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Elucidation of interactive effects of synthesis conditions on the characteristics of mesoporous silicas templated using polyoxide surfactant

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Abstract

A series of mesoporous silicas (MS-1–MS-9) were synthesized at different gel compositions using a triblock copolymer (TCP), poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide), as the surfactant. The interactive effects of acidity, the contents of tetraethyl orthosilicate (TEOS) and the surfactant, and the gelling temperature on the characteristics of the final material were simultaneously characterized. Increasing acidity favored mesopore formation. A material with a surface area of 760 m²/g, mostly in the mesoporous range, was obtained at 1.0(TEOS):0.017(TCP):7.3HCl:115.7H₂O. Mesopore formation was predominantly determined by the TEOS:TCP ratio and was promoted with its increase from 1.56:1 to 2.09:1. A further increase to 2.61:1 was detrimental. Whereas increasing the TCP content to 3.5% w/w improved micellization, a further increase to 4.6% should be avoided. Mesoporous silicas showed low crystallinity but a high degree of hexagonal mesoscopic organization. The weak surface acidity was attributed to surface silanols, the number of which was proportional to mesoporosity.

Keywords: Mesoporous; Silica; Synthesis; Gel composition

1. Introduction

Despite their successful application in many industrial processes, microporous materials such as zeolites become inadequate when processing reactants with sizes above the dimensions of the micropores (> 1 nm) [1]. Thus, mesoporous silica materials have introduced a new degree of freedom in the conception of catalysts. Recently, mesoporous silica materials with larger pore size and better stability were synthesized in an acidic medium using nonionic triblock copolymers (TCPs) as the surfactant [2]. These materials, exemplified by hexagonal (p6mm) SBA-15, have long-range order, large monodispersed mesopores (up to 50 nm) [3] and thicker walls (typically between 3 and 9 nm) [4].

The most commonly used surfactant for mesoporous silica synthesis is poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide), or EOₙPOₘEOₙ, with various m and n values [5]. The successful synthesis of SBA-15 has been reported using EO₂₀PO₇₀EO₂₀, whereas the use of EO₁₀₆PO₇₀EO₁₀₆ results in cubic SBA-16 [6]. The materials display a relatively narrow pore size distribution, larger pores (6–9 nm) and a thicker pore wall (6 nm). All these characteristics are desirable if superior-quality mesoporous catalyst supports or molecular sieves are to be obtained. Furthermore, the correct proportion of acid and silica sources, such as tetraethyl orthosilicate (TEOS), could also significantly improve the quality of the final material [7,8].

A basic understanding of the synthesis conditions is indispensable, because mesoporous materials with desirable characteristics can only be obtained by suitably controlled synthesis procedures and conditions [3]. Therefore, specific behaviors of the synthesis system must be investigated, particularly those concern the relationship between the synthesis conditions and the characteristics of the material [4]. The widening of the range of suitable
working compositions of the synthesis gel will ensure
tolerance in the synthesis process without significant effects
on the quality of finished materials. Unfortunately, in most
reports, the effects of the synthesis conditions on the
characteristics of the final material are investigated
separately [2,7,8]. Erroneous results or misleading conclu-
sions could result, because the synthesis system generally
behaves differently under different synthesis conditions [7].
Therefore, it is suggested that the synthesis process be
studied under a wide range of conditions so that its
behavior under different synthesis conditions can be
characterized. Again, the interactive effects of the synthesis
conditions should also be simultaneously elucidated rather
than studying one condition while fixing the others [6].
Thus, the overall behavior of the synthesis system can be
simultaneously investigated, leading to more meaningful
conclusions.

This study focuses on the in-depth understanding of
interactive correlations between different synthesis condi-
tions, including gel composition and gelling temperature,
with the quality of the mesoporous silica obtained. A wide
range of synthesis conditions, including the HCl, TEOS
and TCP contents in the synthesis gel as well as the gelling
temperature, was used. Particular focus has been placed on
the dominant condition and governing mechanism in-
volved under different synthesis conditions that could lead
to the successful formation of mesoporosity, the distribu-
tion of channel sizes, the interparticle meso/macroporosity
and the surface acidity.

