Chemical Engineering Journal 158 (2010) 325–332

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Deposition of SBA-15 layers on Fecralloy monoliths by washcoating

Hermicenda Pérez[a,*], Paloma Navarro[b], Mario Montes[b]

[a] División Académica de Ciencias Básicas, Universidad Juárez Autónoma de Tabasco, Km 1 Carretera Cunduacán-Jalpa de Méndez, A.P. 24, C.P., 86690 Cunduacán, Tabasco, Mexico
[b] Department of Applied Chemistry, University of the Basque Country (UPV-EHU), Apdo. 1072, 20080 San Sebastián, Spain

ARTICLE INFO

Article history:
Received 22 September 2009
Received in revised form 15 January 2010
Accepted 18 January 2010

Keywords:
SBA-15
Slurry
Viscosity
SBA-15 Washcoating
Metallic monoliths

ABSTRACT

Stable slurries or suspensions were prepared in order to carry out deposition of SBA-15 layers onto Fecralloy monoliths by washcoating. The suspensions presented an important evolution with ageing time under magnetic stirring, that consisted of a change in viscosity. This change was directly related to the abrasive effect of the magnetic stirring, and caused the breakdown of the big aggregates of the parent SBA-15 into rod-shaped units that became more and more irregular, and the slurries to become less viscous compared with the established usual trend. The viscosity was suitable for washcoating after 120 h of magnetic stirring. Although a clear macroscopic effect was observed, the mesoporous nature of the solid was preserved. The amount loaded and the adherence of the coatings depended on the formulation of the slurry. The best results were obtained when colloidal silica was used as a binder.

1. Introduction

Monolithic catalysts are widely used in processes such as purification of car exhaust gases, abatement of NO_x and catalytic combustion of VOCs [1]. The use of monolithic structures is a very good option due to the low-pressure drop associated with the high flow rates of these mentioned processes. The materials most used to construct the monolithic structure are ceramics and metals. In the case of metallic monoliths, these are usually manufactured by rolling or piling up alternate corrugated and flat thin sheets [2]. The malleability and easy to perforate and to cut properties of the metallic substrates make it possible to prepare many different and complicated forms adapted to the needs of each process. Many different metals and alloys have been proposed to manufacture these metallic monoliths, but a good mechanical, chemical and thermal stability, as well as a good surface adherence of the catalytic coating, is always desirable. Two different strategies can be followed to deposit a catalyst coating on a metallic substrate:

- direct in situ growth of the catalytic phase on the metallic substrate, or
- washcoating (or dip-coating) of the synthesised catalyst from a slurry.

Washcoating is widely used to deposit catalytic materials as it provides a uniform coating on complex-structured substrates. In washcoating, the support is immersed in a suspension with the appropriate rheology, and is then withdrawn at a constant rate [3]. The deposited wet film, after drying and calcination, transforms into a solid coating adhered to the support. The properties of the final coating films are determined mainly by the composition parameters of the suspension, such as the pH, solid content and particle size distribution. The homogeneity and adherence of the coating are dependent on the physico-chemical properties of the metallic alloy and on the interaction between the alloy and the coating.

Although monolithic and structured catalysts are commonly used, little information is available in the open and scientific literature on the preparation methods for coating metallic monoliths with catalytic supports or catalytic active phases. More extensive studies on ceramic monoliths exist due to their wide use in three-way automobile catalysts. For this purpose, alumina is the most common catalytic support used to coat cordierite [4–12] but parameters in the slurry such as particle size [13], pH and isoelectric point [14] have to be precisely adjusted to get the main objective: loading the honeycomb with a predetermined amount of washcoat in the form of a uniform and homogeneous layer with a minimum number of impregnation [5]. Agrafiotis et al. have also studied other oxides to coat ceramic monoliths, such as CeO_2 [15–17], TiO_2 [18], ZrO_2 [19] and YSZ [20].

For any catalytic process, the catalysts usually require high surface area, appropriate pore structure, and thermal stability. Since the first reports of the ordered mesoporous material, named

* Corresponding author. Tel./fax: +52 914 33 60928.
E-mail address: hermicenda.perez@dacb.ujat.mx (H. Pérez).

1385-8947/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2010.01.032

SBA-15 in 1998 [21,22], it has became a very popular material due to its textural properties that include: an important surface area, large well-ordered mesopores interconnected by irregular micropores [23,24], thick pore walls, and a notable thermal and hydrothermal stability in comparison with the most popular MCM-41. These characteristics present the SBA-15 as an interesting material for applications such as adsorption [25], catalysis [26,27] and templates in the synthesis of nanowires [28–30], among others. Furthermore, the synthesis of the material can be accomplished using a cheap silica source, sodium silicate [31,32], which makes the synthesis commercially viable. In catalysis, an interesting possibility is to use the high surface area and porosity of the SBA-15 for the dispersion of active phases. Supporting SBA-15 on a metallic monolith should offer the advantages of both technologies, a high surface area to disperse an active phase, as previously said, and those derived from the structure of the metallic monolith.

