A multivariate analysis of the synthesis conditions of mesoporous materials

Gisle Øye a,*, Johan Sjöblom a, Michael Stöcker b

a Department of Chemistry, University of Bergen, Allégaten 41, N-5007 Bergen, Norway
b SINTEF Applied Chemistry, P.O. Box 124 Blindern, N-0314 Oslo, Norway

Received 30 April 1999; accepted for publication 30 August 1999

Abstract

A 2^8−4 reduced factorial design was used to study the influence of different experimental variables in the synthesis of mesoporous materials. Eight variables were investigated at high and low levels. This resulted in 18 experiments, including two center points. X-ray diffraction patterns were used to characterize the samples, which ranged from well-defined MCM-41 structures to amorphous materials. Analysis of the data resulted in two models (Model 1 and Model 2). In Model 1, the materials were simply divided into porous or non-porous materials. Several variables and interaction terms were found to be significant for this model, of which pH turned out to be the most important variable. The quality of the materials was taken into consideration in Model 2. The pH was again found to be the most important variable for the model. Model 2 also indicated that at least one of the variables is non-linear. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: MCM-41; Mesoporous materials; Multivariate data analysis; X-ray diffraction

1. Introduction

The syntheses of mesoporous materials of the so-called M41S family were first reported in 1992 [1,2]. The main members of this family are called MCM-41 and MCM-48. MCM-41 has a hexagonally ordered pore structure, which is considered as one-dimensional. MCM-48 has a three-dimensional, cubic ordered pore system, but has a smaller synthesis regime than MCM-41. Consequently, MCM-48 has been less studied, even though it should be more applicable as catalyst or adsorbent due to its three-dimensional pore architecture.

MCM-41 and MCM-48 materials are both characterized by high surface areas, uniform pore size distributions with pore sizes in the range 15 to 100 Å, and high thermal stability. This type of material has potential applications as acidic catalysts for petrochemical processes, redox catalysts, adsorbents in separation processes, etc. [3–5].

Many variables may influence the synthesis of mesoporous materials. The best way of investigating the effect of several variables at the same time (multivariate data analysis) is to utilize an experimental design. This consists of M variables and N experiments set up to investigate the variables in a systematic way. An N × M matrix will then constitute the variable space (X). A response matrix (Y), containing at least one response variable for each experiment, is necessary for the analysis as well. The purpose of the multivariate analysis is then to perform a screening of the
variables in order to get a model that describes the connection between \( X \) and \( Y \) as well as possible.

In the present work we have applied a \( 2^{8-4} \) reduced factorial design to study eight variables which we believed to have significance for the syntheses of mesoporous materials. We have mainly chosen chemical related variables, but it would be possible to include other variables, such as hydrodynamic effects, at a later time. The design consists of 18 experiments, including two center points, and the results are discussed in view of two alternative models.

2. Experimental

2.1. Chemicals

Chemicals used in the syntheses were hexadecyltrimethylammonium bromide (CTAB, \( \geq 99\% \), Fluka), sodium hydroxide (\( \geq 99\% \), Riedel-de Hain), sodium fluoride (\( \geq 99\% \), Merck), tetraethylorthosilicate (TEOS, \( \geq 99\% \), Fluka) and tetramethylorthosilicate (TMOS, \( \geq 99\% \), Fluka). All the chemicals were used as received.

2.2. Syntheses

The eight synthesis variables under investigation and their high and low experimental levels and center points are given in Table 1. The syntheses were performed according to the synthesis scheme stated in Table 2. The general synthesis procedure was to dissolve CTAB and NaF (if any) in distilled and deionized water at the required pH. NaOH was used to adjust the pH. Then the solutions were stabilized at the desired temperature, before TEOS or TMOS was added. After stirring for 20 min, the samples were transferred to Teflon bottles and left under static conditions at the required temperature for the required time.

Finally, the as-synthesized products were recovered by filtration. They were washed with distilled water and dried at ambient temperature. The samples were calcined under flowing nitrogen for 1 h, followed by 6 h under flowing air. The temperature was 540°C.

