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# Acidity and catalytic behaviors of ordered mesoporous aluminosilicate materials containing zeolite building units

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The structural and acidic properties of two new highly stable meso-/microporous composite materials (MMS-H and RMM-1) developed recently were characterized by various analytical and spectroscopic techniques. Comparing to their structural analogue, Al-MCM-48, these novel aluminosilicates materials comprising zeolite secondary building units were found to have superior catalytic activities, as illustrated by ethylbenzene alkylation reaction.

**KEY WORDS:** mesoporous aluninosilicate material; zeolite building units; characterization; acidity; stability; ethylbenzene alkylation.

## 1. Introduction

Recent research on mesoporous molecular sieves focus on the synthesis of highly stable aluminosilicate mesoporous materials with improved acidity [1]. Several attempts have been made through multi-step synthesis methods, namely either by post-synthesis coating of the mesoporous pore-wall with zeolite secondary building units (SBU) [2–4] or by using zeolite seeds as precursors to form the desirable mesoporous phase [1, 5–7]. However, majority of the mesoporous/microporous composite materials reported in the literature thus far were either prepared under strong acidic medium [1, 5, 6] or synthesized in the presence of NaOH. The latter method requires additional post-treatment procedures, namely ion-exchange and recalcination, to generate acid sites on the framework and thus is more vulnerable to dealumination of the catalysts [1, 5]. On the other hand, materials synthesized under strong acidic conditions ($pH < 1$) [1, 5, 6] are more difficult to incorporate heteroatoms onto the structural framework. More recently, several successful attempts [8, 9] have been made to synthesize ordered mesoporous materials by direct replication using carbon mesoporous (CMKs) materials [10] as templates.

In particular, we reported [8] the first synthesis of highly stable mesoporous aluminosilicate materials, named as replicated mesoporous materials (RMMs), which possess unique microporous characteristics due to the presence of zeolite SBU in the frame work. In particular, two types of mesoporous aluminosilicate mesoporous/microporous composites, namely RMM-1 and RMM-3 that exhibit structures, respectively, analogous to mesoporous Al-MCM-48 [11, 12] and Al-SBA-15 [13], were prepared by replication from CMK-1 and CMK-3, respectively. In a recent study using molecular modeling, Sonwane *et al.* [14] went further to characterize the structures of RMMs by estimating the $N_2$ accessible areas/volumes by Connolly surfaces, X-ray diffraction patterns, methane adsorption, and ice as a probe to study the pore structure. In addition to the aforementioned replication method using multi-step procedures [8]. Successful attempts have also been made in fabricating a highly stable aluminosilicate mesoporous/microporous composite material, MMS-H, by a unique one-step synthesis procedure using tetrapropyl ammonium hydroxide without the assistance of NaOH [15]. The framework structure, porosity and acidity of RMMs and MMS-H materials have been characterized by a variety of analytical and spectroscopic techniques, *viz*. XRD, $N_2$ adsorption/desorption, TGA, SEM/TEM, FT-IR, hyperpolarized (HP) $^{129}$Xe NMR and solid-state $^{27}$Al and $^{31}$P magic-angle spinning (MAS) NMR spectroscopy [8, 15]. Accordingly, these novel RMMs and MMS-H materials were all found to possess multimodal meso- and micro-porosities, high thermal, hydrothermal, steam and mechanical stabilities and superior acidities rendering for advanced catalytic applications.

The objectives of this study are to confirm the acidity of these novel mesoporous aluminosilicates by additional

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$NH_3$-TPD technique and to evaluate their catalytic activities. In particular, we focus on the catalytic performances of RMM-1 and MMS-H, both of which possess a structure analogous to mesoporous MCM-48 but comprise of MFI-type zeolite frameworks, during ethylbenzene (EB) alkylation reaction will be examined and the results are compared to that obtained from conventional Al-MCM-48 and ZSM-5 catalysts.