This paper presents a preliminary study of a method for preparing SBA-15 washcoated Fecralloy monoliths. As a first step, a study of the rheological properties of SBA-15 suspensions was required to obtain stable slurries for washcoating. To our knowledge, little research has been carried out in this area. We then studied the procedure to prepare a stable SBA-15 slurry for washcoating Fecralloy monoliths. We illustrate the evolution of the slurry with ageing time. Different properties of the slurry were studied including the viscosity, particle size and pH. The morphology and textural properties of the solids obtained after drying and calcination of slurry aliquots were also analyzed. Finally, the slurry was applied with several coatings to evaluate the adherence and homogeneity of the resulting washcoated monoliths.

2. Experimental

2.1. Sample preparation

SBA-15 was synthesised according to the literature using triblock copolymer $EO_{20}PO_{70}EO_{20}$ (Pluronics P123) as an organic template [33]. In a typical procedure, 9.6 g of P123 was mixed in 225 g of Millipore water and 150 g of 0.5 M HNO_3 solution at 308 K with vigorous stirring. After 4 h, the stirring was increased and 20 g of tetraethylorthosilicate (TEOS) were added as a silica source. After 1 min, stirring was set to the original value and the mixture was kept under magnetic stirring for 24 h before static hydrothermal treatment at 353 K for 72 h in an oven. After that time the flask was cooled down, the product was filtered, washed with distilled water and dried at 353 K for 24 h, before removing the polymer by calcination in air at 773 K for 6 h (dT/dt = 1 K/min).

Two SBA-15 suspensions were prepared. One of them contained 24% by weight of SBA-15, and in the other the total solid content was kept at 24% and a Ludox AS30 commercial colloid was used as a binder (this commercial colloid contains 30% in weight of amorphous SiO_2 in water). The $SiO_2/(SBA\text{-}15 + SiO_2)$ ratio was 0.16. To prepare the suspension, the SBA-15 was added slowly to the required amount of water under magnetic stirring, after which the binder was mixed. The addition of the binder was selected as the starting time for the ageing step.

Metallic Fecralloy (Goodfellow) monoliths were used as supports in the evaluation of the washcoating technique. The typical analysis of the alloy is Cr 22%, Al 4.8%, Si 0.3%, Y 0.3% and C 0.03%. Cylindrical monoliths were prepared rolling up a corrugated and a flat 50 μm sheet (L = 30 mm, d = 16 mm, V = 6 cm^3, cell density 1400 cells/cm^2). Before washcoating, the metallic monoliths were heated at an air temperature of 1173 K for 22 h in order to induce surface segregation of α-Al_2O_3 whiskers, generating a convenient roughness to insure adherence [1].

Washcoating of the pre-treated monoliths was carried out by dipping them in the slurry and withdrawing them at a constant speed of 3 cm/min [3]. Afterward, they were centrifuged at 400 rpm for 2 min to eliminate the excess of slurry blocking the monolith's channels. They were then dried at 353 K for 30 min. Repeated washcoating was carried out with in-between drying to increase the amount of solids loaded on the monoliths. Finally the monoliths were calcinated after the last washcoating at 773 K for 2 h with a ramp of 2 K/min.

2.2. Characterization

Nitrogen adsorption/desorption isotherms at 77 K were used to determine the textural properties with a Micromeritics ASAP 2020 and a homemade cell that allows analyzing the complete 6 cm^3 monoliths. The surface area was calculated following the BET (Brunauer–Emmett–Teller) method. The total pore volume was determined from the amount adsorbed at a relative pressure of about 0.99. The pore size distribution curve was obtained from the analysis of the desorption branch of the isotherm using the Barrett–Joyner–Halenda (BJH) algorithm.

The rheological properties of the suspensions were determined using a Viscotester VT 500 coaxial cylinder rheometer equipped with a NV sensor. Approximately 10 ml of sample were used for each experiment, with the temperature maintained at 298 K using a water bath. The samples were allowed to settle for 60 s after being placed in the rheometer, after which they were exposed to an increasing shear rate of 75–3000 s^{-1}.

The particle size distribution in the suspensions was monitored using a laser diffraction Master Sizer 2000, Malvern Instrument Ltd., equipment with a Hydro 2000G sonifier. For these measurements, a few drops of each suspension were placed in a container filled with deionised water to create a very diluted suspension, and at least five measurements were recorded to check reproducibility. In all cases the observed values presented a negligible standard deviation.

Adherence of the coating was evaluated following the ultrasound test [34]. The adhesion was evaluated by calculating the amount of coating lost after dipping samples in a beaker containing petroleum ether placed in an ultrasonic bath for 30 min. After the test, the monoliths were dried and calcinated, and the adherence was calculated through the weight difference.

Scanning electron microscopy (SEM) micrographs were taken on a Hitachi S-2700 scanning microscope at a voltage of 15 kV. To prepare the samples, a few drops of the slurry were deposited on a conducting double face adhesive tape, and after drying they were gold coated.

The zeta potential of diluted SBA-15 suspensions (about 2 mg of SBA-15 were dispersed in 50 ml of a 0.03 M NaCl solution) was measured by electrophoretic mobility in a Zeta Potential Analyzer (Malvern Zetasizer Nano-ZS). Nitric acid (0.5 M) and sodium hydroxide (1 M) solutions were used to adjust the pH value. The zeta potential was determined as a function of the pH value.