2. Experimental

2.1. Synthesis of mesoporous silicas

The mesoporous silica materials were synthesized using
TEOS (Merck) as the silica source, a TCP, i.e., poly
(ethylene oxide)–(propylene oxide)–poly(ethylene oxide)
(Aldrich) with a molecular weight of 5800 as the
structure-directing agent, HCl and distilled, deionized
water. The gel molar compositions are given in Table 1.
In a typical synthesis procedure, TCP was first dissolved in
a solution of water and HCl, and the mixture was shaken in
an orbital shaker at 30 °C and 150 rpm for 2 h. Next, the
required amount of TEOS was added to the above
solution. As the gel started to develop, the mixture was
quickly heated to the desired temperature (T) under slow
shaking at 50 rpm for 24 h. The synthesis gel was then
transferred into an oven and aged at 100 °C for another 6 h.
Then, the solid formed was filtered, washed several times
with distilled water and calcined at 500 °C for 6 h. The
mesoporous silica materials obtained were denoted by
MS-1 to MS-9.

2.2. Characterization of mesoporous silicas

All mesoporous silica samples were tested for surface
characteristics using Quantachrome Autosorb-1 equipment
with an outgassing temperature of 300 °C, and X-ray
diffraction (XRD) patterns were obtained using a Siemens
2000X system. The acidity was determined through the
temperature-programmed desorption of NH3 using a
Quantachrome Chembet 3000 system. In this test, the
adsorption of NH3 was carried out at 50 °C, because only
weak acid sites were expected to be present in the samples.
The infrared spectroscopy characterization of each catalyst
sample was carried out using a Perkin Elmer 2000 Fourier-
transformed infrared (FT-IR) system, and the structure of
the samples was characterized using a Philips CM 12
transmission electron microscope.

3. Results and discussion

3.1. Effect of HCl content

Table 2 shows the surface characteristics of all the
mesoporous silica samples. The surface data were auto-
matically calculated on the basis of adsorption isotherm
data, as typically shown in Fig. 1 for MS-3. The isotherm
data are characterized by a sharp nitrogen uptake at higher
relative pressures. The material also exhibits a large
hysteresis loop of type E with a gradually increasing
adsorption branch, but with a relatively steep desorption
branch at $P/P_0$ lower than 0.9. The shape of the hysteresis
loop indicates the presence of different sizes of spheroidal

| Condition | TEOS (g) | TCP (g) | HCl (g) | H$_2$O (g) | T (°C) | Molar ratio |
|-----------|----------|---------|---------|------------|--------|------------|
| 1         | 24.0     | 11.5    | 21.9    | 300.0      | 60     | 1.0(TEOS):0.017(TCP):5.2HCl:144.7H$_2$O |
| 2         | 24.0     | 11.5    | 26.4    | 270.0      | 60     | 1.0(TEOS):0.017(TCP):6.3HCl:130.2H$_2$O |
| 3         | 24.0     | 11.5    | 30.7    | 240.0      | 60     | 1.0(TEOS):0.017(TCP):7.3HCl:115.7H$_2$O |
| 4         | 18.0     | 11.5    | 26.4    | 270.0      | 60     | 1.0(TEOS):0.023(TCP):8.3HCl:173.6H$_2$O |
| 5         | 30.0     | 11.5    | 26.4    | 270.0      | 60     | 1.0(TEOS):0.014(TCP):5.0HCl:104.2H$_2$O |
| 6         | 24.0     | 7.5     | 26.4    | 270.0      | 60     | 1.0(TEOS):0.011(TCP):6.3HCl:130.2H$_2$O |
| 7         | 24.0     | 15.5    | 26.4    | 270.0      | 60     | 1.0(TEOS):0.023(TCP):6.3HCl:130.2H$_2$O |
| 8         | 24.0     | 11.5    | 26.4    | 270.0      | 50     | 1.0(TEOS):0.017(TCP):6.3HCl:130.2H$_2$O |
Table 2
Surface characteristics of the mesoporous silicas

