# STUDIES OF ACID PROPERTIES OF FeSiMCM-41 AND LaSiMCM-41 BY NH$_3$-MICROCALORIMETRIC AND NH$_3$-TPD MEASUREMENTS

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## Abstract

The acidity of mesoporous materials FeSiMCM-41, LaSiMCM-41, SiMCM-41, AlSiMCM-41 and HAlSiMCM-41 has been investigated by microcalorimetric studies of the adsorption of ammonia and temperature programmed ammonia desorption method. In the initial stage, the acid strength sequence is SiMCM-41>HAlSiMCM-41>AlSiMCM-41>FeSiMCM-41>LaSiMCM-41, in agreement with that found for microporous molecular sieves materials. A small number of strong acid sites of SiMCM-41 may result from the aluminum impurity contained in the silica source material. The acid density sequence is HAlSiMCM-41>AlSiMCM-41>FeSiMCM-41>LaSiMCM-41≥SiMCM-41 and can be explained by the studies of existing states of trivalent atoms in these samples reported in previous work. Since some NH$_3$-TPD plots of these samples show the profiles that could not be back to baseline at elevated temperature, the technique of microcalorimetric adsorption is preferable in studying these samples.

## Introduction

Due to the channel diameter within 1.5–10 nm, the synthesis of mesoporous molecular sieves family M41S by Mobil in 1992 threw new light on the conventional concept of synthesis of zeolites [1]. One member of this family, named as MCM-41, exhibits stable regular hexagonal pore channel structure and, therefore, is of special application prospect.

For its potential application, the studies on this family novel materials are very active recently [2]. It is well known that heteroatoms can modify the physico-chemical properties of zeolite molecular sieves, thus numerous papers about heteroatom-containing mesoporous materials have been published [3–12]. However, though a

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Fe-containing MCM-41 sample with Si/Fe molar ratio of 75 has been reported, Fe, and La, two common elements widely used in microporous molecular sieves, have not yet been studied in detail. We have successively incorporated Fe(III) and La(III) into the framework (channel wall) of MCM-41 (designated as FeSiMCM-41 and LaSiMCM-41) using $C_{16}H_{33}(CH_3)_3NBr$ (CTAB) as template and water glass as silicon source [13]. In this paper, we will report the acid properties, which are important for catalysis, of these two samples, as well as the siliceous sample SiMCM-41, Al-containing sample AlSiMCM-41 and its H-type HAlSiMCM-41 by means of $NH_3$-microcalorimetric measurement and $NH_3$-TPD (temperature programmed desorption) techniques.

## Experimental

The synthesis of samples SiMCM-41, AlSiMCM-41, FeSiMCM-41 and LaSiMCM-41 used in the present work has been described elsewhere [13]. XRD, IR, $N_2$-BET measurement and HRTEM techniques determined their structures typical of MCM-41 hexagonal mesoporous materials. The synthesized samples were calcined at 813 K in flowing $N_2$ for 1 h followed by air for 6 h to decompose the template $C_{16}H_{33}(CH_3)_3NBr$ for further experiments. HAlSiMCM-41 was prepared by exchanging template-removed AlSiMCM-41 sample with $NH_4NO_3$ at 353 K for 2 h in the mass ratio, AlSiMCM-41: $NH_4NO_3$:$H_2O$=1:4:30, followed by washing with distilled water, drying at 373 K and calcination at 773 K for 4 h.

Microcalorimetric adsorption studies of $NH_3$ at 423 K were carried out on a Tian-Calvet heat-flux apparatus described elsewhere [14]. The microcalorimeter was connected to a gas-handling and volumetric adsorption system, equipped with a Baratron capacitance manometer for precision pressure measurements. The differential heat of adsorption vs. adsorbate coverage was obtained by measuring the heats evolved when doses of $NH_3$ (1–3 μmol>99.9%) were admitted sequentially onto the catalyst until the surface was saturated by adsorbed species. Before microcalorimetric measurements, the samples were typically dried under vacuum at 673 K for 1 h, calcined twice in 450 Torr $O_2$ at 673 K for 1 h, and evacuated at 673 K about 2 h until $<10^{-5}$ Torr.

