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PII:	S1566-7367(20)30188-6
DOI:	https://doi.org/10.1016/j.catcom.2020.106112
Reference:	CATCOM 106112
To appear in:	Catalysis Communications
Received date:	26 April 2020
Revised date:	17 June 2020
Accepted date:	3 July 2020

Please cite this article as: J. Wen, K. You, F. Zhao, et al., AlCl3 immobilized on silicic acid as efficient Lewis acid catalyst for highly selective preparation of dicyclohexylamine from the vapor phase hydroamination of cyclohexene with cyclohexylamine, *Catalysis Communications* (2020), https://doi.org/10.1016/j.catcom.2020.106112

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AlCl<sub>3</sub> immobilized on silicic acid as efficient Lewis acid catalyst for highly selective preparation of dicyclohexylamine from the vapor phase hydroamination of cyclohexene with cyclohexylamine

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## Abstract

efficient and stable Lewis acid catalyst silicic acid An (SA)-immobilized AlCl<sub>3</sub> (AlCl<sub>3</sub>-SA) has been successfully prepared by the chemical bonding method in this work. The results indicated that the immobilized 15% AlCl<sub>3</sub>-SA exhibited excellent catalytic performance and stability in the vapor phase hydroamination of cyclohexene with cyclohexylamine. 58.5% cyclohexene conversion with 98.7% selectivity to dicyclohexylamine was still maintained a<sup>cter</sup> running for over 150 hours, and the space time yield of dicyclo<sup>1</sup> exylamine was  $142.6 \text{ mol/h} \cdot \text{m}^3$ . The developed AlCl<sub>3</sub>-SA catalyst had dive advantages of low cost and long-time stable activity. Maybe this work provides a promising approach for hydroamination of olefins to amines.

**Keywords**: Immobil<sup>5</sup>zed AlCl<sub>3</sub>-SA catalyst, Dicyclohexylamine, Cyclohexene, Catalytic hydroamination, Vapor phase.

#### **1. Introduction**

The organic amines as important chemical raw materials and intermediates dominated a key role in fine chemicals, pharmaceuticals, pesticides, dyestuffs and petrochemical industries. For example, dicyclohexylamine (DCHA) was used as a useful chemical intermediate for the synthesis of excellent vapor phase corrosion inhibitors [1], rubber vulcanization accelerators, textiles, varnishes and conmercial insecticide [2]. It can be also employed to absorb acidic gases, to plasticize casein and neutralize plant and insect poisons. Its fatty acids and sulfuric acid salts have soap and detergent proper ie, used in the printing and textile industries. Several methods are employed for the manufacture of DCHA, which include the hydrogenation of equimolar amounts of cyclohexanone and cyclohexylamine [3] the lydrogenation of nitrobenzene [4] and the hydrogenation of nitropenzene with phenol [5]. At present, DCHA is industrially manufac ured by vapor phase catalytic hydrogenation of aniline at elevated temperature and pressure [6]. However, DCHA is hard to be separated from the high boiling residues comprised of unreacted aniline, N-phenylcyclohexylamine and DCHA in this process. Therefore, developing an alternative method for the convenient production of DCHA is imperative. Fortunately, the direct hydroamination of olefins to amines is a desirable process, which offers a simple, efficient, and high

atom-economical access. Hence, one-step hydroamination of cyclohexene and cyclohexylamine to DCHA with high atom-economical efficiency is regarded as a promising method.

Previous studies for the catalysts of hydroamination mainly focused on the Brönsted acids [7, 8], zeolites [9-15], noble metals [16] and transition metals [17, 18]. It worth be mentioned that the pentasil zeolites [13, 14] are the only type of catalysts currently applied in the commercialization of the direct amination, as d have an extremely high service time and last for years without descrivation. Based on these patents reported by Wolfgang Hölder cr., the very important intermediate tertbutyl-amine was commercialized in three BASF units, such as Freeport USA (10.000 t/a), Artwerp NL (10.000 t/a) and Nanjing China (30.000 t/a). However, montioned-above these catalysts more or less had some disadvantages (Table S1 in Supporting Information (SI)). Therefore, developing a cheap, highly efficient and stable catalyst for direct hydroaming ion of olefins to amines is highly desirable. To our delight, the Lewis acid catalysts have been widely applied in some organic reaction fields due to its environmental, practical and economical considerations. Especially, some typical Lewis acid catalysts were introduced into the liquid phase hydroamination of olefin to amines [19-24], and an acceptable amine yield was achieved. However, they

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were scarcely used in vapor phase hydroamination of olefin to amines.

