Metal Chlorides Supported on Chiral Mesoporous Silica as Highly Active Lewis Acid Catalyst for the Selective Hydroamination of Cyclohexene

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Metal chlorides supported on chiral mesoporous silica (MCl₆/CMS) as highly active Lewis acid catalyst for the selective hydroamination of cyclohexene

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A B S T R A C T

Metal chlorides supported on chiral mesoporous silica (MCl₆/CMS) as solid acid catalysts were prepared, characterized and their catalytic performance in hydroamination of cyclohexene was evaluated. A series of MCl₆/CMS catalysts were prepared by wet impregnation with various types of metal chlorides (NiCl₂, CuCl₂, AlCl₃, CoCl₂, FeCl₃, ZnCl₂) 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 MCl₆/CMS catalysts can be recovered for reuse for several runs with little activity loss (~5%) and easily handled under the described reaction conditions.

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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 Brønsted acids such as H₂SO₄ [2], trifluoromethanesulfonic acid [3], heteropoly acid [4] or homogeneous basic catalyst such as lithium diethyamide [5]. In 2004, homogeneous Lewis acids (TiCl₄ [6], AlCl₃ [7], FeCl₃ [8]) were first used in hydroamination reactions. The studies found that these Lewis acids are more efficient than the homogeneous Brønsted 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 m²/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...
chiral space utilizable for separation, adsorption and catalysis [28–30].

Several studies have reported that metal chlorides (e.g., ZnCl₂, AlCl₃, FeCl₃) 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 (NiCl₂, CuCl₂, AlCl₃, CoCl₂, FeCl₃, ZnCl₂). The composite catalysts (MClₓ/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 MClₓ/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 C₁₄-t-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 1C₁₄-t-AlaA:1APS:7TEOS:1500H₂O: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 (MClₓ/CMS)

CMS supported metal chlorides (NiCl₂/CMS, CuCl₂/CMS, AlCl₃/CMS, CoCl₂/CMS, FeCl₃/CMS, ZnCl₂/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 catalysts were 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. N₂ 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 Brunauer–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 MClₓ/CMS samples were measured with AAnalyst 200 atomic absorption spectrometer (AAS). In order to determine the chloride content in the composite samples, the dried MClₓ/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 isothermical! 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) and K₂CrO₄ 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 cm², 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 MClₓ/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 MClₓ/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.
The leaching test was performed as follows: the non-activated and activated composite solids were sonicated in chloroform for 30 min using Branson DHA-1000 ultrasonicator (400 W). The photo of the appearance of solutions after sonication was then taken (results will be discussed in Section 3.2.3). In order to investigate the metal and chloride leaching tendency from the MCl/CMS solid catalysts during the catalytic reaction, MCl/CMS solid catalysts after four cycles of catalytic reaction were recovered and washed thoroughly with diethyl ether and ethanol. The catalyst solids were then dried at 100 °C overnight. The metal and chloride contents in MCl/CMS solids were analyzed using AAS and Mohr titration, respectively to determine the amount of metal and chloride leached out from the MCl/CMS catalysts.

3. Results and discussion

3.1. Characterization

Metal chlorides supported on CMS (MCl/CMS) catalysts in this work were prepared in a very simple way. Small amount of metal chlorides were first dissolved in the ethanol solution and then CMS support was introduced to allow impregnation to take place. The ethanol solution was then evaporated and activated at 300 °C giving MCl/CMS powders with different colors as final products (Fig. 2).

The mesostructure of the series of MCl/CMS catalysts was confirmed by X-ray diffraction (XRD) analysis. Fig. 3 displays the XRD patterns of the CMS solids and the d_{100} spacing values are given in Table 1. The parent CMS exhibits an intense signal at 2θ = 2.15° corresponding to (1 0 0) plane and three small signals between 3.5° and 6.0° due to (1 1 0), (2 0 0) and (2 1 0) planes which corresponds to a two-dimensional hexagonal nanoporous structure (Fig. 3a). As wet impregnation took place, the intensity of the diffraction peaks decreased and the signals also slightly shifted toward higher diffraction angles due to a decrease in the pore size resulting from the insertion of metal chlorides into the CMS pores and/or deposition of metal chlorides nanoclusters on the surface of CMS. Nevertheless, the characteristic diffraction peaks (especially (1 0 0), (1 1 0) and (2 0 0) planes) of all series of samples were retained indicating that the long-range order of mesoporous hexagonal channels was still preserved after modification. The width of diffraction peaks also remained almost identical indicating that the structural integrity in CMS materials was not damaged upon gentle modification by wet impregnation and thermal activation. Furthermore, no other diffraction peaks corresponding to metal salts were observed at high diffraction angle (not shown here).