## 2. Experimental

### 2.1. Materials preparation

Highly stable mesoporous aluminosilicate materials, RMM-1 and MMS-H (both with Si/Al ratio of 100), were synthesized following the respective procedures reported earlier [8, 15]. For comparison purposes, a commercial microporous H-ZSM-5 zeolite sample (Si/Al = 80; Strem Chemicals Inc.) and a conventional mesoporous Al-MCM-48 (Si/Al = 100) molecular sieve were also prepared. The latter sample was synthesized according to a known recipe [12] with a molar gel compositions of $5.0SiO_2 : 2.5NaOH : 0.87CTABr : 0.13 Brij30 : 400 H_2O : 0.025Al_2O_3$. Briefly, surfactant mixture solution was first prepared by dissolving both CTABr (7.6532 g) and Brij30 (1.45 g) simultaneously in distilled water(60 mL). Then, sodium hydorxide (2.5 g) solution (in 5 mL water) was added to the surfactant solution and stirred for 0.5 h. The silica solution was then added to the above solution and the resulting mixture was shaken vigorously for 0.5 h and the resultant gel was kept at 373 K for crystallization. After 2 days, the mixture was cooled to room temperature (298 K) and pH of the solution was adjusted to 10 with acetic acid, this procedure was repeated twice. Then, aluminum nitrate was added to the gel and the resulting mixture was kept for 373 K for another 7 days. The resulting final product was filtered and washed with ethanol/water mixture and dried in an oven at 373 K followed by calcined in air at 823 K for 6 h. Unlike RMM-1 and MMS-H catalysts, which warrant direct formation of acid sites after calcination treatment, the protonated Al-MCM-48 catalyst was obtained by ion-exchange of Na-form Al-MCM-48 using 1 M ammonium nitrate solution at 348 K for 6 h, this procedure was repeated for three times, followed by re-calcination in air at 823 K for 6 h.

### 2.2. Characterization methods

The phase purities of all samples were examined by powdered X-ray diffraction (XRD). The diffraction patterns were recorded in the $2\theta$ range of 1–10° using an X-ray diffractometer (Scintag X1) with nickel filtered $CuK_\alpha$ ($\lambda = 0.15418$ nm) radiation. The scanning speed and step size were 0.5°/min and 0.01°, respectively. $N_2$ adsorption/desorption measurements were obtained at 77 K (Micromeritics ASAP 2000); sample was degassed at 573 K for at least 6 h under $10^{-3}$ Torr pressure prior to each run. Fourier-transform infrared (FT-IR; Bruker IFS-28) spectroscopy was used to identify vibrational mode of the zeolite SBU. Elemental analyses were carried out by ICP-AES technique on a Labtam Plasma Lab 8440 equipment. Prior to each experiment, ca. 100 mg of the RMM-1 and MMS-H sample was dissolved with 10 mL of 1:1:1 volume mixture of $HCl:HNO_3:HF$ acid solutions, followed by dilution of resulting solution to 100 mL.

The acid properties of the RMM-1, MMS-H and Al-MCM-48 were studied by temperature programmed desorption of ammonia ($NH_3$-TPD). A Micromeritics AutoChem II 2920 Chemisorption system equipped with a TCD detector was used for the analysis. Each catalyst sample (ca. 100 mg) was first preheated at 383 K in flowing dried He gas for 0.5 h before heating at 823 K for additional 1 h, then cooled to 393 K for $NH_3$ adsorption, which is carried out by adsorbing 5% $NH_3$ in He dried gas at 30 mL/min for 0.5 h, followed by purging with He gas for 1 h to remove physisorbed ammonia. Finally, $NH_3$-TPD experiment was carried out by heating up to 773 K at a rate of 10 K/min.

### 2.3. Catalytic activity test

Ethylbenzene alkylation (ethylation) reaction was carried out in a continuous flow reactor system under $N_2$ atmosphere at the normal pressure and for a time-on-stream (TOS) of 3 h. Pelletized catalysts (10–20 mesh; ca. 0.8 g) was first activated at 773 K for 8 h and then cooled to the desired reaction conditions under flow of $N_2$. Then, 1:1 molar mixture of EB and dry ethanol was feed into the catalyst sample with desirable WHSV and reaction temperature. Reaction products were analyzed by a gas chromatograph apparatus(Shimadzu GC-9A) using 5% SP-1200 + 1.75% Bentone 34 on a 100/120 Suplecoport packed column.

