

Surfactant effects on the physical properties of mesoporous silica and silicates

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Abstract

Mesostructured silicas and silicates have been synthesized using hydrogels with molar composition: $M:26.0SiO_2:5.2(C_2H_5)_4NOH:7.5[CH_3(CH_2)_{15}N(CH_3)_3]_2O:790H_2O$, where $M = 0, Zr(OC_3H_7)_4$ or $Ti(OC_4H_9)_4$. In all preparations, colloidal silica (Ludox) was used as the source of silica. The hydrothermal transformation at $110^\circ C$ of these gels produced solids with the hexagonal structure typical of MCM-41 type materials. The effects of chain length and surfactant terminal alkyl groups on the properties of mesoporous materials containing Ti or Zr, have been investigated by using different surfactants such as cetyl trimethyl ammonium bromide and chloride, cetyl dimethyl ethyl ammonium bromide, and myristyl trimethyl ammonium bromide. When the surfactant's carbonyl chain decreased to 14 from 16 carbon atoms, a reduction in unit cell dimension and average pore diameter was observed in the mesoporous silicas, titaniumsilicates and zirconiumsilicates under study. Replacement of methyl groups with ethyl groups on the surfactant hydrophobic head, had no measurable effects on crystals' properties. However, a surfactant with a bulky aromatic head group, such as cetyl pyridinium chloride, inhibited crystallization. In general, the use of bromide in place of chloride salts yielded more ordered MCM-41 type crystals. The high thermal stability (to $800^\circ C$), surface area ($1000\text{--}1500\text{ m}^2/\text{g}$), pore volume ($0.90\text{--}1.20\text{ cm}^3/\text{g}$) and uniform mesoporosity (with pore diameter in the $2.9\text{ nm}\text{--}3.6\text{ nm}$ range), of these metalsilicates could be of particular interest in the preparation of catalysts requiring siliceous metal supports. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Because of their large internal surface area (SA) and open three-dimensional structure, microporous solids such as zeolites have found widespread use in the chemical and petrochemical industry. New demands for solids capable of providing catalysts for compounds excluded by the microporous structure of zeolites has trig-

gered numerous synthetic efforts that culminated in 1990 with the report of the synthesis of a new family of mesoporous solids. In fact, in 1990, Yanagisawa et al. [1] first reported the preparation of mesoporous silicas with uniform pore dimensions, by reacting kanemite with alkyltrimethylammonium chloride solutions. Shortly after, in 1992, researchers at Mobil published in a letter to Nature [2] the synthesis of several mesoporous aluminosilicates with unique pore structure and stability. Since then, research efforts in academia and in industrial

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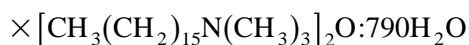
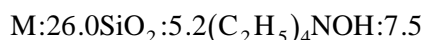
laboratories have been dedicated to the manipulation of synthesis condition in the hope to generate mesoporous solids with unique acidity, pore structure and hydrothermal stability; a recent review of these efforts can be found in Ref. [3].

The ammoxidation of hydroxyacetophenones, the selective oxidation of aromatic [4,5], the hydroxylation of phenols [6], and vinyl acetate production [7], are examples of technologically important catalytic reactions over siliceous supports which depend more on the solid's composition and pore structure than on its acidity [8]. In a companion paper [9], it was shown that the isomorphous substitution of Si with Ti or Zr can modify the weak acidity of the mesoporous silicate framework. It is the purpose of this paper to report and describe the effects that different surfactants have on the synthesis of certain mesoporous silicas and silicates of potential interest in the preparation of catalysts for the above-mentioned chemical reactions.