$NH_3$-TPD experiments were performed with a heating rate of 15 K min$^{-1}$ from 373 to 873 K. Before TPD experiments, samples were activated at 873 K for 2 h in flowing $N_2$ (50 ml min$^{-1}$).

## Results and discussion

Some physico-chemical properties of samples are summarized in Table 1. All the samples show the large surface area with the pore size of 3.3 nm (3.2 nm for SiMCM-41). Although no Al was introduced deliberately, as a result of Al impurity contained in the starting materials (water glass), the siliceous sample SiMCM-41 exhibits a Si/Al ratio of 700.

Figure 1 shows plots of the differential heat of ammonia adsorption as a function of adsorbate coverage on the various samples. At the initial stage, SiMCM-41 and

**Table 1** Some physico-chemical properties of samples

| Sample | Before calcination | | After calcination | | | | | |
|---|---|---|---|---|---|---|---|---|
| | $d_{100}$/nm | $a^a$/nm | $d_{100}$/nm | $a$/nm | pore size (BJH)/nm | S.A.[b] | Si/M[c] | A.D.[d] |
| SiMCM-41 | 4.27 | 4.93 | 4.03 | 4.65 | 3.2 | 1340 | 700 | 266 |
| FeSiMCM-41 | 4.43 | 5.12 | 4.46 | 5.15 | 3.3 | 947 | 31 | 416 |
| LaSiMCM-41 | 4.35 | 5.02 | 4.03 | 4.65 | 3.3 | 932 | 42 | 337 |
| AlSiMCM-41 | 4.29 | 4.95 | 4.15 | 4.79 | 3.3 | 1084 | 29 | 499 |
| HAlSiMCM-41 | – | – | 4.15 | 4.79 | 3.3 | 1057 | 29 | 664 |

[a] Lattice parameter $a=d_{100}2/\sqrt{3}$,
[b] Surface area/m$^2$ g$^{-1}$
[c] Molar ratio, where $M$=Al, Fe, La for the corresponding sample, but $M$=Al for SiMCM-41,
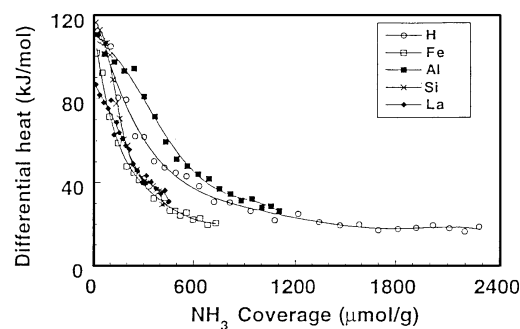[d] Acid density/$\mu$mol g$^{-1}$ (measured by NH$_3$-TPD method)



**Fig. 1** Differential heat *vs.* adsorbate coverage for adsorption of NH$_3$ at 423 K on calcined
× – SiMCM-41; □ – FeSiMCM-41; ♦ – LaSiMCM-41; ■ – AlSiMCM-41 and
o – HAlSiMCM-41

HAlSiMCM-41 exhibited small amount of the strongest acidic sites. The strongest acidic sites in SiMCM-41 may result from the Al impurity. Exchanging AlSiMCM-41 with NH$_4$NO$_3$, followed by calcination at elevated temperature, produced some bridging OH groups which should respond to the strongest acidic sites in HAl-SiMCM-41, just like the well-known case in microporous molecular sieves. From Figs 1 and 2, we can also find that the density of acidic site in HAlSiMCM-41 is much greater than that in AlSiMCM-41, indicating exchanging with NH$_4$NO$_3$ increased the number of acidic sites. However, besides a small amount of strongest acidic sites mentioned above, the increased sites are mainly weak acidic sites exhibiting low NH$_3$ adsorption heat.

