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Tailored synthesis of organized mesoporous aluminas prepared by non-ionic surfactant templating using a Box-Wilson CCF design

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Abstract

Organized mesoporous aluminas (OMA) are materials that present interesting properties as catalytic supports in reactions in which bulky molecules are involved. In this work, a number of OMA were prepared using a non-ionic structure directing agent (a tri-block co-polymer). The study of the quantitative influence of some OMA synthesis conditions (water aluminium ratio ($H_2O:Al$), ageing temperature (T_{ag}), and calcination heating rate (r_{cal})) on the resulting OMA textural properties (specific surface area (S_{BET}), pore volume (V_p) and average pore diameter (APD)) was carried out using a Box-Wilson Central Composite Design Face Centred (CCF, $\alpha:\pm 1$). The models obtained provided a satisfactory adjustment of the experimental data. $H_2O:Al$ was found to be the most

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influencing model term. The influence of T_{ag} and r_{cal} interactions on S_{BET} and V_p was found to be significant. Representative OMA with well differentiated pore size distributions were characterized by N_2 adsorption, XRD and TEM.

Keywords: Organized mesoporous alumina, non ionic surfactants, experiment design

1. Introduction

Organized mesoporous aluminas (OMA) have recently attracted the attention of the scientific community due to their interesting textural properties, such as large surface areas, tuned pore size diameter and various surface properties which may vary depending on their specific synthesis procedure [1]. These characteristics make these materials promising candidates as support in catalytic processes in which large molecules are involved, such as hydrotreating of heavy oil fractions. Available mesoporosity in catalysts used in these processes is of paramount importance in order to facilitate the diffusion of reactants and products by avoiding steric hindrance as well as to reduce catalyst deactivation by coke [2]. Mesoporous materials favour the access of asphaltenes from heavy oils into the catalytic structure, promoting hydrodeasphalting (HDA) and hydrodemetalisation (HDM) reactions[3].

The methods developed to synthesise OMA are based on the use of various structure-directing agents, which can be classified into cationic, anionic or neutral, as reviewed in [1, 4]. The first report on the method of neutral or non ionic surfactant, published by Bagshaw et al. [5, 6], was based in the hydrolysis of an alkoxide (tri-sec-butoxyaluminium) employing structure director agents poly(ethylene oxide) (PEO) based diblock (Tergitol, Igepal, Triton) or triblock co-polymers (Pluronic 64L). The non ionic templating procedure has successfully been applied for OMA synthesis using a number of different aluminium precursors, such as other alkoxides (sec butoxide) [6-8], nitrate [9], chloride [9-11] and Al_{13} Keggin oligocation [8, 9].

Several studies can be found in the literature addressing the effect of the preparation conditions on the textural parameters of the synthesised aluminas. Focusing on the non ionic templating method, alongside the structure directing agent and the aluminium

source used, the synthesis process variables under study are commonly $\text{H}_2\text{O}:\text{Al}$ ratio (also called hydrolysis ratio), ageing temperature and calcination temperature program (final calcination temperature and dwell time). The effect of $\text{H}_2\text{O}:\text{Al}$ ratio was shown to be determinant in the obtained average pore diameter (APD) [12]. High hydrolysis ratios led to an increase of the $\text{H}_2\text{O}:\text{co-solvent}$ ratio. As a consequence, the micelle radii augments [13] and thus, an increase in the pore size was observed [12]. However, no definitive trend could be inferred between the hydrolysis ratio and specific surface area (S_{BET}) and pore volume (V_p).

The study of the influence of the ageing temperature from 25 to 90 °C [7] revealed that V_p decreased with increasing temperature, although it was not significantly correlated to the final S_{BET} . Pores sizes were shifted to smaller diameters at higher temperatures. The same results were observed in [9] with an increase in ageing temperature from 45 to 90 °C.

An increase in final calcination temperatures (from 500 to 800 °C) led to a decrease in S_{BET} and no significant change in the APD or V_p [7]. Other authors also showed a decrease in S_{BET} when calcination temperature was increased [14, 15]. Calcination times of 2 h were needed to stabilise S_{BET} [7]. In the same work, it was shown that prolonged calcination times at 650 °C (up to 32 h) did not affect negatively the structural stability of the prepared mesoporous aluminas.

The study of the influence of the calcination heating rate has attracted considerably less attention, even though this treatment, aimed at surfactant removal, might have an enormous influence on the final textural properties, as pointed out in [1]. This was attributed to the fact that surfactant combustion is highly exothermic and might cause a collapse of the pore structure. Calcination heating rates lower than 5 °C·min⁻¹ are

commonly used in the non ionic templating method [1], although to the best of our knowledge, the influence of the variation of heating rate in the textural properties of OMA prepared by the non ionic templating method has not been studied.