The stability of the slurries was evaluated by two different methods: direct observation and with a Turbiscan Lab Expert equipment. The direct observation is really a simplified settling column test. This test was carried out by putting the suspension into graduated cylinders and leaving them undisturbed for 24 h. Slurry stability was evaluated by measuring the clarified supernatant (sedimented height as a percentage of the total suspension height) for the two different formulations. In the Turbiscan test the sample was placed in a flat-bottomed cylindrical cell and was irradiated by a pulsed near infrared light. A backscattering detector was used to receive the light that was backscattered (at 135°) by the product. The slurries were evaluated after 24 and 48 h of ageing. Readings of the backscattering of the samples were taken every 40 μm along the sample tube for a length of 40 mm. The acquisition scans were repeated with a frequency of 5 min for 30 min.

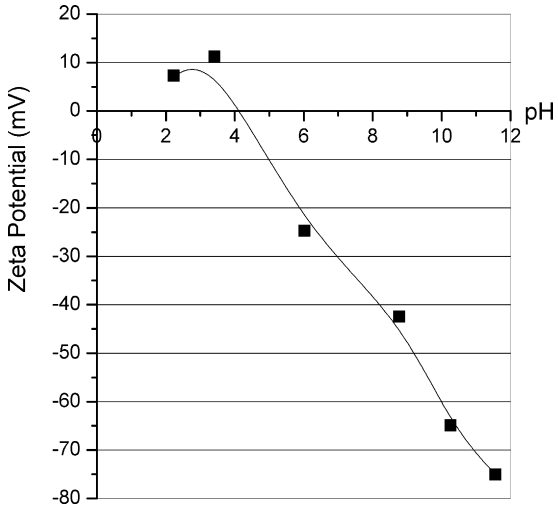

Fig. 1. Zeta potential vs. pH plot for SBA-15.

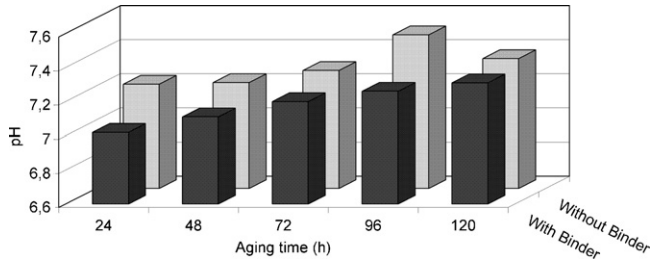

Fig. 2. pH evolution of the suspensions as a function of the ageing time.

3. Results

3.1. Chemistry of the suspension

The isoelectric point (iep) of the silica solids is between 3.5 and 4.2 depending on the solid. Fig. 1 shows the effects of the pH on the zeta potentials of the SBA-15 suspensions. The isoelectric point of the SBA-15 was about pH = 4, which is in good agreement with reported values [35].

The evolution of the pH of the slurries was followed for 120 h of ageing time. The results are shown in Fig. 2. The pH was very stable during the studied ageing time. It presented a slight increase in time from 7 to 7.3 in the case of the suspension without a binder and from 7.2 to 7.3 when AS30 was added. This evolution was not significant and it may be considered that the pH was stable.

The stability of the slurries was evaluated following two different methods: direct observation and using Turbiscan equipment. The direct observations at the end of the ageing test showed that the slurries were stable for up to 4 h, as no clarified supernatant was detected. The setting front advance was 5% at the end of the 24 h test. Analyses were carried out after 24 and 48 h of ageing with the Turbiscan equipment. The results are plotted on Fig. 3. No sedimentation was observed during 30 min for both slurries and the two different ageing times.

3.2. Rheological behaviour

The suspension viscosity vs. shear rates curves at different ageing times are plotted in Fig. 4. As may be seen in the figures, there is a strong dependence of the viscosity on the ageing time. The same behaviour was observed for both suspensions. Every rheogram curve was characterised by a shear-thinning behaviour at low shear rates followed by an almost constant viscosity at high shear rates. For the suspension without a binder, the viscosity decreased during 72 h with no significant evolution after that time. In the case of the suspension with a 16% AS30 binder, no significant evolution was observed after 48 h when the viscosity became stable.

3.3. Particle size distribution

Fig. 5 shows the particle size distribution for the slurries under study. The main features of the particle size distribution are that both slurries presented the same particle size distribution and the same trend with ageing time: smaller particle sizes and a narrower distribution as ageing time increased. The mass median diameters [MMD or D (v, 0.5)] of the samples were centred initially at about 8.3 μm, and moved to 2.5 μm during the 120 h ageing period.

3.4. Morphology of the particles forming the suspension

The morphology of the SBA-15 has been studied by SEM. Fig. 6 shows images of the SBA-15 with its typical fiberlike structure. It can be observed that the smallest units grew with 1.5–3 μm long and 0.6–0.93 μm diameter rod-shaped particles that gave place to segmental fibers or rope-like structures which aggregated to form bundles.

The evolution of the morphology of the SBA-15 with ageing time was studied for both slurries. Fig. 7 shows the morphology of the solid obtained after drying the slurry without a binder on the SEM sample holder. It is evident that the morphology of the solid changed even after 24 h of stirring. No bundles were observed as they were broken into the smaller primary rod-shaped particles (Fig. 7b). As ageing time increased, particles became even smaller and more irregular. Some very small particles can be observed after 120 h of ageing (Fig. 7c). The same may be observed in the case of the slurry with a 16% AS30 binder (Fig. 8).