## 3. Results and discussion

Figure 1 displays the FT-IR spectra obtained from the calcined MMS-H and RMM-1 materials together with Al-MCM-48 and ZSM-5 samples. It is evident that while the IR spectra observed for MMS-H (figure 1b) and RMM-1 (figure 1c) both reveal characteristics of aluminosilicate framework structure similar to that of Al-MCM-48 (figure 1a) mesoporous material, with an exception of an additional band at ca. 550 $cm^{-1}$. This band, which also occurs in the spectrum of the ZSM-5 (figure 1d), can be accounted for the presence of zeolite SBU [1–8, 15] in the samples. Thus, the use of TPAOH as hydrolysis agent [8, 15] during syntheses of MMSH and RMM-1 materials not only provokes the formation of zeolite SBU but also creation of desirable acid sites immediately after the calcination treatment.

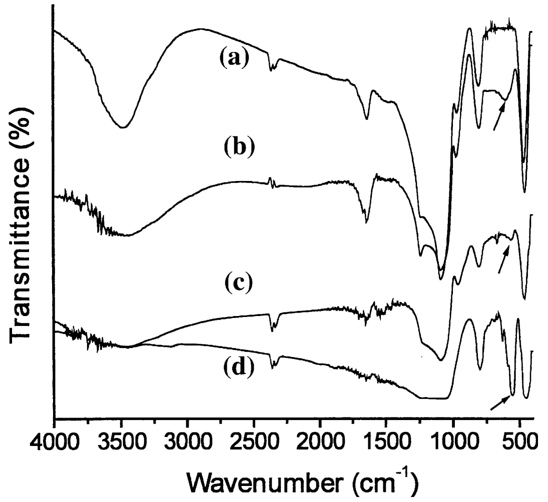

Figure 1. FT-IR spectra of (a) Al-MCM-48, (b) MMS-H, (c) RMM-1, and (d) ZSM-5 samples.

The structures of the novel MMS-H and RMM-1 materials have also been verified by small-angle powdered XRD, as shown in figure 2. It is indicative that the XRD pattern of the calcined MMS-H (figure 2b) reveals characteristic (211) and (220) peaks at a $2\theta$ angle of ca, 2.4° and 2.8°, respectively. This together with the sextet patterns observed at higher angles (4–6°) indicates that MMS-H possesses a structure similar to the calcined mesoporous Al-MCM-48 material (figure 2a). Likewise, the XRD pattern of the RMM-1 sample (figure 2c) also shows a main (211) peak with a weak shoulder (220) together with additional peaks at $2\theta\sim$ 2.5–4° indicating a successful replication of CMK-1 into RMM-1 with structure analogues to MCM-48. That no other diffraction peaks nor any broad background were observed in the $2\theta$ range of 7–35° also reveal the absence of segregated microporous zeolite(ZSM-5) crystals and amorphous phases in both MMS-H and RMM-1 samples [5, 9]. Furthermore, the XRD spectral features of RAW-1 and MMS-H remains practically unchanged after hydrothermal, steam and mechanical treatments [8, 15] indicate that these novel materials are highly stable even under vigorous treatment conditions as compared to the other-mesoporous/microporous composite materials synthesized under acidic conditions [1, 5, 6] and/or using multi-step procedures [1–7].

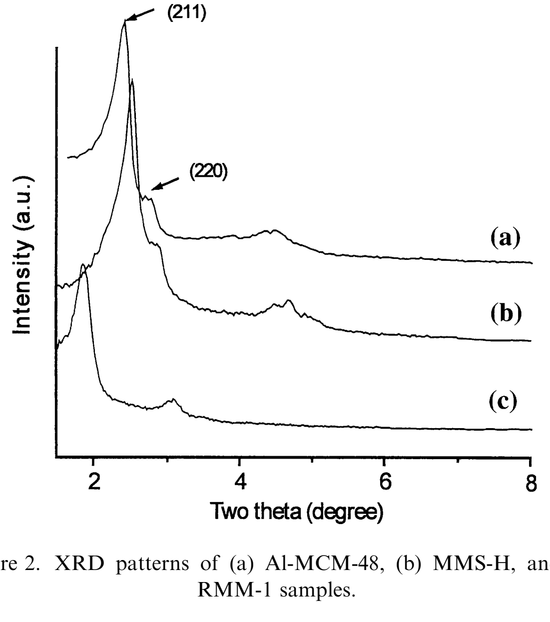

Figure 2. XRD patterns of (a) Al-MCM-48, (b) MMS-H, and (c) RMM-1 samples.