Despite the number of works found in literature, a systematic approach using statistical tools is highly recommended in order to elucidate the effect of the synthesis variables studied on the final properties of the aluminas and to determine the possible synergies between the studied variables. Recently, statistical tools have been used to address the influence of some synthesis variables on the textural properties of the OMA prepared using cationic structure directing agent [16]. Results showed that the main factor influencing the textural properties of the synthesised aluminas was $H_2O:Al$ ratio.

In this work, the quantitative influence of some OMA synthesis conditions (water aluminium ratio ($H_2O:Al$), ageing temperature (T_{ag}), and calcination heating rate (r_{cal})) was studied by its effects on the textural properties (S_{BET} , V_p and APD) using a non-ionic structure directing agent (a tri-block co-polymer) . The manuscript is divided into two sections: in the first one, the influence of the different synthesis conditions on the textural properties is studied and correlated using statistical tools. An augmented model following a Box-Wilson Central Composite Design Face Centred (CCF, $\alpha:\pm 1$) was implemented, providing a satisfactory adjustment of the experimental data obtained. Secondly, a thorough study about the textural and structural properties of some representative OMA synthesised is presented.

2. Experimental

2.1 Materials and Synthesis of OMA

Aluminum isopropanoxide, Pluronic F127 ((EO)₁₀₆(PO)₇₀(EO)₁₀₆) and propanol were purchased from Sigma Aldrich. Absolute ethanol was purchased from VWR UK.

The synthesis of the different aluminas was adapted from a protocol for mesoporous alumina synthesis available in the literature [12]. For each sample of alumina, 50 g of aluminum isopropanoxide were dissolved in 100 mL of ethanol and 100 mL of propanol, while stirring the mixture at 50 °C. When it was homogeneous, 34.7 g of non-ionic surfactant (Pluronic F127) were added and when it was dissolved, water was added to create an emulsion. The H₂O:Al molar ratios studied were 2:1, 11:1 and 20:1, with 8.8, 48.5 and 88 mL of distilled H₂O added in each case, respectively. An additional 15 mL and 13 mL of ethanol and propanol, respectively, were dissolved. The mixture was allowed to age for approximately 22 hours at an ageing temperature of either 20 °C, 50 °C or 80 °C. Then it was vacuum filtered to remove most of the solvents, obtaining a wet paste. Afterwards it was dried and calcined in a muffle furnace with flowing air with the following temperature dwells: 150 °C for 1 hr, 350 °C for 2 hr and finally 550 °C during 4 hr. The temperature ramps during the drying and calcination steps used were 1, 5.5 and 10 °C·min⁻¹.

2.2 Catalyst characterisation techniques

The textural properties were measured by N₂ adsorption at 77 K in a Micromeritics Tristar apparatus. The specific surface areas and pore volumes were calculated by applying the BET method to the respective N₂ adsorption isotherms and the average pore diameter and the pore size distribution were calculated with the BJH method based on the adsorption-desorption branch of the N₂ isotherm.

Transmission Electron Microscopy (TEM) was carried out on a Jeol 2011 microscope equipped with a LaB₆ gun and operating at 200 kV. The samples were firstly finely grounded, dispersed in ethanol and a drop of solution was then deposited on a classical TEM copper grid, previously covered by a lacey amorphous carbon film. Examination of the sample was focused on parts of the samples lying across the holes to obtain information free from the contribution of the supporting carbon film.

Powder X-ray diffraction (XRD) patterns of OMA were acquired in a PANalytical diffractometer equipped with a Ni-filtered Cu K α (λ : 0.154 nm) and a secondary graphite monochromator, using a θ -2 θ configuration. Low angle diffraction with a 2 θ range of 0.8-3° was performed. Counts were accumulated every 0.01° and the step time was 3 s. Wide angle scans were performed at a 2 θ range of 10-80°, step of 0.01° and step time 5s.

2.3 Experimental design and statistical analysis

The study of the quantitative influence of the alumina synthesis conditions (H₂O:Al, T_{ag}, r_{cal}) on the alumina textural properties (S_{BET}, V_p and APD) was carried out using an experimental design. This method is appropriate to study the influence of the experimental variables on the textural properties by applying an empirical modelling technique. Additionally, it is possible to evaluate the interaction between the different synthesis conditions, reducing the number of experiments and optimising resources and time [17]. Firstly, a full factorial design with 3 factors, named H₂O:Al ratio (X_{WA}), ageing temperature (X_T) and calcination heating rate (X_R), and two levels (+1 and -1) was carried out. The specific surface area (Y_S), the pore volume (Y_V) and the average

pore diameter (Y_D) were the studied response variables since they are among the most important textural properties of catalytic supports. The selection of levels of the different factors was carried out on the basis of results obtained previously by other groups, as reviewed in [1]. This work is aimed at studying a wide range of values in order to obtain a high heterogeneity in the textural properties of the prepared aluminas. Therefore, $H_2O:Al$ ratio was varied between 2:1 (level -1) and 20:1 (level +1), the ageing temperature was modified between 20 (level -1) and 80 °C (level +1) and finally, the calcination heating rate was studied between 1 (level -1) and 10 °C·min⁻¹ (level +1). Samples 1-8 are within these variable values.

