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Multivariate approach to zeolite synthesis

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Abstract

The influence of seven variables on the results of zeolite synthesis performed in presence of 1-methyl-1,4-tetramethylen-bis(*N*-methylpiperidinium)-dihydroxide as structure directing agent (SDA) was examined. The syntheses were planned according to a factorial design strategy and run by using a multiautoclave device. The produced data-set (experimental factors values and qualitative XRD responses for 72 syntheses) was explored by stepwise linear discriminant analysis (LDA): SiO_2/Al_2O_3 molar ratio was identified as the most influent synthesis variable, discriminating between a region rich in amorphous materials and a region where the formation of MFI zeolite is favoured.

Keywords: Zeolite synthesis; Dicationic SDA; Multiautoclave devices; Experimental design; Multivariate analysis

1. Introduction

Zeolites are microporous crystalline aluminosilicates with frameworks based on a three-dimensional network of corner-sharing $[TO_4]$ (T = Si, Al) tetrahedra. They are characterised by the presence of regular voids (channels and/or cages) with free dimensions ranging from ~3 to over 10 Å, sufficient to allow the adsorption and diffusion of organic molecules; on this feature is based the use of zeolites as molecular sieves. The presence of Al in the framework induces a negative charge which is compensated by loosely bound extraframework cations (usually, alkali or alkali earth metal ions) which can be readily exchanged with other cations. On this feature is based the use of zeolites as ion-exchangers, for instance, in water softening. When the extraframework cations are replaced by the proton, zeolites assume strong acidic properties which can be exploited for catalysing several important acid-catalysed reactions [1,2]. Compared to compact heterogeneous catalysts, in which the reaction occurs on the solid surface with limited or no steric control, zeolites can be defined as shape selective catalysts because the shape and the size of the pores may influence the diffusion of reactants and products and even the pathway of the reaction. Therefore, the availability of zeolite structures with different pore architecture is fundamental for increasing the number of possible applications of these materials in heterogeneous catalysis. Nowadays, more than 130 framework types are known [3] but several efforts are still devoted for the synthesis of new microporous structures as well as for better understanding the still obscure phenomena occurring during the zeolite nucleation and growth [4,5].

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Typically, a zeolite is synthesised by heating in an autoclave an alkaline reaction mixture containing the silica and aluminium sources, an organic additive (usually a quaternary ammonium cation or a neutral amine), water and optionally, an alkali metal ion (ME). In the crystallisation of a zeolite, the organic additive plays a central role: it usually acts as a structure directing agent (SDA) since, depending on the synthesis conditions adopted, it is able to favour the formation of two or more different microporous structures. Only in a few cases an organic additive acts as a real template (i.e. it favours the crystallisation of a well defined zeolite with the porous structure which resembles the size and the shape of the organic molecule itself) and that implies that for each new organic additive used, an extensive screening of the numerous experimental variables is necessary. In any cases, it is still impossible to design in a rational way the synthesis of a new zeolite; furthermore, such a complex system cannot be efficiently explored by using empirical experimental strategies, such as the *one-variable-at-a-time* approach. For this reason, different approaches to this problem have been proposed:

- The *combinatorial approach* is based on the use of new technologies, in order to increase the number of produced samples and data: according to that, the use of multiautoclave systems for intensive hydrothermal synthesis has been recently reviewed [5].
- The *multivariate approach* is based on the application of mathematical and statistical methods for the a priori selection of sets of informative experiments; multivariate methods can be efficiently used for data mining from data-sets of synthesised samples, as well [9–11].

In this work, both multiautoclave devices and multivariate methods were used in order to get relevant information from explorative zeolite syntheses, performed by using 1-methyl-1,4-tetramethylen-bis(*N*-methylpiperidinium)-dihydroxide as SDA.

This activity was carried out as a part of a wider investigation program on dicationic SDA influence in zeolite synthesis.

Specifically, this class of dicationic derivatives were selected because of the promising results reported in literature for similar compounds [6–8].

The molecular structure of the studied SDA is represented in Fig. 1.

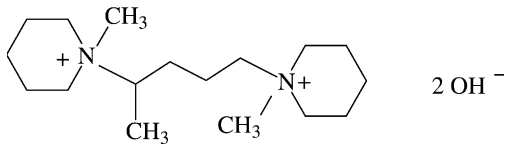

Fig. 1. Molecular structure of the studied SDA.