| Sample | Total surface area (m²/g) | Micropore area (m²/g) | Mesopore area (m²/g) | Average pore diameter (nm) | Pore volume (cc/g) |
|--------|---------------------------|----------------------|---------------------|------------------------|------------------|
| MS-1   | 580                       | 205                  | 365                 | 6.09                   | 0.65             |
| MS-2   | 606                       | 230                  | 396                 | 5.87                   | 0.92             |
| MS-3   | 760                       | 208                  | 552                 | 6.92                   | 0.98             |
| MS-4   | 324                       | 192                  | 132                 | 6.73                   | 0.36             |
| MS-5   | 239                       | 84                   | 155                 | 6.21                   | 0.31             |
| MS-6   | 503                       | 261                  | 242                 | 5.45                   | 0.74             |
| MS-7   | 102                       | 63                   | 39                  | 6.88                   | 0.12             |
| MS-8   | 371                       | 189                  | 202                 | 5.47                   | 0.43             |
| MS-9   | 374                       | 143                  | 230                 | 6.28                   | 0.53             |

*aBET method.  
b&t-method.  
cDR method.  
dMP method.

In the synthesis of MS-3, the gel pH was measured to be 2.1, which is close to the theoretical isoelectric point of silica (pH ≈ 2) [5]. Under this condition, the steady-state condensation of SiO\(_2\) decreased, and the reaction step became rate-limiting. Thus, mesopore development was favored under this condition, provided that the rate of reaction for the hydrolysis of the orthosilicate was slightly higher than that of the condensation of the silica to avoid a large backlog of SiO\(_2\) in the intermicellar spaces.

In this study, the HCl content in the gels was selected (molar ratios between 5.2 and 8.3) such that the pH would not decrease to below 2. At pHs lower than 1.5 (below the isoelectric point), a higher rate of condensation was reported when TEOS was used as the silica source [3]. Similar behavior was demonstrated by various gels utilizing different triblock copolymers [4]. This was attributed to the protonation of the silanol units to produce SiOH\(_2\)\(^+\) groups that could readily eliminate water molecules to enhance the condensation reaction [6]. The increased condensation rate at a low pH would consequently result in the disorder in the mesoporous Si–O–Si network. In this study, this phenomenon was observed at HCl molar ratios of 8.7 and above (data not shown).

3.2. Effect of TEOS content

The content of TEOS in the synthesis gel was increased sequentially in the preparation of MS-4, MS-2 and MS-5. More mesopores formed with an increase in TEOS from MS-4 to MS-2 (Table 2), whereas a further increase resulted in a detrimental effect on the mesopores. The considerable decrease in the surface area and pore volume indicated the failure of the formation of the Si–O–Si network, which was the mechanism that led to the creation of mesoporosity. This result suggested that the content of TEOS must be closely controlled to ensure the development of mesopores in the material. Note that the average

cavities with about the same entrance pore diameter [7]. Different pore sizes could be attributed to large extra-framework mesopores or even macropores entrapped within layers of well-developed arrays of cylindrical pores. This type of porous material can exhibit relatively poor nitrogen uptake and a subsequent facilitated release during the adsorption and desorption steps, respectively. These mechanisms are responsible for the wide hysteresis observed for the mesoporous silica material.

In Table 2, as the HCl content increases from MS-1 to MS-3, the total surface area shows a corresponding increase. These surface areas are primarily contributed to by the mesopores, which constitute between 62% and 73% of the total surface area. The largest mesopores and the highest pore volume are demonstrated by MS-3 with an average size and volume of 6.92 nm and 0.98 cc/g, respectively. There is no clear relationship between the average pore diameter and the pore volume because they are strongly dependent on the pore size distribution of the sample.
pore diameter did not correlate with the formation of mesopores in the samples, suggesting the roles of macropores between SiO₂ particles in the result.

3.3. Effect of TCP content

With an increase in the TCP content from MS-6 to MS-2, more mesopores developed, as indicated by the higher total surface area and mesopore area of the latter. However, a further increase in the concentration of TCP resulted in a severe failure of mesopore formation, as indicated by the low surface area of MS-7. The large average pore diameter of this sample (6.88 nm) was therefore attributed to secondary interparticle mesopores that contributed little to the total surface area.

