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REGULAR ARTICLE

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Preparation, characterization, and post-synthetic modification of layered MCM-22 zeolite precursor

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Abstract. Hydrothermal synthesis of MCM-22(P) was carried out with two different silica sources, colloidal silica (28%) and silicic acid with different gel composition. The synthesis was carried out in stirring and static conditions with different crystallization time. MCM-22(P) modified with swelling-sonication method resulted in swollen MCM-22, while alkali treatment yielded desilicated MCM-22. The materials were characterized by X-ray diffraction, low-angle XRD, FE-SEM-EDX, FT-IR, TGA, N_2 adsorption and NH_3-TPD analysis. The results revealed that MCM-22 has a layered sphere, doughnut like morphology and after modification, swollen and broken sphere was observed. Physicochemical analysis revealed that the materials' mesoporosity increased and acidity also changed. Energy dispersive X-ray analysis revealed the high amount of desilication in alkali-treated MCM-22(P).

Keywords. Colloidal silica; silicic acid; MCM-22(P); swelling-sonication; alkali-treatment.

1. Introduction

Zeolites are microporous, inorganic tetrahedrally coordinated polyaluminosilicate and a promising material having superior catalytic properties. In heterogeneous catalysis, layered zeolites are catalytic materials that combine excellent activity in acid-catalysed reactions with a high stability. MCM-22 is one of such layered zeolites having MWW topology[1] (**M**CM-t**W**enty-t**W**o, Mobil Composition of Matter with sequence number twenty-two) with layered pockets of 10 member ring and surface pockets of 12 member ring channels[2] (Figure 1). Layered as-made MCM-22 has 2D structure while calcined MCM-22 has 3D structure. This is observed due to the external surface of each zeolitic sheet having elevated amount of silanol groups (Si–OH). After the calcination process, these react with other silanols present in contiguous layer covalently condensing between them and facilitating the formation of 3D MWW zeolitic structure.[3–5]

MCM-22 is first layered zeolite which is hydrothermally synthesized in static and stirring conditions.[6] Modifications of MCM-22(P) is possible by methods like alkaline treatment and swelling-sonication which may change its morphology and textural properties.[7] The as-made zeolites are called as a precursor which can be used for further modifications.

The objective of this work is to study the synthesis of parent MCM-22, its modification and comparison of physicochemical properties between parent and modified MCM-22.

2. Experimental

2.1 *Materials*

Layered zeolite (MCM-22) was synthesized hydrothermally with gel composition $2.7Na_2O : Al_2O_3 : 30SiO_2 : 1347H_2O$: 15HMI. The synthesis was performed using two different silica sources, colloidal silica (28%) in stirring condition and silicic acid (Loba-Chemie) in a static condition, respectively. Sodium aluminate (Al_2O_3—53.2%, Na_2O—43.9% Sigma-Aldrich) was used as alumina source. Hexamethyleneimine