<table>
<thead>
<tr>
<th>Variable*</th>
<th>Low level (−1)</th>
<th>High level (1)</th>
<th>Center point (0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( x_1 )</td>
<td>Si source/CTAB</td>
<td>1.5</td>
<td>2.5</td>
</tr>
<tr>
<td>( x_2 )</td>
<td>H_2_O/CTAB</td>
<td>90</td>
<td>200</td>
</tr>
<tr>
<td>( x_3 )</td>
<td>NaF/CTAB</td>
<td>0</td>
<td>0.2</td>
</tr>
<tr>
<td>( x_4 )</td>
<td>pH</td>
<td>10</td>
<td>15</td>
</tr>
<tr>
<td>( x_5 )</td>
<td>Si source TMOS</td>
<td>1</td>
<td>1/2TMOS</td>
</tr>
<tr>
<td>( x_6 )</td>
<td>( T(S) )</td>
<td>30</td>
<td>40</td>
</tr>
<tr>
<td>( x_7 )</td>
<td>( T(H) )</td>
<td>25</td>
<td>100</td>
</tr>
<tr>
<td>( x_8 )</td>
<td>( t(H) )</td>
<td>24</td>
<td>96</td>
</tr>
</tbody>
</table>

- The first three variables \( (x_1, x_2, x_3) \) are given as molar ratios of the additives relative to CTAB.
- \( T(S) \) = temperature at the structure directing solution (°C).
- \( T(H) \) = temperature in the heater (°C).
- \( t(H) \) = time in the heater (h).

2.3. Characterization

X-ray powder diffraction analysis was carried out on a Siemens D5000 diffractometer. Cu K\( \alpha \), equipped with a germanium monochromator, was the source of radiation. The wavelength was 0.15406 nm, and the step size and the step time were 0.020° and 7 s, respectively.

2.4. Data analysis

The data analysis was performed with the software Sirius version 6.0, applying the partial least squares (PLS) method [6]. The 18 samples were analyzed by powder X-ray diffraction (XRD), and the XRD patterns were the basis for the response variables.

The analysis of a \( 2^{8-4} \) reduced factorial design results in an overlap between the main variables and their three-factor interaction terms. In the present work, all three-factor effects are ignored. Also, two-factor interaction terms are obtained from the analysis. Their overlap pattern is shown in Table 3. In order to resolve these overlaps, more experiments have to be carried out. Consequently, the present results are interpreted in view of the main variables and the overlapping two-factor interactions.
the materials was also taken into consideration. The regression coefficients of Model 1 are shown in Fig. 1. The classification of the response values is given in the last column of Table 2. The division was done according to the following criteria.

(a) In the cases of no reflection in the XRD patterns, the response variable was set to 0.
(b) In the cases of one strong and some diffuse reflections in the XRD patterns, the response variable was set to 0.7.
(c) In the cases of one strong reflection in the XRD patterns, the response variable was set to 0.2.
(d) In the cases of one strong reflection in the XRD patterns, the response variable was set to 0.8 (see Fig. 1).
(e) In the cases of a well-defined hexagonally ordered pore structure (MCM-41), the response variable was set to 1.0 (see Fig. 1).

3. Results and discussion

3.1. Model 1

The regression coefficients of Model 1 are shown in Fig. 2. The positive regression coefficients indi-
Fig. 1. XRD patterns of sample 12 (---) and sample 15 (-----). Sample 12 is given the value 1.0 in Model 2, while sample 15 is given the value 0.8 in the same model.

Fig. 2. Regression coefficients determined from Model 1. Only the first term in the overlap pattern of the interaction terms is shown.
icate that the high levels of the current variables enhance the formation of porous materials, while the opposite is the case for the negative regression coefficients. From the figure it is clearly seen that pH ($x_4$) is the most important variable in the model. Other variables of importance are the amount of silicon source ($x_1$), the amount of water ($x_2$), and the time the samples are kept in the heater ($x_8$). In addition, three interaction terms are significant.