In order to analyse inherent variability, three repetitions of the central point were added to the design (samples 9-11). Due to significant curvature obtained after the full factorial design 2³, additional experiments were carried out to augment the model following a Box-Wilson Central Composite Design Face Centred (CCF, $\alpha:\pm 1$) (samples 12-17). In this work, only results obtained with the Box-Wilson CCF model are included. The experimental augmented matrix is presented in Table 1. The textural properties of OMA are also included.

The significance of each model term was determined by means of ANOVA analyses and using the mathematical software Design Expert 7.0.0 (State-Ease Inc). A model term is more significant when its coefficient estimate is larger and its p-value smaller. The factors that significantly affect each textural property were determined using a confidence level of 95% ($p_{value} \leq 0.05$).

3. Results and discussion

3.1. Influence of the preparation variables on the textural properties using statistical analysis

As previously mentioned, Table 1 shows the experimental synthesis conditions used to prepare the materials under study and the results derived from the N₂ adsorption characterization: S_{BET}, V_p and APD. It can be observed that the synthesised OMA provided a wide range of textural parameters, with S_{BET}, V_p and APD ranging from 298.7 to 393.1 m²·g⁻¹, from 0.935 to 1.678 cm³·g⁻¹ and from 8.1 to 17.9 nm, respectively. APD values obtained in this work are significant larger than those reviewed in [1] using the non-ionic templating method. S_{BET} and V_p were in the range of values reported despite the significant variations in the conditions and materials used for the synthesis.

A quadratic model (1) was used to evaluate the effect of the synthesis conditions (X_{WA}, X_T and X_R) in the three response variables (Y_S, Y_V, Y_D) using a Box-Wilson CCF design. Model terms (X_{WA}, X_T, X_R, and theirs interaction factors) are included in the quadratic model as coded factors (-1/+1).

$$Y = a_0 + a_1X_{WA} + a_2X_T + a_3X_R + a_{12}X_{WA}X_T + a_{13}X_{WA}X_R + a_{23}X_TX_R + a_{11}X_{WA}^2 + a_{22}X_T^2 + a_{33}X_R^2 \quad (1)$$

3.1.1. Specific surface area

In Table 2, only the model terms that significantly affected Y_S are included together with their respective coefficient estimate, standard error and p-value. For the experimental range of factors studied, the most significant model term was X_{WA}. Additionally, some interaction factors as X_{WA}·X_T and X_T·X_R also affected Y_S

significantly. The adjustment of the experimental data to the quadratic model (which uses coded factors) resulted in the equation (2) (R^2 : 0.83).

$$Y_S = 333.7 - 21.49 \cdot X_{WA} - 13.15 \cdot X_{WA} \cdot X_T + 10.68 \cdot X_T \cdot X_R \quad (2)$$

Figure 1 shows the contour plots of the specific surface area (Y_S) as a function of X_T and X_R at three different X_{WA} . The highest Y_S values were obtained at the lowest X_{WA} (Figure 1a) in the region where X_T and X_R took their highest values, 80 °C and 10 °C·min⁻¹ respectively. These results are in total agreement with the experimental data since the highest S_{BET} was obtained for the alumina 5 (393.1 m²·g⁻¹), which was prepared under these synthesis conditions. The lowest Y_S values were reached at the highest X_{WA} (Figure 1c). However, in this case, the region corresponded to the highest values of X_T and the lowest values of X_R , 80 °C and 1 °C·min⁻¹, respectively. OMA 7 prepared under these particular conditions showed one of the lowest S_{BET} measured (312.7 m²·g⁻¹).

Analyzing the effect of X_T and X_R , it was observed that for the lowest X_{WA} studied (X_{WA} : 2) (Figure 1a), Y_S increased as the X_T did and finally reached its maximum value at the maximum values of X_T and X_R , as previously commented. According to this model, Y_S did not depend on X_R at X_T : 50 °C, since a straight contour was observed. However, at X_T lower than 50 °C, a decrease of Y_S is observed as X_R increased. The opposite effect was observed above 50 °C.

