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Influence of Ethanol Concentration and Template Ion Exchange Agent on Template Recycling in Mobil Crystalline Material 41 (MCM-41) Synthesis

Jia Yen Lai
Lock Hei Ngu *
Farouq Twaiq
Faculty of Engineering, Computing and Science, Swinburne University of Technology Sarawak Campus, Jalan Simpang Tiga, Kuching 93350, Sarawak, Malaysia
**e-mail:* lngu@swinburne.edu.my

Recycling of surfactant template for several subsequent MCM-41 synthesis is necessary to reduce substantial synthesis solution disposal. In MCM-41 synthesis, ethanol concentration and template ion exchange agent are two significant factors that affect the silicate polymerization, solvating effect on micelles formation, and MCM-41 mesostructure formation. In view of that, this study investigates recycling of surfactant template ions in extract solution in Mobil Crystalline Material 41 (MCM-41) synthesis. Effect of the ethanol concentrations in the solution gel and the types of ion exchange agents on the yield of MCM-41 material and its surface morphology were studied. Hexadecyltrimethylammonium bromide was used as template for MCM-41 synthesis using tetraethylorthosilicate (TEOS) as silica reagent with ethanol-water mixture as solvent at different ethanol concentrations. Template ions of synthesis gel was exchanged with an ion exchange agent (i.e., 1-butyl-3-methylimidazolium chloride or ammonium nitrate) before it is extracted using synthesis solution. After extraction, the extracting solution was added with TEOS, used for second synthesis cycle and the process continued in an extraction. The template ions in the extract solution were further recycled up to eight synthesis cycles. Yield of calcined materials significantly influenced by ethanol solvent concentrations and however did not vary with various ion exchange agents. Nitrogen adsorption isotherms showed that the calcined materials exhibit MCM-41 characteristics with surface areas ranging from 600 – 1000 m^2/g. It is possible to recycle and reuse the surfactant template for several subsequent times of preparing MCM-41 if the ethanol concentration in the solution gel controlled continuously.

Keywords: Ethanol concentration, ion exchange agent, MCM-41 synthesis, template ion exchange, template recycling

INTRODUCTION

Siliceous MCM-41 has unique properties such as high surface area that may reach up to 1600 m^2/g, well-ordered and uniform cylindrical mesoporous

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arrangement with pore size from 2 to 30 nm, and good thermal stability (Kumar et al. 2017, Twaiq et al. 2012). Given its physicochemical properties, MCM-41 has great potential as catalytic materials for chemical separations, catalysis, adsorption and biotechnology devices applications (Kumar et al. 2017, Viswanathan et al. 2002). The as-synthesized MCM-41 material (synthesis gel) is synthesized by hydrolysis and condensation of silica source and self-assembly of surfactant template under a basic or an acidic condition (Owens et al. 2016). The templates are then removed *via* suitable template removal methods to form a mesostructure material (Twaiq et al. 2014).

Two main approaches reported in the literature for synthesizing mesoporous silica material are hydrothermal synthesis approach and the liquid templating approach. In hydrothermal synthesis, heat is utilized in an autoclave with temperature ranging from −4 to 150°C for up to 72 hours under mild-alkaline conditions using a non-organic silica reagent and surfactants (Xu et al. 2009). Whereas, the liquid templating method utilizes surfactants to synthesize the mesoporous silica material from organic silica sources without hydrothermal treatment (Barrera et al. 2011).

Types of surfactants include anionic, cationic and nonionic surfactants are used to synthesize mesoporous silica material. Anionic surfactants have high detergency of potent and lower cost than cationic and nonionic (neutral) surfactants (Cao et al. 2010). Sodium dodecylbenzenesulfonate (SDBS), sodium dodecylsulfate (SDS) and lauric acid sodium salts (LAS) are the typical anionic surfactants which are used as a surfactant template in the synthesis (Yokoi et al. 2004). The cationic surfactants prepared using n-alkyltrimethyl ammonium bromides/chloride has different alkyl chain lengths ranging from C12 to C20. The most common type of cationic surfactant used as surfactant template is CTAB (Du et al. 2013). The type of nonionic surfactants used as template includes primary amine ($C_nH_{2n+1}NH_2$) with carbon atoms of 8 to 20 for instance tetradecylamine, dodecylamine, hexadecylamine and octadecylamine (Satou and Shimizu 2006) and also poly(ethylene oxide) such as Pluronics (poly(ethyleneoxide)x-poly(propyleneoxide)y-poly(ethyleneoxide)z) (Somasundaran 2006).

The characteristics of mesostructure material are affected by the surfactant concentration in the synthesis gel (Naik and Ghosh 2009). The critical micelle concentration (CMC) affects the formation of the micelle structure, varying in hexagonal, cubic or a lamellar arrangement (Donegá 2014). Table 1 shows the CMC of CTAB in different solutions such as water, absolute ethanol and ethanol-water mixture as reported in literature (Li et al. 2005, Li et al. 2006, Wowczyk 2014).

Calcination is a conventional method to remove surfactant template (Twaiq et al. 2014). The surfactant template is burned off when the as-synthesized mesoporous material is calcined under high temperature of 550 °C (Kleitz et al. 2003). However, the as-synthesized mesoporous material is thermally unstable under high temperature and mesopores shrinkage may occur due to mesophase transformation (Du et al. 2013). Solvent extraction is therefore used to treat the as-synthesized mesoporous material to produce less negative effects on the structure of mesoporous material and to intensify the removal of the surfactant template (Jabariyan and Zanjanchi 2012). Also, the extracted surfactant molecules can be recovered and reused for consecutive synthesis cycles.