Similar to Al-MCM-48 (figure 3a), $N_2$ adsorption/desorption measurements of the MMS-H and RMM-1 materials exhibit a typical type-IV isotherm (figure 3b and c) with a sharp inflection at $p/p_0 = 0.35$–0.45 and a broad hysteresis loop; typical characteristics of capillary condensation in mesoporous channels [1]. Their physical properties are summarized in Table 1 along with their Si/Al ratios determined by ICP-AES. Obviously, their unit cell parameters, BJH pore diameters, and BET surface areas all fall in the mesoporous range [5–7]. However, the presence of zeolite SBUs [5] in MMS-H and RMM-1 result in thicker walls compared to Al-MC-48. It is noted that even after vigorous thermal, hydrothermal, steam and mechanical treatments, the MMS-H and RMM-1 materials retain their high BET surface areas. That all the Si/Al ratios observed are smaller than their respective initial molar gel composition may be attributed to incomplete condensation of silica under the strong alkali synthesis condition; some of the residual silicon species retained in the solution during synthesis may have been washed away during filtration [16].

Furthermore, $^{27}$Al MAS-NMR spectra obtained from fully hydrated Al-MCM-48, MMS-H, and RMM-1 materials revealed that, regardless of a small amount (<5%) of octahedral Al species observed near 0 ppm, majority of Al in the samples are tetrahedrally coordinated, as indicated by the intense resonance at ca. 52 ppm (not shown). As such, the acid properties of these materials were further characterized by $NH_3$-TPD measurements, as shown in figure 4. It is well known

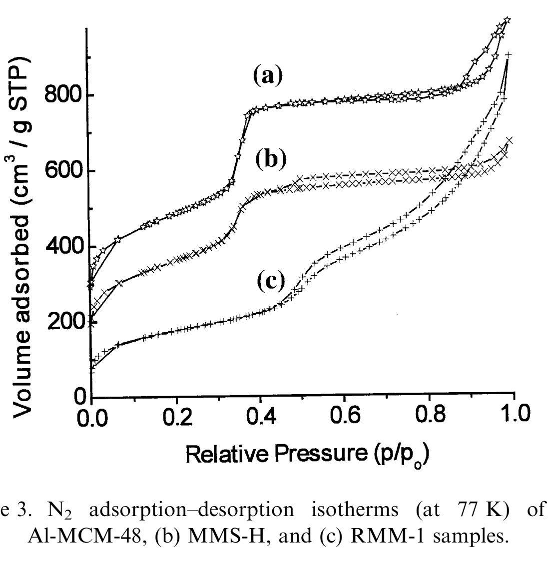

Figure 3. $N_2$ adsorption–desorption isotherms (at 77 K) of (a) Al-MCM-48, (b) MMS-H, and (c) RMM-1 samples.

Table 1
List of physical properties for Al-MCM-48, MMS-H, and RMM-1 materials

| Sample | Unit cell parameter ($\bar{a}$; nm)[a] | Pore diameter ($D$, nm) | Wall thickness ($w$, nm)[b] | BET surface area ($m^2g^{-1}$) | Si/Al ratio | |
|---|---|---|---|---|---|---|
| | | | | | Initial | ICP[c] |
| Al-MCM-48 | 8.3 | 3.4 | 1.0 | 1043 | 100 | 76.8 |
| MMS-H | 8.6 | 2.4 | 1.6 | 949 | 100 | 75.6 |
| RMM-1 | 9.4 | 3.0–5.0 | 1.1–1.6 | 554 | 100 | 71.9 |

[a] $\bar{a} = d_{hkl}(h^2+k^2+l^2)^{1/2}$.
[b] $w = (\bar{a}/3.092) - (D/2)$.
[c] As determined by ICP-AES.