2. Methodology

The best way for simultaneously investigating the effect of several variables is to use a statistical experimental design. This consists of M variables (in a multivariate context, usually called *factors*) and N experiments set up to investigate the variables in a systematic way. An $N \times M$ matrix will then represent the variable space, $\boldsymbol{X}$. A response matrix, $\boldsymbol{Y}$, containing at least one response variable (i.e. a result) for each experiment, is necessary for the data analysis, as well. Then, the purpose of the multivariate analysis is to perform a screening of the variables in order to find out the connection between $\boldsymbol{X}$ and $\boldsymbol{Y}$.

In this case, the preparation of the reaction mixtures was organised as stated by a 2^{5-1} fractional factorial experimental design scheme, with the addition of two experiments performed in the middle of the experimental domain, one for each selected alkali metal ion; this strategy led to the production of 18 slurries of different composition. Syntheses were run according to the general procedure reported in Section 3.3. The following synthesis variables were inspected (the respective lower and upper levels are reported in parentheses):

- Synthesis molar ratios: SiO_2/Al_2O_3 = SA (25–150), nitrogen/SiO_2 = NS (0.30–0.15), ME/SiO_2 = MS (0.10–0.20), H_2O/SiO_2 = HS (20–60).
- Alkali metal ions (ME = Na^+ or K^+, respectively coded as -1 and $+1$ during data evaluation).

Each of the 18 mixtures was charged into a multiautoclave device (described in Section 3.4) in order to study the effect of crystallisation time, TI (7–21 days) and crystallisation temperature, TE (140–180 °C) on the resulting material. TI and TE were varied according to a 2^2 factorial design strategy. Seventy-two samples, corresponding to four different responses for each mixture preparation, were obtained (18 samples crystallised at 140 °C within 7 days, 18 samples

Table 1
Experimental design, XRD characterisation and classification of the synthesised samples (part 1)

Samples	Experimental factors							XRD characterisation	Classes	
	SA (mol/mol)	NS (mol/mol)	HS (mol/mol)	MS (mol/mol)	ME	TI (days)	TE (°C)		C1	C2
A1	25.0	0.150	20	0.10	K	7	140	Am.	A	A
A2						21	140	MFI	M	P
A3						7	180	Am.	A	A
A4						21	180	Am.	A	A
B1	150.0	0.150	20	0.10	Na	7	140	MFI	M	P
B2						21	140	Am.	A	A
B3						7	180	MFI	M	P
B4						21	180	MFI + Quartz	M	I
C1	25.0	0.300	20	0.10	Na	7	140	Am.	A	A
C2						21	140	Am.	A	A
C3						7	180	Am.	A	A
C4						21	180	Am.	A	A
D1	150.0	0.300	20	0.10	K	7	140	MFI	M	P
D2						21	140	MFI	M	P
D3						7	180	MFI	M	P
D4						21	180	MFI	M	P
E1	25.0	0.150	60	0.10	Na	7	140	Am.	A	A
E2						21	140	Am.	A	A
E3						7	180	Am.	A	A
E4						21	180	Am.	A	A
F1	150.0	0.150	60	0.10	K	7	140	Am.	A	A
F2						21	140	MFI + Am.	M	I
F3						7	180	MFI	M	P
F4						21	180	MFI	M	P
G1	25.0	0.300	60	0.10	K	7	140	Am.	A	A
G2						21	140	Am.	A	A
G3						7	180	Am.	A	A
G4						21	180	Am.	A	A
H1	150.0	0.300	60	0.10	Na	7	140	Am.	A	A
H2						21	140	MFI + Am.	M	I
H3						7	180	MFI	M	P
H4						21	180	MFI	M	P
I1	25.0	0.150	20	0.20	Na	7	140	Am.	A	A
I2						21	140	Am.	A	A
I3						7	180	MOR	A	A
I4						21	180	MOR	A	A

crystallised at 180 °C within 21 days, 18 samples crystallised at 140 °C within 21 days and 18 samples crystallised at 180 °C within 7 days). The results obtained by using the miniaturised autoclaves were confirmed by charging eight mixtures (randomly chosen among those suggested by the fractional factorial design) into conventional 250 cm^3 autoclaves. Specifically, the syntheses E3, F3, G3, H3, M3, N3, O3, P3 reported in Tables 1 and 2 were chosen for this aim.