Table 1. The critical micelle concentration (CMC) of CTAB in different ethanol-water solvents (Li et al. 2005, Li et al. 2006, Wowczyk 2014)

System	CMC (mol/L)	Reference
CTAB in pure water	0.0009	Li et al. 2006
CTAB in 50% ethanol in water	0.022	Li et al. 2005
CTAB in pure ethanol	0.24	Wowczyk 2014

Extraction agents (*i.e.*, ion exchange agent) are typically used to enhance the surfactant template recovery from the pores of as-synthesized mesoporous material. Two ion exchange agents, *i.e.*, 1-butyl-3-methylimidazolium chloride (BMImCl) and ammonium nitrate (NH_4NO_3), were recently used to enhance the removal of surfactant template (Lang and Tuel 2004, Martinez-Palou and Aburto 2015). BMImCl is an ionic liquid (IL) with long-chain hydrocarbon radius structure exhibiting the surfactant properties when dissolved in water (Martinez-Palou and Aburto 2015). BMImCl has a high solvent ability, very low vapor pressure and high thermal stability, which enable it to replace the surfactant template in the MCM-41 synthesis in organic environment (Martinez-Palou and Aburto 2015). Moreover, the mesostructure of MCM-41 material could be maintained after the ion exchange process using BMImCl (Zukal et al. 2007).

When using ammonium nitrate (NH_4NO_3) as an ion exchange agent, the weak interaction between ammonium ions (NH_4^+) and the silicate (O_3SiO^-) group resulted in the MCM-41 surface easily produces the silanol group to condensate the desirable silicate (González-Rivera et al. 2014). The mesoporous material produced after repeated NH_4NO_3 ion exchange process, resulted in an ordered channel-like mesostructure with higher surface area and larger mesopores volume (Ariapad et al. 2012). In addition, the adjustment of ethanol volume fraction in the synthesis gel (e.g. CTAB/ethanol molar concentration ratio) is an important step. The ethanol is produced from the TEOS hydrolysis which eventually increasing the concentration of ethanol (Othman and Zeid 2012). After the separation of the as-synthesized mesoporous material from the filtrate, the ethanol in the filtrate mixture is then used as a solvent to extract the surfactant template from the as-synthesized MCM-41 materials (Milea et al. 2011).

Numerous studies on the synthesis and characterization of mesoporous materials have been reported in literature (Hitz and Prins 1997, Keene et al. 1999, Kleitz et al. 2001, Kleitz et al. 2003, Lebeau et al. 2013).

Special attention must therefore be given to the relationship among the selected synthesis method, the final mesostructure and properties of mesoporous materials. A research on the synthesis, mesoscopic structures as well as the template removal *via* calcination of the alkaline-prepared mesostructures (MCM-41 and MCM-48) and acid-prepared mesostructures (SBA-3 and SBA-15) was investigated by Kleitz *et al.* (2003). Moreover, Kleitz *et al.* (2001) analyzed the effect of calcination temperature on the hexagonal phase as well as the physical and chemical aspects of the surfactant degradation within the mesopores.

Keene *et al.* (1999) studied the effects of thermal degradation of surfactant on the porosity and hydrophobicity of the MCM-41 mesophase. The effects of different extraction media (*i.e.*, extraction, calcination and ion-exchanged) in the efficiency of template removal was investigated by Hitz and Prins (1997). The structural aspects of the obtained MCM-41 samples and their catalytic performance in the Friedel-Crafts acetylation of 2-methoxynaphthalene were also investigated. The synthesis routes, formation mechanism, characteristic features and also the potential applications of ordered mesoporous silica-based materials was reviewed by Lebeau *et al.* (2013). There are limited data on the recycling of mother liquor (synthesis solution) to synthesize mesoporous MCM-41 silica materials. Few research works were reported on the recycle and reuse the synthesis solution (mother liquor) to synthesize SBA-15 (Jia et al. 2013, Li 2014). The reuse of crystallized CTAB powder to synthesize MCM-41 for three consecutive synthesis cycles was reported by Ng *et al.* (2013).

Furthermore, studies on the template ion exchange of CTAB template from as-synthesized MCM-41 are scarce (Kim et al. 1995). The template ion exchange is mainly focus on the as-synthesized MCM-41 using nickel nitrate ($Ni(NO_3)_2{\cdot}6H_2O$), vanadium oxalate ($VO(C_2O_4)$), source of ammonium (NH_4NO_3, NH_4Cl and NH_4OAc), sodium ($NaNO_3$, NaCl, NaBr, NaOAc) and potassium (KNO_3, KCl, KOAc, KH_2PO_4) and aluminum isopropoxide ($C_9H_{21}O_3Al$) (Deekamwong and Wittayakun 2017, Lang and Tuel 2004, Lehmann et al. 2012, Wang et al. 2001). Other than the abovementioned research works, comprehensive research works such as the template ion exchange on the as-synthesized MCM-41 using ionic liquid, reuse of the synthesis by-products in the mother liquor as solvent for template extraction, and the recycling of the surfactant template in the extract solution in MCM-41 synthesis, are not yet available.