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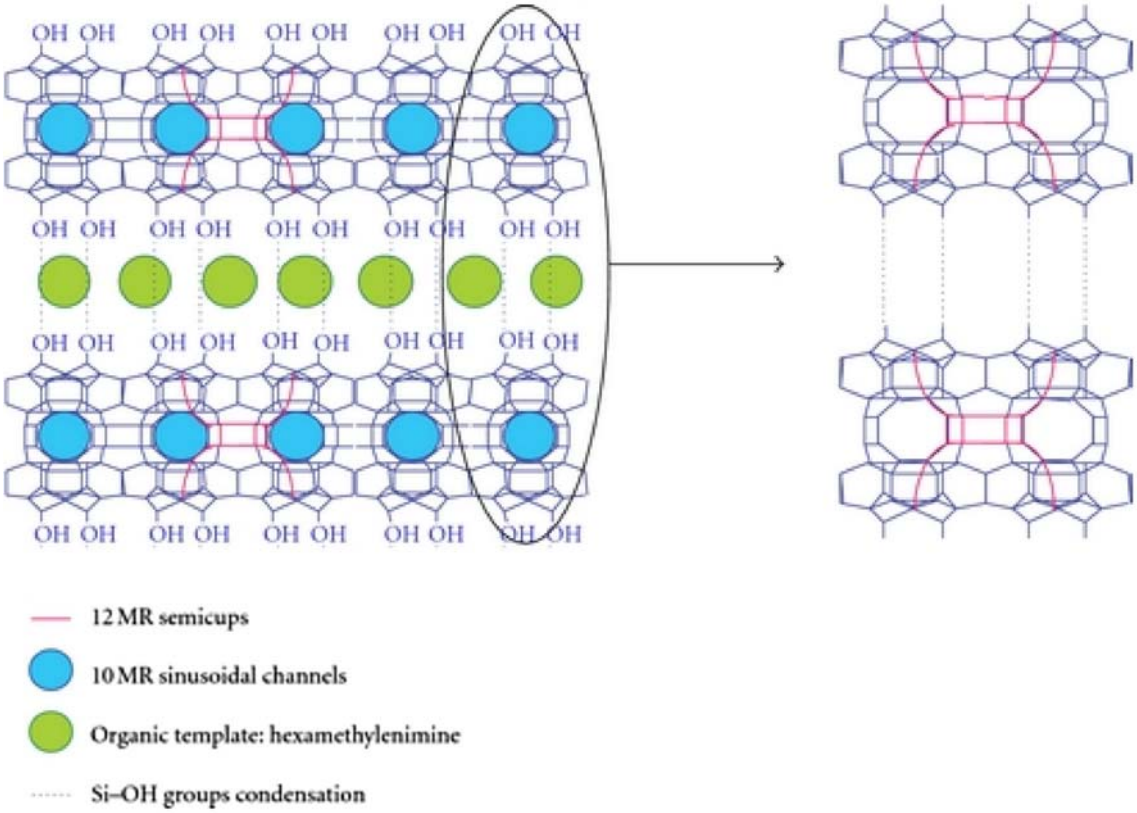

Figure 1. MWW topology of layered MCM-22 precursor.[8,9]

(99% Sigma-Aldrich) worked as an organic structure directing agent. The sodium hydroxide was used as alkali source and balance the sodium content and pH of the synthesis gel. The solvent for the gel was water. Modifications on MCM-22(P) was performed using a surface active agent, tetrapropylammonium hydroxide (TPAOH 40%) and swelling agent, hexadecyltrimethylammonium chloride (CTAB; Sigma-Aldrich) for the swelling-sonication method. The modification by alkali-treatment was performed using excess sodium hydroxide and TPAOH.

2.1a *Synthesis of MCM-22(P)*: Initially, a series of experiments were performed to optimize synthetic parameters of the layered zeolite MCM-22. It was synthesized following published procedure.[10,11] Hydrothermal synthesis was carried out with two different silica sources, colloidal silica and silicic acid with a gel composition: $2.7Na_2O : Al_2O_3 : 30SiO_2 : 1347H_2O : 15HMI$. The gel was transferred to stirring and static autoclaves for hydrothermal synthesis at 423 K for 110 h and 240 h, respectively. The as-synthesized MCM-22 was filtered, washed with deionized water and dried at 393 K for 12 h. The dried zeolite was further crushed to fine powder and calcined at 823 K for 10 h in a flow of dry air to remove organic template. The H-form of MCM-22 was obtained by repeated ammonium exchange with ammonium nitrate solution (10%) followed by calcination at 823 K overnight.

2.2 *Preparation of modified MCM-22(P)*

2.2a *Swelling-sonication method*: MCM-22(P) slurry was mixed with hexadecyltrimethylammonium bromide solution (29 wt.%) and tetrapropylammonium hydroxide (40 wt.%), and refluxed for 16 h at 80°C to create swelling.[12–15] The slurry was placed in an ultrasound bath (50 W, 20 kHz) for 1 h. Finally, pH of the slurry was maintained below 2 by adding concentrated HCl, yielding modified MCM-22(P). The modified slurry was filtered, washed and dried overnight at 373 K, and calcined at 823 K for 10 h.