Each synthesised sample was characterised by X-ray powder diffraction (XRD) to identify the obtained phases (Section 3.5). The obtained samples (mostly MFI zeolite and amorphous materials, coded as Am. in Tables 1 and 2) were ranked according to

Table 2
Experimental design, XRD characterisation and classification of the synthesised samples (part 2)

Samples	Experimental factors							XRD characterisation	Classes	
	SA (mol/mol)	NS (mol/mol)	HS (mol/mol)	MS (mol/mol)	ME	TI (days)	TE (°C)		C1	C2
J1	150.0	0.150	20	0.20	K	7	140	MFI	M	P
J2						21	140	MFI	M	P
J3						7	180	MFI	M	P
J4						21	180	MFI + Quartz	M	I
K1	25.0	0.300	20	0.20	K	7	140	Am.	A	A
K2						21	140	Am.	A	A
K3						7	180	MFI + Am.	M	I
K4						21	180	MFI + LEV + MCM68 + Am.	M	I
L1	150.0	0.300	20	0.20	Na	7	140	MFI + Am.	M	I
L2						21	140	MFI + Am.	M	I
L3						7	180	MFI + MOR + Quartz	M	I
L4						21	180	MOR + Quartz	A	A
M1	25.0	0.150	60	0.20	K	7	140	Am.	A	A
M2						21	140	Am.	A	A
M3						7	180	Am.	A	A
M4						21	180	Am.	A	A
N1	150.0	0.150	60	0.20	Na	7	140	MFI + Am.	M	I
N2						21	140	MFI	M	P
N3						7	180	Am.	A	A
N4						21	180	MFI	M	P
O1	25.0	0.300	60	0.20	Na	7	140	Am.	A	A
O2						21	140	Am.	A	A
O3						7	180	Am.	A	A
O4						21	180	Am.	A	A
P1	150.0	0.300	60	0.20	K	7	140	MFI + Am.	M	I
P2						21	140	MFI	M	P
P3						7	180	MFI	M	P
P4						21	180	MFI + Quartz	M	I
Q1	87.5	0.225	40	0.15	K	7	140	MFI + Am.	M	I
Q2						21	140	MFI + Am.	M	I
Q3						7	180	MFI	M	P
Q4						21	180	MFI	M	P
R1	87.5	0.225	40	0.15	Na	7	140	MFI + Am.	M	I
R2						21	140	MFI	M	P
R3						7	180	MFI	M	P
R4						21	180	MFI	M	P

two different criteria, both based upon XRD results (see columns C1–C2 in Tables 1 and 2):

- Classification criterion 1: MFI-containing samples (class M, 34 samples), MFI-free samples (class A, 38 samples).
- Classification criterion 2: samples containing pure MFI (class P, 23 samples), samples containing impure MFI (class I, 15 samples), MFI-free samples (class A, 34 samples).

Finally, the obtained data-set containing experimental factors values and qualitative XRD responses for 72 syntheses (Tables 1 and 2) was inspected by using a multivariate classification method (stepwise linear discriminant analysis (LDA) described in Section 4),

in order to find out the factors that better discriminate the classes of materials.

Notice that the multiautoclave device was only employed to parallelise the crystallisation of the obtained mixtures (as known, hydrothermal treatment represents the bottleneck in zeolite synthesis, especially when long crystallisation times are considered); conversely, the preparation of the mixtures, the work-out of the samples and their XRD characterisation were run by using conventional laboratory equipment.

3. Experimental

3.1. Materials

Sodium hydroxide (Carlo Erba, RPE), potassium hydroxide (Carlo Erba, RPE), 1,4-dibromopentane (Fluka, purity >95%), 1-methylpiperidine (Lancaster, purity >97%), Sylobloc 47 (Grace, purity 99%) and aluminium-tri-isopropoxide (AiP, Fluka, purity >98%) were used as purchased.

3.2. Synthesis of the SDA

1-Methyl-1,4-tetramethylen-bis(*N*-methylpiperidinium)-dihydroxide was synthesised according to the following procedure: 0.8 mol of 1,4-dibromopentane and 380.0 g of ethyl alcohol were mixed in a three-necked flask under vigorous stirring. 0.4 mol of 1-methylpiperidine was added dropwise over a period of 1 h and the mixture was refluxed until the formation of a clear yellow solution (normally after 4 h). After cooling at room temperature, the solution was concentrated in a rotary evaporator to obtain a very high density residue. The yield was almost quantitative and the purity, determined by ^{1}H and ^{13}C NMR, was >92%.

