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Preparation and application of HMCM-22 zeolite as an efficient solid acid catalyst for the synthesis of acetals

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ABSTRACT

HMCM-22 with a Si:Al molar ratio of 15:1 has been shown to effectively catalyze the synthesis of acetals with 100% selectivity by the reaction of aldehydes with methanol under reflux conditions. Platelet HMCM-22 particles were prepared by the static strategy and characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR), BET techniques and N_2-adsorption/desorption analysis. The catalyst was recovered by simple filtration and reused for several cycles without considerable loss of activity.

Keywords: HMCM-22, Heterogeneous catalyst, Acetals, Protection.

1. Introduction

The protection of the carbonyl functional group can play an essential role in multistep organic syntids as catalysts like H_2SO_4, HCl, HF, and H_3PO_4 [1-4]. Recently, several studies were conducted regarding the use of heterogeneous acid catalysts for acetalization of different carbonyl compounds with alcohol such as ion exchange resins [5], zeolites [6], heteropolyacids [7,8], various clays [9], oxidants [10], ionic liquids [11], metal salt [12-14], or nanoparticle catalysts [15].

Mesoporous materials have been used technically as adsorbents, drug delivery systems, catalysts, and catalyst supports because of their high surface area [16,17]. The first synthesis of an ordered mesoporous material was described in the literature in 1971 [18]. However, due to a lack of analysis, the remarkable features of this material were not recognized [19]. Silica-based mesoporous materials have been investigated for practical applications.

In particular, the success of scientists in the discovery of a new family of mesoporous molecular sieves with a unique structural pore system (MCM-22) has been followed by an enormous amount of research worldwide [20-24]. MCM-22 with two independent pore systems: two-dimensional, sinusoidal, 10MR channels and 12MR interlayer supercages interconnected by the 10MR windows has been a focus of recent applications for organic transformations [25-28]. This pore system possesses acidity properties. Undoubtedly, the external surface acidity of MCM-22 zeolite plays an unquestionable role in many catalytic reactions [29,30]. Generally, MCM-22 is synthesized under rotating or static conditions. Large and complex equipment is needed when preparing MCM-22 under rotating conditions.

The crystallization of zeolite MCM-22 under static synthesis conditions is slow, while the impurity phase(s) have higher growth rates nucleating later in the crystallization process, which results in forming a final pure crystalline product. However, regarding the rotating synthesis conditions, the crystallization rate is higher resulting in a smaller final particle size. In other words, although the overall synthetic process obtained in the rotating method is shorter than the static conditions, the reproducibility of crystallizations carried out under the rotating is usually poor [31,32].

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In this contribution, MCM-22 zeolite was prepared under static conditions by two-stage varying-temperature hydrothermal synthesis and then the zeolite framework was modified to HMCM-22. After that, the catalytic performance of HMCM-22 in the synthesis of acetals by the reaction of methanol and aldehydes was investigated.

2. Experimental

2.1. Materials and methods

All of the chemicals were commercial products. Reactions were monitored by TLC (0.2 mm thickness, Merck). Products were characterized by comparison of their physical data with known samples [35-36]. Infrared spectra of the catalysts and reaction products were recorded on a Perkin-Elmer RX1 FTIR spectrometer in KBr disks. XRD patterns were recorded on a PANalytical X-ray diffractometer Model X'Pert Pro. Scanning electron micrograms (SEM) was obtained using a Philips XL30 instrument. Nitrogen adsorption/desorption isotherms of samples were measured at -196℃ on a BElSORP Mini instrument.