In the present study, MCM-41 was synthesized using liquid templating method in the presence of cationic surfactant with different ethanol concentrations. The template ion exchange on the as-synthesized MCM-41 is carried out using ionic liquid, 1-butyl-3-methylimidazolium chloride (BMImCl) prior to solvent extraction to ion exchange the surfactant template ions from its pores. Ammonium nitrate (NH_4NO_3) was used to ion exchange the template for comparison purpose. The synthesis by-products in the mother liquor was reused as solvent for template extraction and the extracted surfactant template in the extract solution was recycled and utilized to synthesize MCM-41. The effect of the ethanol concentrations in the solution gel and the types of ion exchange agents on the yield of MCM-41 material was investigated. The recycling of the surfactant template in the extract solution in MCM-41 synthesis was also evaluated.

EXPERIMENTAL

Materials

For MCM-41 synthesis, tetraethyl-orthosilicate (TEOS, $C_8H_{20}O_4Si$, 98% purity, Sigma-Aldrich) was used as a silica source while hexadecyltrimethylammonium bromide (CTAB, $C_{19}H_{42}BrN$) obtained from R&M (R and M Chemicals) was used as a surfactant template. Nitric acid (HNO_3) (65% purity, Fisher Scientific) was used as catalyst for TEOS hydrolysis and pH adjustment. Ethanol (C_2H_5OH), 95% purity, HMBG (HmbG Chemicals) was used as a solvent. Ammonium nitrate (NH_4NO_3) (98% purity, R&M) and BMlmCl ($C_8H_{15}ClN_2$) (98% purity, Sigma-Aldrich) were used as ion exchange agents.

MCM-41 synthesis procedure

The silica source solution was prepared using 5 ml TEOS added to 15 ml of distilled water to form the first solution (S1). The surfactant template was prepared using 3.17 g of CTAB dissolved into 20 ml 50% ethanol in water and stirred for 5 min to form the second solution (S2). Both S1 and S2 were mixed under vigorous stirring for 20 min and the resulting mixture (Mix-1) was kept for homogenization for 1.5 h. The mass ratio of Mix-1 is 0.12 TEOS:0.082 CTAB:0.39 distilled water:0.41 ethanol. 2 ml HNO_3 was added drop wise into Mix-1 under stirring for 1 h and kept for crystallization without mixing for 48 h to form the synthesis gel. After the completion of gel formation, a thin layer of solid in Mix-1 underneath was obtained. pH of the gel was monitored to obtain desired pH value of 0.5. The resulting gel was then filtered to separate the as-synthesized MCM-41 powder and the filtrate. The synthesized sample was labeled as MCM-41-MX, MCM-41-NX, and MCM-41-PX, where M, N and P indicate the as-synthesized sample were obtained at water:ethanol volume ratio of 1:1 or 0.4:1 using BMlmCl or NH_4NO_3 as ion exchange agent, respectively (Table 2).

A mixture of 1 g of ion exchange agent, as-synthesized MCM-41 powder and distilled water was prepared under vigorous stirring for 1 h named Mix-2. Mix-2 then filtered to separate the as-synthesized MCM-41 powder from the resulting solution. The as-synthesized MCM-41 powder was then subjected to solvent extraction for 4 h at 70 °C under reflux using the filtrate obtained from Mix-1 as solvent. The concentration of surfactant in the extract was measured using UV-vis spectroscopy. The extract, which contains ethanol and the extracted ion-exchange templates (ionic liquid or ammonium ions) was then reused for second (2^{nd}) MCM-41 synthesis cycle. While, the MCM-41 powder was dried at room temperature and further calcined at 550 °C for 6 h. 30 ml of water was added into the extract solution for 2^{nd} MCM-41 synthesis cycle. A complete synthesis procedure of MCM-41 and surfactant template reuse cycles is illustrated in Fig.

1. Detailed parameters changed and MCM-41 samples obtained are shown in Table 2.

Characterization

Calcined materials were characterized using nitrogen (N_2) adsorption-desorption isotherms using Autosorb Quanta Chrome 6B analyzer. The specific surface area of the calcined material was determined using Brunauer-Emmett-Teller (BET) method, whereas the Barrett-Joyner-Halenda (BJH) method was used to calculate the corresponding pore size and pore volume. Ex-situ XRD analysis was performed using model D8 Advance X-Ray Diffractometer-Bruker AXS by operating with 40 kV and 40 mA at ambient temperature to calculate the diffractogram and lattice constant/indexing of calcined material using DIFFRACplus-EVA software. The remaining amount of surfactant template after calcination or solvent extraction was determined using thermogravimetric analysis (TGA) using a Mettler-Toledo TGA/SDTA 851e analyzer which was operated in the temperature range of 30 – 700 °C and heating rate of 5 °C/min.

