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# Al-MCM-41 as methanol dehydration catalyst

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# ABSTRACT

Al-MCM-41,  $[SiO_2]/[Al_2O_3] = 30$ , mesoporous catalysts were synthesized using tetraethylorthosilicate (TEOS) as a source of silica and hexadecyltrimethylammonium bromide (CTAB) as a structure-directing agent (SDA) in the presence of tetrapropylammonium hydroxide (TPAOH) as a co-surfactant additive. The catalytic activities of the calcined samples were evaluated for the dehydration of methanol to dimethyl ether (DME) at 250–450 °C and a gas hourly space velocity (GHSV) of 14,000–80,000 mL g<sup>-1</sup><sub>cat</sub> h<sup>-1</sup>. Al-MCM-41 samples synthesized in the presence of TPAOH showed higher activity than those synthesized in its absence. The improvement in catalytic activity correlates with the increase in acidity brought about by the enhanced condensation of aluminosilicate framework in the Al-MCM-41 structure. Al-MCM-41 synthesis DME from CO<sub>2</sub>/H<sub>2</sub> at temperature, 260 °C; pressure, 735 psi; GHSV, 2000 mL g<sup>-1</sup><sub>cat</sub> h<sup>-1</sup> in a fixed-bed reactor.

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# 1. Introduction

Mesoporous silica [1,2] belongs to the M41S class of materials and is an ordered porous material with a long-range structural order. It comprises interconnected or straight pore channels of diameter 2–50 nm (mesopore range) in the bulk of its structure. Mesoporous silica has a high surface area and is thermally stable. Its pore dimensions can be tailored to specific requirements. Various metal ions or metal oxides can also be introduced to have a uniform dispersion of active components in its structure. As a result there is a significant interest in the synthesis and applications of mesoporous silica in catalysis, adsorption, etc.

Ordered mesoporous silica can exist in the form of hexagonal, cubic, or lamellar structures which may be prepared using a source of silica together with a structure-directing agent (SDA) usually a surfactant, through a self-assembly process under a range of synthesis conditions [2].

Hexagonal MCM-41 mesoporous silica has been the subject of a large number of studies in recent years. Purely siliceous MCM-41 does not have appreciable acidity, but acidity can be introduced through the incorporation of metal ions such as aluminum, titanium, and zirconium into its framework structure [3–6]. Surface

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E-mail addresses: s.naik@utah.edu, spnaik@gmail.com (S.P. Naik), w.zmierczak@utah.edu (W. Zmierczak). functionalization of the hydroxyl groups in mesoporous silica with silanes containing acidic groups provides an alternate method to introduce acidity in mesoporous silica [7]. The acidity generated by the incorporation of metals is usually associated with the nature of the chemical linkages produced by the metal ions in the silica framework. When a trivalent cation such as Al<sup>3+</sup> substitutes for Si<sup>4+</sup>, the framework possesses a negative charge that can be compensated by a proton to form a Bronsted acid site (Fig. 1). The extra framework Al<sup>3+</sup> species can also be a source of Lewis acidity in the structure. Such metal–ion incorporated mesoporous silica is a candidate acid catalyst for several organic reactions [8–14].

Although Al-MCM-41 is a useful catalyst in organic reactions, the aluminosilicate framework in the walls of its structure does not have short-range order similar to that in zeolites, and hence the structure is amorphous in nature. The degree of condensation of aluminosilicate in the framework of Al-MCM-41 proceeds only to a limited extent during synthesis and calcination, which decreases both the acidity and the hydrothermal stability of Al-MCM-41. Several efforts are on-going to improve the acidity and hydrothermal stability of mesoporous silica for applications in catalysis.

Nevertheless, metal-incorporated mesoporous materials and zeolites are increasingly replacing conventional acid catalysts, usually mineral acids, in organic reactions of industrial importance [8–14]. Use of such catalysts has been demonstrated in Friedel–Crafts, aldol condensation, epoxidation, and Diels–Alder reactions. Al-MCM-41, due its larger pore diameter than that of zeolites, is useful in the catalytic transformation of bulky organic molecules. The use of solid acid catalysts is also environmentally beneficial as these catalysts are easy to handle, can be separated from the reaction medium without difficulty, are reusable, and can

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Fig. 1. A schematic illustration of Al-MCM-41 structure and the aluminosilicate framework in its walls.

be further functionalized to introduce multiple catalytic sites in the structure.