Apart from SiMCM-41 and HAlSiMCM-41, the other samples exhibited the acid strength sequence as: AlSiMCM-41>FeSiMCM-41>LaSiMCM-41, in consistence with that found and well known for microporous molecular sieves.
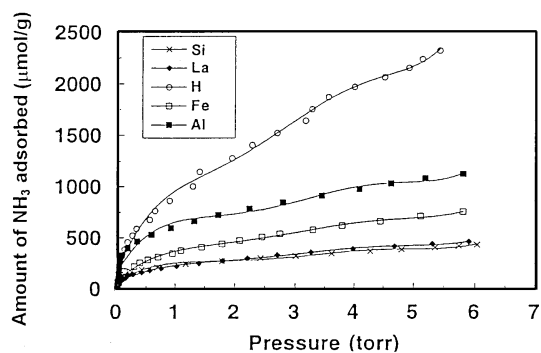
**Fig. 2** Amount of NH₃ adsorbed *vs.* the balanced pressure of NH₃ at 423 K on calcined
× – SiMCM-41; □ – FeSiMCM-411; ♦ – LaSiMCM-41; ■ – AAlSiMCM-41 and
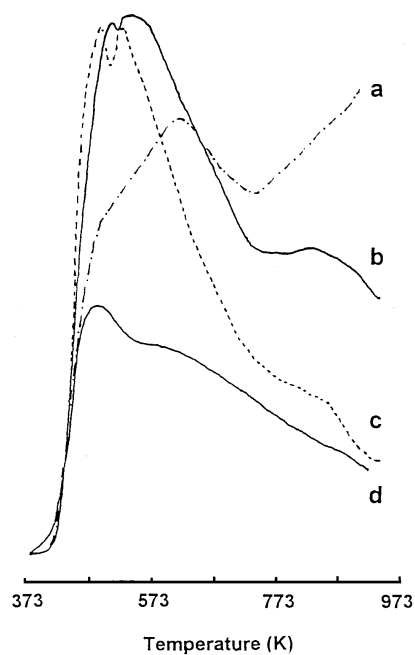o – HAlSiMCM-41



**Fig. 3** NH₃-TPD curves of a – FeSiMCM-41; b – HAlSiMCM-41; c – AlSiMCM-41 and
d – LaSiMCM-41

The acid densities for all the samples are shown in Fig. 2. The sequence of acid density can be found to be:

HAlSiMCM-41≫AlSiMCM-41>FeSiMCM-41>LaSiMCM-41≥SiMCM-41,

which is in agreement with that obtained by the $NH_3$-TPD method (Table 1). However, because some $NH_3$-TPD plots of these samples show the profiles that could not be back to baseline at elevated temperatures (Fig. 3, especially for FeSiMCM-41), which may lead to error in determining the acid densities, it is concluded that techniques of microcalorimetric adsorption is preferable in studying these samples.

The synthesized FeSiMCM-41 and LaSiMCM-41 exhibited greater XRD d-spacing values than that of synthesized SiMCM-41, which is the result of substitution of longer Fe–O (1.97) or La–O (2.54) bond for shorter Si–O bond (1.61 nm) [13]. It is also found that the wavenumbers of bands of infrared spectra for the framework of synthesized FeSiMCM-41 and LaSiMCM-41 shift toward lower frequency as compared with that of the synthesized SiMCM-41, further indicating the insertion of Fe or La into the channel wall in these two samples. Moreover, the electron spin resonance (ESR) study for synthesized FeSiMCM-41 shows a strong signal at $g$=4.3 characteristic of tetrahedrally coordinated Fe(III) species in framework [15]. This tetrahedrally coordinated condition is also proved by the isomer shift value of 0.28 mm s$^{-1}$ (<0.3 mm s$^{-1}$, meaning Fe(III) existing in a tetrahedral coordination state [16]) in the Mössbauer spectrum of synthesized FeSiMCM-41. All above information support the incorporation of Fe(III) and La(III) in the channel walls of these two samples. The thermogravimetric (TG) analysis results as shown in Fig. 4 further confirm this incorporation. From Fig. 4 we observe two steps in the TG curves of synthesized SiMCM-41 and AlSiMCM-41. The low-temperature step (450–620 K) was attributed to the decomposition of template interacting with siloxy group and
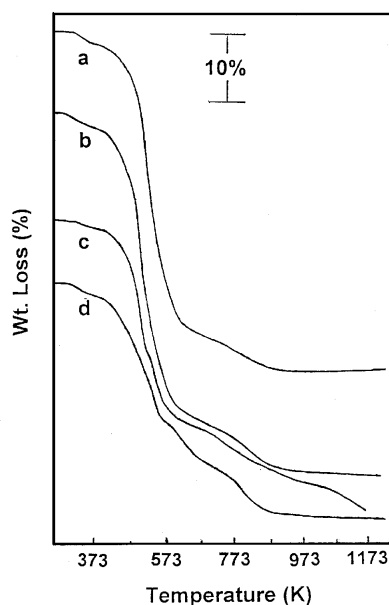