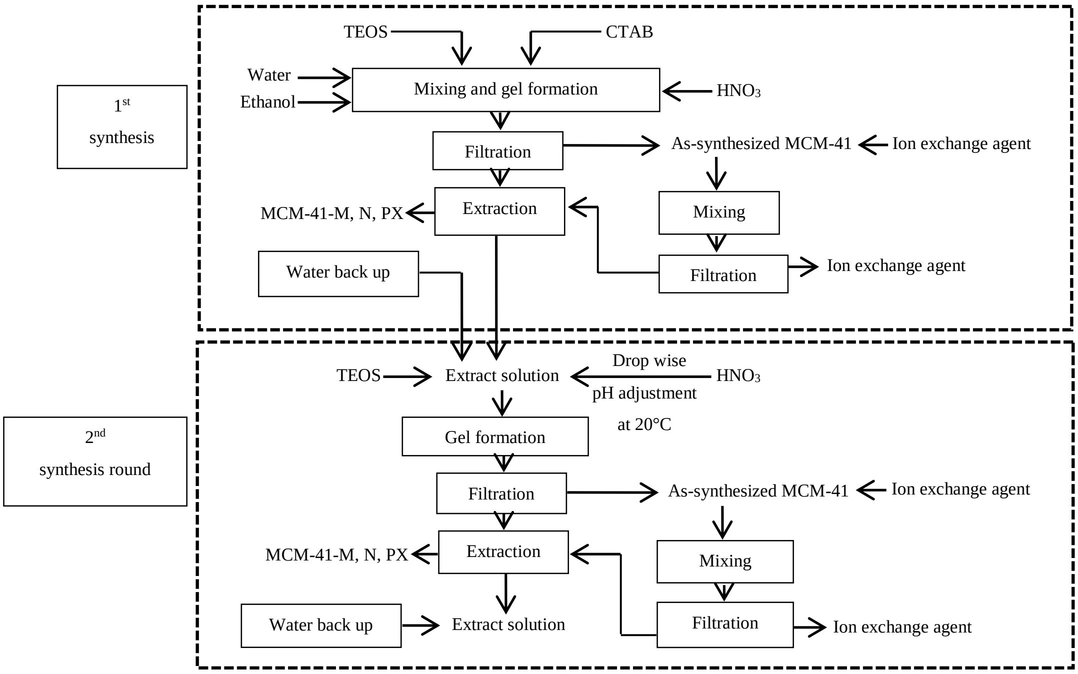

Fig. 1: Schematic diagram of MCM-41 synthesis and surfactant template recycle using different template extraction parameters and reuse cycle test

Table 2. Synthesis parameters of MCM-41 synthesis samples using 5 ml TEOS, 3.17 g CTAB and 1 g of ion exchange agent

Ethanol-water volume ratio	Type of ion exchange agent	Resulting MCM-41 sample name
1:1	BMImCl	MCM-41-MX
1:1	NH_4NO_3	MCM-41-NX
0.4:1	NH_4NO_3	MCM-41-PX

RESULTS AND DISCUSSION

The current study investigates the effect of two extraction parameters on the recycling and reuse of CTAB in the MCM-41 synthesis process. The two extraction parameters are the use of two different ion exchange types and the use of different solvent composition. Below sections will discuss the results obtained by varying these two parameters on the recycling and reuse of the surfactant template in the MCM-41 synthesis process. With reference to Fig. 1, the synthesis carried out using 1 g of BMlmCl ion exchange agent, is indicated as MCM-41-MX and using 1 g NH_4NO_3 ion exchange agent is indicated as MCM-41-NX. MCM-41 referring to the siliceous mesoporous material, M is the BMlmCl ion exchange agent, N is the NH_4NO_3 ion exchange agent and X is the synthesis cycle starting at 1 for the fresh chemicals.

The resulting yield of MCM-41 synthesized using two different types of ion exchange agent are compared. The surfactant template was used for up to eight MCM-41 synthesis cycles. The mass and physical properties of the calcined MCM-41 material produced in the respective experimental set was presented in Table 3 and 4, respectively. When using a BMlmCl ion exchange agent, relatively a large yield of calcined material was obtained, for instance 1.65 wt% and 3.06 wt% were obtained in the 3rd and 5th synthesis cycles at CTAB/ethanol molar concentration ratio of 0.023 and 0.024. When CTAB/ethanol molar concentration ratio decreased from 0.028 to 0.021, the yield of calcined MCM-41 material decreased from 1.19 wt% in MCM-41-M1 to 0.070 wt% in MCM-41-M8. A yield of 0.53 wt% in MCM-41-M2 (CTAB/ethanol ratio = 0.022) was increased to 1.65 wt% obtained in the 3rd synthesis cycle (MCM-41-M3) which has a CTAB/ethanol molar concentration ratio of 0.023. At the same time, a 1.79 wt% yield of calcined material obtained in MCM-41-N1 compared to 1.56 wt% obtained in MCM-41-N2.

The effect of the CTAB/ethanol molar concentration ratio on the yield of calcined MCM-41 was also observed. There was no systematic correlation between both parameters. The CTAB/ethanol molar concentration ratio in the consequence recycling experiment was measured as a result to ratio changing due to losses in CTAB recycled and increase in ethanol content which is a by-product of the TEOS hydrolysis. Monitoring the surfactant to ethanol ratio is important to ensure the formation of micelles at the appropriate CMC conditions. Maintaining the minimum CMC condition is the guarantor for the crystallization and MCM-41 formation. The high dilution of ethanol performed during the extraction for the previous synthesis cycle affected the molar ratio of CTAB/ethanol that causes less as-synthesized MCM-41 material produced at the silicate polymerization for the next synthesis cycle.

Besides, water addition into the extract solution (mother liquor) also influenced the calcined material amount produced. Increase water addition into the mother liquor has accelerated the polymerization rate of silicate (Milea et al. 2011).

The concentration of CTAB also

affected the formation of gel. More gel was formed when the CTAB concentration is higher due to increase interaction of silicate anions and surfactant cations. The interaction between the surfactant cations and silicate anions decrease which lead to the reduction of the calcined MCM-41 material yield (Ahmed and Ramli 2011).