Even at the low TCP content (2.3% w/w) in the synthesis of MS-6, the critical micelle concentration (cmc) was exceeded, because a material with significant mesoporosity was produced. This cmc concentration was slightly lower than the reported value for Pluronics 123 (3.2% w/w) or Pluronics 127 (2.8% w/w) [8]. The higher surface area of the material that resulted from an increase in TCP content to 3.5% w/w in the synthesis of MS-2 was associated with the improved micellation activity in the synthesis mixture. However, a further increase to 4.6% resulted in a marked drop in the mesoporosity, as shown by MS-7. This result was partly due to the penetration of the ethylene-oxide end of the TCP molecule into the condensing silica wall covering the micelles [4]. The congestion in the core of the micelles due to the presence of an excessive amount of hydrophobic propylene-oxide groups may cause the deformation of micelles. As a result, the regular arrays of mesopore channels failed to satisfactorily form, as suggested by the poor surface characteristics of MS-7.

Data in Table 2 suggested that among all the synthesis variables studied, the contents of TEOS and TCP in the synthesis gel were most critical in the development of mesopores in the material. Despite their important role in the synthesis of mesoporous silica, the content of HCl and the gelling temperature in the range used in this study did not have a strong effect. Thus, the governing mechanisms leading to mesopore formation were predominately influenced by the satisfactory formation of micelles and the condensation of silane. This resulted from the optimal balance between the contents of TCP and TEOS in the synthesis gel. However, this balance appeared to occur in a narrow range.

During the synthesis, the ethylene-oxide end groups were protonated under sufficient acidity, while the orthosilane underwent the rate-determining hydrolysis to form silicate oligomers. Interactions between the protonated TCP with the positively charged silicate oligomers were then mediated by Cl⁻ anions from the acid [9]. Under the moderate acid concentration in the synthesis of MS-1 and MS-2, the condensation of the silica oligomers was faster than the hydrolysis of TEOS. This was due to the strong nucleophilicity of the deprotonated silanol (SiO⁻), which favors the condensation process [5]. As a result, the mesopore channels did not satisfactorily form, because the silicate oligomers tended to undergo condensation, which limited their opportunity to assemble themselves into mesoscopic channels. This explained the relatively low mesopore surface areas of MS-1 and MS-2 compared with that of MS-3.

Increasing the TEOS:TCP ratio from 1.56:1 to 2.09:1 in the synthesis of MS-4 and MS-2, respectively, brought about the desired effect on the formation of mesopores. This observation could be explained using the model proposed by Kitazawa et al. [9]. According to their model, the hydrophilic ethylene-oxide groups of TCP interact with the cationic oligomeric silica through an electrostatic interaction and hydrogen bonding. By increasing the concentration of silica oligomers, the rate of silica polymerization increased, and fewer defects occurred in the mesopore walls because of a sufficient number of silica building blocks. As a result, more mesopores formed and correspondingly, a higher surface area resulted. However, the higher concentration of silica oligomers also resulted in the shrinkage of the micelles, and subsequently, the average pore size of the silica material decreased. A further increase in the TEOS:TCP ratio to 2.6:1.0 in the MS-5 synthesis was demonstrated to be detrimental, because excessive TEOS interrupted the condensation of the silica network on the micelles.

3.4. Effect of gelling temperature

MS-8, MS-9 and MS-2 samples were synthesized with a gelling stage at temperatures of 40, 50 and 60 °C, respectively. It is evident in Table 2 that mesopores did not satisfactorily form at low temperatures (40, 50 °C), because MS-8 and MS-9 had lower surface area and lower pore volume compared with those of MS-2. However, the main contributor to the surface area in the former two samples was still the mesopores, which accounted for between 54% and 61% of the total surface area. This result suggested that at 40 and 50 °C, the synthesis of orthosilane and the condensation of silica can still take place, although they proceed at lower rates. With an increase in the temperature of the gelling stage to 60 °C, more ordered mesopores developed as clearly indicated by the higher surface area and pore volume of MS-8 compared with those of MS-9 and MS-2.