Figure 1b shows the contour plot of Y_S at the medium X_{WA} (X_{WA} :11). Due to the symmetry found in the results, the maximum values of Y_S were reached at both the lowest and the highest values of X_T and X_R .

Finally, when X_{WA} was increased up to 20 (Figure 1c), the opposite behaviour as respect to that in Figure 1a was observed. In this case, the maximum value of Y_S was obtained at the lowest values of X_T and X_R , and as X_T increased, a decrease in Y_S was observed.

In summary, a wide range of Y_S values were obtained depending on the alumina preparation conditions. The Y_s ranged approximately between 300 and 400 $m^2 \cdot g^{-1}$ and the most influential variable was X_{WA} . Y_s was found to increase as X_{WA} decreased. However, both X_T and X_R affected slightly the Y_S for a given X_{WA} .

3.1.2. Pore Volume

The model terms that significantly affected Y_V are listed in Table 3 together with its coefficient estimate, standard error and p-value. In this case, the most significant model term was X_{WA}^2 , followed by X_{WA} and $X_T \cdot X_R$. The adjustment of the experimental data to the model resulted in equation (3) (R^2 : 0.84).

$$Y_V = 1.520 + 0.16 \cdot X_{WA} + 0.096 \cdot X_T \cdot X_R - 0.33 \cdot X_{WA}^2 \quad (3)$$

In Figure 2, Y_V is represented as a function of the X_{WA} at the medium X_T and X_R (the same trend was observed regardless the values of X_T and X_R). Curvature was well appreciated and the maximum value of Y_V was obtained at approximately the intermediate X_{WA} ($X_{WA} \approx 11$). Besides this, the minimum value of Y_V was obtained at the lowest X_{WA} (X_{WA} : 2) and a medium value of Y_V was obtained at the highest X_{WA} (X_{WA} : 20).

Despite the clear effect of X_{WA} on Y_V , the effect of the interaction term $X_T \cdot X_R$ has to be taken into account and it is represented in Figure 3 at three different X_{WA} . The same trend as in Figure 2 was observed. When X_{WA} : 2 (Figure 3a), Y_V had the lowest values,

ranging from 0.961 to 1.089 cm³·g⁻¹. When the value of X_{WA} was increased to 11 (Figure 3b), Y_V reached the maximum values (1.451-1.580 cm³·g⁻¹). Finally, when X_{WA}: 20 (Figure 3c), Y_V values slightly decreased to 1.289-1.417 cm³·g⁻¹. In all cases, a symmetric trend was detected, observing two maxima and two minima in values of Y_V for each X_{WA}. These points were located on opposite corners. The maximum values of Y_V were observed when both X_R and X_T were in the same level (+1 or -1) and the minima were observed when they were in different levels. For example, in Figure 3a, when X_T was 80 °C (level +1) and X_R was 10 °C·min⁻¹ (level +1) a maximum value of Y_V was reached. However, for X_T: 80 °C (level +1) and X_R: 1 °C·min⁻¹ (level -1), a minimum value was obtained.

3.1.3. Average pore diameter

Y_D was strongly influenced by X_{WA}. Both, X_{WA} and X_{WA}² significantly affected Y_D. Each model term along its coefficient estimate, standard error and p-value are presented in Table 4. In this case, interaction terms were found to be no significant (p-value > 0.05) and therefore have not been considered. The adjustment of the experimental data to the model resulted in equation (4) which only includes X_{WA} effects (R²: 0.76).

$$Y_D = 16.4 + 2.57 \cdot X_{WA} - 3.77 \cdot X_{WA}^2 \quad (4)$$

In this case, only a one-factor figure is plotted since only X_{WA} significantly affected Y_D. In Figure 4, Y_D is represented as a function of X_{WA} at the medium X_R and X_T (the same trend was observed regardless of these synthesis conditions for the other X_W studied). Again, a significant curvature was observed. According to the statistical model, the maximum values of Y_D were reached at values slightly above the medium value of X_{WA} (≈14:1). In addition, the model predicted that higher Y_D values are obtained at high values of X_{WA} (20:1) than at low values (2:1).

3.2. Textural and structural properties

Four aluminas presenting well differentiated APD were selected to gain more insight into their textural and structural properties as well as their porous architecture. Thus, the characterization of OMA 3 (8.1 nm), 2 (11 nm), 10 (15.5 nm) and 5 (17.9 nm) by N₂ adsorption, TEM and XRD is presented in the following section.