3.5. Textural properties of the solids

Aliquots of the suspensions were dried and calcinated at each ageing time and the obtained solids were characterised by N_2 adsorption, in order to study the evolution of the textural properties of the solids. All the solids had a type IV isotherm with a H2 hysteresis loop, which is a typical adsorption for mesoporous materials with cylindrical pores. Fig. 9a shows the isotherm of the parent SBA-15 and that of the solids obtained by drying and calcinating the slurry containing the 16% AS30 binder at different ageing times. All the isotherms exhibited a sharp inflection in the P/P_0 range from 0.60 to 0.80, that is characteristic of capillary condensation within uniform pores. Fig. 9b shows the pore size distribution of the solids. The pore size distributions are narrow and centred at around 60–70 Å, and do not change significantly with ageing time. In all cases, the solids obtained from the slurries had surface areas smaller than that of the parent SBA-15 (Fig. 10). The longer the ageing time, the bigger the loss of surface area. This was slightly more accentuated when the slurry contained the AS30 binder.

3.6. Washcoating

After the slurries were characterised, they were used to washcoat Fecralloy monoliths. Two and four washcoatings were applied in these experiments. Results are shown in Fig. 11. The loadings were approximately of 300 mg of solid per monolith after two coatings with the slurry containing the 16% AS30 binder, and of 500 mg when four washcoatings were carried out. Loads were 100 and 500 mg for two and four washcoats respectively when the slurry without a binder was used. The adherence tests showed that the

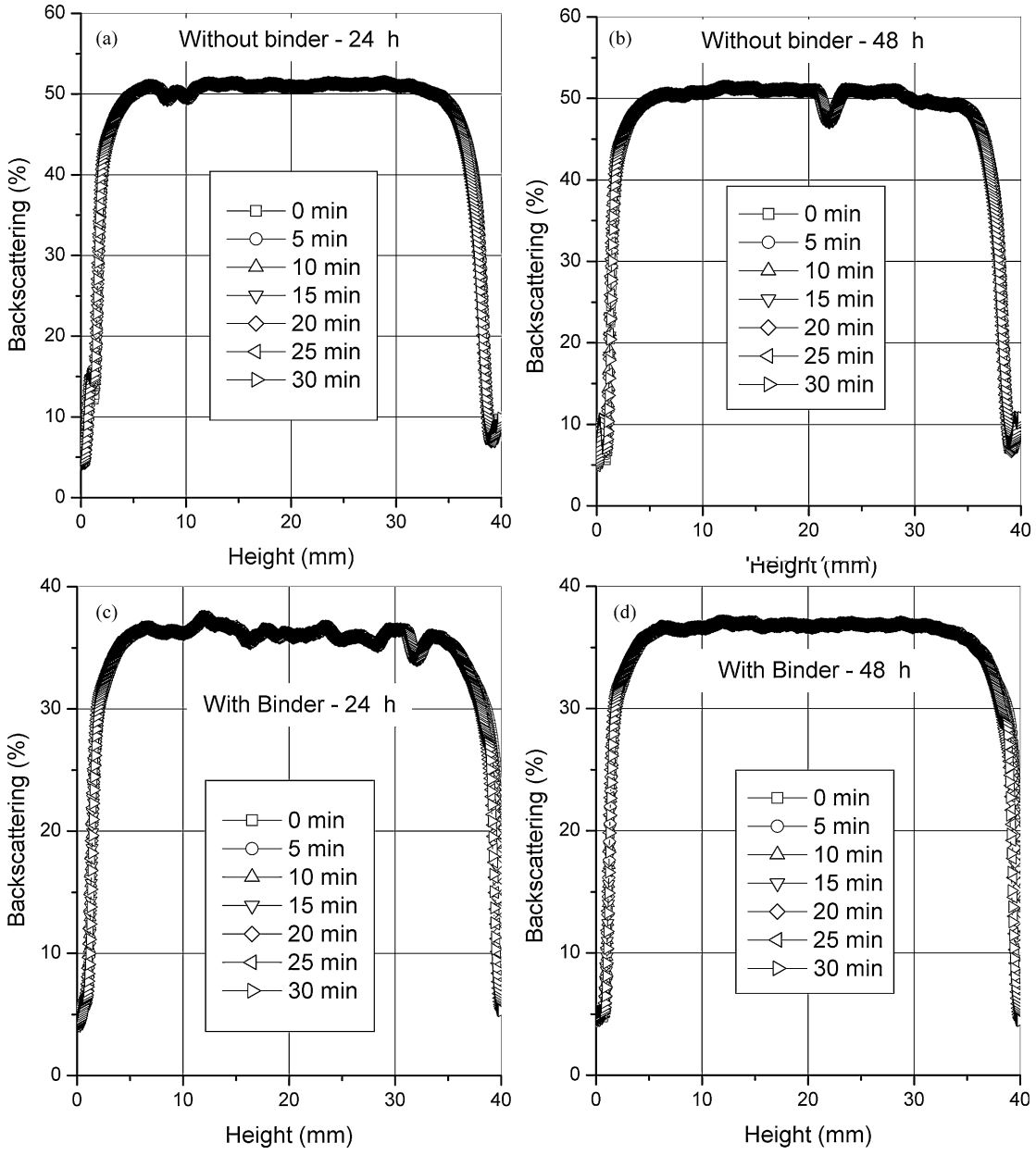

Fig. 3. Turbiscan analysis for both slurries at 24 and 48 h of aging time.

coating loss was between 20% and 40% when no binder was used in the slurry (Fig. 11b), and below 10% when the binder was present.