Herein, we had successfully prepared a new mesoporous silicic acid (SA)-immobilized AlCl<sub>3</sub> (AlCl<sub>3</sub>-SA) as a highly efficient and stable Lewis acid catalyst by chemical bonding method. The mesoporous AlCl<sub>3</sub>-SA catalyst exhibited excellent catalytic performance and stability in the vapor phase hydroamination of cyclohexene with cyclohexylamine to DCHA (**Scheme 1**). The obtained results from the vapor phase hydroamination process will be reported in det ils in this paper.



Scheme 1 One-step catalytic hydroamination of cyclohexene to DCHA over immobilized mesopcroup AlCl<sub>3</sub>-SA.

## 2. Experimental Section

#### 2.1 Reagents and matruments

Cyclohexene (AR) and cyclohexylamine (AR) was purchased from Shanghai Macklin Biochemical Co., Ltd, China. Other chemicals (AR) used were obtained from Sinopharm Chemical Reagent Co., Ltd., China. The gas chromatograph (GC) (Agilent 7890B) equipped with a HP-5 capillary (30mx0.25mmx0.25µm) column and a hydrogen flame ionization detector (FID) was employed as the quantitative analysis of products. The gas chromatography-mass spectrometer (GCMS-QP2010 Plus Shimadzu) was employed as the qualitative analysis of products by the internal standard method (toluene was used as internal standard substance).

#### 2.2 Preparation process of immobilized AlCl<sub>3</sub>-SA catalyst

The immobilized Lewis acid catalysts were prepared by chemical bonding method. Typically, the preparation process of immobilized AlCl<sub>3</sub>-SA catalyst (**Scheme 2**) was as follows:

The preparation of SA: Firstly, 35.0 g sodium silicate was dissolved in 200 ml deionized water. Firen, 30.8 g hydrochloric acid was added into the solution under starting. The resulting gel was aged for 24 h at room temperature. Finally, the gel was washed until the filtrate became neutral, and the obtained  $5^{\circ}$  (Silicic acid) was dried at 100 °C for 12 h in a vacuum oven.

The preparation of immobilized AlCl<sub>3</sub>-SA catalyst: Firstly, in order to avoid the hydrolysis of anhydrous AlCl<sub>3</sub>, a certain amount of anhydrous AlCl<sub>3</sub> was rapidly dissolved in 20 mL anhydrous ethanol. Then, 2 g of dried silicic acid as precursor was added into the above solution. The resulting suspension was vigorously stirred and refluxed at 80 °C for 4 h in N<sub>2</sub> atmosphere. After then, the solvent was removed by rotary evaporated at 60 °C under vacuum. Finally, the obtained white solid powder was calcinated at 300 °C for 4 h in N<sub>2</sub> atmosphere. The resulting catalysts impregnated with 0.1g, 0.2 g, 0.3 g, 0.4 g, 0.5 g and 0.6 g of anhydrous AlCl<sub>3</sub> were named as 5%AlCl<sub>3</sub>-SA, 10%AlCl<sub>3</sub>-SA, 10%AlCl<sub>3</sub>-SA, 15%AlCl<sub>3</sub>-SA, 20%AlCl<sub>3</sub>-SA, 25%AlCl<sub>3</sub>-SA and 30%AlCl<sub>3</sub>-SA (wt%), respectively. The spent catalyst was regenerated by calcination at 550 °C in air for 4 h.



Scheme 2 Preparation of immobilized AlCl<sub>3</sub>-SA catalyst 2.3 Typical experimental procedure

The vapor phase h; dr/amination of cyclohexene with cyclohexylamine was carried out in a fixed bed straight tubular reactor of 850 mm length with 10 mm inner diameter. 3.5 g catalyst was placed at the center of the reactor. The hydroamination reaction was performed at a set reaction tempera ure under atmospheric pressure. The mixture of cyclohexene and cyclohexylamine were introduced into the reactor using a high pressure constant flow pump with 0.02 ml/min flow rate, and the flow of N<sub>2</sub> as carrier gas was controlled by a mass flow meter. The condensed with mixtures from the outlet of reactor were a low-temperature cooling liquid around 2-6 °C. The liquid products were identified and quantified by GC-MS and GC, respectively. Toluene was

used as internal standard sample for the quantitative analysis of products. The conversion of cyclohexene and selectivity to DHCA and *N*-cyclohexylidenecyclohexanamine (CCA) were calculated using the following equations:

Conversion of cyclohexene = 
$$\frac{\text{the mole of cyclohexene reacted}}{\text{the mole of cyclohexene added}} \times 100\%$$

Selectivity to DCHA= 
$$\frac{\text{the mole of DCHA}}{\text{the mole of cyclohexcreacted}} \times 100\%$$

Selectivity to CCA= 
$$\frac{\text{the mole of CCA}}{\text{the mole of cycloi-exene reacted}} \times 100\%$$

# 2.4 Characterization of catalysts

X-ray diffraction (XRD) paterns of samples were recorded on a Japan Rigaku D/Max-2550VE<sup>+</sup> 18 KW powder diffractometer with a monochromatic Cu Ka radiation source ( $\lambda$ =1.5418 Å) at 40 kV voltage and 300 mA electric corrent. The infrared spectra of pyridine adsorption (Py-FTIR) of can ples were examined on a Thermo Nicolet 380 FT-IR  $\mathrm{cm}^{-1}$ . spectrometer in the 1400-1650 The range of  $N_2$ adsorption-desorption isotherms of samples were measured on an American Mike Instruments 3Flex Physisorption analyzer at 77 K. The temperature-programmed desorption of ammonia (NH<sub>3</sub>-TPD) of samples were performed on a CHEMBET-3000 instrument from 100 to 700 °C at heating of 10 °C/min. Thermogravimetric/derivative rate a

thermogravimetric (TG/DTG) analysis of samples were conducted on a Mettler TGA/DSC1/1600HT thermogravimetric analyzer under 40 ml/min of nitrogen flow and 10 °C/min of heating rate from 30 to 800 °C.

#### **3. Results and discussion**

# 3.1 Catalytic performance of various catalysts in the vapor phase hydroamination reaction

In an effort to seek the suitable catalyst for schedule hydroamination of cyclohexene with cyclohexylamine to DCHA, everal typical catalysts were screened under the identical reaction conditions at atmospheric pressure, and the obtained results were summarized in Table 1. As expected, DCHA was not ob air ed in the absence of catalyst. The cyclohexene conversion and selectivity to DCHA were improved in different degrees as the microporous molecule sieves with strong Broensted acidic sites (such as HZSM-5, HY) and the weakly acidic catalysts with surface hydroxyl groups (such as SA and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) were introduced into the hydroamination reaction. In addition, compared with strongly acidic HZSM-5, the weakly acidic catalysts, iron modified ZSM-5 (Fe/ZSM-5), cobalt modified ZSM-5 (Co/ZSM-5) and boron modified ZSM-5 (B/ZSM-5) obviously improved the cyclohexene conversion and selectivity to DCHA. The cyclohexene conversion and selectivity to DCHA were futher improved over typical Lewis acid

catalysts (such as AlCl<sub>3</sub>, FeCl<sub>3</sub> and ZnCl<sub>2</sub>). Unfortunately, these Lewis acid catalysts have poor stability and are easy to be hydrolyzed in air, which makes the difficulties in operation. To our delight, an acceptable cyclohexene conversion and selectivity to the desired product DCHA were achieved over the immobilized Lewis acid catalysts. Especially, the immobilized 15% AlCl<sub>3</sub>-SA catalyst gave the satisfactory results with 41.6% of cyclohexene conversion and 97.3% of celectivity to DCHA. These results showed that the catalyst played a c ucial role in the vapor phase hydroamination of cyclohexene to  $\Gamma$  CEA.

 Table 1 Comparison of catalytic performance of various catalysts in the

 hydroamination reaction<sup>a</sup>

Catalyst	Conversion of cyclohexene	Selectivity (%)		
	(%)	DCHA	CCA	
None	- 7	-	-	
HZSM-5	4.3	85.4	14.6	
HY	6.4	88.8	11.28	
$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	17.6	71.6	28.4	
SA	18.3	75.4	24.6	
Fe/ZSM-5	10.5	88.3	11.7	
Co/ZSM-5	8.7	86.5	13.5	
B/ZSM-5	12.5	88.7	11.3	
AlCl <sub>3</sub> <sup>b</sup>	28.5	97.1	2.9	
FeCl <sub>3</sub>	26.8	95.8	4.2	
$ZnCl_2$	27.6	90.6	9.4	
$15\%H_2SO_4/SiO_2$	36.9	91.1	8.9	

15%FeCl <sub>3</sub> -SA	41.5	91.4	8.6	
15%ZnCl <sub>2</sub> -SA	44.9	71.3	28.7	
15% AlCl <sub>3</sub> -SA	41.6	97.3	2.7	
15% AlCl <sub>3</sub> -MCM-41	35.9	97.2	2.8	
<sup>a</sup> Reaction conditions: the	reaction temperature	e is 280 °C, th	ne molar	ratio

of cyclohexene to cyclohexylamine is 1:1.5, residence time is 14.6 s, time on stream is 6 h, and GHSV is 246.6  $h^{-1}$ .