Dehydration of alcohols to ethers or hydrocarbons is an industrially important acid catalyzed reaction. Dimethyl ether (DME) is gaining prominence as a next-generation synthetic fuel [15–19]. It is produced by the direct dehydration of methanol or by a twostep process from CO/CO<sub>2</sub> and H<sub>2</sub>, via intermediate formation of methanol, on a bifunctional catalyst comprising methanol synthesis and methanol dehydration components.

In fact, it is necessary to develop new improved methods for the efficient reductive conversion of CO<sub>2</sub> to methanol and/or DME in order to manage the growing problem of excess CO<sub>2</sub>, a green house gas, in the environment [18].

DME is a clean fuel for diesel engines and has a very high thermal efficiency compared to other synthetic fuels. Vehicular engines running on DME have considerably lower  $NO_x$  emissions and nearzero production of solid particulates. By using DME as a starting material, several useful chemicals or other fuels such as ethanol, hydrocarbons, and higher oxygenates can be produced. Furthermore, DME is a useful carrier of hydrogen for applications such as in fuel cells, etc.

Synthesis of DME requires a dehydration catalyst component of high specificity and durability. The catalyst should have an optimum acidity to selectively produce DME [18,19]. Usually the presence of strong acid sites in the catalyst will promote side reactions to generate undesired hydrocarbons, which may lead to coke formation and reduction of the yield of DME, and ultimately shorten the life of the catalyst.

In this paper, studies on the synthesis of active Al-MCM-41 catalysts for the selective dehydration of methanol to DME are reported. The activity and selectivity of Al-MCM-41 catalysts are enhanced by modification of the conventional synthesis process. Specifically, small amounts of tetrapropylammonium hydroxide (TPAOH) were added during synthesis, which enhanced the activity of Al-MCM-41 catalysts. The catalytic activity of the calcined material was evaluated for the direct synthesis of DME from methanol in a fixed-bed reactor. The most-effective Al-MCM-41 catalyst was then admixed with a commercial methanol synthesis catalyst to form a bifunctional (mechanical mixture) catalyst [15,18–20] for the synthesis of DME from CO<sub>2</sub>/H<sub>2</sub> in a high-pressure fixed-bed reactor.

#### 2. Experimental

## 2.1. Synthesis of Al-MCM-41

Al-MCM-41 samples were prepared by modifying the conventional synthesis process. The  $SiO_2$ -to- $Al_2O_3$  molar ratio was kept equal to 30 in all samples. A clear solution (A) was first prepared by dissolving aluminum isopropoxide (Alfa Aesar, 99%) in tetraethylorthosilicate (Sigma–Aldrich, 99.9%) in a polypropylene (PP) bottle and stirred at 25 °C for 2 h. Another solution (B) was prepared by dissolving hexadecyltrimethy-

#### Table 1

List of the synthesized Al-free and Al-MCM-41 samples, their acidity values, and their catalytic activity toward dehydration of methanol, [CTAB/TPAOH] is the molar ratio.

Catalyst code	Catalyst type	[CTAB/TPAOH]	Acidity, $\mu m/g(250500^\circ\text{C})$	Methanol conversion, %	Selectivity, %	
					DME	C-1-C-3 <sup>a</sup>
MC-1	Al-free MCM-41	-	-	6	100	0
MC-2	Al-MCM-41	$\infty$	140	45	98	2
MC-3	Al-MCM-41	0.75	260	72	98	2
MC-4	Al-MCM-41	0.20	460	73	97	3

Reaction conditions: temperature, 400 °C; GHSV, 14,000 mLg<sup>-1</sup><sub>cat</sub> h<sup>-1</sup>; time on-stream, 5 h; methanol vapor pressure, 97.48 mm of Hg. <sup>a</sup> Hydrocarbons.