2.2. Preparation of HMCM-22

The synthesis of MCM-22 was carried out using silicic acid as Si source, hexamethylene imine (HMI) as the template and $NaAlO_2$ as Al source with the gel composition of SiO_2: $HMI:Al_2O_3:H_2O:NaOH$ = 0.30:0.01:0.01:0.037. In a typical procedure, 11.87 g hexamethyleneimine (HMI, 99%) was added to an aqueous solution containing 1.87 g $NaAlO_2$ (50% Al_2O_3, 45% Na_2O) and 1.55 g sodium hydroxide (granular, 97%). After 30 min, 23.38 g silicic acid (H_2SiO_3, 20%) was slowly added to the solution under continuous stirring for 1h at room temperature. The mixture was transferred to an autoclave. The sealed autoclave was heated to 45℃ for 24 h. Then, the temperature was increased to 150℃ and kept at that temperature for 9 days under static condition. At the end of the 9th day, the autoclave was lifted from the heater and cooled rapidly by immersion in cold water. The white crystalline product was filtered and washed well with distilled water and dried for 8h at 120℃. The template was removed by calcining the as-prepared materials at 538℃ for 20 h in an electric furnace with flowing zero air. The protonated forms of MCM-22 samples were obtained by two successive exchanges with an aqueous solution of NH_4NO_3 (1M) at 80℃ under reflux condition for 6 h. Then, it was filtered, washed with distilled water, dried at room temperature overnight and calcined at 500℃ for 4 h.

2.3. General procedure for the synthesis of acetal derivatives

To a solution of aldehyde/ketone (1 mmol) and HMCM-22 (0.01 g) in a 50 mL round-bottomed flask equipped with a condenser and a magnetic stirrer, methanol (5mL, excess) was added. The reaction mixture was refluxed for the appropriate time indicated in Table 2. The progress of the reaction was monitored by TLC. Upon completion of the reaction, the catalyst was washed thoroughly with ethylacetate (3.5mL) and then treated with acetone (5mL). The combined washings and decanted liquid were treated with water to remove the excess methanol. The organic layer was dried over anhydrous sodium sulfate, and then concentrated under vacuum. The crude product was directly charged on a small silica gel column and eluted with a mixture of (n-hexane/ethylacetate: 10/3) to afford the pure product.

3. Results and Discussion

3.1. Catalyst characterization

The structure of MCM-22 is well known and has been reported in many papers [33-36]. However, due to small differences in the recipe of the MCM-22, the necessity for characterization of the prepared samples is indefeasible.

The morphology of HMCM-22 was studied by SEM. Fig. 1 clearly shows that the HMCM-22 sample is composed of two main forms including lamellar particles as an aggregation of platelets (Fig. 1b) as well as regular spherical particles (Fig. 1c). Amorphous material was not observable in the acquired micrographs.

FT-IR spectrum of HMCM-22 is shown in Fig. 2. MCM-22 materials show main peaks at 469 cm^{-1} (Si–O-Si bending vibration), 589 and 694 cm^{-1} (double ring), 775cm^{-1} (Si–O–Si internal symmetric stretching), 798cm^{-1} (Si–O–Si external symmetric stretching), 1074 cm^{-1} (Si–O–Si internal asymmetric stretching), 1244 cm^{-1} (Si–O–Si external asymmetric stretching) and 3439, 3467 cm^{-1} (silanol group), which is in agreement with the previous report [33].