<sup>b</sup> The reaction temperature is 190 °C.

Moreover, the hydroamination reaction crother amines and olefins over immobilized AlCl<sub>3</sub>-SA catalyst were also examined, and some satisfactory results were summarized in Table 2. 42.6% cyclohexene conversion and 98.5% selectivity to N-methylcyclohexylamine was obtained in the hydroamination of cyclohexene and methylamine. In addition, for the hydroaming tion of styrene and diethylamine, 55.3% of conversion with 94.1% of styrene the selectivity to N,N-diethylphenetin annine was achieved. Furthermore, an acceptable conversion and selectivity to the desired product were also obtained over AlCl<sub>3</sub>-SA catalyst in the hydroamination of isobutylene with ethylamine, and cyclohexene with aniline. These results demonstrated that the immobilized AlCl<sub>3</sub>-SA catalyst exhibits good catalytic performance in the hydroamination of olefins and amines.

Olefins	Amines	Products	Conversion (%)	Selectivity (%)
cyclohexene	methylamine	N-methylcyclohexylamine	42.6	98.5
styrene	diethylamine	N,N-diethylphenethylamine	55.3	94.1
isobutylene	ethylamine	N-tert-butylethylamine	20.1	96.7
cyclohexene	aniline	N-cyclohexylaniline	15.3	90.2

 Table 2 Hydroamination reaction results of other amines and olefins over

 15% AlCl<sub>3</sub>-SA catalyst<sup>a</sup>

<sup>a</sup>Reaction conditions: the reaction temperature is 2% °C, the molar ratio of cyclohexene to cyclohexylamine is 1:1.5, residence time is 14.6 s, time on stream is 6h, and GHSV is 246.6 h<sup>-1</sup>.

## 3.2. Optimization of reaction conditic ns

In order to find out optimal eaction conditions in hydroamination reaction, a single factor experiment was performed in present work. **Table S2** in SI showed the offects of immobilized AlCl<sub>3</sub>-SA catalysts with different AlCl<sub>3</sub> loadings on the catalytic hydroamination reaction of cyclohexene with cyclohexylamine. **Fig. S1** in SI depicted the effects of reaction temperature on the catalytic hydroamination reaction. The results indicated that properly increasing the reaction temperature was beneficial to the generation of target product DCHA. **Fig. S2** in SI showed the effects of residence time on the catalytic hydroamination reaction. It can be clearly seen that the cyclohexene conversion gradually increased with prolonged the residence time, and the selectivity to DCHA was basically

unchanged. However, further prolonging the residence time more than 20 s, the cyclohexene conversion increased slowly, while the selectivity to CCA obviously increased. The formation mechanism of CCA may be a follow-up dehydrogenation reaction of DCHA over solid acid catalyst under the longer residence time. Fig. S3 in SI displayed the effects of the molar ratio of cyclohexene to cyclohexylamine on the hydroamination enhancing concentration reaction. The results showed that of cyclohexylamine facilitated the formation o' DCHA. From the single-factor experiment results, 58.5% conversion of cyclohexene with 98.7% was achieved selectivity DCHA over immobilized to 15% AlCl<sub>3</sub>-SiO<sub>2</sub> catalyst under the optimal reaction conditions that 270 °C of reaction temperature, 1:4 of the molar ratio of cyclohexene to cyclohexylamine, 16.7 s of residence time and 215.6 h<sup>-1</sup> of gas hourly space velocity (GHSV).

# 3.3 Stability test of Symmobilized 15%AlCl<sub>3</sub>-SiO<sub>2</sub> catalyst in the vapor phase hydroamics tion reaction

It is well known that the catalyst stability is one of the crucial issues in the development of efficient catalysts. Therefore, in order to verify the stability of immobilized 15% AlCl<sub>3</sub>-SA catalyst, a long-term performance test was performed under the optimal reaction conditions, and the obtained results were depicted in **Fig. 1**. It was clearly seen that 58.5% of

cyclohexene conversion with 98.7% selectivity to dicyclohexylamine was still maintained after running for over 150 hours under the optimal demonstrated conditions. These results the immobilized that 15% AlCl<sub>3</sub>-SA catalyst exhibited excellent stability and activity in the vapor phase hydroamination of cyclohexene with cyclohexylamine to DCHA. Furthermore, in order to further investigate the leaching problem of immobilized 15% AlCl<sub>3</sub>-SA catalyst, the second and third run over the regenerated catalyst were performed in this work, and the obtained results were depicted in Fig. S4 and Fig. S5 in SI. These results demonstrated that there were no leaching problems over the time for the immobilized 15% AlCl<sub>3</sub>-SA catalyst, and the ne mos-stability of AlCl<sub>3</sub> is significantly improved by the immobilization methods.