2.2b *Alkali-treatment method*: The alkaline treatment of MCM-22(P) was carried out in the presence of a mixture of 0.1 M NaOH and 40% Tetrapropylammonium hydroxide at 70°C for 5 h, yielding alkali-treated MCM-22(P).[16–18] The other procedure of filtering, drying, calcination and converting to H-form of catalyst remained same as that of MCM-22.

2.3 *Physicochemical characterization*

Crystallinity and phase purity was determined by powder X-ray diffraction for both as-made and calcined samples using PANalytical X'Pert pro XRD equipment. The operational parameter was CuKα radiation at 40 kV/40 mA, with a goniometer speed of 2°/min and a step of 0.02° in the 2θ

range from 5° to 50°. The morphology and elemental composition of samples were evaluated using field emission scanning electron microscopy combined with energy dispersive X-ray ZEISS equipment. FT-IR was performed on PerkinElmer's FTIR spectrometer model 'Spectrum Two'. TGA was performed on Mettler Toledo Star^e system. Zeolite's textural properties were confirmed using Quantachrome Autosorb IQ nitrogen adsorption–desorption pore size and surface area analyzer. The acidity of catalyst was carried out by NH_3-TPD method using Micromeritics Autochem 2920.

3. Results and Discussion

3.1 *Influence of the silica source/synthesis procedures*

The effectiveness of the silica sources and synthesis conditions during the synthesis of MCM-22 was observed in the difference in crystallinity. MCM-22 synthesized using silicic acid in static condition shows high crystallinity and purity, while that synthesized using colloidal silica in stirring condition has comparatively low crystallinity. The powder XRD pattern of as-made and calcined MCM-22 are shown in the Figures S1 and S2 of Supplementary Information (SI).

MCM-22 synthesized from two different silica sources having different physical properties influences the shape of the layered structure of MCM-22, and this was observed in FE-SEM images. MCM-22 (silicic acid) shows doughnut like morphology having paper-like layers, and MCM-22 (colloidal silica) shows spherical shape having a regular arrangement of layers. However, MCM-22(P) formed from colloidal silica was further modified with swelling-sonication and alkaline treatment, showing significant changes in morphology. Modification shows swelling of parent sphere and breaking of a sphere with agglomerated layers. FE-SEM images are shown in the Supplementary Information (SI), Figure S3.

Zeolite framework properties like framework stretching and bending vibrations are studied through FT-IR analysis. The bending and stretching observed in mid-infrared due to internal vibrations of the TO_2 tetrahedra (T = Si or Al). Zeolite's framework vibration of calcined samples was observed in the range of 1300–400 cm^{-1}. The analysis results are shown in the Figure S4 of Supplementary Information (SI).

3.2 *Analysis of synthesized MCM-22 and modified MCM-22(P)*

MCM-22 prepared from two different silica sources has high crystallinity than modified MCM-22(P). Low angle peak below $2\theta = 2°$ was observed in the case of modified MCM-22 (swelling-sonicated) indicating the formation of mesoporosity. XRD pattern shows that the alkali-treated sample maintains the crystal structure of the MCM-22 zeolite. Generally, the alkali-treatment process under certain conditions can extract Si atoms from the framework and partially damage the topology of the zeolite showing decreased crystallinity than their parent zeolite. The XRD pattern in Figure 2 shows a mixture of different peaks comprising sharp, broad and tiny peaks.

Thermal stability of zeolites is one of the important features that make zeolites applicable as selective sorbents and potential catalysts. Kinetics of the dehydration of zeolites is normally studied between 25°C to 250°C.