3.2.1. N₂ adsorption

Figure 5 shows the N₂ isotherms of the OMA under consideration. They presented specific surface area values in the range 339.8-374.2 m²·g⁻¹. Sample 3 presented the highest S_{BET} among the four aluminas under consideration (374.2 m²·g⁻¹), followed by the alumina 5 (353.5 m²·g⁻¹). Aluminas 2 and 10 showed similar values (338.6 and 339.8 m²·g⁻¹, respectively), being the lowest values in S_{BET} among all 4 samples under study.

N₂ adsorption-desorption isotherms showed a relatively steep increase in the adsorbed amount starting at P/P₀ about 0.6-0.8. Sample 3 presented a type IV isotherm, which corresponds to a mesoporous material, and a hysteresis of type H1, typically assigned to capillary condensation taking place in mesopores [18]. The isotherm ended with a nearly horizontal plateau indicating a relative narrow pore size distribution (PSD), as discussed below. On the other hand, aluminas 2, 10 and 5 showed a N₂ adsorption-desorption isotherms of type IV with a H3 hysteresis loop, which can be assigned to crystalline metal oxide aggregates of slit-like shape [18]. The adsorption at high P/P₀ pointed out at the presence of a larger pore size and a wider PSD as compared to the alumina 3. A transition in the shape of the isotherms between the samples 3 and 5 was observed. This fact is related to the differences in PSD, as observed in the inset on Figure 5. Sample 3 showed a narrow PSD centred around 8 nm, as it was anticipated

from the plateau in the isotherm. The maximum in the PSD for the alumina 2 was also centred at ca. 8 nm, although the appearance of wider pores shifted the APD towards higher values (11 nm). Aluminas 10 and 5 presented similar PSD curves centred at ca. 17 nm, although sample 5 presented a larger fraction of larger pores than alumina 10. This promoted a shift of the APD to larger values as compared to the alumina 10 (from 15.5 nm to 17.9 nm), similar to what happened with alumina 2.

3.2.2. TEM study

A TEM study was carried out in order to elucidate the differences in the structure and pore architecture of the prepared OMA. Thus, Figure 6 shows two micrographs at different magnifications (10,000X and 100,000X) for each of the four aluminas under study. The low magnification TEM image of sample 3 (Figure 6a) shows a typical worm-like motif, typically observed for self-assembled aluminas using the surfactant templating method [6, 19]. The packing of the channel system appeared to be random, therefore indicating the non-existence of long-range channel packing order. Figure 6b shows that alumina 3 was formed by an intricate mixture of short corrugated platelets as previously reported by other authors [12, 15]. Some of these platelets adopted a rounded morphology, thus providing the relative narrow PSD observed from the N₂ adsorption study (Figure 5).

The worm like motif was fairly retained in the OMA 2 (Figure 6c), although high magnification (Figure 6d) provided evidence of the enlargement of the platelets when compared to sample 3. This fact was more discernible as the APD of the OMA increased. For instance, in the low magnification TEM images of aluminas 10 and 5 (Figures 6e and 6g, respectively) the edge of the platelets could clearly be observed forming slit-shaped mesopores. On the other hand, the high magnification micrograph

of sample 10 (Figure 6f) confirmed the presence of long straight platelets of ca. 20-40 nm length. Figure 6h (high magnification micrograph of alumina 5) shows the presence of platelets of ca. 60-80 nm long.

Thus, it can be concluded that the APD increased as the platelets became larger and less rounded, giving rise to a wider pore size distribution. No discernible pattern regarding the wall thickness of the platelets, taking values in the 2-3 nm range, could be inferred from the TEM study. As the platelets became larger, a transition between a wormlike motif to lamellar or slit-like was observed, as previously reported in [9]. This observation confirms the interpretation of the N₂ adsorption-desorption isotherms shown in Figure 5, in which two well-differentiated shapes were observed.

As further discussed below, H₂O:Al ratio played an important role in the length of the platelets. Thus, this TEM study revealed that larger and more lamellar platelets were obtained at medium (11:1) and high (20:1) H₂O:Al ratios (samples 10 and 5, respectively), therefore explaining the difference in APD observed.

3.2.3 XRD study

Figure 7a shows the wide angle XRD diffractograms of the studied aluminas. Samples 2 and 3 showed no diffraction lines characteristic of an ordered oxide phase, which is indicative of mesostructure with amorphous framework walls [9]. Three broad, low intensity peaks that are typically assigned to gamma alumina (38°, 46° and 67°) were observed in the aluminas with wider pore size distribution (5 and 10). This suggests the appearance of some degree of ordering, although the framework walls can still be considered amorphous due to the poor reflection obtained. The slight differences in crystallinity may be related to the H₂O:Al ratio used. It was reported [12, 20, 21] that a high H₂O:Al ratio strongly influences the aluminium phases in the final products,

leading to more crystalline materials. In this case, aluminas 5 and 10 were prepared with $\text{H}_2\text{O}:\text{Al}$ ratios of 11 and 20, respectively, as compared to the hydrolysis ratio of 2 used to synthesise the aluminas 2 and 3.