The MCl/CMS supported catalysts were further studied by HRTEM analysis. As can be seen in Fig. 4a, the parent CMS solids have a twisted rod-like morphology with left-handed fringes chirality, indicating that the handedness of helices is directed by the handedness of the surfactants [16]. As the metal chlorides were supported on the CMS support, all the composite materials exhibited ultra small metal chloride nanocrystals with an average size of 8–10 nm distributed on the CMS solids (Fig. 4b–f). According to Yan et al. [42], the (supported or unsupported) nanoparticles have better catalytic reactivity compared to their micron-sized counterparts due to their high surface energy. Among all the supported catalysts, AlCl₃/CMS, FeCl₃/CMS and ZnCl₂/CMS had the most dense metal chloride nanoclusters deposited on the CMS support (Fig. 4d–f). These observations are in line with the XRD data (Fig. 3).

In order to verify whether the supported nanoparticles contained metals and chloride element, AAS elemental analysis and Mohr titration were carried out (Table 2). The results revealed

![Fig. 2. Physical appearance of (a) parent CMS, (b) NiCl₂/CMS, (c) CuCl₂/CMS, (d) FeCl₃/CMS, (e) AlCl₃/CMS, (f) CoCl₂/CMS, and (g) ZnCl₂/CMS.](image)

![Fig. 3. XRD patterns of samples after heat treatment: (a) parent CMS, (b) NiCl₂/CMS, (c) CuCl₂/CMS, (d) AlCl₃/CMS, (e) CoCl₂/CMS, (f) FeCl₃/CMS, and (g) ZnCl₂/CMS.](image)

### Table 1

<table>
<thead>
<tr>
<th>Samples</th>
<th>d₁₀₀ spacing (nm)</th>
<th>S_{BET} (m²/g)</th>
<th>V_{total} (cm³/g)</th>
<th>Pore diameter (nm)</th>
<th>Lewis acid sites (μmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMS</td>
<td>3.69</td>
<td>1130</td>
<td>0.89</td>
<td>3.78</td>
<td>0/0</td>
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<tr>
<td>NiCl₂/CMS</td>
<td>3.69</td>
<td>1076</td>
<td>0.83</td>
<td>3.71</td>
<td>37.6/4.2</td>
</tr>
<tr>
<td>CuCl₂/CMS</td>
<td>3.85</td>
<td>1197</td>
<td>0.70</td>
<td>3.69</td>
<td>16.4/0.9</td>
</tr>
<tr>
<td>AlCl₃/CMS</td>
<td>3.90</td>
<td>864</td>
<td>0.53</td>
<td>3.66</td>
<td>29.2/2.1</td>
</tr>
<tr>
<td>CoCl₂/CMS</td>
<td>3.89</td>
<td>736</td>
<td>0.49</td>
<td>3.54</td>
<td>37.0/9.1</td>
</tr>
<tr>
<td>FeCl₃/CMS</td>
<td>3.76</td>
<td>958</td>
<td>0.66</td>
<td>3.19</td>
<td>29.9/12.1</td>
</tr>
<tr>
<td>ZnCl₂/CMS</td>
<td>3.97</td>
<td>696</td>
<td>0.43</td>
<td>3.18</td>
<td>33.5/14.4</td>
</tr>
</tbody>
</table>

* a Calculated using BJH method.