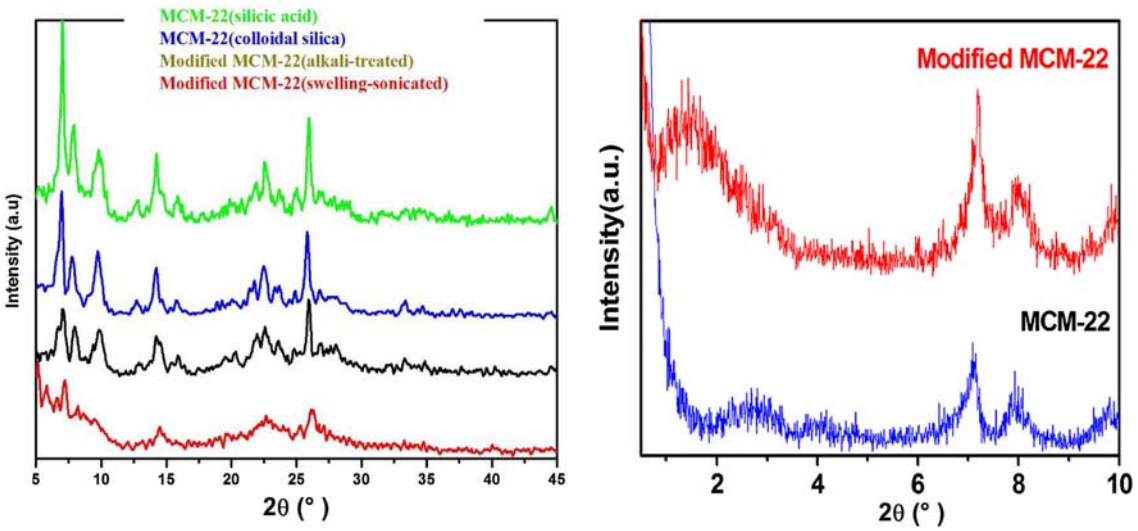

Figure 2. Powder XRD and LAXRD of parent and modified MCM-22.

Table 1. Chemical composition and textural properties of all zeolite samples studied.

Name	SiO_2/Al_2O_3 ratio	$S_{BET}(m^2g^{-1})$[a]	$S_{ext}(m^2g^{-1})$[b]	$V_{tot}(cm^3g^{-1})$[c]	$V_{mic}(cm^3g^{-1})$[c]	$V_{mas}(cm^3g^{-1})$[c]
MCM-22[d]	30.30	432.7	94.63	0.2232	0.1442	0.0790
MCM-22[e]	30.30	377.4	123.4	0.2606	0.1121	0.0285
Modified MCM-22[f]	30.25	463.4	427.6	0.5627	0.0980	0.4647
Modified MCM-22[g]	14.36	524.1	203.6	0.4601	0.1315	0.3286

[a] S_{BET} = BET surface area. [b]S_{ext} = external surface area. [c]V_{tot}, V_{mic} and V_{mas} correspond to the total, micro and meso pore volume of the zeolites. [d]MCM-22 = synthesized by silicic acid. [e]MCM-22 = synthesized by colloidal silica. [f]MCM-22 = swelling-sonicated. [g]MCM-22 = alkali-treated. The silica/alumina ratio from EDX analysis.

