}^1A_{1g}$, $^1T_{2g} \leftarrow {}^1A_{1g}$ and ligand to metal charge transfer (LMCT) electronic transition, respectively, which could be attributed to electronic transitions of *trans*-Co(Cl_2)(cyclam)$^+$ complex. Upon addition of axially bound pyridine co-ligand, the lambda maximum of the $^1T_{1g} \leftarrow {}^1A_{1g}$, $^1T_{2g} \leftarrow {}^1A_{1g}$ peaks blue-shifted to higher wavelength due to stronger ligand field of pyridine than Cl^-.

The catalytic activity of the Co(III)-SBA-15 was investigated through the aerial oxidation of ethylbenzene. The catalyst showed good catalytic activity on the ethylbenzene oxidation to give acetophenone as a major product and the other products were found to be phenylethanol and 2-hydroxy-1-phenylethanone (Scheme 2). The time-course showed an absence of induction period indicating that the Co species was mainly in its higher oxidation state at the beginning of the reaction [8]. The catalyst could be reused and, as shown in Fig. 3A, the catalyst exhibited higher catalytic activity in the early reaction period and slightly decreased after 5 h reaction. The higher catalytic activity was supposed mainly due to the remaining reaction products of the first run inside the mesopore of the catalyst. And the slight decrease in the activity after 5 h reaction could be due to the pore blocking of the catalysts by bulky polymeric products.



Scheme 2. Aerial oxidation of ethylbenzene.

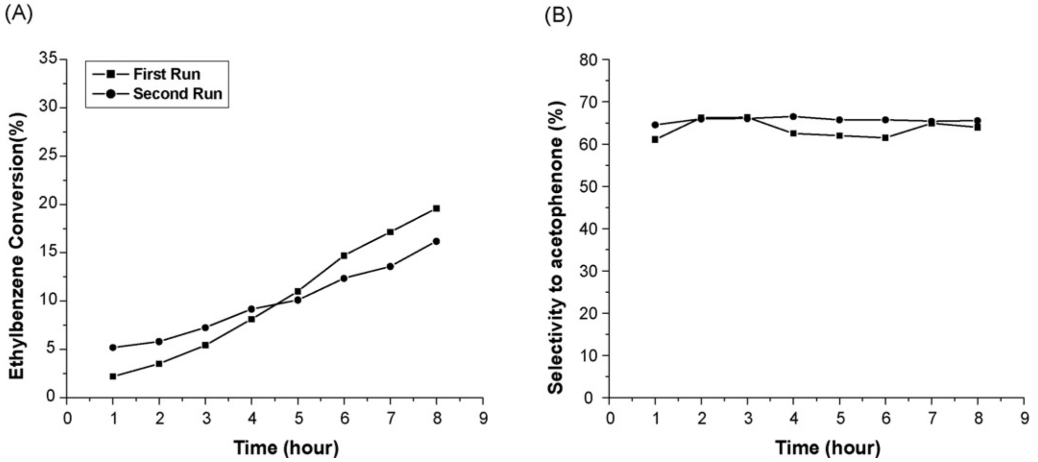


Fig. 3. Aerial oxidation of ethylbenzene over Co(III)cyclam-SBA-15 catalyst.

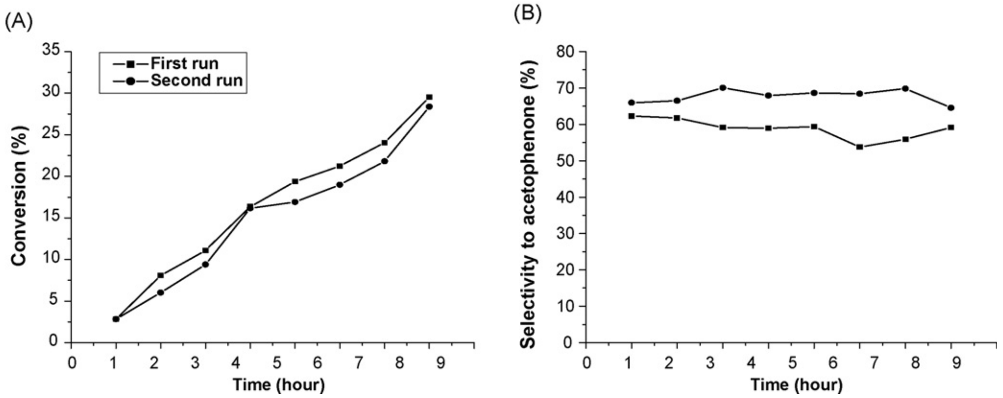


Fig. 4. Aerial oxidation of ethylbenzene over Co(III)(cyclam)py_2-SBA-15.

The pyridine modified catalyst, Co(III)(cyclam)py_2-SBA-15, showed improvement in catalytic activity by 10% in conversion with similar selectivity to acetophenone (Fig. 4). The reused catalyst also showed similar catalytic activity with slight decrease in acetophenone selectivity. It had been reported that axially bound co-ligands with basic property such as imidazole, pyridine and derivatives thereof could improve catalytic activity of high oxidation state metal complexes in oxidation reactions by accelerating the oxidation of the low oxidation state species to their higher oxidation state valent species and concurrently stabilizing the higher oxidation state species [17,18]. In the aerial oxidation of ethylbenzene, the aerial oxidation of Co(II) to Co(III) active species is a slow process and therefore was rate limiting (Das et al.). In the Co(III)(cyclam)py_2-SBA-15, the pyridine co-ligand seemed to enhance the Co(II) to Co(III) step and stabilize the Co(III) species in the catalytic cycle and can be attributed to the increase in the catalytic activity as compared to Co(III)cyclam-SBA-15.

4. Conclusions

Cobalt(III) species has been successfully immobilized on cyclam ligand tethered SBA-15 mesoporous silica which was obtained from surface chemical modification of chloropropyl-functionalized SBA-15. The Co(III)cyclam-SBA-15 showed high catalytic activity in the aerial oxidation of ethylbenzene to acetophenone as the major product. The presence of axially bounded pyridine co-ligand to the Co(III) metal center enhanced the catalytic activity by 10% without changing the catalytic selectivity. The increase in catalytic activity was attributed to the enhancement of Co(II) to Co(III) step and the stabilization of the Co(III) species by the axially bound pyridine co-ligand.

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