**Fig. 1** Stability test of immobilized 15% AlCl<sub>3</sub>-SA catalyst in the hydroamination of cyclohexene with cyclohexylamine

## 3.4 Characterization of catalysts

The XRD patterns for the wide-angle of SA and immobilized 15% AlCl<sub>3</sub>-SA samples were displayed in Fig. S6 in SI. Obviously, a characteristic broad diffraction peak at  $2\theta = 22^{\circ}$  was observed in all samples, which belonged to the typical amorphous structure [25]. Moreover, the diffraction peaks of AlCl<sub>3</sub> were hardly observed in the immobilized 15% AlCl<sub>3</sub>-SA samples, indicating that no free AlCl<sub>3</sub> molecular species existed in the catalyst. The N adsorption-desorption isotherms and pore diameter distribution (urves of SA and 15% AlCl<sub>3</sub>-SA samples were presented in Fig. S7 ir SI, and the textural properties (surface area, pore volume, and pore diameter) were summarized in **Table S3** in SI. The BET surface area of SA is 588  $m^2/g$ , while the BET surface area decreased to 524  $m^2/g$  after impregnation. Fig. S8 in SI depicted the thermo-ctacility of SA, AlCl3 and 15% AlCl3- SA samples. The results derion trated that the thermo-stability of AlCl<sub>3</sub> was significantly improved after immobilizing on the mesopores SA by forming the stronger bond of Si-O-Al-Cl<sub>2</sub>.

To further verify the acidic sites and acid strength of catalysts, the FT-IR spectra of adsorbed pyridine and  $NH_3$ -TPD curves of SA and 15%AlCl<sub>3</sub>-SA catalysts were measured, and the obtained results were depicted in **Fig. 2**. As shown in **Fig. 2** (**A**), no significant IR signals were

observed in the range of 1400-1650 cm<sup>-1</sup> in the pyridine adsorbed FT-IR spectra of SA. While AlCl<sub>3</sub> was introduced to mesoporous SA, four characteristic peaks were observed at 1447, 1490, 1547 and 1609 cm<sup>-1</sup>. The high-intensity peaks appeared at 1447 and 1609 cm<sup>-1</sup> were ascribed to the characteristic adsorption of pyridine on strong Lewis acidic centers [26], the low-intensity peak at 1547 cm<sup>-1</sup> was attributed to the adsorption of pyridine on Brønsted acidic centers [27], and the charp peak at 1490 cm<sup>-1</sup> was assigned to the interaction of pyridine a disorbed on both Lewis and Brønsted acidic sites [28]. These results demonstrated that the Lewis acidity of catalyst was significantly improved after AlCl<sub>3</sub> was immobilized on the SA, and 15 %  $_{2}$  JCr<sub>3</sub>-SA catalyst possessed the strong Lewis acidic sites.



**Fig. 2** FT-IR spectra (A) of adsorbed pyridine and NH<sub>3</sub>-TPD curves (B) of SA and 15%AlCl<sub>3</sub>-SA samples

**Fig. 2 (B)** described the NH<sub>3</sub>-TPD profiles of SA and 15%AlCl<sub>3</sub>-SA samples. Obviously, the immobilized 15%AlCl<sub>3</sub>-SA samples exhibited

the strong NH<sub>3</sub> desorption peak while SA only showed the weak NH<sub>3</sub> desorption peak at around 170 °C, which was assigned to the desorption of ammonia bonded on weak acid centers [29]. The results indicated that the acid amounts of the weak acid centers of catalyst were remarkably improved as  $AlCl_3$  was immobilized on SA. Moreover, a new  $NH_3$ desorption peak at around 520 °C was observed in 15% AlCl<sub>3</sub>-SA samples, which was ascribed to the desorption of ammonia builded on strong acid centers [30]. This acid sites may be created by the interaction between Al species and the Brönsted acid sites [31] In addition, the intensities of desorption peaks for spent 15% AlCl<sub>3</sub>: 5/x catalyst was almost unchanged, indicating that the acid amount, and acid strength of catalyst were well maintained during the hydrocymination reaction. Furthermore, the FT-IR spectra of adsorbed pyridine and NH<sub>3</sub>-TPD curves of regenerated catalyst also indicated that there was no obviously loss in chloride and aluminum after regeneration