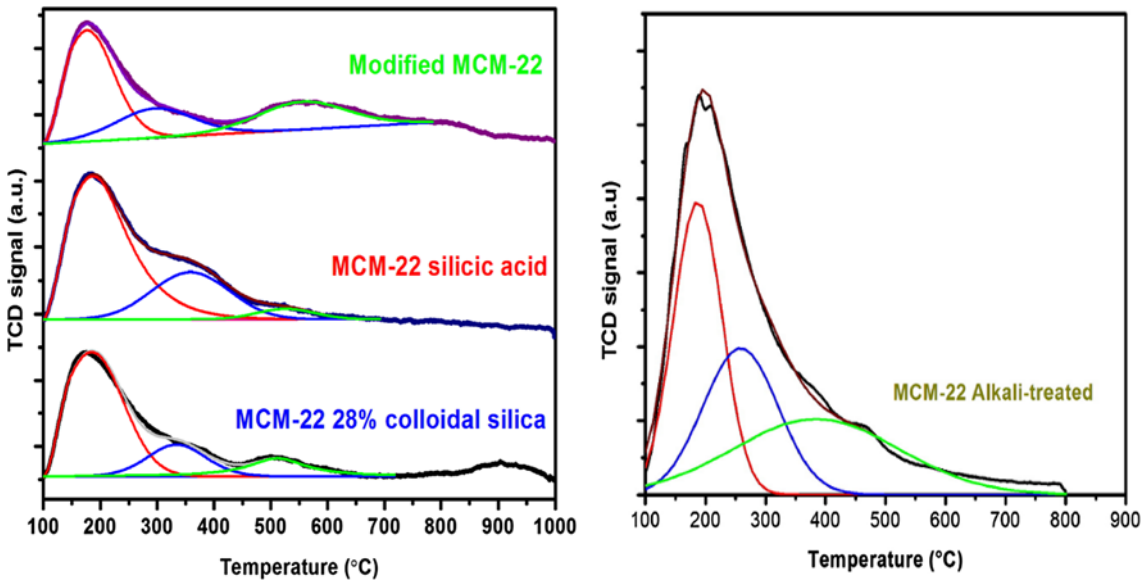

Figure 3. Deconvoluted ammonia TPD of zeolite samples.

Table 2. NH3-TPD qualitative and quantitative results.

Material name	Temperature (°C)	Acid sites concentration (mmol NH_3/g)
Modified MCM-22[a]	178.7	0.281
Modified MCM-22[a]	546.9	0.077
MCM-22 (silicic acid)	183.2	0.526
MCM-22 (colloidal silica)	176.5	0.423

[a]MCM-22 = swelling-sonicated modification.

Oxidative decomposition of the occluded organic template is observed at 250°C to 600°C. The TG curve showed 4% water loss and 15% template loss for the as-synthesized MCM-22, while 10% water loss was observed in modified HMCM-22. The result is shown in Figure S5 of Supplementary Information (SI).

The N_2 adsorption/desorption analysis revealed zeolite's textural properties like surface area and pore size as described in Table 1. The formation of mesoporosity in modified MCM-22 was supported by its high surface area. Modified MCM-22 shows high surface area and mesoporosity with a major difference in the external surface area. Moreover, parent MCM-22 synthesized using two different silica sources showed the difference in surface area and porosity distributions with each other indicating influence of different silica sources during synthesis.

The influence on silica and alumina amount after modifications were analysed by energy dispersive X-ray analysis. There was no significant change in silica/alumina ratio of swelling-sonicated modified MCM-22, while alkali-treated modified MCM-22 shows desil-

ication due to high pH of gel, resulting in a decrease in the silica/alumina ratio, about half of that of parent MCM-22.

Layered zeolite MCM-22 has acidic nature, which has great applications in acid catalysed organic reactions.[19] The acidic nature of the catalyst was observed by TPD of ammonia (Figure 3). The TPD pattern confirms the presence of acid sites and strength of the acid sites. Deconvolution of ammonia shows acid sites as weak, medium and strong sites according to the temperature of the release of ammonia from these sites over a large temperature range. The first peak (<200°C) represented mainly physisorbed ammonia molecules. The second peak (200°C–400°C) was associated with ammonia molecules adsorbed on hydroxyl groups. The third peak (>400°C) was associated with dehydroxylation and strong acid sites.[20] The first peak at around 183°C for parent and modified samples are assigned to the weak acid sites and physically adsorbed ammonia. Modified MCM-22 seems to have higher acidity showing a peak with higher peak area at around 550°C. On the other hand, the alkali-treated MCM-22, shows lesser acidity having insignificant acid sites compared to the parent sample. The amount of ammonia desorbed from zeolitic acid sites is shown in Table 2.

4. Conclusions

Synthesis of MCM-22 with different silica sources yielded microporous materials with different crystallinity, while modified MCM-22(P) showed partial mesoporous properties. The comparative study of parent MCM-22 and modified MCM-22 revealed significant changes in physicochemical properties. The silica/alumina ratio also changes after modification indicating the influence of swelling-sonication and alkali-treatment method as a novel development of catalyst. Surface area and pore size analysis after modification suggest presence of mesoporosity having high surface area. These synthesized and modified materials would be further studied in various organic reactions to complement their physicochemical characteristics. Processing of such layered zeolites could be extended to broad application in petrochemical and fine chemical industries.

Supplementary Information (SI)

The XRD plot of as-made and calcined MCM-22 prepared by two different silica sources are reported as Figures S1 and S2 (Supplementary Information). FE-SEM, FTIR and TG analysis of MCM-22 and modified MCM-22 are reported as Figures S3–S5 (Supplementary Information) and are available at www.ias.ac.in/chemsci.

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