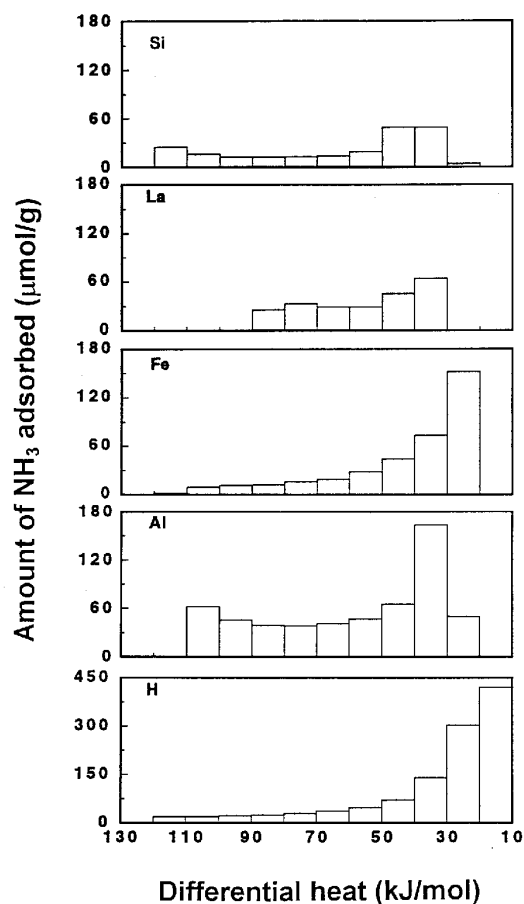**Fig. 4** Thermogravimetric (TG) curves of synthesized a – SiMCM-41; b – AlSiMCM-41; c – FeSiMCM-41 and d – LaSiMCM-41

**Fig. 5** Histograms of the distribution of interaction strengths for $NH_3$ adsorption at 423 K on calcined SiMCM-41 (Si), LaSiMCM-41 (La), FeSiMCM-41 (Fe), AlSiMCM-41 (Al) and HAlSiMCM-41 (H)

Brönsted sites, while the high-temperature step (740–920 K) was ascribed to both the decomposition of template associated with aluminum species and the condensation of hydroxide groups [17–18]. However, a new step (600–710 K) and two steps (one at 530–620 K, the other at temperature higher than 850 K) appear in the TG curves for synthesized LaSiMCM-41 and FeSiMCM-41, respectively. We assign these new bands to the decomposition of template associated with Fe(III) or La(III) species, suggesting the insertion of Fe(III) or La(III) into the channel wall of these two samples.

However, as reported in our previous work [13], Fe(III) species in FeSiMCM-41 will partially change from tetrahedrally coordinated state into octahedrally coordinated non-framework state during calcination at high-temperature, suggesting that

some Fe(III) may exist in the form of iron oxides on the surface of channel wall. Thus it is understandable that FeSiMCM-41 showed a lower acid density than Al-SiMCM-41. Moreover, our experimental results demonstrate that after calcination at 813 K for 6 h, La(III) species in LaSiMCM-41 may almost completely transform into lanthanum oxide species which are highly dispersed on the surface of channel wall, leading to a similar acid density of LaSiMCM-41 to that of SiMCM-41. As being basic in character, this high-dispersed lanthanum oxide species will not only cover some acid sites and, therefore, lead to the decrease of acid density, but also particularly kills all strong acid sites. Figure 5 shows the histograms of the distribution of interaction strengths for ammonia adsorption. From Fig. 5, we can also found that Fe(III) only partially shift from the framework to the surface of channel wall during calcination, since some intermediate strength acid sites are still remained. Since only a small fraction of Al shift from the framework to the surface of channel wall during calcination [17] for the AlSiMCM-41, it possesses a much larger number of intermediate strength acid sites than the FeSiMCM-41 and LaSiMCM-41 samples.

<p align="center">*   *   *</p>

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