lammonium bromide (CTAB, Sigma–Aldrich, 99%) in a 30% aqueous solution of NH<sub>4</sub>OH (Sigma–Aldrich), tetrapropylammonium hydroxide (TPAOH, 40% aqueous, Sachem) and de-ionized water in a PP bottle, under stirring at 25 °C. The solution (A) was then added in a drop-wise manner to the solution (B) which was kept under stirring at 25 °C. This procedure resulted in the formation of a precursor gel of molar composition of  $1SiO_2:0.033Al_2O_3:0.12CTAB:7.37NH_4OH:0-0.62TPAOH:75H_2O$ . The gel was stirred for 30 min, followed by hydrothermal treatment at 100 °C for 3 days. The white precipitate obtained was filtered and dried at room temperature for 24 h, followed by further drying at 110 °C for 1 h.

A series of samples as MC-1 to MC-4, as shown in Table 1, were prepared by varying the amount of TPAOH in the synthesis mixture. The variation in amounts of TPAOH added to each of the samples during their preparation is expressed as a molar ratio of CTAB to TPAOH, as shown in Table 1. An aluminum-free MCM-41 sample was also prepared by the same method but without aluminum and TPAOH in the gel. The dried samples were calcined at 550 °C in air for 10 h in a muffle furnace at a heating rate of 5 °C/min.

#### 2.2. Characterization

X-ray diffraction (XRD) analysis of the calcined samples was performed in the 2- $\theta$  range of 1.5–10°, by using a Philips XRD instrument employing Ni-filtered Cu K $\alpha$  radiation at 45 kV and 50 mA. The N<sub>2</sub> adsorption/desorption isotherms were obtained using a Micromeritics ASAP 2000 instrument. Prior to the measurements, the catalysts were degassed at 250 °C for 1.5 h. Infrared spectra were collected on a Spectrum RX-1 (PerkinElmer) instrument using the KBr pellet technique and a resolution of 2 cm<sup>-1</sup>. The composition of 95% KBr and 5% calcined sample was used for FTIR analysis and maintained for all measurements.

Temperature-programmed desorption (TPD) of ammonia was performed on a Micromeritics Chemisorb 2720 instrument equipped with a thermal conductivity detector. Typically 0.1 g of the catalyst was charged in a U-shaped quartz cell and pretreated in helium at 300 °C for 1 h. The catalyst was then saturated with NH<sub>3</sub> at room temperature using a gas mixture of 5% NH<sub>3</sub> and 95% He. The catalyst was heated to 700 °C at a rate of 5 °C/min for desorption of NH<sub>3</sub>. The amount of desorbed NH<sub>3</sub> was quantitatively analyzed by a thermal conductivity detector and recorded as a function of temperature. Scanning electron microscopy (SEM) measurements on the samples were conducted on a Topcon SM-300 instrument equipped with an energy dispersive X-ray spectrometer (EDS) allowing visualization of the elemental distribution and their quantification.

#### 2.3. Catalytic property measurements

#### 2.3.1. Methanol dehydration reaction

The activity of the different catalysts for methanol dehydration was evaluated in a tubular fixed-bed stainless steel reactor operating at 250–400 °C and gas per hourly velocity (GHSV) of 14,000–80,000 mL g<sup>-1</sup><sub>cat</sub> h<sup>-1</sup>. Prior to the catalytic activity measurements, the calcined samples were finely powdered in an agate mortar, pelletized (50 MPa pressure), crushed, and sieved to 25–40 mesh size using the standard US sieve series. Methanol was introduced to the reaction zone by bubbling ultrapure helium gas through a thermostated glass saturator filled with methanol and maintained at 20 °C. A fresh catalyst was used for each run. The catalyst was activated at 400 °C in flowing air for 3 h, after which the temperature was brought down under flowing He and the flow of methanol was started. The reaction time on-stream was 5 h.

Fig. 2. Small-angle XRD patterns of the calcined Al-free and Al-MCM-41 samples.