Fig. 3 shows the fitted regression curve for the present model, it is represented as follows.

\[
\text{Response} = 0.333 - 0.125x_1 + 0.125x_2 + 0.375x_4 \\
+ 0.125x_4 + 0.125x_1x_2 \\
- 0.125x_1x_4 + 0.125x_1x_8.
\]

The slope of the curve, the intersection with the y-axis and the correlation coefficient are given in Table 4.

In the following the variables and their interaction terms will be discussed more closely. The significance of each variable, with reference to Fig. 2, will be accounted for by plausible explanations.

Fig. 3. Regression curve for Model 1. Response = 0.333 – 0.125$x_1$ + 0.125$x_2$ + 0.375$x_4$ + 0.125$x_4$ + 0.125$x_1$$x_2$ – 0.125$x_1$$x_4$ + 0.125$x_1$$x_8$.

Table 4: The slope, intersection and correlation coefficient of the regression curves of Model 1 and Model 2.

<table>
<thead>
<tr>
<th>Model</th>
<th>Slope</th>
<th>Intersection</th>
<th>Correlation coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model 1</td>
<td>0.94</td>
<td>0.02</td>
<td>0.986</td>
</tr>
<tr>
<td>Model 2</td>
<td>0.93</td>
<td>0.02</td>
<td>0.96</td>
</tr>
</tbody>
</table>

$x_1$ (the amount of silicon source relative to CTAB). It is observed that increased amounts of the silicon source (TMOS or TEOS) will oppose the formation of porous materials. This is found to be in agreement with recently published results by Behrens et al. [7]. They reported a decrease in the ordering of the pore structure, and finally an amorphous material, as the amount of TEOS in their syntheses was increased.

This observation may be accounted for by the reaction mechanism for the formation of this type of mesoporous material, suggested by Huo et al. [8]. The mechanism involves interactions between positively charged micelles or surfactant monomers and negatively charged silicon species, ranging from monomers to oligomers of different sizes.
Consequently, anionic silicate species are accumulated at the micelle surfaces or associated with surfactant monomers [9]. When the amount of silicon source in the system is increased, the amount of silicate species in the bulk solution will increase too. These may then polymerize to give less porous or non-porous materials, and the negative regression coefficient can be accounted for.

$x_3$ (the amount of water relative to CTAB). Increasing the water content seems to have a favorable effect on the formation of porous materials. This is effectively the same as decreasing the relative amount of silicon in the system, and has been reported to result in mesoporous structures [7,10].

$x_4$ (pH). In this model the increase of pH has the most pronounced positive effect on the formation of porous materials. High pH means high concentration of hydroxyl ions, which may have several possible effects on the system. Firstly, these anions will act as counterions in the electrical double layer around the micelles. This reduces the thickness of the double layer, and the surfactants in the micelles become packed more tightly. These compact aggregates may enhance the porosity of the materials. Secondly, high pH results in fast and complete hydrolysis. Also the polymerization of monomers to oligomers, and later to three-dimensional particles, occurs within a few minutes. Due to the high pH, all these species will be negatively charged, and consequently interact more readily with the positively charged micelles. In this way the formation of porous materials may be improved. Finally, both the solubility and the rate of dissolution of silica are promoted at high pH. This evokes a rapid ripening process, where small particles (which are most soluble) dissolve and reprecipitate at larger particles. The result is a decrease of the total interfacial area and a more long-range pore ordering.

$x_5$ (the silicon source). The source of silicon, and implicitly the alcohol produced during the

![Fig 4. Regression coefficients determined from Model 2. Only the first term in the overlap pattern of the interaction terms is shown.](image-url)
syntheses, has no significance in the present model.

\( x_6 \) (the temperature of the structure directing solution). This variable has no significance in the present model.

\( x_4 \) (the time the samples are kept under static conditions). The formation of porous materials seems to be promoted by increased time in the heater. During this aging process internal hydroxyl groups will be eliminated by further condensation reactions. The result is a strengthening of the pore wall structure, and collapse during calcination is less probable.

Another process that appears during aging is the ripening of the particles, which was commented on under the \( x_4 \) variable. Finally, several reports have also been published regarding phase transformations of the porous materials during aging of the synthesis gel [11,12].

