The discovery of a new family of mesoporous molecular sieves called M41S was reported by researchers at Mobil R&D corporation. The influence of surfactant/silica molar ratio (Sur/Si) in M41S synthesis was studied in the simple synthesis system consisting of tetraethoxysilyl orthosilicate (TEOS), water and cetyltrimethylammonium (CTMA) cation at 100°C. As the Sur/Si increased from 0.5 to 2, the silicious products obtained were identified and could be classified into four groups: MCM-41 (hexagonal), MCM-48 (cubic), thermally unstable M41S and a molecular species, the organic octamer (CTMA)SiO2. One of the thermally unstable structures has been identified as a lamellar phase. These results are consistent with micellar phase transformations that occur at various surfactant concentrations and reinforce the concept that micellar structures serve as templating agents for the formation of M41S type materials.

In this paper, in continuation of earlier work, a novel lamellar type aluminosilicate molecular sieves, NCL-5, was synthesized and characterized by various physicochemical techniques such as XRD, SEM, TG/DTA, FT-IR and MAS NMR. The results have been compared with Si-MCM-41 samples synthesized using the same template.

Materials and Methods

Synthesis of Si-MCM-41

A Si analog of MCM-41 was prepared hydrothermally using a gel with the following molar composition in terms of oxides: SiO2: 0.27, (CTMA)2O: 0.13, (TMA)2O: 60 H2O. Sodium silicate (28.48% SiO2, 9.03% Na2O, 62.5% H2O), cetyltrimethylammonium bromide (99%, Aldrich, USA), tetramethylammonium hydroxide (TMAOH, 25% aqueous solution, Aldrich) and fumed silica (Cab-O-Sil, 99%, Fluka, USA) were used in the synthesis.

In a typical synthesis TMAOH (18.9 g) was added to sodium silicate (16.86 g) diluted with 100 g water. In another beaker CTMABr (19.68 g) was dissolved in 50 g water and 30 g ethanol and aqueous ammonia (1.9 g) were added to it (solution A). Solution A was then added to the above mixture of sodium silicate and TMAOH and then fumed silica (7.06 g) was added to it. The mixture was stirred for 1 h. The gel formed (pH 11.5) was then transferred to an autoclave and heated at 110°C for 5 days. The product was then filtered, washed with distilled water, and dried at ambient temperature. The sample was calcined at 540°C in nitrogen flow for 1 h and then in air for 6 h.

Synthesis of lamellar type aluminosilicate, NCL-5

NCL-5 samples prepared hydrothermally using a gel with the following molar compositions in terms of oxides: SiO2:0.02, Al2O3:0.27, (CTMA)2O: 0.13, (TMA)2O:xNa2O:60 H2O. The preparation procedure was similar to that of Si-MCM-41 excepting that sodium hydroxide (0.035 g) dissolved in 8 g water was added to the mixture of sodium silicate and TMAOH and a calculated quantity of Al2(SO4)3.
18 H₂O (2.52 g) dissolved in 30 g water was added to the final gel and stirred well. The gel was crystallized as described earlier (110°C for 5 days). The sample was calcined at 550°C in air for 6 h.

**Characterization**

The sample synthesized during the course of the work was analyzed for qualitative identification by X-ray powder diffraction (Rigaku, Model D/MAX III VC, Japan; Ni filtered Cu-Kα radiation, λ = 1.5404Å; graphite crystal monochrometer; computer controlled automated diffractometer). The morphologies of the aluminophosphate synthesized was investigated using a scanning electron microscope (JEOL, JSM 5200). The framework region (400-1300 cm⁻¹) of the synthesized aluminophosphates were analyzed using a Nicolet 60SXB FT-IR instrument in the diffuse reflectance mode using a 1:30 ratio of the sample to KBr mixture. Simultaneous TG/DTA analysis of the crystalline phases was performed on an automatic derivatograph (Setaram TG-DTA 92). The thermograms were recorded in flow of nitrogen with heating rate 10 K/min. MAS NMR spectra were recorded in the solid state with a Bruker DRX 500 spectrometer operating at a field of 11.7 Tesla. ⁴⁷Al spectra were recorded at a frequency of 130.3MHz, with a pulse length of 2μs and a spinning speed of 3-5 KHz. ²⁹Si NMR spectra were recorded at 99.3 MHz, 2μs (45°) pulse width and repetition time of 2s. Tetramethylsilane (for silicon) and 1M Al(NO₃)₃ solution (for aluminium) were used as standards.