#### 2.3.2. Dimethyl ether synthesis from $CO_2/H_2$

A bifunctional DME synthesis catalyst was prepared by mechanical mixing of 1.8 g of commercial methanol synthesis catalyst (MK-121, Haldor Topsoe) and 0.12 g Al-MCM-41, the methanol dehydration catalyst prepared in this work. The reaction was performed in a high-pressure tubular stainless steel fixed-bed reactor operating at 260 °C, 735 psi, and GHSV of 2000 mL g<sup>-1</sup><sub>cat</sub> h<sup>-1</sup>, using the reactant gas of composition 25% CO<sub>2</sub>:75% H<sub>2</sub>.

## 2.3.3. Analysis of reaction products

The reaction products exiting the reactors were analyzed using an online GC (Agilent 7890) equipped with a thermal conductivity detector and an HP-Plot Q (bonded polystyrenedivinylbenzene) capillary column (15 m length). The tail gas lines in the reactors were kept heated at 150 °C all the time to avoid condensation of the products. The identity of the products was further confirmed on a gas chromatograph coupled with mass spectroscopy (GC-MS) on a Hewlett Packard (5897 series) instrument equipped with a single quadruple detector.

#### 3. Results and discussions

The XRD patterns of the prepared mesoporous catalysts shown in Fig. 2 confirm their hexagonal mesoporous structure. A very intense(100) diffraction peak with additional higher order peaks of lower intensity which could be indexed to the *p6mm* structure [2]. In Fig. 3, the SEM images of the samples captured under the same magnification are shown. All the samples showed almost identical morphology of aggregated spheroid particles. The size of the particles was 1-2 µm in samples MC-1, MC-2, and MC-3, however, MC-4 had slightly larger particles of size from 3 to 4 µm. MC-4 was prepared at a much higher concentration of TPAOH in the gel, and therefore the increase in the size of particles could be a direct effect of the extra TPAOH in the gel. The EDAX analyses of all the samples confirmed their SiO<sub>2</sub>-to-Al<sub>2</sub>O<sub>3</sub> ratio to be ~30. Furthermore, the uniform distribution of Si and Al in the material was also confirmed by the mapping of Si and Al obtained from EDAX. The mapping results obtained on MC-4 are shown as an example in Fig. 4.

Table 1 shows the catalytic activities of the calcined materials for the dehydration of methanol at 400 °C, GHSV 14,000 mL  $g^{-1}_{cat}$  h<sup>-1</sup> and time on-stream of 5 h. The molar ratio of CTAB and TPAOH,





Fig. 3. SEM images of the Al-free and Al-MCM-41 samples.



Fig. 4. EDS maps of MC-04 sample, light and dark spots in the two images correspond to the distribution of Si, and Al, respectively, in the sample.



**Fig. 5.** Conversion of methanol at different temperatures on MC-2 and MC-4 samples. GHSV, 14,000 mL  $g^{-1}_{cat}$  h<sup>-1</sup>; time on-stream, 5 h; methanol vapor pressure, 97.48 mm of Hg.

maintained in the synthesis gel during sample preparation, is also shown in this table. MC-1 showed the lowest methanol conversion 6%, among all the samples; evidently, this lower conversion of Alfree MCM-41 is due to its lower acidity, as it does not contain Al. MC-2, synthesized in the absence of TPAOH showed 45% methanol conversion at a DME selectivity of 98%. Significant increases in catalytic activity were observed from MC-3 and MC-4 samples that were prepared in the presence of TPAOH in the synthesis gel. MC-3 prepared at [CTAB]/[TPAOH] = 0.75 showed methanol conversion of 72%, whereas MC-4 prepared at [CTAB]/[TPAOH] = 0.20 showed methanol conversion of 73%, at a DME selectivity of 98% and 97%, respectively. The magnitude of acidity, measured in terms of desorbed ammonia on the catalysts in the range of 250-500 °C shown in Table 1, indicated a direct correlation between total acidity and the activity of the catalysts. The total acidity increased with the increase of TPAOH to the gel.