Small angle XRD diffractograms are shown in Figure 7b. The absence of broad reflections in the small angle region near 2° indicates the irregularity in the separation between single channels [6]. However, the TEM study revealed that alumina 3 showed a worm like pore packing in which, to some extent, uniformity between pores can be inferred (Figure 6a). In fact, several examples of similar worm-like structures, which present characteristic reflections at low angles, can be found in the literature [6, 9, 19, 22]. This apparent discrepancy in the results of this work can be tentatively explained attending to the larger APD shown by OMA used in this work, as compared to the related structures reported in the studies previously mentioned. This causes a shift in the expected broad reflection to 2θ value lower than 1° , where X-ray diffraction cannot be measured with sufficient accuracy. Similar low angle XRD plots for aluminas showing wide pores (higher than 8 nm) as those found in this work can be found in [21].

4. Discussion

The non ionic templating method using Pluronic F127 as surfactant and aluminum isopropanoxide as aluminum source was used to prepare a number of aluminas varying the synthesis conditions. A Box-Wilson Central Composite Design Face Centred (CCF, $\alpha:\pm 1$) was used to model the influence of the synthesis conditions on the textural properties of the as prepared OMA.

Some differences were observed comparing Y_S , Y_V and Y_D models. In all cases, the model showed a strong dependence on model term X_{WA} (or X_{WA}^2). In the case of Y_S and Y_V models (equations 2 and 3, respectively), the influence of X_T and X_R interaction was significant since they modified the response values. In addition, the quadratic term (X_{WA}^2) contributed significantly to the model curvature of Y_V and Y_D models. This led to the presence of two maximum and two minimum values of the corresponding response variables in the contour plots (Figure 3 for Y_V , figure not included for Y_D), regardless the value of X_{WA} (2:1, 11:1 or 20:1). Furthermore, the effect of X_{WA} on the Y_V and Y_D models was very similar.

Therefore, $H_2O:Al$ can be considered as the most determinant synthesis variable since it is the only term that appeared (as X_{WA} , X_{WA}^2 and/or $X_{WA} \cdot X_T$) in the three models (equations 2-4) obtained. Characterisation data shown in Section 3.2. revealed the paramount effect of $H_2O:Al$ on the OMA structure. The TEM study showed that larger and more lamellar platelets were obtained at medium (11:1) and high (20:1) $H_2O:Al$ ratios (samples 10 and 5, respectively), resulting in marked variations in the APD, as N_2 adsorption study showed. The analysis of data in Table 1 revealed a clear trend for V_p and APD as a function of the $H_2O:Al$ ratio. Thus, the highest values of V_p and APD were mainly obtained at medium (11:1) $H_2O:Al$ ratio, and in less extent at high (20:1) ratio. However, no clear trend can be observed between $H_2O:Al$ ratio and S_{BET} , despite the fact that highest S_{BET} values were obtained at low (2:1) $H_2O:Al$ ratio. This fact is probably due to the presence of two interaction factors ($X_{WA} \cdot X_T$ and $X_T \cdot X_R$) in the Y_S model (equation 2). The effect of $H_2O:Al$ ratio in the APD was previously addressed using the non-ionic templating method, while no clear relationship between $H_2O:Al$ ratio and the S_{BET} was reported [12], similarly to the results here reported. However, in

this work a clear relationship between H₂O:Al ratio and V_p was found, as opposed to results published in [12].

T_{ag} effect was found to be less important than H₂O:Al ratio. No significant effects were detected for the single X_T factor in the equations presented in section 3.1. However, interactions factors including T_{ag} effect appeared as X_{WA}·X_T and X_T·X_R in the Y_S model and as X_T·X_R in Y_V equation. Neither the single factor (X_T) nor the interaction factor involving T_{ag} were included on the Y_D equation. Since the single factor (X_T) was not significant (p-value > 0.05) for any textural property and the T_{ag} effect was influenced by other factors, no obvious trend as a function of T_{ag} can be inferred from data in Table 1. However, a decrease of the V_p and APD as T_{ag} increased was reported [7, 9]. In our case, V_p was influenced by T_{ag} but its effect depended on the heating temperature rate value due to the interaction factor (X_T·X_R) included in the Y_V equation, while no significant influence of the T_{ag} on the APD was observed.