Also, the X-ray diffraction pattern of MCM-22 is presented in Fig.3. As shown in this figure, X-ray powder diffraction of the MCM-22 gave peaks at 2θ= 7.1, 8.0, 9.6°, 13.5°, 20.8°, 22.5°, and 26.6°. These diffraction peaks are consistent with the characteristic diffraction pattern of the typical MCM-22 [34].
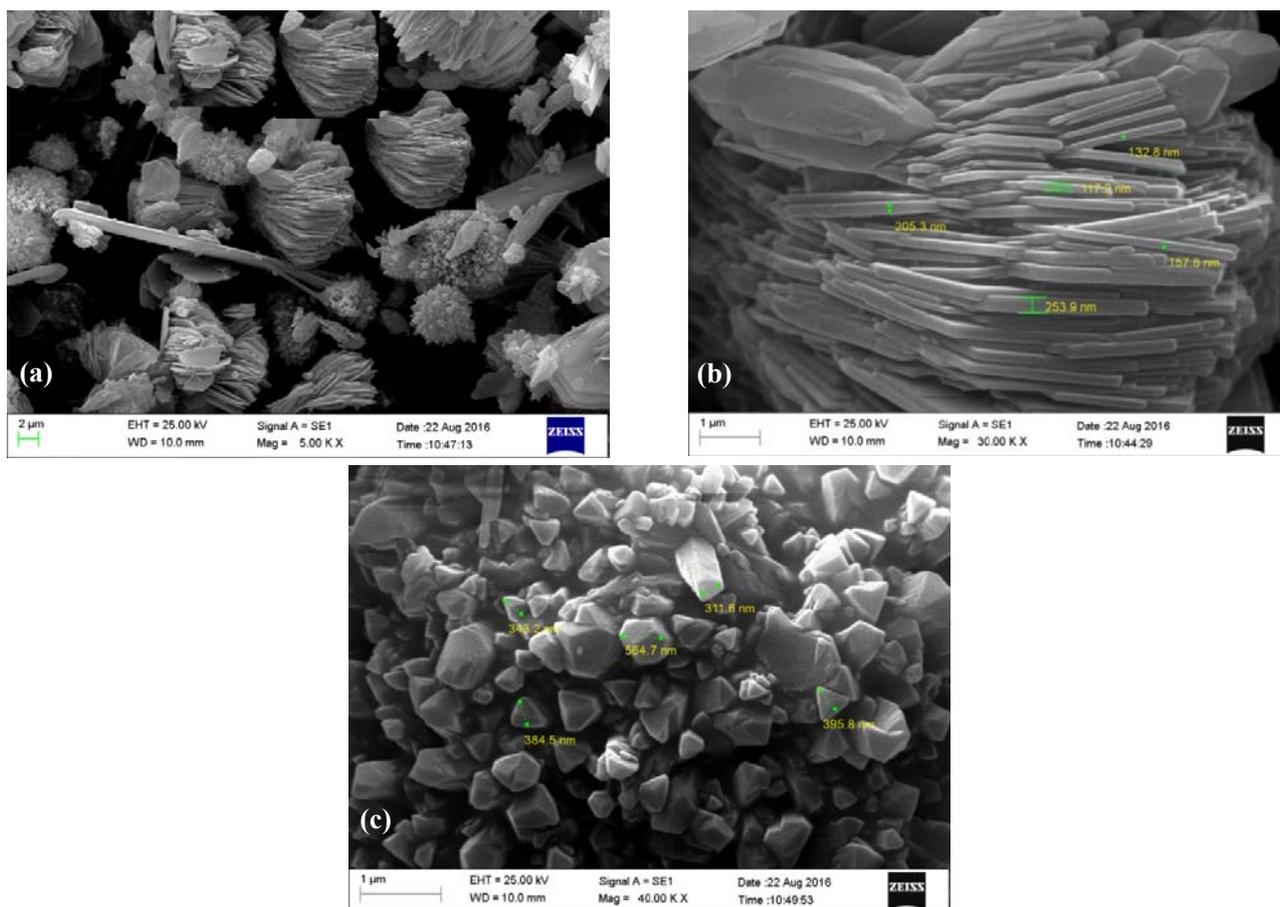
Fig. 1. SEM images of HMCM-22. Wide view (a), lamellar structures (b), and aggregated spherical particles (c).

Fig. 4 shows the N_2 adsorption-desorption isotherms for HMCM-22. These isotherms belong to type IV according to the IUPAC classification and exhibit H_1 loop hysteresis that is representative of mesopores [37]. The BET surface area, total pore volume and average diameter of the pores were $107.57 m^2/g$, 0.066 $m^3.g^{-1}$, and 2.47 nm, respectively.