The activities of MC-2 and MC-4 prepared in the absence and presence respectively of TPAOH in the synthesis gel, were further evaluated at different temperatures and GHSVs, as shown in Figs. 5 and 6, respectively. MC-4 performed superiorly to MC-1 over a range of temperatures and GHSVs. At GHSV of 14,000 mLg<sup>-1</sup><sub>cat</sub> h<sup>-1</sup>, the conversion of methanol increased with the increase in temperature ranging from 250 to 400 °C for both catalysts, but the selectivity to DME decreased slightly at higher temperature. However, there was a substantial difference between the activities of two catalysts. Similarly at 400 °C, with the increase in GHSV, the conversion of methanol decreased, but the conversion was much lower for MC-2 in the investigated GHSV range. The selectivity to DME was however not much affected for the investigated GHSV range. Clearly, MC-4, synthesized in the presence of TPAOH, showed much higher activity over a range of temperature and GHSV than MC-2, prepared in the absence of TPAOH.

 $N_2$  adsorption/desorption measurements on Al-MCM-41 were conducted at -195.85 °C to obtain the texture properties of the catalysts. All studied samples showed type IV adsorption isotherms, indicating cylindrical mesopores with hysteresis loops in the  $p/p_0$ 

able 2		
Fexture	properties of Al-MCM-41	samples



**Fig. 6.** Conversion of methanol for different GHSVs on MC-2 and MC-4 samples. Temperature, 400 °C; time on-stream, 5 h; methanol vapor pressure, 97.48 mm of Hg.



Fig. 7. N<sub>2</sub> adsorption/desorption isotherms measured on Al-MCM-41 samples.

range of 0.2–0.3 (Fig. 7), that is typical of MCM-41 materials [21,22]. It is known that the BJH method does not correctly estimate the mesopore size. Thus, for capillary condensation in this pressure range, the mesopore size was estimated according to the correlation obtained from nonlocal density functional theory [21–23] (NLDFT), and the obtained data are listed in Table 2. The BET surface areas, determined from the linear part of the BET equation ( $p/p_0$  equal to 0.05–0.3), were in the range of 900–1200 m<sup>2</sup>/g. MC-4 showed the highest surface area among the samples. The

Catalyst code	[CTAB/TPAOH]	BET surface area (m²/g)	External surface area (m²/g)	Total pore volume (cm <sup>3</sup> /g)	Macropore volume (cm <sup>3</sup> /g)	Mesopore volume (cm <sup>3</sup> /g)	Pore diameter (Å)	a0 (Å)	Wall thickness (Å)
MC-2	$\infty$	900	880	1	0.40	0.60	33	43.34	10.34
MC-3	0.75	980	900	1	0.30	0.70	30	41.77	11.77
MC-4	0.20	1200	1000	0.95	0.10	0.85	27	40.39	13.39

pore diameter was found to decrease with a decrease of the [CTAB]/[TPAOH] ratio in the precursor gel. The wall thickness of the pores, as estimated from the difference between the unit cell parameter (*a*<sub>0</sub>) calculated from XRD and pore diameter, was found to be in the range of 10–13 Å for the calcined samples and increased with a decrease in [CTAB]/[TPAOH] ratio. The mesopore volume was found to increase with a decrease in [CTAB]/[TPAOH] ratio. MC-4 showed the lowest average pore diameter and the highest wall thickness among the three samples. The increase of surface areas for MC-3 and MC-4 was due to the presence of better quality mesostructure and a higher degree of aluminum incorporation in the framework [4,24]. Such Al-MCM-41 samples with superior mesostructure and high surface areas therefore showed higher activity toward methanol dehydration, as discussed earlier.