Before its use in the hydrothermal syntheses, the di-bromide salt was dissolved in demineralised water and exchanged into the hydroxide form by

Fig. 2. Multiautoclave device utilised during explorative zeolite synthesis.

electrodialysis. The resulting solution was concentrated in a rotary evaporator and the OH^- concentration determined by titration.

3.3. Zeolite synthesis

NaOH or KOH, AiP and the SDA were dissolved in demineralised water and the resulting solution was heated at 70–80 °C. Then Sylobloc 47 was added gradually under vigorous stirring, resulting in a 30.0 g mixture which was aged for 4 h, cooled at room temperature and then divided into four 15 cm^3 stainless-steel autoclaves. The autoclaves were then inserted into the holder described in Section 3.4. The crystallisation conditions are reported in Tables 1 and 2 together with the molar ratios.

After crystallisation the autoclaves were cooled to room temperature with cold water. The solid products were collected by filtration, repeatedly washed with demineralised water and finally dried overnight at 150 °C.

3.4. Multiautoclave device description

Fig. 2 shows the multiautoclave device employed for hydrothermal syntheses, inserted into the conventional oven used during experimental runs. It consists into a mechanically oscillated holder (a particular of which is illustrated in Fig. 3), able to carry a maximum of 39 autoclaves, each having an internal volume of 15 cm^3 (a single autoclave is depicted in Fig. 4). Both the autoclaves and the holder are made by stainless steel.

3.5. XRD characterisation

The XRD patterns were collected with Ni-filtered Cu Kα radiation ($\lambda = 1.54178$ Å) on a Philips X'Pert vertical diffractometer equipped with a pulse height analyser and a secondary curved graphite-crystal monochromator. Data were collected in the range $5 \leq 2\theta^\circ \leq 53$ with a 0.05° 2θ-step and 5 s per step.

4. Data analysis

The data analysis was performed with the software STATISTICA, version 5 for Windows [12].

The experimental variables inspected by means of a factorial design are varied independently one to each other (factorial designs are *orthogonal* by definition). The absence of statistical correlation among the factors guarantees independent estimations of the effect of each variable on the obtained response, apart from the chosen data analysis methodology. The experimental strategy adopted in this work corresponds to the combination of two factorial designs, one considering the crystallising mixture preparation variables (the molar ratios SiO_2/Al_2O_3 = SA, nitrogen/SiO_2 = NS, ME/SiO_2 = MS, H_2O/SiO_2 = HS and the kind of

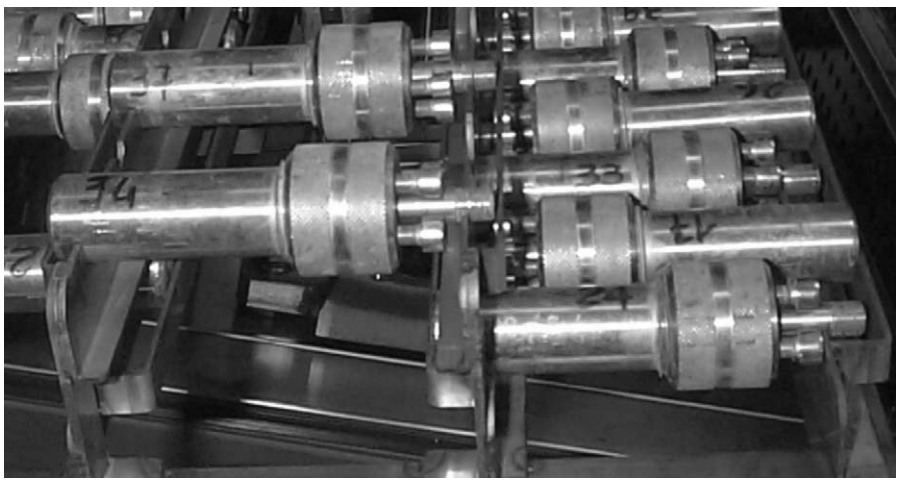

Fig. 3. Particular of the oscillating holder.