4. Discussion

The purpose of this study was to washcoat Fecralloy monoliths with SBA-15 as a first step to support a catalytic phase on the SBA-15 on a structured monolith. Previous studies carried out by our research group have shown that the adherence of the SBA-15 on Fecralloy substrates is quite poor. The use of binders is a widespread method to favour adherence between different materials. After considering several binders, it was decided to use AS30 and preparation of the slurries was started. The first prepared slurry presented a high viscosity of 15 mPa s when working without a binder at 3000 s^{-1} of shear rate, and a viscosity of 12 mPa s when using a binder in the slurry after 24 h under magnetic stirring. According to Nijhuis et al. [36] the length of monolithic blocks that can be washcoated is mainly controlled by the viscosity of the washcoating solution. If the viscosity of the solution is kept bellow 30 mPa s, washcoating monolith bodies up to 25 cm long poses no problems. Although our monoliths length was of 3 cm and the viscosity should be adequate [19] it was impossible to perform the washcoating. Nijhuis et al. do not mention anything about the size of the channels but we think that this is an important parameter to take into account when the viscosity of the slurry is too high and the size of the channel too small. To washcoat a monolith it is immersed for a short period into the washcoating solution at a certain speed. As the monolith is dipping into the solution, the solution should flow up into the channel by capillarity. If the slurry is too viscous the phenomena does not happen as it was our case. This fact made us redirect the study so as to understand the rheology of our suspension and make it successful with respect to the purpose of washcoating Fecralloy monoliths with SBA-15.

When the first SBA-15 suspensions were prepared, it was realised that the viscosity evolved throughout several days. Taking into account that viscosity is a first parameter that controls the

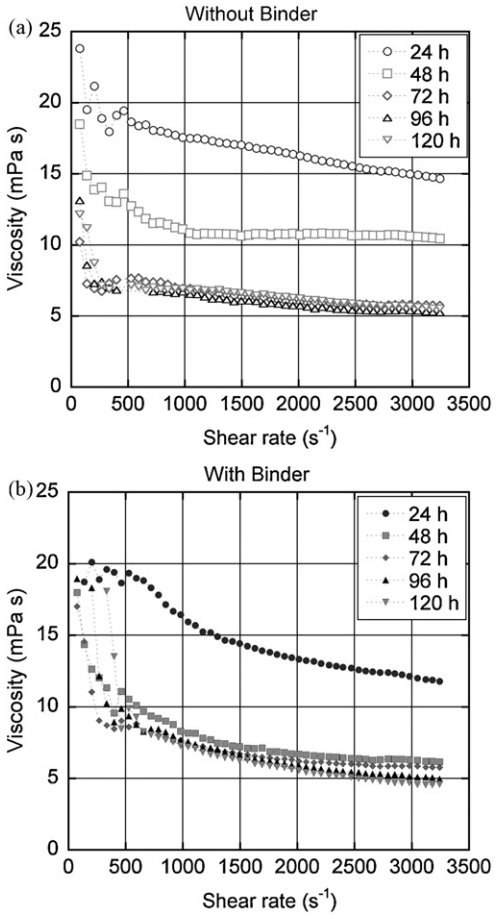

Fig. 4. Viscosity vs. shear rate plot at different ageing time.

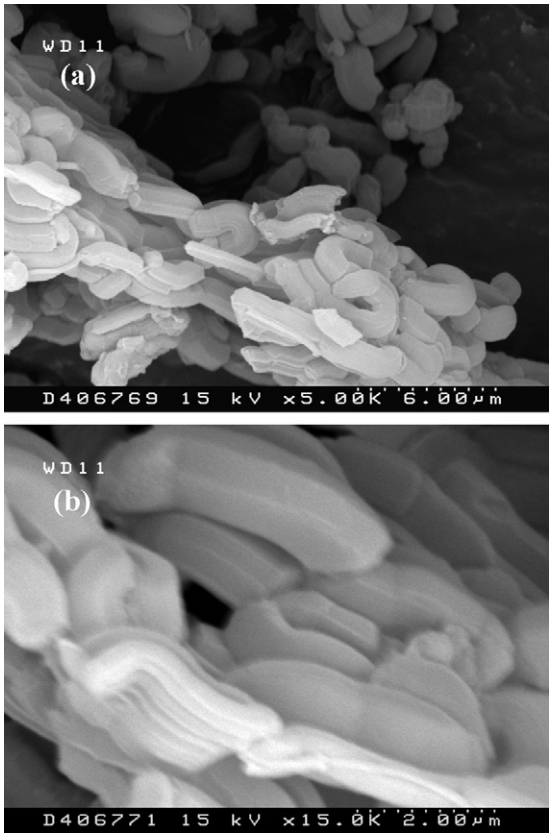

Fig. 6. SEM micrographs of the parent SBA-15 used to prepare the slurries.

washcoating procedure, a target range (5–15 mPa s) [37] needs to be attained to obtain good coating results, and this makes it necessary to study the ageing of the SBA-15 slurry. The purpose of this study was double: on the one hand to understand this ageing phenomenon, and on the other to establish standard conditions to allow the study of the effect of the other preparation variables.