3.2. Catalytic activity of HMCM-22

To testify the catalytic activity, the synthesis of acetals through coupling of aldehydes (1 mmol) with methanol as the reagent and solvent is selected in the presence of HMCM-22 to represent the activity of the prepared catalyst.
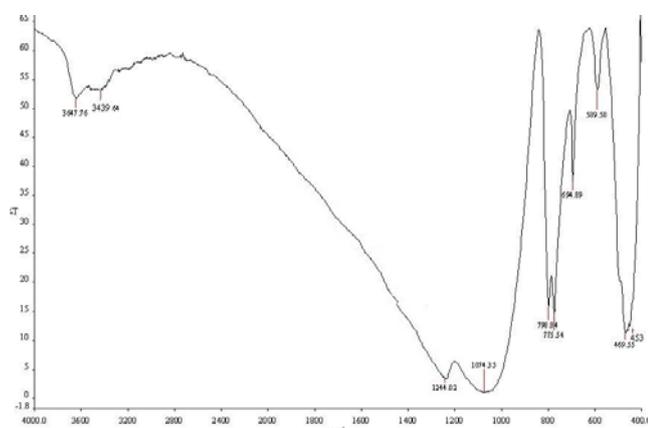
Fig. 2. FT-IR spectrum of HMCM-22
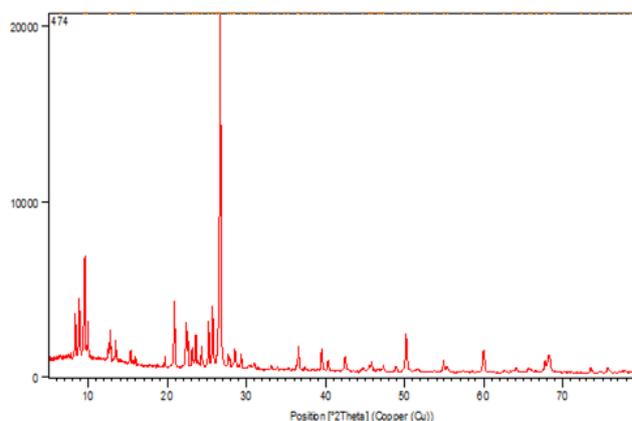
Fig. 3. X-ray diffraction pattern of HMCM-22
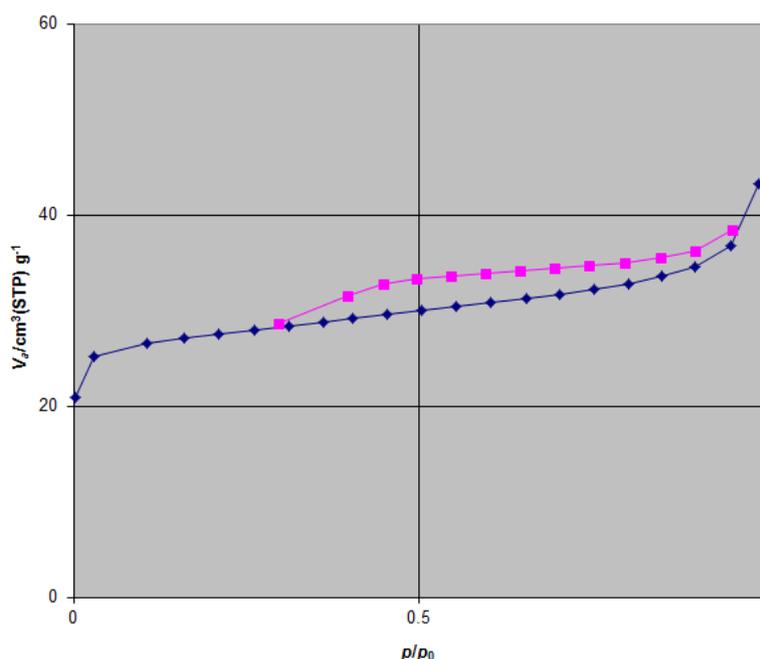
Fig. 4. N_2 adsorption-desorption isotherms of HMCM-22.

Initially, to optimize the reaction conditions, the reaction of benzaldehyde and methanol was selected as a model reaction. The best result was obtained under the reflux condition with 0.1 g of the catalyst and 100% selectivity for the formation of the corresponding acetal (Table 1).

A similar reaction in the absence of HMCM-22 was studied to show the merit of the catalyst. The reaction did not proceed even after 24h. Noteworthy, when the reaction was carried out in the presence of MCM-22, it was not completed and up to 40% conversion was achieved after 6 h under reflux conditions.