2. Experimental

2.1. Synthesis

Microporous materials were prepared by heating, at 110°C/3 days without stirring, hydrogels with molar composition:



where $M = 0$, $\text{Zr}(\text{OC}_3\text{H}_7)_4$ or $\text{Ti}(\text{OC}_4\text{H}_9)_4$. The hydrogels were prepared by adding to colloidal silica (Ludox, 40% SiO_2 from DuPont), a mix-

ture obtained by reacting the chosen surfactant with a solution prepared by adding 70% (in 1-propanol) zirconium propoxide (ZrPOX, from Aldrich) or by adding Ti(IV) *n*-butoxide (TiBOX, from Aldrich), to 20% tetraethyl ammonium hydroxide ($(\text{C}_2\text{H}_5)_4\text{N}^+\text{OH}^-$) from Sachem) in water. The surfactant tested were: (1) cetyl trimethyl ammonium Br and Cl (CTMA-Br, Cl) (25% aqueous $\text{C}_{16}\text{H}_{33}(\text{CH}_3)_3\text{N}^+\text{Cl}^-$ solution from Aldrich), (2) cetyl dimethyl ethyl ammonium Br (CDMEA-Br) and (3) myristyl trimethyl ammonium Br (MTMA-Br), both from Zeeland Chemicals. Hydrogels were then heated at 110°C/3 days in Teflon lined 750 cm^3 Berghof autoclaves equipped with temperature controllers and stirring mechanism. Crystals were separated from the mother liquor by filtration, washed with an excess of DI water at about 60°C and then dried in air at 110°C overnight. The oven temperature was then raised at a rate of 2°C/min to 600°C and maintained at this value for 12 h.

2.2. Characterization

X-ray diffractograms were obtained with a Scintag diffractometer using Cu K α radiation at a speed of 1.0°/min. Chemical analyses were performed by Galbraith Laboratories, Knoxville, TN. SA and pore volume (PV) were measured by nitrogen sorption at 77°K with an ASAP-2010 porosimeter from Micromeritics. Prior to nitrogen adsorption, the samples were degassed in vacuum at 350°C/12 h. Pore size distributions were obtained with Density Functional Theory methods using DFT-Plus software from Micromeritics. Thermogravimetric analyses (TGA and DTA) were obtained on a Seiko 210/310

Table 1

Surface properties of mesoporous silica. All samples have been calcined in air at 600°C/12 h

Surfactant	SA (m ² /g)	PV (cm ³ /g)	APD (nm)	d_{001} (nm)	a_o (nm)	W (nm)
CTMA-Cl	1214	1.16	3.4	4.22	4.87	1.47
CTMA-Br	1234	1.39	3.4	3.96	4.57	1.17
CDMEA-Br	1143	1.19	3.4	3.94	4.55	1.15
MTMA-Br	1437	0.96	2.9	3.40	3.93	1.03

Table 2

Surface properties of mesoporous titaniumsilicates. All samples have been calcined in air at 600°C/12 h

Surfactant	SA (m ² /g)	PV (cm ³ /g)	APD (nm)	<i>d</i> ₁₀₀ (nm)	<i>a</i> ₀ (nm)	<i>W</i> (nm)
CTMA-Cl	1246	0.83	3.2	3.77	4.35	1.15
CTMA-Br	1211	1.06	3.4	3.91	4.51	1.11
CDMEA-Br	1163	1.00	3.4	3.86	4.46	1.06
MTMA-Br	1238	0.84	2.9	3.55	4.10	1.20

analyzer equipped with 3.0 version software and a Perkin-Elmer 7.0 analyzer. Samples were heated at a rate of 5.0°/min to 800°C.

3. Results and discussion

The effects of surfactants such as CTMA-Br, CTMA-Cl, CDMEA-Br and MTMA-Br on the properties of Si-MCM-41, (Si,Zr)-MCM-41 and (Si,Ti)-MCM-41 crystals have been collected in Tables 1–3. The X-ray diffractogram in Fig. 1A is typical of calcined mesoporous materials prepared with CTMA-Cl. In addition to a sharp *d*₁₀₀ reflection line near 2θ = 2.5°, there is a broad peak in the 3° to 5° 2θ range that has been attributed to broadening effects of higher reflection lines due to small particle sizes [5]. When using CTMA-Br, instead of CTMA-Cl, the *d*₁₁₀, *d*₂₀₀, and *d*₂₁₀ lines are better resolved indicating the influence of the surfactant counter-ion on the solid long-range order (Fig. 1B). It is for this reason that in this study, bromides have been the salts of choice.

