AlCl$_3$-Grafted MCM-41 as a New Catalyst for the Catalytic Cleavage of the Si-Si Bond of Methylchlorodisilanes to Methylchloromonosilanes

Zhongping Zhang[a]; Chao Chen[a]; Zhiyong Ao[a]; Li Chen[a]; Ning Zhang[a]

[a] Department of Chemistry, Nanchang University, Nanchang, P.R. China

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AlCl$_3$-GRAFTED MCM-41 AS A NEW CATALYST FOR THE CATALYTIC CLEAVAGE OF THE Si–Si BOND OF METHYLCHLORODISILANES TO METHYLCHLOROMONOSILANES

Zhongping Zhang, Chao Chen, Zhiyong Ao, Li Chen, and Ning Zhang

Department of Chemistry, Nanchang University, Nanchang, P.R. China

Mesoporous MCM-41 silica-immobilized aluminum chloride was employed as a new catalyst for cleaving methylchlorodisilanes to methylchloromonosilanes. The parent and AlCl$_3$-grafted MCM-41 samples were characterized by X-ray powder diffraction, N$_2$ sorption, and EDAX. The nature and concentration of the acid sites of AlCl$_3$-grafted MCM-41 samples were monitored by in situ IR using pyridine as a probe molecule. The result of catalytic cleavage reveals that the synthesized catalysts possess considerable activity in the catalytic decomposition reaction and high selectivity to methylchloromonosilanes. The AlCl$_3$-grafted MCM-41 catalyst can be used for the cleavage of methylchlorodisilanes under atmospheric pressure. The influence of reaction time on the performance of the catalyst was also investigated. The conversion of methylchlorodisilanes and yield to methylchloromonosilanes can reach 70.5% and 63.4% over the AlCl$_3$-grafted MCM-41 catalyst, respectively.

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Keywords AlCl$_3$-grafted MCM-41; cleavage; methylchlorodisilanes; methylchloromonosilanes

INTRODUCTION

Organochlorosilanes, particularly methylchlorosilanes (MCSs), are well-known reactive chemical intermediates utilized extensively in silicon industries. Direct process, which was discovered by Rochow,[1] is the main method for the synthesis of MCSs. While methylchlorosilanes are produced by the direct process, there are some byproducts formed, such as a high-boiling residue whose boiling point is above 353 K. The high-boiling residue contains some compounds that have linkages such as Si–Si, Si–Si–Si, and Si–C in molecules, and their ratios depend on the reaction conditions, structure of reactor, silicon purity, and nature of the catalyst.[2] In current commercial operations for performing the

direct process, the high-boiling residue can constitute as much as 5–10 wt% of the resultant products.[3–5] The reaction of high-boiling residue with water or combustion of high-boiling residue into fumed silica leads to the formation of hydrogen chloride, which is detrimental to the environment. Therefore, it is desirable to convert the high-boiling residue into commercial products without pollution of the environment to both reduce waste disposal and to improve raw material utilization.

Except for some reports dealing with the Si–Si bond cleavage via thermal scission, a large part of the reported literature is concerned with the use of Lewis acids, such as $AlCl_3$, $NiCl_2$, $CuCl_2$, and their complex compounds, as cleavage and redistribution catalysts. Among them, $AlCl_3$ is investigated extensively because of its low price and high selectivity to monosilanes.[6–9] However, it also shows some drawbacks: (1) High pressure is needed to impede $AlCl_3$ vaporizing, resulting in inconvenience of operation as well as high cost; (2) $AlCl_3$ is a stoichiometric reagent, which cannot be recovered, and has to be disposed, thus producing a large volume of solid waste. In order to improve the shortcomings of this catalyst, the immobilization of $AlCl_3$ onto an inorganic solid support could be an effective strategy. With uniform mesopores, long-range order, and extensive specific area,[10,11] MCM-41 has attracted wide attention in heterogeneous catalysis.[12] However, the weak acid strength of terminal silanol groups, both on the external and internal surface of the MCM-41, limits its application. Therefore, immobilization of aluminum chloride onto MCM-41 would not only overcome the drawbacks of $AlCl_3$, but would also improve the limitation of MCM-41.

In the present work, aluminum chloride was immobilized onto mesoporous MCM-41 silica. The synthesized samples were characterized by X-ray powder diffraction, N_2 sorption, and EDAX. Acid site concentrations (Brønsted and Lewis) were estimated from sorption of pyridine using in situ IR. The activity of all the catalysts was evaluated by the cleavage reaction of methylchlorodisilanes to methylchloromonosilanes.