A declining trend of surface area was observed as tabulated in Table 3 and 4 when CTAB/ethanol molar concentration ratio decreased due to hydrolysis solvating effect of alcohol that causes the slow equilibrium toward TEOS, resulting in slow micelles growth on the surface of the center of the spherical particles (Liu et al. 2003).

Water/ethanol molar concentration ratio varied in both synthesis and extraction steps (Table 3 and 4). The water/ethanol molar concentration ratio influences the specific surface area of MCM-41 material. The specific surface area of MCM-41 material increases with the increase of water/ethanol molar concentration ratio in two experiments. Low surface area was observed in MCM-41 materials formed at high water/ethanol molar concentration ratio. This indicates that the solvating effect of alcohol influenced the micelle formation that resulted in slow micelles growth on the surface of the center of the particles (Liu et al. 2003).

The calcined MCM-41 materials MCM-41-M1, MCM-41-M3, MCM-41-M4, MCM-41-M5, MCM-41-M7, and calcined MCM-41 materials MCM-41-N2, MCM-41-N3, MCM-41-N4 and MCM-41-N5, were tested to determine the BET specific surface area, pore size and pore volume. A comparison purpose on these random selections of calcined MCM-41 materials for characterization is studied to investigate the possibility of recycling the surfactant template ions to synthesize calcined MCM-41 materials and their mesostructure stability upon the surfactant template recycling.

Table 3. The yield and physical properties of calcined MCM-41 material produced, TEOS/ethanol ratio, CTAB/ethanol ratio and water/ethanol ratio utilizing BMlmCl ion exchange agent and an ethanol volume fraction of 0.5

Sample name	Yield of calcined material (%weight, wt%)	TEOS/ethanol molar concentration ratio	CTAB/ethanol molar concentration ratio	Water/ethanol molar concentration ratio	Specific surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (Å)
MCM-41-M1	1.19	0.8	0.028	15.09	1052	0.56	21.4
MCM-41-M2	0.53	0.5	0.022	3.43	-	-	-
MCM-41-M3	1.65	0.6	0.023	1.83	854	0.54	25.2
MCM-41-M4	2.39	0.5	0.021	2.61	720	0.80	44.3
MCM-41-M5	3.06	0.6	0.024	8.82	682	0.58	34.1
MCM-41-M6	1.38	0.5	0.021	1.24	-	-	-
MCM-41-M7	2.00	0.5	0.021	6.60	720	0.48	26.5
MCM-41-M8	0.07	0.5	0.021	2.75	-	-	-

Table 4. The yield and physical properties of calcined MCM-41 material produced, TEOS/ethanol ratio, CTAB/ethanol ratio and water/ethanol ratio utilizing NH_4NO_3 ion exchange agent and an ethanol volume fraction of 0.5

Sample name	Yield of calcined material (wt%)	TEOS/ethanol molar concentration ratio	CTAB/ethanol molar concentration ratio	Water/ethanol molar concentration ratio	Specific surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (Å)
MCM-41-N1	1.79	0.8	0.026	17.97	1052	0.56	21.4
MCM-41-N2	1.56	0.5	0.021	10.17	1016	0.49	19.4
MCM-41-N3	2.44	0.6	0.022	1.29	936	0.59	25.0
MCM-41-N4	1.77	0.5	0.021	2.06	734	0.78	42.4
MCM-41-N5	4.14	0.6	0.022	2.12	600	0.38	25.1
MCM-41-N6	0.78	0.5	0.022	2.69	-	-	-
MCM-41-N7	0.16	0.6	0.022	7.55	-	-	-

Fig. 2 and 3 are showing the N_2 adsorption-desorption isotherms for the calcined materials produced (MCM-41-MX, X = 1, 3, 4, 5 and 7 and MCM-41-NX, X = 2-5). The IUPAC physisorption isotherms classification and IUPAC hysteresis loop type classifications were used as reference for identifying the isotherms and hysteresis loops presented for the samples (Thommes et al. 2015).

In Fig. 2, MCM-41-M1 and MCM-41-M3 have type I (b) isotherms according to IUPAC classification which indicates that the calcined materials produced in the 1st and 3rd synthesis cycles are mesoporous material with narrow mesopores size of 2.14 nm and 2.52 nm. The BET data shows that MCM-41-M1 has a narrower distribution of mesopores size than MCM-41-M3 since MCM-41-M1 has a steeper capillary condensation step at higher P/P0 than MCM-41-M3. MCM-41-M4 has type IV (a) isotherm whereas MCM-41-M5 has type IV (b) isotherm. The isotherms of MCM-41-M4 and MCM-41-M5 show that the calcined materials obtained in the 4th and 5th cycles of MCM-41 synthesis have non-uniform cylindrical mesopores with larger pore sizes of 4.43 nm for MCM-41-M4 and 3.41 nm for MCM-41-M5. Moreover, similar isotherm behaviour illustrated in MCM-41-M5 is also apparent in the isotherm of MCM-41-M7. This indicates that MCM-41-M7 has non-uniform mesopores size of 2.65 nm.