As expected, these high SA silicas and silicates with the MCM-41 structure give type IV nitrogen sorption isotherms characteristic of mesoporous solids [10,11] (Fig. 2A). In contrast, the reference (commercially used) silica

gel powders and silica support, exhibit type I isotherms typical of microporous materials such as zeolites (Fig. 2B–C). SAs were calculated using the BET equation. This equation was developed to estimate the specific SA of a flat surface [12]. In a cylindrical mesopore (~ 3.0 nm in diameter), multilayer coverage of the solid surface is only negligibly affected by the wall curvature and by the presence of the pore walls. Since in the case of nitrogen adsorption within MCM-41 type crystals, the size (~ 0.30 nm) of the adsorptive molecule is small compared to the size (~ 3.0 nm) of the pore diameter, the BET equation can be justifiably used to estimate the specific SA of these solids [13]. Pore size distributions were calculated using Density Functional Theory [14,15]; the usefulness of DFT methods to characterize MCM-41 type materials has been discussed elsewhere [13].

In Tables 1–3, the total mesopore volume was derived from the amount of vapor adsorbed at *P*/*P*₀ = 0.50 by assuming that all the mesopores were filled with condensed liquid nitrogen in the normal liquid state. In addition, the wall thickness (*W*), was calculated by subtracting the average pore diameter (APD) calculated by DFT methods, from the hexagonal unit cell dimension: *a*₀ = 2*d*₁₀₀/√3. Results in Tables 1–3

Table 3

Surface properties of mesoporous zirconiumsilicates. All samples have been calcined in air at 600°C/12 h

Surfactant	SA (m ² /g)	PV (cm ³ /g)	APD (nm)	<i>d</i> ₁₀₀ (nm)	<i>a</i> ₀ (nm)	<i>W</i> (nm)
CTMA-Cl	1136	0.99	3.4	3.83	4.42	1.02
CTMA-Br	906	1.02	3.6	4.44	5.13	1.53
CDMEA-Br	1205	1.28	3.4	3.94	4.55	1.15
MTMA-Br	1369	1.20	2.9	3.46	3.99	1.09