The rheology of a suspension is complex and there is no single parameter that can solely explain it. The physical and chemical parameters of a slurry such as solids content, particle size distribution, particle shape, pH and viscosity have a significant influence on the rheology of the slurry.

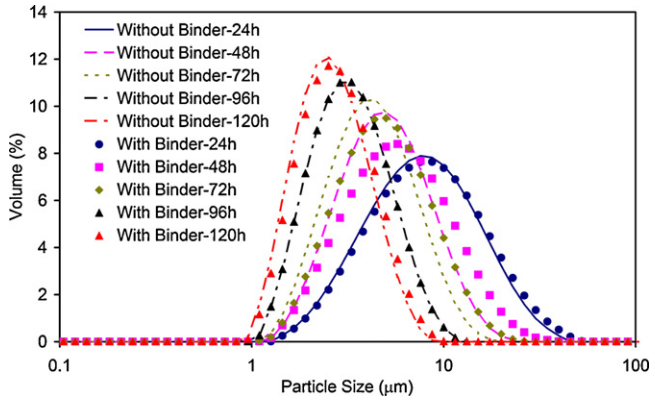

Fig. 5. Particle size evolution with ageing time. Distributions with lines correspond to the slurry without binder and the distributions with symbols correspond to the slurry with 16% of AS30 as binder.

Surface charge is an important characteristic of suspended particles, as it determines the dispersion and stability of suspensions. The zeta potential of a suspension is an indication of the magnitude of the repulsive force between the particles. The higher the absolute value of the zeta potential, the more predominant the electrostatic repulsion between particles. According to the literature [38], when the zeta potential is between 20 and 50 mV the dispersion is stable, when it is between 50 and 80 mV the stability is good, and above that it is excellent. When the SBA-15 and AS30 are immersed in water, charged species start to migrate across the solid/liquid interface until equilibrium is reached. We determined that the isoelectric point of the synthesised SBA-15 occurred at a pH of 4 (Fig. 1). At higher pH values, the absolute value of the zeta potential increased helping to stabilise suspensions by repulsive interactions. It was decided to work at a pH of 7 which corresponds to a zeta potential of about −35 mV. The stability of the slurries was evident from the Turbiscan measurements, as these showed no evidence of flocculation, coalescence, creaming or sedimentation during the 30-min tests. The settlement test at the end of the ageing time showed no clarified supernatant during the first 4 h that could be considered large enough for the washcoating procedure.

Once the stability of the slurries was proven, the next step was to confirm the presence of a good rheology to insure the success of the washcoating. It was difficult to disperse the SBA-15 during the preparation of the slurry. At the very beginning when the SBA-15 was added to the water, a very viscous slurry was formed probably due to the hydrophobic character of the SBA-15. It was decided to let the slurry age under magnetic stirring and follow the evolution of the viscosity (Figure 4). As is stated above, the slurries under study showed a shear-thinning behaviour, but for each ageing time the suspension reached an almost constant viscosity at high shear rates, with this value becoming lower as ageing time increased. Considering that in these experiments the solid content of the slur-

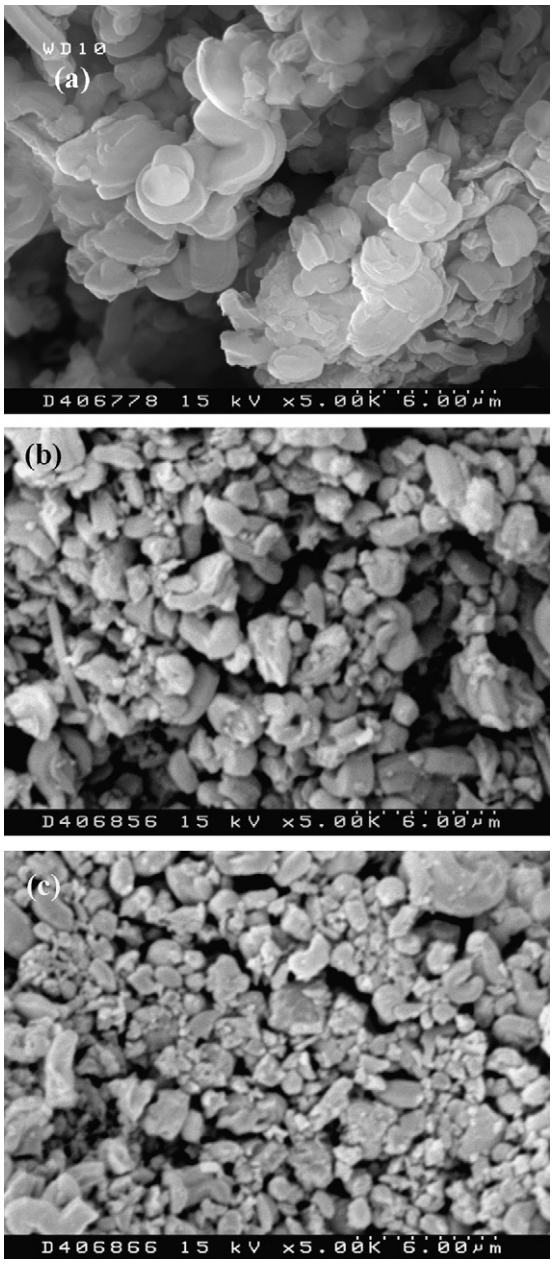

Fig. 7. Evolution of the morphology of the SBA-15 particles with the aging of the slurry without binder.