that the temperatures at which $NH_3$ desorbs during TPD measurement depend on the acidic strengths of the catalyst [16, 17]. Accordingly, the desorption peaks at lower temperatures (around 350–500 K) are attributed to weak acid sites arising from surface hydroxyl groups, whereas the higher temperature peaks (around 510–700 K) correspond to moderate or strong (Brønsted and Lewis) acid sites. While Brønsted acid sites are mainly due to the presence of bridging hydroxyl (Si–OH–Al) groups, the existence of extraframework trivalent aluminum species normally gives rise to Lewis acidity [17]. In this context, the $NH_3$-TPD results shown in figure 4 clearly indicate that the MMS-H and RMM-1 samples possess more Brønsted acid sites with moderate or strong acidic strengths than the Al-MCM-48 sample having nearly the same Al content. Again, this is ascribed due to the presence of zeolite SBU's in the structural framework of MMS-H and RMM-1 samples. Separate acidity characterization of these materials using solid-state $^{31}P$ MAS-NMR of adsorbed trimethylphosphine oxide (TMPO) as the probe molecule [18] also indicated that in addition to the resonance peak at chemical shift of ca. 5.0 ppm, which arises strictly from physisorbed TMPO, the multiple resonance locate at 62–71 ppm region represent TMPO adsorbed on Brønsted acid sites [8, 15] (not shown). More specifically, three distinct $^{31}P$ NMR resonances at chemical shifts of 62, 66, and 71 ppm were observed for Al-MCM-48, MMS-H, and RMM-1 materials, indicating the presence of three types of Brønsted acid sites with different acidic strengths. Furthermore, that the observed total peak area of the three resonance accounting for total Brønsted acidity present in the MMS-H and RMM-1 materials are greater than the Al-MCM-48 sample [8, 15] provides additional support to the notion that more amounts of acid sites are present in the two former novel (MMS-H and RMM-1) materials than their conventional counterpart (Al-MCM-48) having a similar Si/Al ratio (Table 1).

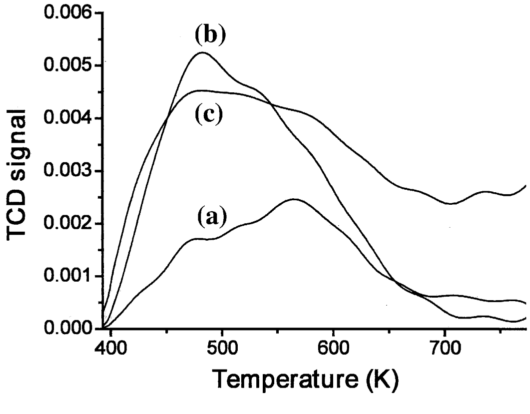

Figure 4. $NH_3$-TPD profiles of (a) Al-MCM-48, (b) MMS-H, and (c) RMM-1 samples.

Alkylated product of ethylbenzene (EB), namely 1,4-diethylbenze (DEB) is an important intermediate for the manufacture of cross-linked styrene [19–21]. Thus, we have chosen EB alkylation as a test reaction for evaluating the catalytic activities of the novel MMS-H and RMM-1 materials. A schematic representation of possible reaction pathways [21] is shown in figure 5. Figure 6 displays the variations of EB conversion and total DEB selectivity over time-on-stream (TOS) for MMS-H and RMM-1 materials and the results are also depicted in Table 2 together with those obtained from conventional mesoporous Al-MCM-48 and microporous H-ZSM-5 (Si/Al = 80) zeolite catalysts. As can be seen from figure 6, a rapid decrease in EB conversion was observed in both MMS-H and RMM-1 catalysts during initial TOS then it gradually reached to a steady state at TOS $>1.5$ h. The deactivation occurs during initial TOS $<1.5$ h in both catalysts is most likely due to blocking of strong acid sites by cooking. By comparison, the RMM-1 sample appeared to be less vulnerable to deactivation than MMS-H. Nevertheless, the DEB selectivity observed for the latter is lifted from its initial value of ca. 83% to a plateau value of ca. 90% at prolonged TOS. That a higher catalytic activity was observed in RMM-1 than MMS-H (at TOS = 1.5 h; see Table 2) may be associated with the presence of more strong acid sites on the replicated material (figure 4). It is noted that while the catalytic activity observed for MMS-H and RMM-1 is less than that of H-ZSM-5, notable increases in DEB selectivity and substantial reductions in by-product yield were found for the two novel mesoporous aluminosilicate materials. Furthermore, although similar DEB selectivity and