The variation in the reaction temperature between 40 and 50 °C evidently did not have a significant impact on the development of mesoporosity in the mesoporous silica materials. These temperatures were considered to be too low for the efficient hydrolysis of TEOS as well as for the sufficient mobility of silica oligomers required for organization on the micelles. Thus, MS-8 and MS-9 demonstrated almost similar surface characteristics. When the gelling temperature was increased to 60 °C, the acceleration of the rates of reactions and the subsequent molecular arrangement were sufficient to eventually produce a material with significantly increased mesoporosity.
An increase in gelling temperature was also observed to result in an increase in the mesopore area leading to an overall pore volume increase. The effect can be explained by considering the stages in the formation of mesopores. The micelles of TCP in an aqueous solution consist of cores and shells formed by the hydrophobic and hydrophilic parts of the molecule, respectively. The dependence of the micelle core radius \( R_c \) on the temperature of the solution can be expressed by the following empirical equation [10]:

\[
R_c \sim (T - T_c)^{0.2},
\]

where \( T \) is the temperature of the aqueous solution and \( T_c \) is the critical micellization temperature. As the temperature increases, the aggregation number \( N_g \) of the block copolymer in the micelle and the hydrophobicity of the ethylene-oxide block also increase [11]. At the same time, the density of the core of the micelle, constructed by the hydrophobic part of the TCP, increases with the growth of the latter and directly influences \( R_c \). Therefore, \( R_c \) increases when the gelling temperature is raised.

### 3.5. TEM study of the mesopores formed

Figs. 2(a)–(d) show the different characteristics of mesopores formed in different mesoporous silica samples. Generally, MS-3 showed relatively well-developed mesopores, characterized by an array of straight and uniform-sized pores (Fig. 2(a)). The well-formed mesopores correlated with the high surface area and pore volume of this sample, as suggested by the data in Table 2. At a low TCP content of the synthesis gel, mesopores also formed, but in a less orderly manner (with relatively random and irregular pore widths), as seen in Fig. 2(b) for MS-6. This type of pore was described as wormlike by Chen et al. [11]. Meanwhile, at the high TEOS content in the synthesis of MS-5, mesopores failed to form satisfactorily, as suggested by Fig. 2(c). In this sample, only part of the silica mass showed mesoporosity, while the remaining fraction was a mass of nonporous silica. As shown in Fig. 2(d), mesopores also failed to form (there were no visible arrays of straight channels) when the TCP content of the synthesis gel was greater than the suitable range for the formation of micelles (2.3–3.5% w/w).

Figs. 2(a)–(d) suggest that the optimal balance between the contents of TCP and TEOS was critical for the development of mesoporosity. A low TCP caused the formation of less orderly micelles in the synthesis gel. Consequently, when TEOS was added, slow hydrolysis took place, and the resulting silane started to fill the hydrophilic intermicellar spaces. Since the TCP micelles
failed to arrange themselves (to form orderly arrays of straight micelles) below the cmc, the resultant silica material demonstrated a wormlike structure, as depicted in Fig. 2(b). The too high TCP content in the synthesis gel of MS-7 (34.8% higher than that for MS-3) also disturbed the orderly formation of micelles. This was because the additional TCP molecule disturbed the already formed micelle system through interactions between their hydrophobic poly(propylene oxide) group and their hydrophilic poly(ethylene oxide) ends. By comparing Figs. 2(c) and (d), it can be concluded that this undesirable effect was apparently more severe than that obtained by increasing the TEOS content by 25% in the synthesis of MS-5, compared with that of MS-3.