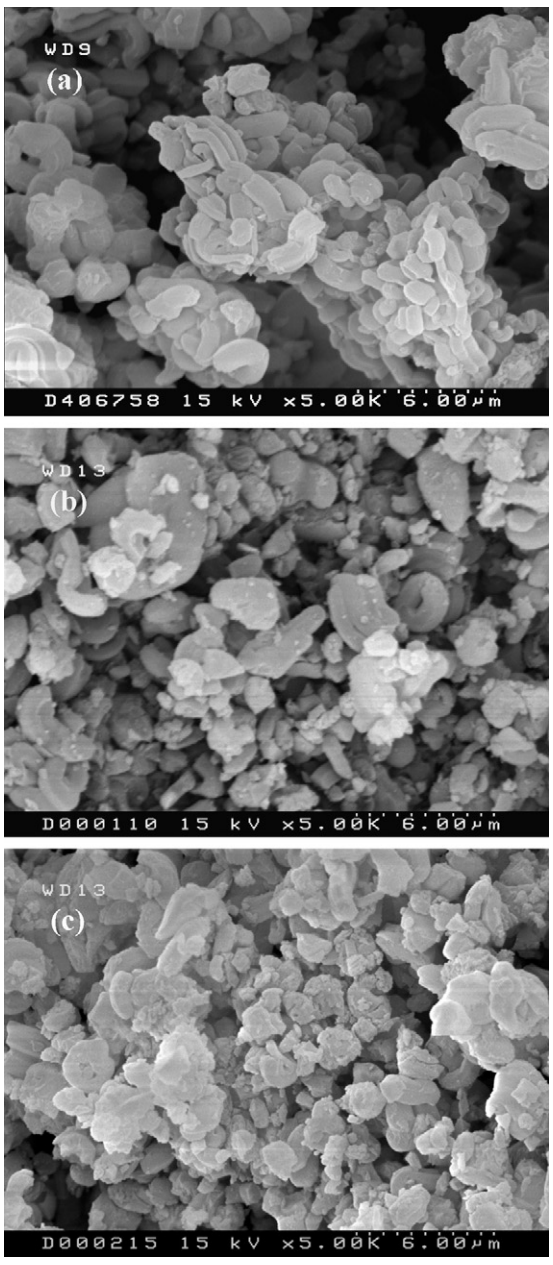

Fig. 8. Evolution of the morphology of the SBA-15 particles with the aging of the slurry with 16% of AS30 as binder.

ries was a fixed variable and the pH remained constant (Fig. 2), it was other parameters that had to be affecting the viscosity of the slurries.

Many models have been proposed to describe the viscosity of slurries, both for diluted and concentrated suspensions, starting from Einstein's first studies on spheres [39,40]. In the proposed models, viscosity is directly related to the volumetric fraction of the solids [41] or/and the maximum packing fraction [42]. In most of the cases, only rigid spheres are considered, but when working with concentrated slurries the particle asymmetry and the maximum packing fraction have a strong effect on viscosity [43]. This packing fraction, as well as being controlled by the type of packing, is very sensitive to particle-size distribution and particle shape [44]. Broader particle-size distributions have higher values of maximum packing fraction, as the smaller particles fit into the gaps between the bigger particles. On the other hand, non-spherical particles lead to poorer space filling, and hence lower maximum packing fraction. A number of studies have shown that any deviation from spherical particles means an increase in viscosity for the same phase volume; generally speaking, rods have a greater effect than discs in increasing viscosity [45,46]. Thus, the viscosity of the suspensions may be affected by two parameters: particle size distribution and particle shape.

It was observed (Fig. 5) that the particle size distribution of both slurries presented the same behaviour as a function of ageing time: the particle size decreased and the particle size distribution became narrower at increasing ageing times. So, viscosity decreased with ageing time and the particle size distribution became narrower. According to the literature, viscosity decreases when coarse particles are added to a slurry [47] or when a broad particle size is observed [48]. However, the opposite occurred in our system, an additional parameter had to be playing a decisive role, and particle shape was the best option.

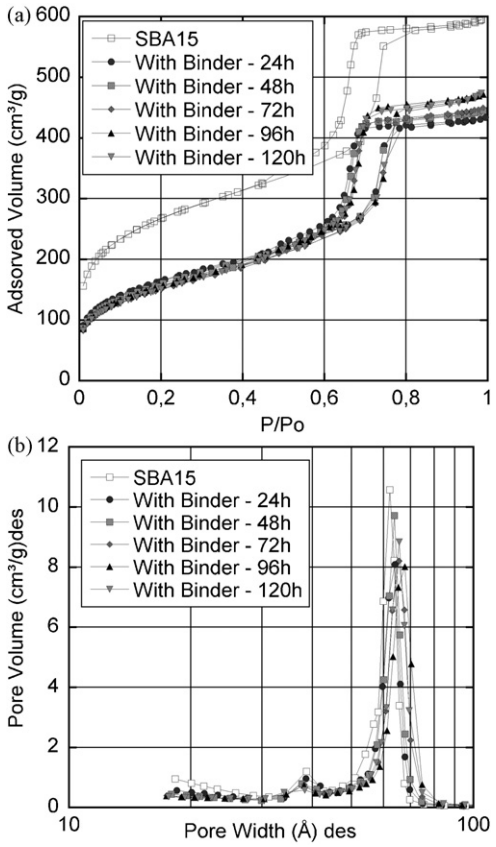

Fig. 9. Nitrogen isotherms and pore size distributions of the solid dried from the two slurries after different aging times.