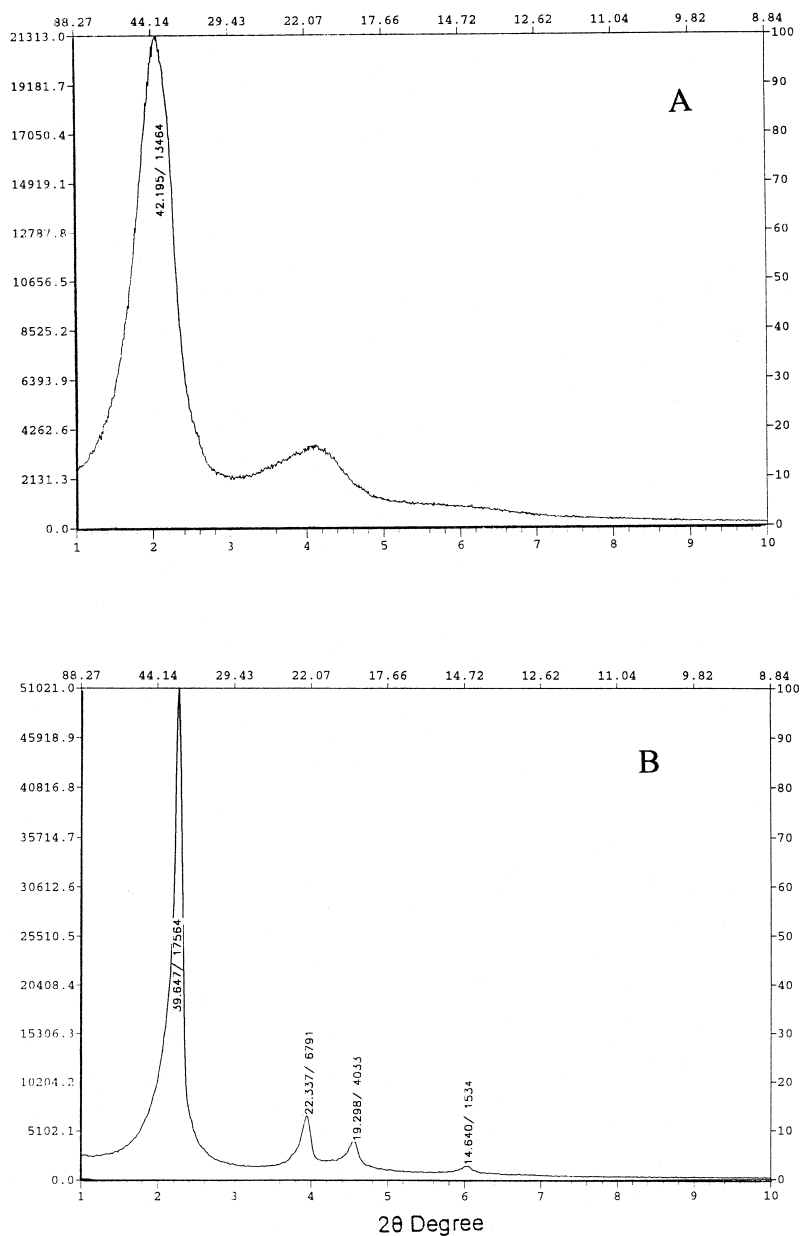


Fig. 1. Powder X-ray diffractogram of Si-MCM-41 synthesized with: (A) CTMA-Cl and (B) CTMA-Br; crystals have been calcined at 600°C/12 h.

indicate that the use of CTMA-Br, instead of CTMA-Cl, in the synthesis mixture yields a more ordered crystalline phase with larger unit cell dimensions and APD size. By decreasing the surfactant alkyl chain to C₁₂ from C₁₅, that is, by replacing equimolar amounts of CTMA-Br with MTMA-Br, the crystals' APD size de-

creases in all the mesoporous silicas and silicates synthesized. Replacement of methyl groups in CTMA-Br with ethyl groups as in CDMEA-Br, induce only small variations in APD values whereas if instead of ethyl groups, large benzyl groups are introduced in the surfactant hydrophobic $\geq N^+$ head, crystallization (at the