Fig. 8 shows the FTIR spectra for the studied samples. For Si-MCM-41, two intense bands ( $\nu$ 1 and  $\nu$ 2) at 1252 and 1087 cm<sup>-1</sup> were assigned to the asymmetric T-O-T (T# Si or Al) stretching vibration were observed. The band at  $817 \text{ cm}^{-1}$  (v4) is associated with symmetric T–O–T (T = Si or Al) stretching, and the band at  $458 \text{ cm}^{-1}$  ( $\nu 5$ ) is assigned to a TO<sub>4</sub> bending mode. The silanol group stretching vibration ( $\nu$ 3) occurs at 965 cm<sup>-1</sup>. Generally, the FTIR spectra of Al-MCM-41 samples show a low intense peak at ~960 cm<sup>-1</sup>, assigned to Si–O–H or Si–OH vibrations. The substitution of silicon by aluminium causes a shift of the lattice vibration band to a lower wave number. These shifts are due to the increase of mean T-O distances in the walls of the mesostructure. In this case, it is caused by the substitution of the small silicon atom by the larger aluminum atom. The two intense bands ( $\nu$ 1 and  $\nu$ 2) at ~1252 and  $1087 \text{ cm}^{-1}$  for MC-1 are assigned to the asymmetric T–O–T (T = Si or Al) stretching. These vibrations were shifted to lower wave numbers in the case of MC-2, MC-3, and MC-4 samples. The shift at 1087 cm<sup>-1</sup> was more prominent for MC-3 and MC-4, the Al-MCM-41 samples prepared in the presence of TPAOH in the synthesis gel. In addition, MC-2 showed a peak of low intensity at  $\sim$ 570 cm<sup>-1</sup>. The intensity of this peak increased with the addition of TPAOH. For



Fig. 8. FTIR spectra of calcined Al-free and Al-MCM-41 samples in the region of  $400-1500\,\mathrm{cm}^{-1}$ .

zeolitic aluminosilicates this peak is observed at  $\sim$ 550 cm<sup>-1</sup> and is assigned to the asymmetric stretching mode of the five-membered aluminosilica rings [25–28]. The position of this peak can shift to a higher wavenumber depending upon the size of the crystallites and crystallinity of the material [29]. The intensity ratio of the 570 cm<sup>-1</sup> to 450 cm<sup>-1</sup> peaks for MC-4, MC-3, and MC-2 were 0.14, 0.12, and 0.07, respectively, proving that the addition of TPAOH has clearly facilitated the formation of catalytically active five-member aluminosilicate rings which promoted the higher acidic activity of MC-3 and MC-4 materials (Fig. 9).

The acidity determination data shown in Table 1 also confirm that Al-MCM-41 synthesized in this work has a moderate acidity



Fig. 9. FTIR spectra of calcined Al-free and Al-MCM-41 samples in the region of 400-650 cm<sup>-1</sup>.



**Fig. 10.** CO<sub>2</sub> conversion on bifunctional DME catalysts prepared using MK-121 as methanol synthesis components, and MC-4 and MC-2 as methanol dehydration components. Gas mixture, 25% CO<sub>2</sub>: 75% H<sub>2</sub>; temperature, 260 °C; pressure 735 psi; GHSV, 2000 mL g<sup>-1</sup><sub>cat</sub> h<sup>-1</sup>.

which was enhanced by the addition of a small amount of TPAOH to the synthesis gel. It has been reported that only moderate Lewis acid sites are required for the dehydration of methanol to DME [30]. The TPD of NH<sub>3</sub> measures the total acidity in the material, however, it may be difficult to exactly differentiate between the types of acid sites, such as Lewis or Bronsted, using this technique. Therefore, care must be exercised in interpretation of the data obtained using TPD of NH<sub>3</sub> technique.

