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Metal chlorides supported on chiral mesoporous silica (MCl_x/CMS) as highly active Lewis acid catalyst for the selective hydroamination of cyclohexene

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ABSTRACT

Metal chlorides supported on chiral mesoporous silica (MCl_x/CMS) as solid acid catalysts were prepared, characterized and their catalytic performance in hydroamination of cyclohexene was evaluated. A series of MCl_x/CMS catalysts were prepared by wet impregnation with various types of metal chlorides ($NiCl_2$, $CuCl_2$, $AlCl_3$, $CoCl_2$, $FeCl_3$, $ZnCl_2$) on CMS support and further heat treated at mild temperature. The supported catalysts showed catalytic synergistic effect (~60% of conversion) and 100% selectivity in hydroamination of cyclohexene under mild reaction condition (60 °C). Furthermore, the influence of reaction parameters and supports on activity of the catalyst was also investigated. The MCl_x/CMS catalysts can be recovered for reuse for several runs with little reactivity loss (~5%) and easily handled under the described reaction conditions.

1. Introduction

The synthesis of amines is of considerable importance due to their key role in fine chemicals, pharmaceuticals and petrochemical industries. Among the techniques used for the formation of C–N bond from N–H bond, hydroamination of unsaturated C=C bonds has both the advantages of economy and feasibility, and it is widely used by many researchers worldwide [1]. Typically, this reaction is carried out using strong homogeneous Brönsted acids such as H_2SO_4 [2], trifluoromethanesulfonic acid [3], heteropoly acid [4] or homogeneous basic catalyst such as lithium diethylamide [5]. In 2004, homogeneous Lewis acids ($TiCl_4$ [6], $AlCl_3$ [7], $FeCl_3$ [8]) were first used in hydroamination reactions. The studies found that these Lewis acids are more efficient than the homogeneous Brönsted acid catalysts in the aforementioned reaction. These homogeneous acids, however, cause serious problems resulting in equipment corrosion, difficulty in handling, safety and waste disposal. Moreover, separation of products from the catalyst is tedious and energy-consuming when both compounds are mixed. In view to this, an attempt to search for a more eco-friendly, efficient and safer catalyst for the hydroamination process is worthy of academic pursuit.

Recently, hydroamination of alkenes have been successfully demonstrated by using Au [9], Pt [10], Rh [11], Cu [12], lanthanides [13] and other noble transition metal complexes [14]. Although hydroamination reactions based on noble metal complexes are widely pursued, it should be noted that these catalysts have the drawbacks of high cost, toxicity and demanding reaction conditions as most of the noble metal complexes are very sensitive to air and moisture. Metal chloride salts, on the other hand, are expected to show comparable or better catalytic performance than these noble metal catalysts, with the additional benefits of low cost and ease of separation when supported on a suitable heterogeneous support [15].

Mesoporous materials such as MCM-41 [16] and SBA-15 [17] are one of the promising candidates for catalyst supports due to their unique characteristics such as extraordinarily high surface area (*ca.* 700 m^2/g), uniform pore size distribution, tunable pore size and adjustable surface hydrophobicity/hydrophilicity. As a result, they have been used as inorganic matrix to support organic compounds, metal salts and metal complexes for catalyzing many chemical reactions such as oxidation [18,19], hydrogenation [20], hydroformylation [21], epoxidation [22], alkylation [23,24] and many others [25,26]. In 2004, a new type of mesoporous materials called chiral mesoporous silica (CMS) with chiral pore channelshas been synthesized by Che and her co-workers [27]. These materials have been well proven as an excellent support due to their unique structure that provides

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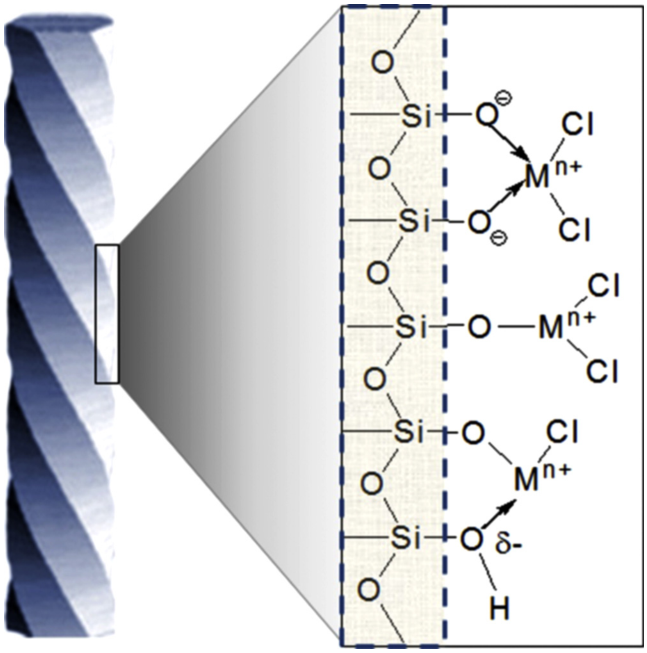

Fig. 1. Binding model for the metal chlorides ($M^{n+}Cl_x$) with the CMS inorganic matrix. The arrows represent dative covalent bonds.

chiral space utilizable for separation, adsorption and catalysis [28–30].