3.6. XRD study of mesoporous silica samples

The XRD patterns for different mesoporous silica samples are shown in Fig. 3. Generally, all samples were of amorphous or low-crystallinity materials. Weak (1 0 0) peaks were only detectable in MS-1, MS-2 and MS-3. In these three samples, strong (1 1 0) peaks (2θ = 1.8–1.9°), and very weak (2 0 0) (2θ = 2.4–2.5°) and (2 1 0) (2θ = 3.1–3.4°) signals were also detected, suggesting a high degree of hexagonal mesoscopic organization. MS-3 showed the highest crystallinity among all the samples synthesized in this study, with an extra (2 1 1) signal occurring at 2θ = 5.3°. No scattering signal was detectable for MS-7, indicating that this sample was almost completely amorphous. MS-4, MS-5, MS-8 and MS-9 exhibited only very weak (1 1 0) diffraction peaks, which indicated the formation of poorly ordered mesoporous materials.

From Bragg’s law (nλ = 2d sinθ) and the relationship \(1/d_{hkl}^2 = (h^2 + k^2 + l^2)/a_0^2\) between the hexagonal lattice parameter (a₀) and the planar distance (d_{hkl}) at different Miller indices (h k l), if the first peak belongs to the (1 0 0) diffraction peak of the hexagonal phase, the (2 0 0) and (2 1 0) diffraction peaks should appear at 2θ = 2.4° and 3.4°, respectively [11]. Thus, the XRD result matched the theoretical result. The increase in HCl content in the synthesis gels of MS-1, MS-2 and MS-3 appeared to result in the disappearance of the overall crystallinity of the materials. The XRD result was consistent with the TEM and surface analyses.

Because the (1 0 0) peaks only appear in the profiles of MS-1, MS-2 and MS-3, further analysis of the unit cell properties was only performed on these materials. The unit cell size (a₀) and the pore wall thickness (t) were calculated from the values of \(d_{100}\) spacing, and the results are summarized in Table 3. Increasing the acid content of the synthesis gel was found to result in the enlargement of the unit cell size from 8.07 nm for MS-1 to 9.24 nm for MS-3. These values were similar to the reported values obtained using the same surfactant but under slightly different synthesis conditions [6]. These values in the mesosize range suggested a high degree of mesoporosity in these materials. The pore wall thickness was also found to show a corresponding increase from MS-1 to MS-2. However, there was not much difference in the wall thicknesses of MS-2 and MS-3. This result suggested that an increase in the acidity of the synthesis gel favored the formation of mesoporosity in the material, while at the same time promoting the growth of thicker pore walls.

At a lower acid content, there was competition between the condensation of partially hydrolyzed silica species and the hydrolysis of remaining alkoxysilane moieties [2]. Residual organic groups weakened the interactions

![Fig. 3. XRD patterns of mesoporous silica samples.](image)

Table 3

| Sample | Spacing \(d_{100}\) (nm) | Unit cell size a \(a_0\) (nm) | Pore diameter \(D\) (nm) | Pore wall thickness b \(t\) (nm) |
|--------|-----------------|------------------|----------------|------------------|
| MS-1   | 8.07            | 9.32             | 6.09           | 3.23             |
| MS-2   | 8.32            | 9.61             | 5.87           | 3.74             |
| MS-3   | 9.24            | 10.67            | 6.92           | 3.75             |

\(a_0 = 2d_{100}/\sqrt{3}\).  
\(t = a_0 - D\).
between the hydrophilic part of the block copolymer and the silica oligomer. The promoted hydrolysis of TEOS at higher acid content in the synthesis gel also resulted in the enhancement of the condensation of the hydrolyzed silica species on the intermicellar spaces, leading to the assembly of the mesophase. This phenomenon was attributed to the higher concentration of Cl\(^-\) which mediated the interaction between the surfactant head groups and the positively charged oligomeric inorganic species through weak hydrogen-bonding forces [5]. Note that the hydrolysis and condensation reactions initially proceeded at a higher rate, which gradually decreased with time as the concentrations of the reactants decreased. Consequently, the silica network in the intermicellar spaces proceeded at a higher rate, leading to the formation of well-ordered pores with thicker pore walls. The smaller pore diameter of MS-2 compared with that of MS-1 could be the result of the congestion occurring in the presence of the higher concentration of silica species in the synthesis mixture. This congestion was deemed to be the main cause for the decrease in the size of the micelles. In MS-3, the rate controlling mechanism was neither hydrolysis nor condensation of the silica species, because a similar pore wall thickness was obtained at a significantly larger pore diameter.