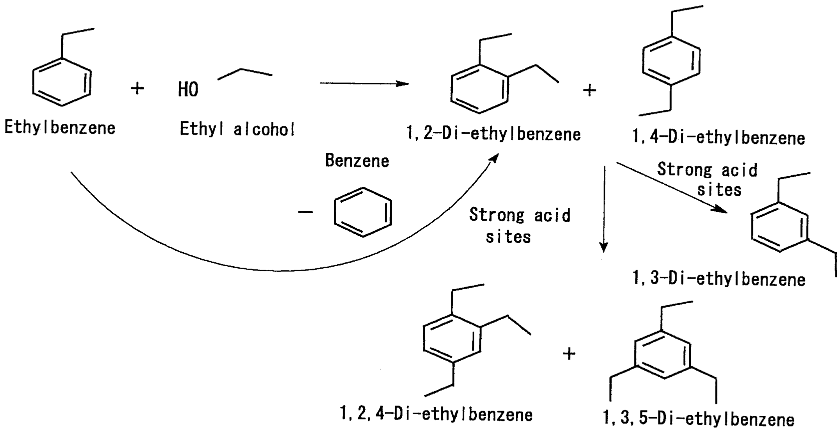

Figure 5. Schematic representation of possible pathways during ethyl benzene alkylation reaction [21].

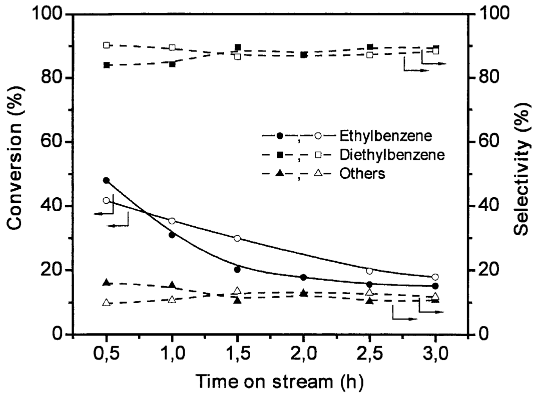

Figure 6. Effects of time on stream on conversion and selectivity during EB alkylation reaction over MMS-H (filled symbols) and RMM-1 (open symbols) catalysts. Reaction conditions: temperature 623 K, WHSV = 4.6 $h^{-1}$, ethylbenzene/ethanol = 1:1, $N_2$ flow = 50 mL $min^{-1}$.

by-product yield were found in MMS-H and RMM-1 materials comparing to Al-MCM-48, their catalytic activities are nearly 2- and 3-fold higher than their mesoporous analogue, respectively. This, again, is attributed to the presence of SBU's on the structural frameworks of the former novel mesoporous/microporous composite materials, as evidenced by the FT-IR and $NH_3$-TPD results in the present study and $^{31}P$ MAS-NMR of adsorbed TMPO, $^{27}Al$ MAS-NMR, and HP $^{129}Xe$ NMR of adsorbed xenon reported earlier [8, 15]. The higher catalytic activity observed for RMM-1 compared to MMS-H is likely due to the larger pore diameter (Table 1), higher textual porosity (figure 3), and higher Al content and hence more strong acid sites (figure 4) presence in the catalyst material.

Table 2

Catalytic data obtained from various samples during ethylbenzene alkylation reaction[a]

| Catalystic perfomrance | MMS-H | RMM-1 | Al-MCM-48 | H-ZSM-5 |
|---|---|---|---|---|
| Ethylbenzene conversion (%) | 20.2 | 29.9 | 11.9 | 44.1 |
| Diethylbenzene selectivity (%) | 89.6 | 86.6 | 88.3 | 69.0 |
| Others[b] | 10.4 | 13.4 | 11.7 | 31.0 |

[a] Reaction conditions: temperature = 623 K; WHSV = 4.6 $h^{-1}$; ethylbenzene:ethanol = 1 : 1 (molar ratio); TOS = 1.5 h.

[b] Other products including benzene, cracking products and trace amount of trialkylbenzene.

## 4. Conclusions

The results obtained from various characterization techniques and ethylbenzene alkylation test reaction reported herein verify that both of these novel, highly stable mesoporous aluminosilicate materials, namely MMS-H and RMM-1, respectively, prepared by direct synthesis and multi-step replication methods, possess zeolite secondary building units that lead to the co-existence of meso- and micro-porosities and improved Brønsted acidities, and hence are more superior as acid catalysts over their mesoporous analogue, i.e., conventional Al-MCM-48.

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