**Interaction terms**: the two-factor regression coefficients contain information on the effects of interacting variables. As mentioned above, several two-factor effects are overlapping. One could argue, however, that it is possible to assume that only the significant variables contribute to the interaction terms. Then the overlap patterns for the three interaction terms of significance are reduced to the following: \( x_1x_2 = x_4x_8 \), \( x_1x_4 = x_2x_8 \), and \( x_1x_8 = x_2x_4 \). More experiments have to be carried out in order to resolve this overlap, and thereby to be able to give any further interpretation.

### 3.2. Model 2

Fig. 4 reveals the regression coefficients obtained for Model 2. As for Model 1, pH is clearly the most important variable. Furthermore, the other variables and cross terms which were significant in Model 1 are of approximately the same importance in this model as well. In addition, several other variables and cross terms show small contributions to the present model.

The regression curve for Model 2 is shown in

![Regression curve for Model 2](image)
Fig. 5. The model for the fitted curve is as follows.

Response = 0.306 - 0.094x₁ + 0.106x₂ + 0.006x₁x₃
+ 0.319x₄ - 0.031x₅ - 0.031x₆
+ 0.006x₇ + 0.119x₈ + 0.094x₁x₂
- 0.006x₁x₅ - 0.119x₃x₄ + 0.031x₁x₅
- 0.019x₂x₆ - 0.056x₃x₇ + 0.131x₁x₈

The slope of the curve, the intersection with the y-axis and the correlation coefficient are given in Table 4. Note that the model predicts response values for the two center points that are larger than the measured values. This indicates that at least one of the investigated variables shows non-linear behavior.

In the following, only the variables with small regression coefficients (those which were insignificant in Model 1) will be discussed with reference to Fig 4. It must be emphasized that the small values of these coefficients make the interpretation more uncertain. The variables with larger coefficients were examined in Model 1, and because their significance is approximately the same in the present model, their interpretation should be similar.

x₁ (the amount of NaF relative to CTAB). The presence of NaF seems to have a small positive effect on the quality of the porous materials. This may be accounted for by the compression of the electrical double layer that this salt addition contributes to. The micellar aggregates become well-defined and this should be reflected in the pore structure. Another property of the fluoride anions is their catalytic effect on dissolution of silica, and thereby their promotion of ripening processes.

x₂ (the silicon source). TMOS appears to be slightly favorable in the syntheses of better porous materials. Reactions involving TMOS normally occur faster than those involving TEOS, and this may influence the observed tendency.

x₃ (the temperature of the structure directing solution). The fine structure of the materials seems to be enhanced by lower temperature of the micellar, structure directing solution. Increasing the temperature of cationic micellar solutions results in an increase of the critical micellar concentration (CMC) and a reduction of the aggregation number of the micelles. Hence, less well-defined pore structures can be expected.

x₄ (the temperature in the heater). The temperature at which the samples are kept under static conditions appears to be only slightly important in improving the quality of the mesoporous materials. This is quite surprising since the temperature is expected to affect several of the processes occurring during the aging of the samples. Examples are continued polymerization processes to improve the wall structure and ripening processes.

Interaction terms: the interaction terms have a complicated overlapping pattern, and more experiments are necessary in order to give reasonable explanations of these. The presence of the interaction terms, however, indicates that the systems under investigation are quite complex.

4. Conclusions

Two models for the synthesis of mesoporous materials have been developed. In Model 1, only the formation or not of porous materials was taken into consideration. The quality of the material was ignored. In Model 2, the materials were ranked from well-defined MCM-41 structures to non-porous materials. The XRD patterns were the basis of the classification in both the models.

Both models clearly revealed that pH was the most important of the investigated synthesis variables. Several other variables and cross terms showed approximately the same significance. Finally, Model 2 revealed variables that had small regression coefficients. These have been interpreted as factors that enhance the quality of the mesoporous materials. Model 2 also suggested that at least one of the variables is non-linear.

Acknowledgements

G.Ø thanks the Norwegian Research Council (NFR) for a Dr. Scient. Grant. Dr. H. Kallevik and G.R. Flåten are acknowledged for clarifying discussions regarding the multivariate methods.
References