As observed from Fig. 2, the isotherms of MCM-41-M4 and MCM-41-M5 show a steeper increase than other three isotherms during the capillary condensation with wider pore size distribution. Therefore, MCM-41-M4 and MCM-41-M5 have larger pore sizes than the other three samples as same shown by the BET data tabulated in Table 3. When comparing MCM-41-M4 to MCM-41-M5, the capillary condensation step position in the isotherm of MCM-41-M4 shifted to higher relative pressures. MCM-41-M4 exhibited wider pore size distribution than MCM-41-M5 in the pore distribution graph (Fig. 2). This can be concluded that MCM-41-M4 has larger pore size compared to the other four samples that was similar to the BET data presented in Table 3.

In comparison to MCM-41-NX samples,

the calcined material produced in the 1st synthesis cycle was assumed to possess uniform mesopores as similar to MCM-41-M1 because the same synthesis method was repeated for the 1st cycle of MCM-41 synthesis except that different ion exchange agent type was used. In Fig. 3, the isotherm of MCM-41-N2 shows type I (b) isotherm. This can be said that MCM-41-N2 has uniformly smaller mesopores with the pore size of 1.94 nm. For MCM-41-N3, type I (b) isotherm is illustrated in the isotherm. The isotherm shows that MCM-41-N3 has regular sphere-shaped particles with narrow slit-like mesopores diameter of 2.50 nm. Other than that, MCM-41-N4 has type IV (a) isotherm whereas type I (b) isotherm is presented in the isotherm of MCM-41-N5. This indicates the calcined material obtained in the 4th synthesis cycle has non-uniform mesopores while the calcined material produced in the 5th synthesis cycle contains uniform and narrow mesopores. The respective pore sizes of MCM-41-N4 and MCM-41-N5 as shown in Table 4 are 4.24 nm and 2.51 nm. The isotherm of MCM-41-N4 has a steeper increase capillary condensation step at higher P/P0 when compared to other three isotherms. In addition, MCM-41-N4 has wider pore size distribution among the four samples as observed from the pore distribution graph. This showed that MCM-41-N4 has a larger pore size than MCM-41-N2, MCM-41-N3 and MCM-41-N5 which was in agreement with the BET data as tabulated in Table 4.

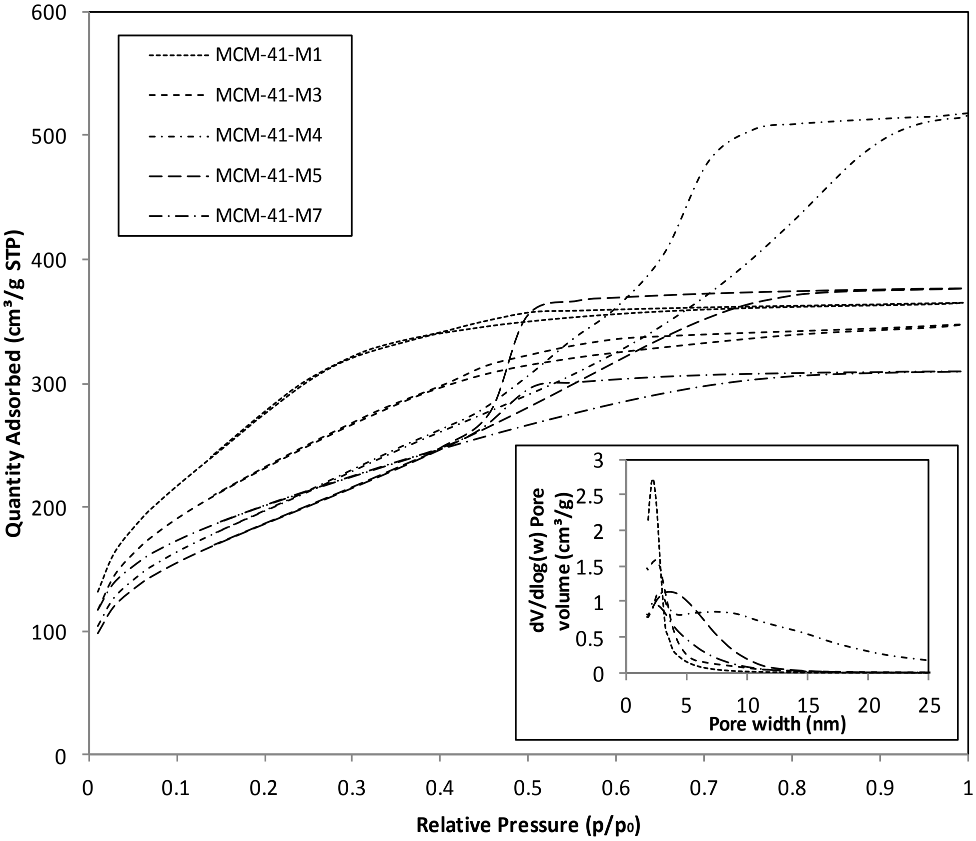

Fig. 2: N_2 adsorption-desorption isotherms for MCM-41-M1, MCM-41-M3, MCM-41-M4, MCM-41-M5 and MCM-41-M7