RESULTS AND DISCUSSION

Catalysts Characterization

The XRPD patterns for purely siliceous MCM-41 and $AlCl_3$-grafted MCM-41 catalysts are shown in Figure 1. A typical diffractogram of MCM-41 shows four peaks at low angles, the angles of which can be indexed to a hexagonal unit cell.[13] In the XRPD patterns of parent MCM-41 (Figure 1a), a strong peak at $2\theta = 2.198°$ corresponding to (100) reflection and three weaker peaks at higher angles assigned to (110), (200), and (210) reflections are observed. The hexagonal unit cell or lattice parameter, measuring the spacing between the hexagonal layers, is calculated as the $\alpha_0 = d_{100} (2/\sqrt{3})$. For the MCM-41, this parameter is 51.2 Å (Table I). The main intense peak shifts towards slightly higher d-spacing, resulting in an increase in the unit cell constant of treated samples with a decrease in the Si/A1 ratio after immobilizing with $AlCl_3$ (see Figure 1), but the (110) and (200) reflections become less well defined, while the (210) peak is almost not detected, suggesting the partial loss the hexagonal symmetry of the sample.[13] The calculated XRD d value and lattice parameter value of all samples are shown in Table I.

The N_2 adsorption–desorption on the MCM-41 and all the $AlCl_3$-grafted MCM-41 samples (Figure S1, Supplemental Materials, available online) shows as a typical type-IV isotherm, which is a typical shape for mesoporous MCM-41.[14] Four well-defined stages were identified as follows: (1) adsorption at low relative pressure, attributed to the adsorption of monolayers of N_2 on the pore walls; (2) a light inflection point at intermediate relative
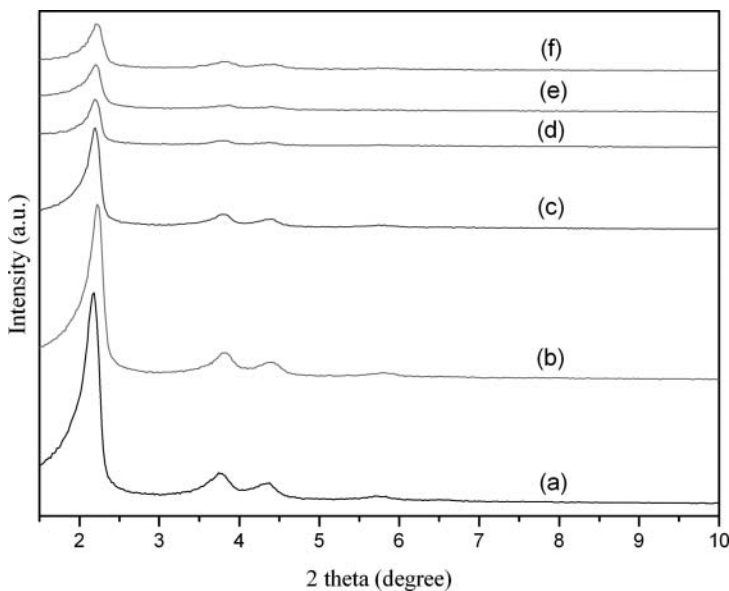
Figure 1 XRD powder patterns of (a) the parent MCM-41, (b) catalyst A, (c) catalyst B, (d) catalyst C, (e) catalyst D, and (f) catalyst E.

pressure, corresponding to capillary condensation in the pores; (3) a plateau with a slight inclination at high relative pressure due to the adsorption of multilayers on the material surface;[12] and (4) a sharp rise in N_2 uptake filling all other available pores when the pressure reached saturation ($P/P_0 = 1$).[15] The isotherms of all the AlCl₃-grafted MCM-41 samples are comparable with that of the parent sample, suggesting that the mesoporosity of the treated samples is largely preserved during the refluxing process. As shown in Table I, the structure of MCM-41 is retained, but the surface area, pore volume, and average pore diameter of treated samples decrease with the decrease in the Si/A1 ratio after the modification with anhydrous AlCl₃.

Figure S2 (Supplemental Materials) shows the infrared spectra of the pyridine adsorbed on the catalyst C, D, and E in the region 1650–1350 cm^{-1} at 423 K. Prior to the adsorption experiment, the samples were calcined in vacuum at 573 K for 2 h. The calcined samples were exposed to pyridine at 423 K followed by evacuation at 423 K for 30 min to remove physisorbed pyridine. As expected, all the samples exhibited the bands due to