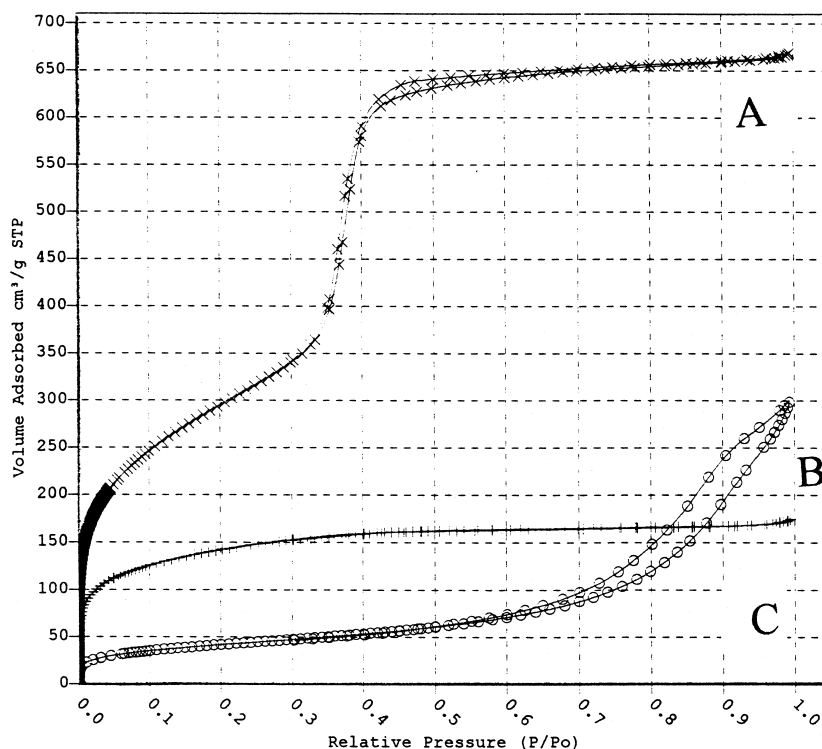


Fig. 2. Nitrogen sorption isotherms for: (A) Si-MCM-41 calcined at 600°C/12 h, (B) Silica gel and (C) Silica support (1/8 in. extrudates).

condition used in this research) does not occur. The hexagonal unit cell dimension a_0 decreases as the surfactant in the reaction mixture is changed from CTMA-Br to CDMEA-Br and to CDMEA-Br (see Tables 1–3). Similar results have been reported for mesoporous aluminosilicates with the MCM-41 structure [16]. In addition, when in the starting hydrogel CTMA-ions are replaced with CDMEA or with MTMA-cations, the wall thickness, W , decreases in Si-MCM-41 crystals whereas no clear trend is observed in mesoporous silicates containing either Ti or Zr (see Tables 1–3).

TGA [16–19] of the crystals show distinct weight losses that depend, in part, on the solid composition. Representative thermograms are given in Fig. 3. For the parent Si-MCM-41, the minor ($\sim 2\%$) weight loss below 150°C corresponds to the desorption of physisorbed water (or ethanol) in the voids formed by the crystals' agglomeration. Above 150°C, breakage, decomposition and thermal desorption of organic frag-

ments occur. The large ($\sim 34\%$) weight change in the 150–300°C temperature region is attributed to losses of occluded water (and ethanol molecules) and to the thermodesorption of alkyl chains resulting from the surfactant decomposition. Above 300°C, combustion of residual organics occurs and a small ($\sim 6\%$) but sudden weight loss can be seen in Fig. 3A. The last $\sim 6\%$ weight decrease above 350°C is attributed to water losses generated by dehydroxylation reactions at the silicate surface (Fig. 3A). Replacement of CTMA with CDMEA or MTMA ions has negligible effects on the crystals' thermograms. The observed changes in distribution of weight losses reflect the different structure and molecular weight of the surfactants used. Similar results have been observed when the same surfactants were used to prepare the zirconosilicates and the titaniumsilicates described in Tables 2 and 3. The zirconosilicate thermogram in Fig. 3B is similar to the one in Fig. 3A for Si-MCM-41. In contrast, the ther-