# 3.5 The possible reaction pathways for the hydroamination of cyclohexene with cyclohexylamine over Lewis acid $AlCl_3$ -SA catalyst

In general, the reaction pathways for vapor phase catalytic hydroamination of olefin with amine catalyzed by Lewis acid catalyst are regarded as the electrophilic addition [24, 32, 33]. According to the results obtained in this work, the possible mechanistic pathways of the hydroamination of cyclohexene with cyclohexylamine over Lewis acid AlCl<sub>3</sub>-SA catalyst were proposed in **Scheme 3**. Firstly, cyclohexene and cyclohexylamine were adsorbed on the immobilized AlCl<sub>3</sub>-SA surface. Since Al<sup>3+</sup> has higher affinity to cyclohexylamine than cyclohexene because of the electronegativity of the lone pair electron of nitrogen atom, the adsorption step results in the activation of cyclohexylamine [34]. Thus, the Al-coordinated amine species was formed, which generated the proton as electrophilic reagent [35]. Then, the carbocation of cyclohexene was generated by the electrophilic addition between Al-coordinated amine species as protic acid and cyclohexene. The formed carbocation of cyclohexene was attacked by the lone electron pair of Al-coordinated amine species to generate the brechate. Finally, the free Lewis acid site of catalyst was regenerated again by the release of DCHA product.



Scheme 3 Possible catalytic hydroamination reaction mechanism of cyclohexene with cyclohexylamine over Lewis acid AlCl<sub>3</sub>-SA catalyst

#### 4. Conclusions

In summary, a simple and efficient approach for the selective catalytic hydroamination of cyclohexene and cyclohexylamine to DCHA in vapor phase has been successfully developed in this work. The immobilized AlCl<sub>3</sub>-SA catalyst with strong Lewis acid sites was successfully prepared by the chemical bonding between AlCl<sub>3</sub> and surface silicon hydroxyl groups (Si-OH). 52.5% of cyclohexene conversion with 98.7% of selectivity to DCF A vas obtained under the optimized reaction conditions. Moreover, he immobilized 15% AlCl<sub>3</sub>-SA high thermal stability catalyst exhibited and activity in the hydroamination reaction. Finally, the possible catalytic hydroamination reaction mechanism of cyclohexene with cyclohexylamine over Lewis acid AlCl<sub>3</sub>-SA catalyst web suggested. Maybe the present work provides a promising strategy for the hydroamination of olefin to valuable amines employing the in xp nsive immobilized Lewis acid as catalyst, and has important industric. application prospects.

#### Acknowledgements

We are grateful for the financial support by the National Natural Science Foundation of China (21676226), the Natural Science Foundation for Distinguished Young Scholars in Hunan Province (2018JJ1023), Key Research and Development Program in Hunan

Province (2019GK2041), Hunan Key Laboratory of Environment-Friendly Chemical Process Integrated Technology and Collaborative Innovation Center of New Chemical Technologies for Environmental Benignity and Efficient Resource Utilization.

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# **Credit Author Statement**

Jingbin Wen: Experimental, Methodology, Characterization, Writing-Original draft

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# **Declaration of Interest Statement**

We declare that we have no any financial and personal relationships with other people or organizations that can inappropriately influence our work, there is no professional or other personal interest of any nature or kind in any product, service and/or company that could be construed as influencing the position presented in, or the review of, the manuscript entitled, "AlCl<sub>3</sub> immobilized on silicic acid as officient Lewis acid catalyst for highly selective preparation of dicyclohexylamine from the vapor phase hydroamination of cyclohexe is with cyclohexylamine".



Meso immobilized AlCl<sub>3</sub>-SA

# Highlights

- A new mesoporous immobilized Lewis acid catalyst had been successfully prepared.
- AlCl<sub>3</sub> can be grafted on the silicic acid (SA) by chemical bonding method.
- Immobilized AlCl<sub>3</sub>-SA catalyst exhibited excellent catalytic performance and stability.
- Immobilized AlCl<sub>3</sub>-SA had the advantages of low cost, long-time stable activity and reusability.
- This work provides a promising approach for the catalytic hydroamination of olefin to amines.