* b Pyridine desorbed at 100 °C/280 °C, 1 h.
Table 1
Metal and chloride contents in freshly activated catalysts and in used catalysts after four cycles of hydroamination reaction.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Freshly prepared Metal (%)</th>
<th>Freshly prepared Chloride (%)</th>
<th>After four cycles Metal (%)</th>
<th>After four cycles Chloride (%)</th>
<th>Leaching (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiCl₂/CMS</td>
<td>7.8</td>
<td>9.1</td>
<td>6.5</td>
<td>7.1</td>
<td>19.3</td>
</tr>
<tr>
<td>CuCl₂/CMS</td>
<td>8.5</td>
<td>8.6</td>
<td>6.1</td>
<td>6.2</td>
<td>28.1</td>
</tr>
<tr>
<td>AlCl₃/CMS</td>
<td>8.5</td>
<td>13.5</td>
<td>7.1</td>
<td>11.3</td>
<td>16.4</td>
</tr>
<tr>
<td>CoCl₂/CMS</td>
<td>16.1</td>
<td>17.9</td>
<td>9.7</td>
<td>11.1</td>
<td>38.9</td>
</tr>
<tr>
<td>FeCl₃/CMS</td>
<td>15.2</td>
<td>15.4</td>
<td>12.7</td>
<td>13.0</td>
<td>16.0</td>
</tr>
<tr>
<td>ZnCl₂/CMS</td>
<td>18.1</td>
<td>15.6</td>
<td>15.1</td>
<td>12.9</td>
<td>16.9</td>
</tr>
</tbody>
</table>

* Degree of leaching was estimated by:

\[
\text{leaching} = \left(\frac{1 - \text{Metal after 4 cycles}}{\text{Metal after 4 cycles}}\right) + \left(\frac{1 - \text{Chloride after 4 cycles}}{\text{Chloride after 4 cycles}}\right) \times 100\%.
\]

that NiCl₂/CMS, CuCl₂/CMS and AlCl₃/CMS had quite low metal and Cl contents (∼8.0% and ∼10.0%, respectively) whereas CoCl₂/CMS, FeCl₃/CMS and ZnCl₂/CMS contained high loading of metal and chloride contents on the CMS support (∼16.0% and ∼16.3%, respectively).

The textural properties of MClₓ/CMS composites were further investigated using N₂ adsorption-desorption analysis. All solids showed type IV isotherms with H1 hysteresis loops [23] (Fig. 5). Upon impregnation treatment of the parent material with various types of metal chlorides, changes in the N₂ sorption isotherm curves and consequently decreases in the N₂ gas uptake were observed. This could be explained by the deposition and occupation of metal chloride molecules onto the surface of the inner pores (Table 1). In addition, a decrease in the pore volume and pore diameter was also observed and confirmed the presence of metal chloride nanoparticles on the parent CMS solid as observed in the TEM study (Table 1 and Fig. 4).

The amount, type and strength of acid sites of supported CMS catalysts were investigated using pyridine adsorption and were monitored with FTIR spectroscopy. The pyridine adsorption was first carried out at room temperature to allow saturation adsorption on the catalysts and followed by evacuation of pyridine at 100 and 280 °C. The wave numbers and the intensities of the IR bands after pyridine desorption were then recorded. It was observed in the IR spectrum of parent CMS that no IR absorbance bands were detected at 1445 and 1595 cm⁻¹ after pyridine evacuation at 100 °C, which confirmed the parent CMS has no acidity (Table 1). On the other hand, the MClₓ/CMS solids showed extra bands at 1490 and 1450 cm⁻¹ after pyridine desorption at 100 °C (not shown). These two bands are assigned to pyridine interacting via the nitrogen lone-pair electrons, with Lewis (aprotic) acidic sites on the composite catalysts [43]. The Lewis acidity of the MClₓ/CMS solids was calculated from the peak areas of the signals and was shown in Table 1. Based on the pyridine adsorption study, NiCl₂/CMS and CoCl₂/CMS had the highest...
amount of Lewis acid sites (~37.0 μmol/g) whereas CuCl2/CMS contained the lowest amount of Lewis acid sites (16.4 μmol/g).

In order to measure the strength of acid sites, the samples adsorbed with pyridine were further evacuated at 280 °C. NiCl2/CMS, CuCl2/CMS, AlCl3/CMS, and CoCl2/CMS at the beginning showed fairly high pyridine adsorption after evacuation at 100 °C. As evacuation temperature was increased to 280 °C, a significant decrease in the intensity of IR bands for these catalysts was observed. This indicated that these four CMS composites have Lewis acidity with mild acid strength (Table 1). In contrast, the IR bands with moderate intensity was still observed at 1490 and 1450 cm⁻¹ in the IR spectra of ZnCl2/CMS and FeCl3/CMS after evacuation at 280 °C. Based on the calculation, ZnCl2/CMS and FeCl3/CMS were found to have 14.4 μmol/g and 12.1 μmol/g of strong Lewis acid sites, respectively. In other words, these results of chloride species. Thus, we can conclude that the nanoparticles supported on CMS support after activation at 300 °C exist in the form of chloride rather than oxide form.