Table I Texture properties of all the samples studied by XRD and N_2 sorption

Sample	XRD d_{100} value (Å)	Lattice parameter α_0 (Å)	BET surface area ($m^2 \cdot g^{-1}$)	Pore volume ($mL \cdot g^{-1}$)	Si/Al ratio	Average pore diameter (Å)
MCM-41	44.3	51.2	1013	0.93	∞	30.3
Catalyst A	44.3	51.2	897	0.79	14.5	29.5
Catalyst B	44.8	51.7	818	0.70	7.0	29.2
Catalyst C	44.9	51.8	780	0.60	4.7	28.5
Catalyst D	45.0	52.0	702	0.51	4.3	28.4
Catalyst E	45.0	52.0	484	0.45	4.5	28.9

strong Lewis-bonded pyridine (1455 and 1620 cm^{-1}) and pyridinium ion ring vibration due to pyridine bonded to Brønsted acid sites (1544 and 1637 cm^{-1}). The signal at 1492 cm^{-1} is assigned to a combination band associated with both Brønsted and Lewis sites.[16] A careful investigation of the band position of the Brønsted acid sites at 1544 cm^{-1} reveals that as we go from catalyst C to E, the peak intensity increases, which is consistent with the report of Chakraborty and Viswanathan.[17] Examination of the band at 1455 cm^{-1} shows that the intensity of this band is the highest for catalyst E, though the difference is not great between catalyst D and E. Also, the infrared spectra of the pyridine adsorbed on the catalyst D subjected to different thermal treatment in the range 363–573 K was investigated (Figure S3). The bands at 1596 cm^{-1} and 1445 cm^{-1} were associated with hydrogen-bonded pyridine and the combination of Lewis sites and hydrogen bonded pyridine, respectively (see Figure S3a). These bands basically disappear at 423 K (see Figure S3c), and the band at 1445 cm^{-1} shifts to 1455 cm^{-1}, which is assigned to Lewis sites bonded pyridine. All IR spectra in Figure S3 indicate that increasing evacuation temperatures reduces the number of acid sites capable of interacting with pyridine. With thermal treatment, the intensity of all bands decreases, and the band at 1544 cm^{-1} almost disappears at 513 K, but the reduction in the intensity of Lewis acid sites seems to be relatively less than that of the Brønsted acid sites.

Catalytic Studies

The results of all the catalysts for catalytic decomposition reactions of methylchlorosilanes are shown in Table II. The activity of the catalysts with different Si/Al ratio is summarized for the catalytic decomposition reactions under the given reaction conditions. The MCM-41 without AlCl$_3$ shows a very low conversion (5%) and yield of methylchloromonosilanes (3.8%). The increased amounts of AlCl$_3$ immobilized onto MCM-41 leads to a clear increase of conversion and yield. However, the total amount of methylchloromonosilanes increases less when the Si/Al ratio reaches 4.7. For the E catalyst, the conversion and yield both decrease, which is probably ascribed to blocking of the pore network of MCM-41 caused by excessive AlCl$_3$. This is consistent with the result of N$_2$ adsorption–desorption, which shows the BET surface area of catalyst E is much lower than that of catalyst D.

The results of comparisons of various catalysts for catalytic decomposition reactions of methylchlorodisilanes are shown in Table III. It is remarkable that AlCl$_3$-grafted MCM-41 catalyst is far more active than the MCM-41, indicating that AlCl$_3$ plays the key role in

Table II Catalytic properties of all the catalysts under the reaction conditions indicated

Samples	X (g)^a	Si/Al	Conversion (%)^b	Products (%)^c
MCM-41	0	∞	5.0	3.8
Catalyst A	0.2	14.5	50.7	46.2
Catalyst B	0.3	7.0	64.5	57.1
Catalyst C	0.4	4.7	68.5	62.7
Catalyst D	0.5	4.3	70.5	63.4
Catalyst E	0.6	4.5	67.4	60.6

Reaction conditions: CHCl$_3$ refluxing temperature, 0.1 MPa, reacting for 5h.

^{a}The amount of AlCl$_3$ added to react with 1 g MCM-41 in the synthesis procedure of catalyst.

^{b}Conversion of methylchlorodisilanes.

^{c}Yield of methylchloromonosilanes products.

Table III Comparison of various catalysts for catalytic decomposition reactions

Catalyst	Temperature (K)	Pressure MPa	Conversion (%)[a]	Products (%)[b]	Reference
Tri-n-butyl amine	403–423	0.15	∼91.6	∼85.0	18
LiAlH₄	503	3.4	∼85.0	∼74.0	19
AlCl₃	573–623	4.8–6.9	∼83.2	65.5	9
MCM-41	333–353	0.1	5.0	3.8	This work
Catalyst D	333–353	0.1	70.5	63.4	This work

[a]Conversion of methylchlorodisilanes.
[b]Yield of methylchloromonosilanes products.

the cleavage reaction. Although the amine catalysts show the best conversion and selectivity to methylchloromonosilanes, only the reactants having at least two chlorine atoms attached to a silicon atom could be cleaved in the presence of hydrogen chloride.[18] Also, limitations of this system include difficult separation of products and catalysts and the need for large dosages of catalyst, as well as difficult recovery of the catalyst, a large volume of liquid waste, and the fact that catalyst cannot be used for subsequent batches. Compared to AlCl₃[9] or LiAlH₄[19] catalysts, which show high activity for the cleavage of the Si–Si bond, the AlCl₃-grafted MCM-41 catalyst also exhibits a remarkable activity. Additionally, the highlight of our present catalytic system is that the cleavage of the Si–Si bond can be conducted under atmospheric pressure. This facilitates the operation and reduces the cost caused by high pressure.