In this study, well-ordered Al-MCM-41 structures were obtained up to a CTAB-to-TPAOH molar ratio of 0.15 (data not shown) in the synthesis gel. Further increase in the amount of TPAOH leads to the formation of disordered mesoporous zeolitic silica, as reported by Chiang and co-workers [23]. The addition of TPAOH during synthesis of Al-MCM-41 favors a higher extent of condensation in the mesoporous aluminosilicate framework that facilitates incorporation of Al<sup>3+</sup> ions in the framework [31,32]. An improved condensation of aluminosilicate framework meant an increased concentration of catalytically active acidic sites in the aluminosilicate framework, leading to a higher conversion of methanol for the MC-3 and MC-4 samples. From the data shown in Table 2, it is clear that the addition of TPAOH increases the wall thickness of mesoporous Al-MCM-41. Previous reports [33-35] also suggest that mesoporous silica of enhanced stability could be synthesized simply by increasing the pore wall thickness and the extent of silica condensation. In fact, Mokaya [36] has reported improvement of silica condensation and an increase in wall thickness of MCM-41 by increasing the period of hydrothermal treatment during synthesis of MCM-41. Therefore, in our approach too, the addition of TPAOH improved the silica condensation in the walls of Al-MCM-41, thereby modifying the structural, acidic and catalytic properties of Al-MCM-41 (Tables 1 and 2).

MC-2 and MC-4 were chosen as dehydration components of a bifunctional DME synthesis catalyst prepared by mechanical mixing of methanol synthesis catalyst, MK-121, with MC-2 or MC-4 as methanol dehydration components. The DME synthesis was performed using  $\rm CO_2/H_2$  as reactants at 260 °C, 735 psi, and GHSV of 2000 mL g<sup>-1</sup><sub>cat</sub> h<sup>-1</sup>. The MC-4-based bifunctional DME synthesis catalyst showed CO<sub>2</sub> conversion of ~11%, and the MC-2-based catalyst showed ~8%, both at the end of 4.8 days of time on-stream, as shown in Fig. 10. The activity of the MC-4-based catalyst seems to have stabilized after 2.5 days as compared to that of MC-2-based catalyst in which the activity to DME for the MC-4-based catalyst,



**Fig. 11.** DME selectivity on bifunctional DME catalysts prepared using MK-121 as methanol synthesis components, and MC-4 and MC-2 as methanol dehydration components. Gas mixture, 25% CO<sub>2</sub>: 75% H<sub>2</sub>; temperature, 260 °C; pressure 735 psi; GHSV, 2000 mLg<sup>-1</sup><sub>cat</sub> h<sup>-1</sup>.

shown in Fig. 11, was 76% after 4.8 days of time on-stream whereas it was only 32% for MC-2-based catalyst for the same period. The other major product was methanol, and only traces ( $\sim$ 1%) of hydrocarbons were detected in the products.

It is clear that MC-4 functions as a superior acidic component to MC-2 in the bifunctional DME synthesis catalyst for the preparation of DME from  $CO_2/H_2$  mixtures. Highly porous and ordered active materials, such as Al-MCM-41 or Al-SBA-15, are of interest for the preparation of bifunctional DME catalyst as their mesopores could be loaded uniformly with active components of methanol synthesis catalysts to form robust and novel catalyst systems.

### 4. Conclusions

Al-MCM-41 mesoporous catalysts of [SiO<sub>2</sub>]/[Al<sub>2</sub>O<sub>3</sub>]=30 samples were prepared using tetraethylorthosilicate (TEOS) as the source of silica, and hexadecyltrimethylammonium bromide (CTAB) as the structure-directing agent. The synthesis was performed under alkaline synthesis conditions at 100 °C in the presence and absence of tetrapropylammonium hydroxide (TPAOH) in the synthesis gel. MC-3 and MC-4 samples, prepared at CTAB/TPAOH of 0.75 and 0.20, respectively, showed methanol conversions of 72% and 73%, respectively. MC-2 prepared in the absence of TPAOH showed a methanol conversion of 45%. The improvement in the activities of the catalysts was correlated with the enhancement of acidity the catalysts generated by better incorporation of Al species in the aluminosilicate framework by the enhanced aluminosilicate condensation effected by TPAOH. MC-4 and MC-2 catalysts were studied as the dehydration components of bifunctional catalysts for the synthesis of DME from CO<sub>2</sub>/H<sub>2</sub> gas mixture at temperature of 260 °C, pressure of 735 psi and GHSV of 2,000 mLg<sup>-1</sup>cat h<sup>-1</sup>. The MC-4-based catalyst showed higher conversion and stability as compared to MC-2-based catalyst.

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