**Results and Discussion**

The XRD pattern of the as-synthesized Si-MCM-41 is similar to those reported for Si-MCM-41 samples. However, the NCL-5 XRD pattern did not match with any of the reported materials. The X-ray diffraction pattern of the as-synthesized lamellar material (NCL-5) exhibited a high intensity peak having d-spacing of approximately 24.39 Å and three high angle peaks having d spacings (12.55, 8.48 and 6.37 Å) consistent with lamellar indexing of 001 reflections as shown in Fig. 1b. Upon calcination at 550°C, the X-ray diffraction was featureless.

The lamellar phase could be represented by sheets or bilayers of surfactant molecules with the hydrophilic ends pointed towards the oil-water interface, while the hydrophobic ends of the surfactant molecules face one another. Any silicate structures produced from this liquid crystal phase would be similar to that of two dimensional layered materials such as magadiite or kenyite. However, the lack of any observable peaks in the XRD pattern of the lamellar material in the region of 20-25° C suggests that these silicate layers of this lamellar phase are not well ordered as those of layered silicates. This lack of order may be due to the higher concentration of silanol groups resulting in less condensation of the silicate species as suggested by the NMR data. Removal of the surfactant from between the silicate sheets could result in a condensation of layers, collapsing any structure and forming a dense phase with little structural order or porosity.

Elemental analysis gave the Si/Al ratio of the NCL-5 is 23.0. The morphology of the samples as observed by SEM (Fig. 2) image reveals that the sample is highly crystalline without any amorphous material. Both the samples Si-MCM-41 and NCL-5 are having spherical morphology with 6.36 μm and 0.25 μm particle sizes, respectively.

The TG-DTA curves of the template containing NCL-5 and Si-MCM-41 samples are presented in Fig. 3. In the low temperature region up to 138.5 and 156.7°C there is an endothermic weight loss of 6.1 and 7.6% mainly due to the loss of adsorbed water. In the temperature regions of 138.5 to 650.4 and 156.7 to 666.8°C, there are one and two stages of exothermic weight loss (45% and 49.2%, 15.6%) due to the oxidative decomposition of the organic template occluded in the sample. Single stage oxidative decomposition in NCL-5, may be due to the nanocrystalline morphology of the sample. Similar results were also reported for nanocrystalline ZSM-35 sample. In the 156.7 to 293.4°C region, occluded template molecules in the pores oxidatively
decompose with probably a part of the hydrogen burning. While in the region 293.4 to 666.8°C, the coke is eliminated by oxidation. Based on the total loss due to template removal and the carbon and nitrogen analysis (C = 29.43%, N = 2.08% for NCL-5) and (C = 44.59%, N = 2.55% for Si-MCM-41) respectively, 0.149, 0.182 template molecule per 100 g of the sample is calculated.

The FT-IR spectrum of the as-synthesized Si-MCM-41 and NCL-5 in the framework region is shown in Fig. 4. The different modes of tetrahedral linkages give bands at 1215 (m), 1059 (vs), 964 (m), 912 (w), 785 (m), 719 (m), 604 (w) and 448 (s). The bands can be assigned to asymmetric stretching, symmetric stretching, pore opening and bending vibrations of T-O-T linkages as described in earlier literature. The difference between the spectra of Si-MCM-41 and NCL-5 is that the peaks at 1215 (m) and 604 (w) are stronger in the case of Si-MCM-41.

The 27Al MAS NMR spectra of as-synthesized NCL-5 are presented in Fig. 5a. The sample shows a
Fig. 5—$^{27}$Al (a) and $^{29}$Si (b) MAS NMR spectra of NCL-5 single signal with $\delta = 1.986$ ppm due to Al in octahedral co-ordination. The other weak signals at -34 and -38 ppm are due to non-octahedral co-ordination. The remaining two signals at 20, -58 ppm are due to side bands. The results were in contradiction with the results of Al-MCM-41 samples$^5$, where aluminium was found in tetrahedral co-ordination. $^{29}$Si MAS NMR spectra of as-synthesized NCL-5 samples show 3 distinct lines at -90, 98 and 110 ppm attributed to $Q^2$, $Q^3$ and $Q^4$ species respectively$^8$.

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References