Fig. 4. Miniaturised 15 cm^3 autoclave (a 250 cm^3 one and one Euro coin are reported for comparison).

the alkali metal counterion, ME) and the other involving the crystallisation parameters (the crystallisation time, TI, and the crystallisation temperature, TE). The correlation matrix reported in Table 3 confirms that no correlation among the seven inspected experimental factors exists (notice that the statistical correlation index $\rho_{i,j}$ is always comprised between −1 and 1; the minimum correlation between two variables, namely i and j, is expressed by values of correlation index near to zero).

A qualitative response (from XRD) identifying the type of synthesised materials was obtained from each experimental run: for this reason the relation between responses and factors was explored by means of a multivariate supervised pattern recognition method. Specifically, linear discriminant analysis was employed. Linear discriminant analysis (LDA) is a statistical multivariate classification procedure that renders a number of orthogonal linear discriminant functions equal to the number of categories minus one. Each linear discriminant function is obtained as linear combination of the original variables. The method maximises the variance between categories and minimises the variance within categories [9,12]. In order to allow fast identification of the most discriminating factors, the LDA procedure was coupled to a stepwise-forward variable selection algorithm [12]. For each of the two ranking criteria described in the Introduction, the performances of the LDA procedure, in correspondence of the selected factors, were evaluated by analysing the corresponding classification matrix, which shows the number of samples that were correctly classified (along the matrix diagonal) and those that were misclassified. For each classification matrix the observed classifications are reported along the rows while the computed ones are reported along the columns.

Table 3
Correlation matrix computed for the studied seven factors

	SA	NS	HS	MS	ME	TI	TE
SA	1	0	0	0	0	0	0
NS	0	1	0	0	0	0	0
AQ	0	0	1	0	0	0	0
HS	0	0	0	1	0	0	0
ME	0	0	0	0	1	0	0
TI	0	0	0	0	0	1	0
TE	0	0	0	0	0	0	1

5. Results and discussion

Table 4 illustrates the classification matrix obtained for the first ranking criteria (MFI-containing samples, M, MFI-free samples, A). Notice that the

Table 4
Classification matrix obtained by adopting stepwise linear discriminant analysis as classification method and SA as discriminant variable (class A = MFI-free samples; class M = samples containing MFI)

	A	M
A	29	5
M	3	35

Table 5
Classification matrix obtained by adopting stepwise linear discriminant analysis as classification method and SA as discriminant variable (class A = MFI-free samples; class P = samples containing pure MFI, class I = samples containing impure MFI)

	A	P	I
A	29	5	0
P	6	17	0
I	5	10	0

Table 6
Classification matrix obtained by adopting stepwise linear discriminant analysis as classification method and SA, ME, MS, TE, HS as discriminant variables (class A = MFI-free samples; class P = samples containing pure MFI, class I = samples containing impure MFI)

	A	P	I
A	29	5	0
P	4	15	4
I	5	6	4

factor selected by the LDA stepwise algorithm (the SiO_2/Al_2O_3 = SA molar ratio) allows an excellent classification of the samples (about 90% of the samples are correctly classified).

Tables 5 and 6 represent the classification matrices obtained for the second ranking criteria (samples containing pure MFI, P, samples containing impure MFI, I, MFI-free samples, A). It is evident that the classes of samples respectively containing impure MFI and pure MFI are not well separated even if the algorithm is allowed to select more factors. In other words, in the considered experimental domain and in presence of the studied SDA agent, the SiO_2/Al_2O_3 molar ratio discriminates between a region rich in amorphous materials and a region where the formation of MFI zeolite is favoured, apart from the values set for the other six factors. In particular, by observing the results reported in Tables 1 and 2 it is evident that most of MFI-containing samples were obtained for $SiO_2/Al_2O_3 \geq 87.5$.

6. Conclusions

The effectiveness of multivariate methods applied to explorative zeolite synthesis (performed by using a multiautoclave device) has been successfully tested. Specifically, the qualitative results of 72 syntheses, planned according to a multivariate experimental design strategy, were analysed by stepwise linear discriminant analysis. The obtained results show clearly that, in presence of 1-methyl-1,4-tetramethylen-bis(*N*-methylpiperidinium)-dihydroxide as structure directing agent, the SiO_2/Al_2O_3 synthesis molar ratio discriminates between a region rich in amorphous materials and a region where the formation of MFI zeolite is favoured, independently on the values set for the other studied factors (specifically, nitrogen/SiO_2, ME/SiO_2, H_2O/SiO_2 molar ratios, kind of alkali metal counterion, time and temperature of crystallisation).

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