3.2. Catalytic study

3.2.1. Effect of catalysts and reaction time

The catalytic activity of metal chlorides supported on CMS solids were used as catalysts in hydroamination of cyclohexene at 60 °C where cyclohexylamine was used as the amination reagent (Eq. 1). It was found that there was almost no reaction without catalyst (conversion <0.5%) even after 24 h of reaction. In the presence of bare CMS, the conversion rate of hydroamination into dicyclohexylamine increased up to 7.05% after 8 h, showing that the parent CMS was relatively in active (Fig. 6a).

\[
\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}_2 + \text{H}_2\text{N} \rightarrow \text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}_2-\text{N}+\text{H}_2\text{O} \quad \text{(Eq. 1)}
\]

When MClx/CMS catalysts were introduced into the reactant mixtures, a remarkable catalytic activity was observed. As shown in Fig. 6, it was surprisingly observed that the catalytic activity of the catalysts followed the same trend as the number of Lewis acid strength of the catalysts. Best catalytic performance was achieved by ZnCl2/CMS with 61.52% of cyclohexene conversion and 100% selectivity to dicyclohexylamine. On the same side, FeCl3/CMS appeared as the second best catalyst, giving 58.22% conversion and 100% selectivity to a single product. In contrast, CuCl2/CMS which 1 possessed large amount of mild Lewis acid sites (as revealed by pyridine adsorption) only achieved 36.36% conversion in this catalytic reaction. Thus, the results concluded that hydroamination of cyclohexene with cyclohexylamine depended mainly on the strength of Lewis acid site instead of the number of Lewis acid site.

3.2.2. Effect of free and supported metal chloride catalysts

The catalytic performance of free and supported metal salts on CMS mesoporous materials was also evaluated. In order to perform the study, same amount of metal salts used for impregnation
(5.0 mmol) was introduced into the reactants mixture. It was shown that free AlCl$_3$, FeCl$_3$, and ZnCl$_2$ salts which as traditional homogeneous Lewis acid catalysts gave higher conversion (25–30%) than other free metal chloride salts (<20%) (Fig. 7). Interestingly, when the salts were supported on CMS materials, the catalytic activity improved tremendously. For instance, NiCl$_2$/CMS, CuCl$_2$/CMSand CoCl$_2$/CMS evidenced a three-fold increment in the reaction conversion which was higher than fora single component catalyst (Fig. 7). Thus, the boost in catalytic performance can originate from the synergistic effect of Lewis acidity, electrostatic and the confined nature in the chiral channel of MCl$_x$/CMS mesoporous catalysts. Among the supported CMS catalyst tested, ZnCl$_2$/CMS was the best catalyst for the hydroamination of cyclohexene.

### 3.2.3. Effect of temperature

The effect of temperature on hydroamination reaction was investigated at 25, 40 and 60 °C. At 25 °C, low conversion rate was achieved by all supported catalysts (Fig. 8). As expected, the conversion rate increased steadily as the temperature was raised from 25 °C to 40 °C and 60 °C. It is because a raise in temperature increases the reaction rate. In principal, a chemical reaction occurs only when the reactant molecules acquire sufficient kinetic energy, which needs to overcome the activated energy, as well as proper orientation of collision. From the kinetic theory, the more energy provided to the reactant molecules, the faster the molecules move and the more frequently they collide [46]. As a result, the reaction rate will increase simultaneously. The catalytic reaction was also carried out at 80 °C without success due to the volatility of chloroform solvent and cyclohexene reactant at that temperature. Thus, based on the obtained results, the optimum catalytic condition (best conversion and selectivity to dicyclopentylamine) was at 60 °C.

#### 3.2.4. Effect of support

Recently, mesoporous materials such as MCM–41 [47,48] and SBA–15 [49,50] have been explored as good supports for heterogeneous catalysis. These materials exhibit unique pore channel characteristics, high surface areas, narrow pore size distributions, and large pore diameters and volumes. For instance, MCM–41 has an array of uniform hexagonal channels [16] whereas SBA–15 has a feature of micropores interconnecting hexagonally ordered mesopores [17]. The effect of catalyst support in hydroamination was investigated by impregnating similar amount of ZnCl$_2$ on different MCM–41, CMS and SBA–15 supports (The preparation procedures, nitrogen adsorption data and acidity characterization can be found in the Supplementary Information, Figs. S2–S5, Table S1). It was found that the textural properties of support influence significantly the catalytic activity of hydroamination reaction. The results showed that CMS support (61.52%) with chiral channel has better performance in comparison with MCM–41 (52.72%) and SBA–15 (55.30%) containing merely straight channels (Fig. 9). According to Carrillo et al., the reason for this phenomenon is that the helical mesostructure can slightly affect the activity in the materials by improving the accessibility of active sites [51,52]. As a result, more contact of substrates to the Lewis acid sites during diffusion takes place and hence a higher catalytic activity is achieved.