The influence of the variation of r_{cal} in the textural properties of OMA prepared by the non ionic templating method has received little attention. High r_{cal} may cause structure collapse since surfactant combustion is highly endothermic [1]. A r_{cal} lower than 5°C·min⁻¹ is commonly used, as reviewed in [1]. In this work, r_{cal} appeared as an interaction factor (X_T·X_R) in Y_S and Y_V models. r_{cal} effect was found to be less significant than H₂O:Al ratio effect, and no clear trend was observed for any textural property. However, it is worth mentioning that high values of S_{BET} (393.1 m²·g⁻¹, OMA 4), V_p (1.574 cm³·g⁻¹, OMA 15) and APD (17.2 nm, OMA 15) were obtained when using a r_{cal} of 10°C·min⁻¹, providing evidence that no structure collapse occurred when high calcination heating rates were used.

4. Conclusions

A number of OMA were prepared using the non-ionic templating method and a tri-block co-polymer as structure directing agent. An experimental design based on a Box-Wilson Central Composite Design Face Centred (CCF, $\alpha:\pm 1$) was employed to study the effect of some synthesis conditions ($H_2O:Al$, T_{ag} and r_{cal}) on the resulting OMA textural properties (S_{BET} , V_p APD). The models obtained provided a satisfactory adjustment of the experimental data. $H_2O:Al$ was found to be the most determinant synthesis variable since it influenced significantly S_{BET} , V_p and APD. No significant effects were detected for the single T_{ag} or r_{cal} terms. However, interactions factors including these terms modified S_{BET} and V_p values. Characterization of some representative OMA showed the formation of platelets of different length upon the synthesis conditions, giving rise to different pore size distributions. The statistical analysis carried out in this work provided useful information that allows the tailored synthesis of OMA with well differentiated textural properties.

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References

- [1] C. Márquez Alvarez, N. Zilkova, J. Pérez-Pariente, J. Čejka, *Catal. Rev.* 50 (2008) 222-286.
- [2] C. Song, T. Nihonmatsu, M. Nomura, *Ind. Eng. Chem. Res.* 30 (1991) 1726-1734.
- [3] J. Ancheyta, M.S. Rana, E. Furimsky, *Catal. Today* 109 (2005) 3-15.
- [4] J. Čejka, *Appl. Catal. A, Gen.*, 254 (2003) 327-338.
- [5] S.A. Bagshaw, E. Prouzet, T.J. Pinnavaia, *Science* 269 (1995) 1242-1244.
- [6] S.A. Bagshaw, T.J. Pinnavaia, *Angew. Chem. Int. Edit.* 35 (1996) 1102-1105.
- [7] W. Deng, P. Bodart, M. Pruski, B.H. Shanks, *Micropor. Mesopor. Mat.* 52 (2002) 169-177.
- [8] Z. Zhang, R.W. Hicks, T.R. Pauly, T.J. Pinnavaia, *J. Am. Chem. Soc.* 124 (2002) 1592-1593.
- [9] Z. Zhang, T.J. Pinnavaia, *J. Am. Chem. Soc.* 124 (2002) 12294-12301.
- [10] P. Yang, D. Zhao, D.I. Margolese, B.F. Chmelka, G.D. Stucky, *Nature* 396 (1998) 152-155.
- [11] C. Boissière, L. Nicole, C. Gervais, F. Babonneau, M. Antonietti, H. Amenitsch, C. Sanchez, D. Grosso, *Chem. Mat.* 18 (2006) 5238-5243.
- [12] C. Lesaint, W.R. Glomm, Ø. Borg, S. Eri, E. Rytter, G. Øye, *Appl. Catal. A Gen.* 351 (2008) 131-135.
- [13] P. Alexandridis, L. Yang, *Macromolecules* 33 (2000) 5574-5587.
- [14] W. Zhang, *Chem. Commun.* (1998) 1185-1186.
- [15] -, C. Márquez-Alvarez, E. Sastre, J. Pérez-Pariente, *Micropor. Mesopor. Mat.* 44-45 (2001) 203-210.
- [16] M. Akia, S.M. Alavi, M. Rezaei, Z.-F. Yan, *Micropor. Mesopor. Mat.* 122 (2009) 72-78.
- [17] G.E.P. Box, J.S. Hunter, W.G. Hunter, *Statistics for Experimenters: Design, Innovation, and Discovery*, Jhon Wiley & Sons, New Jersey, 2005.
- [18] K.S.W. Sing, D.H. Everett, R.A.W. Haul, L. Moscou, R.A. Pierotti, J. Rouquerol, T. Siemieniowska, *Pure Appl. Chem.* 57 (1985) 603-619.
- [19] J. Čejka, P.J. Kooyman, L. Veselá, J. Rathouský, A. Zúkal, *Phys. Chem. Chem. Phys.* 4 (2002) 4823-4829.
- [20] Z. Shan, J.C. Jansen, W. Zhou, T. Maschmeyer, *Appl. Catal. A Gen.* 254 (2003) 339-343.
- [21] H.C. Lee, H.J. Kim, C.H. Rhee, K.H. Lee, J.S. Lee, S.H. Chung, *Micropor. Mesopor. Mat.* 79 (2005) 61-68.
- [22] R. Zhao, F. Guo, Y. Hu, H. Zhao, *Micropor. Mesopor. Mat.* 93 (2006) 212-216.