Several studies have reported that metal chlorides (*e.g.* $ZnCl_2$, $AlCl_3$, $FeCl_3$) supported on MCM-41, SBA-15, clay and amorphous silica are active in several acid catalyzed reactions such as Friedel–Crafts [31–34], isomerization [35], esterification [36], cyclo addition [37], hydroxylation [38] and tetrahydropyranylation [39] reactions. However, to the best of our knowledge, no catalytic study focused on hydroamination reaction using metal chlorides supported on mesoporous materials as catalysts has been studied. Herein, this work reports on the preparation and characterization of CMS supported with various types of metal chlorides ($NiCl_2$, $CuCl_2$, $AlCl_3$, $CoCl_2$, $FeCl_3$, $ZnCl_2$). The composite catalysts (MCl_x/CMS) involve (i) the chemical interaction of SiO^- groups of CMS surface with the metal chlorides, (ii) reacting some surface silanol (Si–OH) groups of CMS with the metal chlorides, and (iii) electrostatic interaction between surface silanol groups and the metal chlorides (Fig. 1). The prepared MCl_x/CMS composite catalysts were then studied in the hydroamination of cyclohexene.

2. Experimental

2.1. Preparation of CMS support

In a typical synthesis of chiral mesoporous silica, N-miristoyl-L-alanine (denoted as C_{14}-L-AlaA, 0.3331 g) was first prepared according to ref. [40] and was dissolved in diluted NaOH solution (30.073 g, 0.03 M) at 80 °C with stirring. The surfactant solution was cooled to 60 °C before a mixture of tetraethoxysilane (denoted as TEOS, 1.6537 g, Merck, 98%) and 3-aminopropyltriethoxysilane (denoted as APS, 0.2513 g, Merck, 98% in methanol) were added with stirring to give a final chemical composition ratio of $1C_{14}$-L-AlaA:1APS:7TEOS:$1500H_2O$:0.8NaOH. After 10 min, the stirring was stopped and the reaction mixture was hydrothermally treated at 60 °C for 48 h. The precipitates were filtered, washed with hot water, dried at 60 °C, and calcined at 600 °C for 6 h to remove organic template.

2.2. Preparation of CMS-supported metal chlorides catalysts (MCl_x/CMS)

CMS supported metal chlorides ($NiCl_2$/CMS, $CuCl_2$/CMS, $AlCl_3$/CMS, $CoCl_2$/CMS, $FeCl_3$/CMS, $ZnCl_2$/CMS) were prepared as follows: Anhydrous metal chloride (5.0 mmol) was first fully dissolved in ethanol (20 ml, 99%) before the CMS support (1.500 g) was added into the solution. The mixture was magnetically stirred and refluxed at 80 °C for 2 h. The solvent was then rotary evaporated at 90 °C before the dried catalysts were collected and activated at 300 °C for 3 h. All the catalystswere stored in desiccators.

2.3. Characterization

XRD patterns were obtained using a Bruker Advance D8 using a Siemens 5000 diffractometer with Cu Kα radiation at 40 kV and 30 mA within the 2θ range of 1.7–10° at the scanning rate of 0.02° per second with step time 2 s. TEM analysis was performed using JEM-2100 Electron Microscope with acceleration voltage of 200 kV. N_2 adsorption and desorption isotherms were measured at 77 K with Quantachrome Nova 4200E. Prior to the measurement, the samples were degassed at 250 °C overnight to remove adsorbed moisture. The specific surface area was calculated using Bruneuer–Emmett–Teller (BET) method. The average pore size and total pore volume were calculated by the Barrett–Joyner–Halenda (BJH) method.

The metal contents in the MCl_x/CMS samples were measured with AAnalyst 200 atomic absorption spectrometer (AAS). In order to determine the chloride content in the composite samples, the dried MCl_x/CMS solid (0.10 g, 300 °C, 1 h) was fused with small piece of Na metal and extracted with distilled water (10 mL). *Caution: this reaction isexothermic!* The filtrate was then diluted to 25 mL. The chloride content dissolved in the solution was then determined by the Mohr titration method using silver nitrate solution (0.1 M) andK_2CrO_4 as then titration agent and end-point indicator, respectively [41].

Pyridine FTIR spectra were recorded using a Nicolet 6700 FT-IR spectrometer. The CMS composites were ground and pressed to obtain a wafer (area 2 cm^2, mass of 11–13 mg) before being introduced into the vacuum IR cell. The samples were then pre-activated under vacuum (10^{-6} mbar) at 280 °C for 2 h. The reference spectrum was first recorded after cooling and then pyridine was introduced to the sample for 30 s. The sample was then allowed to evacuate at 25, 100, 200 and 280 °C to desorb the pyridine and the spectra were recorded (4 cm^{-1} resolution and 200 scans accumulation) after each evacuation step.

2.4. Catalytic experiments

Hydroamination reactions were performed as follows: Freshly activated MCl_x/CMS (0.20 g, 300 °C, 1 h) was loaded into a 50 mL round bottom flask containing cyclohexene (15 mmol, Merck), cyclohexylamine (10 mmol, Fluka) and chloroform (10 mL) as solvent. The mixture was stirred and the reaction was carried out at 60 °C. The products were withdrawn after the reaction and analyzed using a gas chromatograph (Thermo Focus GC) equipped with a SPB-1 column.

2.5. Reusability and leaching studies

The reusability test was performed as follows: the MCl_x/CMS solid catalysts were separated after the first cycle, washed with diethyl ether and activated at 300 °C for 3 h before being used for subsequent cycle of catalytic reaction. The reaction solution was again withdrawn and analyzed with a gas chromatograph.

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