The hydrophilic ethylene oxide moiety of the TCP can serve as a large and reactive surface for silica condensation and attracts the anionic silica oligomer to effectively catalyze silica polymerization on the surface of the micelles [4]. The silicated micelles further assemble and form a three-dimensional hexagonal architecture of mesoporous silica with moderate electrostatic or hydrogen-bonding interaction between the silica and the surfactant. These phenomena are schematically shown in Fig. 4. A significant portion of the silica and surfactant in the gel form an organic–inorganic composite that precipitates. Therefore, an excessive or insufficient silica source in the gel polymerized on the micellar surface seems unfavorable for establishing the hexagonal architecture of mesoporous silica. This theory was confirmed by the relatively low crystallinity of MS-5 compared with those of MS-2 and MS-4, as observed in the XRD result. However, no significant effect of an increase in the temperature on the hydrolysis and condensation of silane on the surface of the micelles was detected in the XRD result. This meant that the effect of the temperature in the 30–60 °C range was not as critical as the balance between the contents of TCP and TEOS and the acidity in the synthesis gel.

### 3.7. Study of acidity of mesoporous silica

Fig. 5 shows the desorption peaks of NH\(_3\) as a function of temperature. All samples showed a single and almost symmetrical desorption peak with low acidity, as suggested by the small peak area (0.005–0.009 mmol NH\(_3\)/g). The desorption started at about 70 °C and peaked below 110 °C. This low-temperature desorption suggests the predominantly weak surface acidity of the materials. The single desorption peak demonstrated by all samples implied that only one type of acid site was present. Higher-mesoporosity silicas such as MS-1, MS-2, MS-3 and MS-6 showed both desorption peaks shifted towards higher temperatures and larger peak areas. This observation indicated that they contained higher numbers of acid sites.

Many researchers have attributed the weak acidity of mesoporous silica primarily to the silanol groups (Si–OH) terminating the Si–O–Si network [1,2,6]. Through \(^{29}\)Si MAS NMR analysis, Aramendia et al. [12] and Wang et al. [13] detected and confirmed the presence of silanols on the surface of mesoporous silicas synthesized under different conditions. In this study, the presence of silanol groups was confirmed by the presence of an infrared absorption peak at a wave number of 3735 cm\(^{-1}\) [14], particularly for MS-1, MS-2 and MS-3, as shown in Fig. 6. Although only detectable as small humps rather than forming well-separated peaks, the transmittances at this wave number

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**Fig. 4.** Mesoporous wall formation from the polymerization and subsequent condensation of silica oligomers.

**Fig. 5.** NH\(_3\)-TPD profiles of mesoporous silicas.
were not negligible. It was also observed that the hump was not detectable for MS-7, in which mesopores failed to form. Thus, this result indicated a positive correlation between the number of silanol groups and the weak acidity of the sample. Qualitatively, a higher number of silanols (indicated by more intense transmittance at 3735 cm\(^{-1}\)) followed the increase in mesoporosity. This observation led to the conclusion that this functional group was mainly concentrated in the inner walls of the mesoporous channels.

4. Conclusions

Because of the accelerated TEOS hydrolysis and condensation of silica, increasing acidity favored the formation of mesopores. A material with a surface area of 700 m\(^2\)/g, mostly in the mesoporous size range, was synthesized at 1.0(TEOS):0.017(TCP):7.3HCl:115.7H\(_2\)O and a pH of 2.1. The cmc of the TCP was slightly lower than that commonly reported for poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide). The mesopore formation was greatly influenced by the TEOS:TCP ratio. Increasing the ratio from 1.56:1 to 2.09:1 promoted the formation of mesoporosity, whereas a further increase to 2.61:1 was detrimental. Whereas increasing the TCP content to 3.5% w/w improved micellization, a further increase to 4.6% should be avoided. The weak acidity of the mesoporous silica was attributed to silanol groups at the inner walls of the material, the number of which correlated well with the degree of mesoporosity.

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