#### 3.2.5. Leaching and reusability studies

Leaching and reusability are a major concern for supported solid catalysts in liquid phase reaction [18]. Thus, the leaching test of the non-activated and activated MCl$_x$/CMS solids was performed under severe condition by using ultrasonication treatment. The results showed that the activated MCl$_x$/CMS samples evidenced little leaching problem after 30 min sonication treatment (400 W) whereas serious leaching was observed in the non-activated catalysts (Fig. S6). Thus, the results demonstrated that activation of
solid catalysts at mild condition (300 °C) is very important to improve leaching problem by enhancing electrostatic attachment of metal chlorides nanoparticles onto the CMS support.

The main advantage of heterogeneous catalyst is reusability. However, many impregnated solid acid catalysts commonly suffer from rapid deactivation owing to the loss of active species. So, it is of great importance to evaluate the catalyst lifetime. The reusability of MClₓ/CMS was performed for four cycles. All the MClₓ/CMS catalysts exhibited high reusability with small decrease in conversion (averagely ~5.4%) and 100% selectivity was remained (Fig. 10). Among them, ZnCl₂/CMS sample showed the best reusability, it remained above 51.95% conversion of cyclohexene even after being used for four times. Thus, this suggested that the activation thermal treatment of the MClₓ/CMS catalysts helped in binding metal salts and minimizing leaching problem from the CMS support since the nanoparticles of metal salts were electrostatically bonded to the surface of CMS mesoporous support.

The leaching study was further carried out by measuring the metal and chloride contents in the MClₓ/CMS solid catalysts after four cycles of catalytic reaction. As shown in Table 2, CoCl₂/CMS suffered severe leaching (38.9%) which led to decrease in catalytic conversion (36.6%) after four cycles of hydrogenation reaction. On the other hand, AlCl₃/CMS, FeCl₃/CMS and ZnCl₂/CMS experienced lower leaching (~16.0%) in comparison with CoCl₂/CMS. Thus, having reasonable conversion and low leaching problem after four reaction cycles, the elementary analysis and catalyst reusability study suggested that AlCl₃/CMS, FeCl₃/CMS and ZnCl₂/CMS are potential candidates as recyclable heterogeneous catalysts in replacing non-recyclable homogeneous catalysts for hydrogenation of cyclohexene.

4. Conclusion

In conclusion, the current work highlights the study of metal chlorides supported on chiral mesoporous silica (MClₓ/CMS) and their use as highly active Lewis acid catalysts for hydrogenation of cyclohexene. The series of composite catalysts was systematically characterized and the studies revealed that metal chloride nanoparticles with 8–10 nm sizes were well dispersed on CMS rod particles. All the supported catalysts possessed only Lewis acidity where ZnCl₂/CMS contained the largest amount of strong Lewis acid sites followed by FeCl₃/CMS, CoCl₂/CMS, NiCl₂/CMS, AlCl₃/CMS and CuCl₂/CMS. The catalytic hydrogenation of cyclohexene over free metal chloride salts and MClₓ/CMS supported catalysts was also successfully explored. The supported catalysts evidenced a catalytic synergistic effect attributed to the Lewis acidity, electrostatic and the confined nature in the chiral channel of CMS mesoporous catalysts. All the catalysts especially ZnCl₂/CMS and FeCl₃/CMS were catalytically active (conversion ~60%) and showed 100% selectivity to dicyclopentadiene. On the other side, leaching problem of salts from CMS support was significantly improved by activation treatment at 300 °C. The reusability study showed that the catalysts (especially AlCl₃/CMS, FeCl₃/CMS and ZnCl₂/CMS) can be reused with little reactivity loss due to low leaching problem. Thus, being easily recovered and non-corrosive, this group of supported heterogeneous catalysts offers another eco-friendly replacement for conventional Lewis acids catalysts.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jtice.2013.12.011.

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