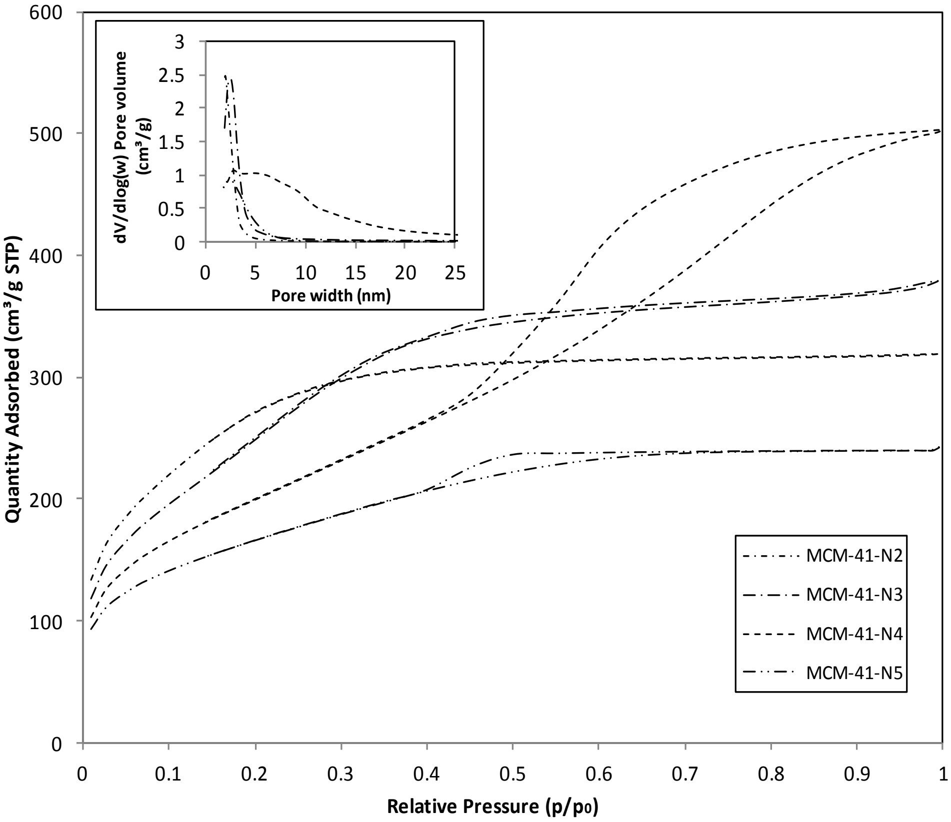

Fig. 3: N_2 adsorption-desorption isotherms for MCM-41-N2, MCM-41-N3, MCM-41-N4 and MCM-41-N5

N_2 adsorption-desorption isotherms indicate that materials prepared utilizing BMImCl have a larger pore size and pore volume than those prepared using NH_4NO_3 as observed in Figs. 2 and 3. The difference in the charge density on the surfactant micelles surface which composed of alkylammonium and 1-alkyl-3-methylimidazolium head groups occurred after the ion exchange process performed using a BMImCl ion exchange agent (Zukal et al. 2007). The charge difference causes the formation of larger particles and therefore forming a larger volume in the mesopores materials such for MCM-41-M4.

The relationship between the specific surface area of calcined material and the molar ratio of CTAB/ethanol for the respective synthesis cycles was investigated through utilizing two different extraction agents. It was reported that the effect of molar ratios of CTAB/ethanol on the surface morphology lead to the formation of more spherical particles occurring at an increase molar ratio of CTAB/ethanol (Ahmed and Ramli 2011). Shrinkage of spherical shape occurs due to the slight increase in the CTAB/ethanol molar concentration ratio, which led to small spherical aggregates to form in a reduced surface area without changing the micelles size during the gel crystallization. In the 1st synthesis cycle, materials were produced with a specific surface area of 1052 m^2/g at CTAB/ethanol molar concentration ratio of 0.028. As compared to the 3rd synthesis cycle (MCM-41-M3), the specific surface area of calcined material obtained decreased to 854 m^2/g when the molar ratio of CTAB/ethanol decreased to 0.023. When the CTAB/ethanol molar concentration ratio further decreased and remained constant at 0.021, the specific surface area for MCM-41-M4 and MCM-41-M6 was 720 m^2/g. The specific surface area of the calcined material decreased along with the decrease of CTAB/ethanol molar concentration ratio except MCM-41-M5 when the MCM-41 synthesis was repeated for consecutive cycles. When NH_4NO_3 was used as ion exchange agent, specific surface area of 1016 m^2/g, 936 m^2/g, 734 m^2/g and 600 m^2/g was obtained for MCM-41-N2, MCM-41-N3, MCM-41-N4 and MCM-41-N5 as tabulated in Table 4 when the CTAB/ethanol molar concentration ratio decreased and remained constant at approximately 0.020.

In comparison between the two types of ion exchange treatment, using BMImCl produced larger pore diameter of calcined materials than the materials synthesized after the ion exchange treatment with NH_4NO_3. The BET data tabulated in Table 3 and 4 show that the calcined material synthesized using both types of ion exchange agents have pore size which the characterize mesoporous material with pore diameter ranging from 2 to 50 nm (Othman and Zeid 2012). The volume fraction of ethanol was varied from 0.5 to 0.3 in the first synthesis cycle and investigated with utilizing NH_4NO_3 as ion exchange agent (Table 5) in order to study whether the ethanol volume fraction would affect the yield of calcined MCM-41 material. Relatively, a large yield of calcined MCM-41 material was obtained in the 1st synthesis of 1.49 wt% and a yield of 2.07 wt% in the 3rd synthesis cycle with the respective CTAB/ethanol molar concentration ratio of 0.029 and 0.021. As observed from Table 5, lesser yield of calcined MCM-41 material was produced at higher CTAB/ethanol molar concentration ratio, whereas higher yield was obtained at lower CTAB/ethanol molar concentration ratio. When compared MCM-41-N1 and MCM-41-P1, a higher yield of calcined material was obtained in those using higher ethanol/TEOS ratio.