After that, the optimized reaction conditions were explored for the synthesis of acetal derivatives (Scheme 1). The results are summarized in Table 2. A regular trend is observed based on the activity of benzaldehyde derivatives. The results show that the electron with-drawing substituent possesses a superior activity among the applied aldehydes.

The efficiency of HMCM-2 was also compared with other similar heterogeneous catalytic systems in the same reaction condition (Table 3). The obtained results indicated that HMCM-22 was an equally efficient but much cheaper and reusable catalyst.

Table 1. Optimization of reaction conditions for the synthesis of acetals in the presence of HMCM-22.

No	Temp. (°C)	Catalyst amount(g)	Conv. (%)[a]
1	r.t	0.1	25
2	30	0.1	40
3	40	0.1	68
4	50	0.1	75
5	reflux	0.1	100
6	reflux	0.08	70
7	reflux	0.9	80
8	reflux	0.11	100
9	reflux	-	trace

[a]Reaction conditions: Benzaldehyde (1 mmol), CH_3OH (5 mL), reaction time (6h).
[b]Determined by GC.

$R_1 = $ aryl
$R_2 = $ H, CH_3
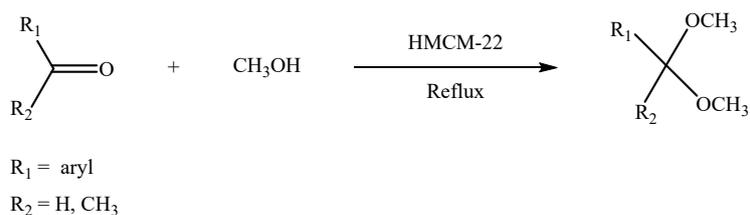
Scheme 1.

Table 2. HMCM-22 catalyzed synthesis of acetals.

No	R_1	R_2	Time(h)	Conv. (%)[a]
1	Ph	H	6	100
2	4-Cl–C_6H_4	H	6	100
3	4-Me–C_6H_4	H	9	100
4	4-MeO–C_6H_4	H	12	40
5	4-O_2N–C_6H_4	H	4	100
6	3-O_2N–C_6H_4	H	12	45
7	4-Br–C_6H_4	H	5	100
8	4-N(-CH_3)$_2$ –C_6H_4	H	12	-
9	4-F–C_6H_4	H	4	100
10	2,4-Cl–C_6H_3	H	5	100
11	C_6H_4	CH_3	12	30

[a]Determined by GC.

Table 3. Comparison of the catalytic activity of HMCM-22 on the acylation of 4-nitrobenzaldehyde.

Catalyst	Catalyst load (mol %)	Time (h)	Yield (%)	Ref.
Cu(OTf)$_2$	2.5	4	94	[38]
AlPW$_{12}$O$_{40}$	0.1	45[b]	89	[8]
Cu(BF$_4$)$_2$. xH$_2$O	1	3	92	[39]
InBr$_3$	0.1	15[b]	99	[40]
In(TFA)$_3$[a]	0.8	3	79	[41]
SSA	0.52	25[b]	86	[35]
HMCM-22	0.01	4	100	This work

[a]Acylation of benzaldehyde.
[b]In minute.

Reusability of the catalyst was investigated in the model reaction under the optimized reaction conditions. The catalyst was separated from the model reaction and reused two times with the moderate loss of the catalytic activity (Table 4). Blockage of the active sites of the catalyst and/or partial leaching of protons from the catalyst may be responsible for this observation. Activity amelioration after calcination of the recovered catalyst from cycle 2 confirms partial blockage of active sites of the fresh catalyst (Table 4, cycle 3).

Table 4. Reusability of the catalyst in the model reaction.

Entry	Fresh	Cycle 1	Cycle 2	Cycle 3[a]
Conv. (%)	100	96	90	93
Time (h)	6	6	6	6

[a]The catalyst was calcined at 550 ℃ for 2h before using in cycle 3.

4. Conclusion

In this paper, we reported a simple method for the preparation of HMCM-22 and its application as a catalyst for the synthesis of acetals/ketals. The reusability, simple workup, and non-toxicity of the catalyst are some of the advantages of the method.

Acknowledgements

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