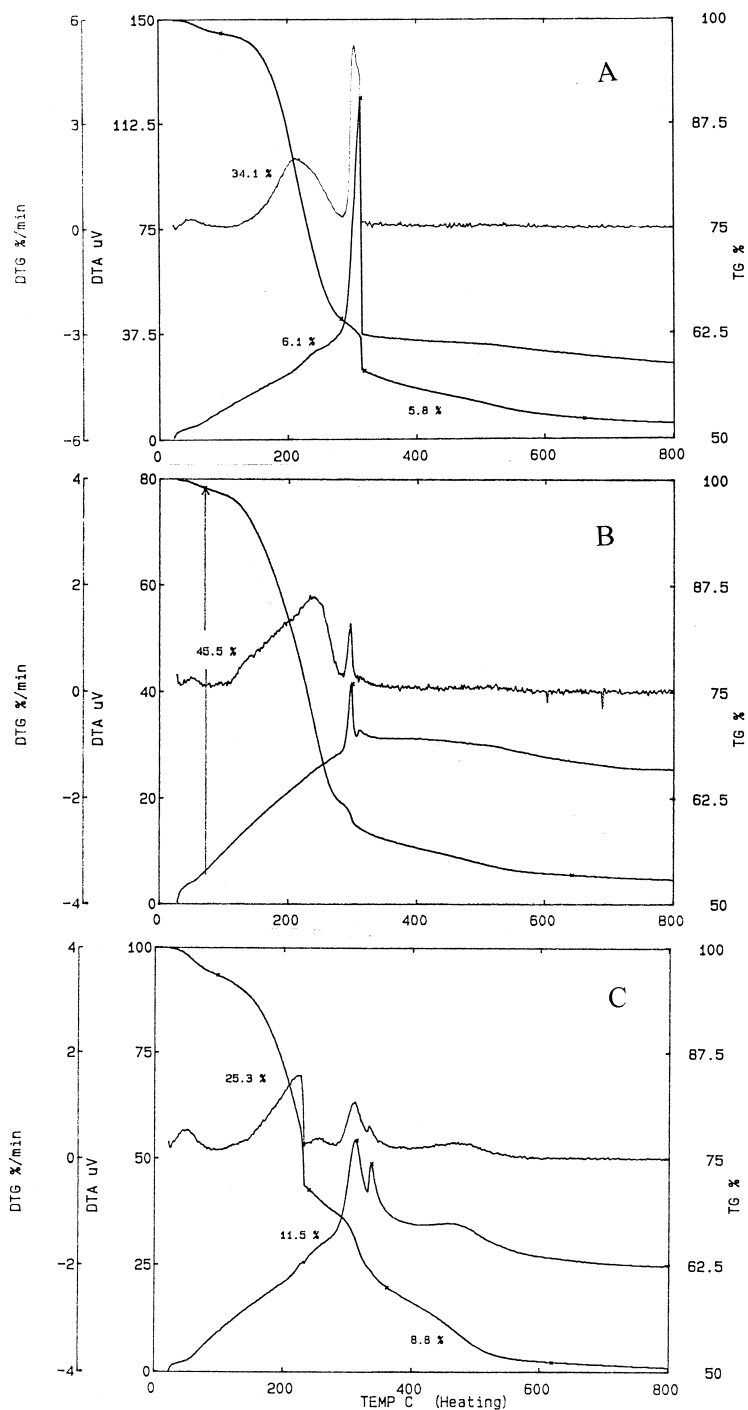


Fig. 3. Representative thermograms in air of: (A) Si-MCM-41, (B) (Si,Zr)-MCM-41 and (C) (Si,Ti)-MCM-41. Crystals have been prepared with CTMA-Br.

mograms in Fig. 3C more closely resemble those obtained for aluminosilicates [13] indicat-

ing that these mesoporous titaniumsilicates contain different adsorption site and that the genera-

tion of these sites is not affected by the nature of the surfactant used. The effects of the isomorphous substitution of Si with Zr or Ti on the solids acidity has been discussed elsewhere [9].

4. Summary and conclusions

Surfactants such as CTMA-Br, CTMA-Cl, CDMEA-Br, and MTMA-Br can be used to synthesize mesoporous silicas and metasilicates (containing Ti or Zr atoms), having high SA, PV and APD values in the 2.9 nm to 3.6 nm range. At the synthesis condition used in this study, surfactants with a bulky aromatic head group, such as cetyl pyridinium chloride, inhibited crystallization. The different surfactants have little effects on the thermogravimetric profiles of these solids. Changes in the distribution of weight losses reflect the different structure and compositions of the organic phase in the solid. The high SA, PV, moderate acidity [9] and thermal stability of these mesoporous metasilicates could be of particular interest in the preparation of a variety of commercially important catalysts requiring a siliceous support for metal promoters.

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