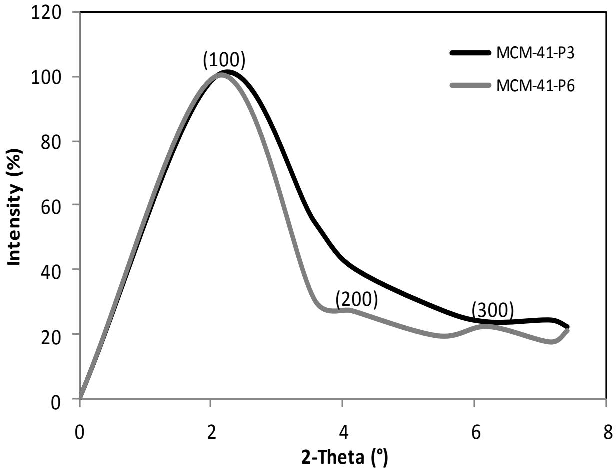

Fig. 4: XRD patterns of MCM-41-P3 and MCM-41-P6

Table 5. The yield of calcined MCM-41 material produced, TEOS/ethanol ratio, CTAB/ethanol ratio and water/ethanol ratio utilizing NH_4NO_3 ion exchange agent and an ethanol volume fraction of 0.3

Sample name	Yield of calcined material (wt%)	TEOS/ethanol molar concentration ratio	CTAB/ethanol molar concentration ratio	Water/ethanol molar concentration ratio
MCM-41-P1	1.49	0.8	0.029	32.26
MCM-41-P2	0.70	0.5	0.020	6.10
MCM-41-P3	2.07	0.5	0.021	2.58
MCM-41-P4	0.61	0.6	0.023	3.54
MCM-41-P5	0.32	0.6	0.024	7.09
MCM-41-P6	1.08	0.5	0.018	4.22
MCM-41-P7	0.25	0.5	0.022	0.64
MCM-41-P8	0.16	0.5	0.021	4.12

The calcined materials from the 3rd (MCM-41-P3) and 6th (MCM-41-P6) synthesis cycles were characterized for ex-situ XRD analysis as shown in Fig. 4. Typical hexagonal ordered array with low-angle reflection that indexed as (100) Bragg peaks is obtained with the *d*(100)-spacing diffraction peak indicating that the calcined material produced in the 3rd synthesis cycle has hexagonal mesophase after the removal of surfactant template. As compared MCM-41-P3 to MCM-41-P6, three low-angle reflections with the index of (100), (200) and (300) Bragg peaks indicated the typical hexagonal ordered array measured for MCM-41-P6. The diffraction peak at *d*(100) reflection is observed in 2-theta angle equal 2.09°. The characteristics peak was found to shift towards lower 2-theta values when the water/ethanol molar concentration ratio in the synthesis gel was increased. The observation is in agreement as reported by Meléndez-Ortiz *et al.* (2012). As a result, the calcined material exhibit the hexagonal ordered mesopores structure in the mesophase even after surfactant template utilization in the extract solution for the third time and sixth time in the MCM-41 synthesis. This is evidenced by the typical low angle characteristic reflections for mesoporous silica material as similarly reported by Kleitz (2002).

CONCLUSIONS

Two surfactant template extraction parameters were used in the MCM-41 synthesis to investigate the effect of template extraction parameters on the production of MCM-41 and its surface morphology. The resulting production of calcined material did not vary significantly when different type of ion exchange agent was used in fixed ion exchange agent quantity and ethanol volume fraction. Relatively larger amount of calcined material was obtained when higher ethanol volume fraction was used in the synthesis. High dilution of ethanol during the extraction and lower molar ratio of CTAB/ethanol caused less calcined material to produce. In addition, higher concentration of TEOS due to non-reacted silicate anions remained in the mother liquor and fresh TEOS added to the next synthesis cycle also increase the silicate polymerization and led to more synthesis gel to form. From BET analysis, the calcined material produced in the ascending random synthesis cycle selected from MCM-41 synthesis using 0.5 ethanol volume fraction with either type of ion exchange agent has pore sizes within the pore diameter range of mesoporous material and exhibit the characteristics of MCM-41. The ex-situ XRD analysis indicated that hexagonal ordered mesopores structure was observed in the mesophase of the calcined material produced in the 3rd and 6th synthesis cycles of MCM-41 with 0.3 ethanol volume fraction and 1 g NH_4NO_3 ion exchange agent. In conclusion, the surfactant template is possible to recycle and reuse for preparing several subsequent MCM-41 synthesis cycles by exhibiting the conventional MCM-41 characteristics in the mesophase of the calcined materials. Future research should aim to continuously control the ethanol concentration in the solution gel that enhances the template recycling in MCM-41 synthesis.

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NOMENCLATURE

MCM-41-MX : Synthesis experiment using BMlmCl as ion exchange agent at 0.5 ethanol volume fraction (M) and X is a number refers to the synthesis cycle.

MCM-41-NX : Synthesis experiment using NH_4NO_3 as ion exchange agent at 0.5 ethanol volume fraction (N) and X is a number refers to the synthesis cycle.

MCM-41-PX : Synthesis experiment using NH_4NO_3 as ion exchange agent at 0.3 ethanol volume fraction (P) and X is a number refers to the synthesis cycle.

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