In order to optimize the reaction time, the catalytic cleavage reaction was carried out with catalyst D and a reaction that time that ranged from 1 to 5 h. The strong influence of the reaction time on the catalyst activity and selectivity is concluded from the results shown in Figure S4. The ideal results were obtained when the reaction was conducted for 3 h, and the conversion and selectivity reached 68.4% and 62.1%, respectively. In order to maximize the catalytic cleavage reactions, 5 h was chosen for the reaction time. The influence of the reaction temperature was not investigated in the present work since the catalytic cleavage reactions were performed under the CHCl₃ refluxing temperature.

In conclusion, a series of AlCl₃-grafted MCM-41 catalysts were prepared by reacting anhydrous AlCl₃ with the terminal Si–OH groups of MCM-41, and their catalytic performance was tested for cleavage of Si–Si bonds in the conversion of methylchlorodisilanes to methylchloromonosilanes. The influence of different Si/Al ratios and reaction times on catalytic properties was also investigated. The cleavage reaction could be carried out under relatively gentler conditions, which may reduce the cost of high-pressure reactions in the cleavage conversion of methylchlorodisilanes to methylchloromonosilanes.

EXPERIMENTAL

Synthesis

The preparation of the siliceous MCM-41 sample was carried out by hydrothermal synthesis, according to the literature.[20] AlCl₃ immobilized on MCM-41 was prepared by reacting X g anhydrous AlCl₃ (Alfa Aesar) with 1 g of MCM-41, according to the literature.[21] Here, X = 0.2, 0.3, 0.4, 0.5, and 0.6, and the corresponding AlCl₃-grafted catalyst samples, were marked as catalyst A, B, C, D, and E, respectively.

Characterization

X-ray powder diffraction (XRPD) patterns were recorded on a Rigaku DMAX2400 instrument using Cu Kα radiation ($\lambda = 0.15418$ nm, 40 kV) at the scanning step width of 0.02°/sec. Elemental analysis for determining the Si/Al ratio was performed by EDAX (SIRION-100). Textural properties were determined from the N_2 adsorption isotherm at 77 K with Micromeritics instrument (APSP2020). The pore size distribution was determined using the BJH analysis, and the specific surface area was calculated using the standard BET method. The acidic nature of MCM-41 materials was investigated by FTIR spectroscopy in the region of pyridine complexes. FTIR spectra of chemisorbed pyridine were measured in situ using a Nicolet 5700 FTIR spectrometer.

Catalytic Tests

The decomposition reactions of methylchlorodisilanes over the $AlCl_3$-grafted MCM-41 catalysts were carried out in a magnetically stirred glass reactor under atmospheric pressure and at the $CHCl_3$ refluxing temperature. For each catalytic test, high boiling residue (10 mL), which mainly constituted of $Me_2ClSiSiClMe_2$, $MeCl_2SiSiCl_2Me$, $MeCl_2SiSiCl_3$, $MeCl_2SiSiMe_3$, and $MeCl_2SiSiClMe_2$ (about 91 wt%), and $CHCl_3$ (Aldrich) (15 mL) were introduced into a three-necked flask equipped with a condenser and a N_2 container. The reaction was started with the introduction of catalyst (100 mg). All the catalysts were activated at 300 °C for 3 h under N_2 atmosphere before introduction into the reaction mixture. The cleavage reaction of methylchlorodisilanes was also carried out employing MCM-41 as catalyst. After the decomposition reactions completed, the crude products whose boiling points are below 353 K were isolated through distillation method. The decomposition conversion of high boiling residue (HBDC) was calculated by the following formula:

$$\text{HBDC} = \left(\frac{M_0 - M_e}{M_0} \right) \times 100\%$$

where M_0 and M_e was the initial weight of the high boiling residue and the weight of the unreacted high boiling residue, respectively. The yield of monosilanes (Y) was calculated by the following formula:

$$\text{Y} = \left(\frac{M_c - M_t}{M_0} \right) \times 100\%$$

where M_c was the weight of the crude products and the M_t was the weight of $CHCl_3$, which was determined by GC method.

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