Table 1. Summary of the synthesis conditions used and textural properties of the synthesized OMA.

Sample	H ₂ O:Al	T _{ag} (°C)	R _{cal} (°C·min ⁻¹)	S _{BET} (m ² ·g ⁻¹)	V _p (cm ³ ·g ⁻¹)	APD* (nm)
1	2	20	1	392.4	1.037	9.2
2	2	20	10	338.6	0.935	11.0
3	2	80	1	374.2	0.954	8.1
4	2	80	10	393.1	1.051	9.2
5	20	20	1	353.5	1.678	17.9
6	20	20	10	341.2	1.215	12.0
7	20	80	1	312.7	1.297	15.4
8	20	80	10	313.1	1.406	16.0
9	11	50	5.5	345.0	1.529	15.5
10	11	50	5.5	339.8	1.501	15.5
11	11	50	5.5	340.0	1.572	17.6
12	2	50	5.5	335.7	1.18	12.1
13	11	20	5.5	319.4	1.434	15.3
14	11	50	1	314.2	1.566	17.7
15	11	50	10	329.2	1.574	17.2
16	11	80	5.5	310.4	1.421	16.1
17	20	50	5.5	298.7	1.202	13.9

*BJH model applied to the adsorption branch of the isotherms

Table 2.

Specific surface area (Y_s , $m^2 \cdot g^{-1}$)				Significant model terms that fit the evolution of the specific surface
Model term	Coefficient estimate ($m^2 \cdot g^{-1}$)	Standard error ($m^2 \cdot g^{-1}$)	p-value (-)	
X_{WA}	-21,49	2,97	< 0,0001	
$X_{WA} \cdot X_T$	-13,15	3,32	0,0022	
$X_T \cdot X_R$	10,68	3,32	0,0081	

area by means of analysis of variance.

Table 3. Significant model terms that fit the evolution of the pore volume by means of analysis of variance.

Pore volume (Y_V, $\text{cm}^3\cdot\text{g}^{-1}$)			
Model term	Coefficient estimate ($\text{cm}^3\cdot\text{g}^{-1}$)	Standard error ($\text{cm}^3\cdot\text{g}^{-1}$)	p-value (-)
X_{WA}	0,16	0,34	0,0004
$X_T\cdot X_R$	0,096	0,038	0,027
X_{WA}^2	-0,33	0,058	0,0001

Table 4. Significant model terms that fit the evolution of the average pore diameter by means of analysis of variance.

Average pore diameter (Y_D, nm)			
Model term	Coefficient estimate	Standard error	p-value
	(nm)	(nm)	(-)
X_{WA}	2,57	0,52	0,0003
X_{WA}^2	-3,77	0,88	0,0009

FIGURE CAPTIONS

Figure 1 Contour plots of S_{BET} as a function of T_{ag} and R_{cal} at three different $\text{H}_2\text{O}:\text{Al}$ ratio: 2:1 (a), 11:1 (b) and 20:1 (c).

Figure 2. V_p as a function of $\text{H}_2\text{O}:\text{Al}$ ratio (T_{ag} : 50°C and R_{cal} : $5.5^\circ\text{C}\cdot\text{min}^{-1}$)

Figure 3. Contour plots of V_p as a function of T_{ag} and R_{cal} at three different $\text{H}_2\text{O}:\text{Al}$ ratio: 2:1 (a), 11:1 (b) and 20:1 (c).

Figure 4. APD as a function of $\text{H}_2\text{O}:\text{Al}$ ratio (T_{ag} : 50°C and R_{cal} : $5.5^\circ\text{C}\cdot\text{min}^{-1}$)

Figure 5. N_2 isotherm of OMA 2, 3, 5 and 10. Inset: pore size distribution calculated using desorption branches of the isotherm based on BJH model.

Figure 6. Low (10.000X) and high (100.000X) magnification TEM images of samples 3 (a and b), 2 (c and d), 10 (e and f) and 5 (g and h).

Figure 7. Wide angle (a) and low angle (b) diffractograms of OMA 2, 3, 5 and 10.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7