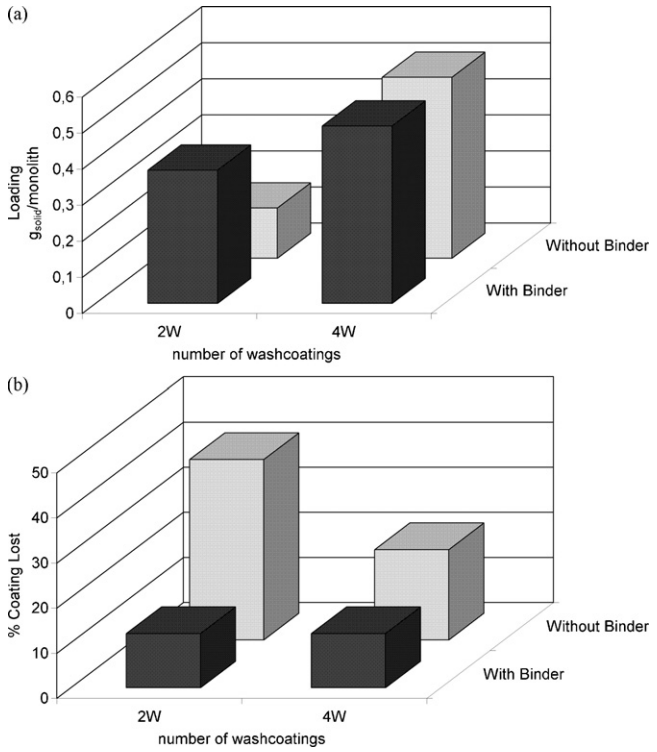

Fig. 11. Effect of the number of washcoatings in the loading (a) and in the coating lost after the adherence test (b) for both slurries.

Very little information has been published with respect to this, and it has to do with different systems. It is an accepted fact that for the same phase volume percentage, viscosity is greater for rod particles than for plates, grains and spheres [27,28]. This is because the irregular, and especially the rotational, motion of non-spherical particles is more impeded than that of spheres. Figs. 7 and 8 show that particles changed shape with ageing time. The parent SBA-15 was a solid with a rope-like structure (Fig. 6) formed by particles with a uniform elemental diameter of less than 1 μm, which aggregated into wheat-like macrostructures. After 24 h under magnetic stirring, the SBA-15 elemental units showed a similar particle morphology, but a different aggregation pattern. When the slurry was aged under magnetic stirring for longer times, the particles became smaller and irregular. We believe that magnetic stirring with flat cylindrical stir bars without spinning rings is very abrasive, and that long ageing times definitively destroyed the macroscopic structure of the SBA-15. The friction made the wheat-like structures break into the smaller rod units, and these units became even smaller and more irregular with longer times. This hypothesis was confirmed when the bottom of the stir bar used in this study showed the Teflon coating worn away and the naked magnet showing through.

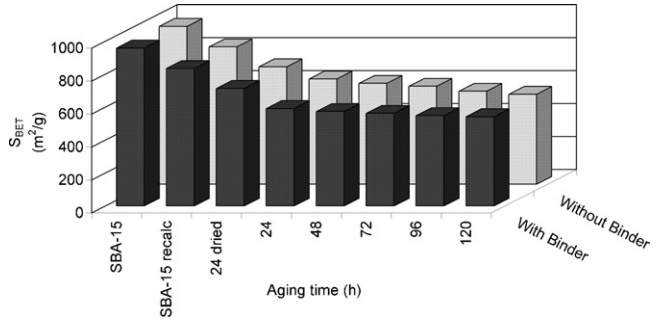

Fig. 10. Surface area of the dried slurries at different aging times.

Nevertheless, this abrasion did not affect the mesoporous structure of the SBA-15, as was confirmed by N_2 adsorption (Fig. 9). The shape of the isotherms, and consequently the corresponding pore size distribution, indicated a uniformity in the cylindrical shape of the pores and in the mesopore size distribution. Only a small loss of specific surface area was observed: the longer the ageing time, the smaller the specific surface area.

To understand this loss of surface area, two additional experiments were carried out. The first one consisted of dispersing the SBA-15 in water and maintaining it under mechanical stirring for 24 h, after which time the suspension was dried and a loss of approximately 25% of the surface area was observed. In the second experiment, the original SBA-15 was re-calcinated and 13% of the surface area was lost (Fig. 10). The main conclusion is that SBA-15 is a meta-stable solid and any additional thermal or hydrothermal treatment produces a decrease in surface area that does not change the mesoporous structure. The solid obtained from the first aliquot after 24 h under magnetic stirring, drying and calcination lost about 35.8%, which agrees with the addition of the loss of surface area due to calcination and that of the hydrotreatment. The loss of surface area was very small for longer ageing times, and it seemed to reach a stage at which the loss was minimum. This behaviour was the same in both slurries, so the presence of the silica binder in the suspension did not affect the evolution of the texture.

Once the slurries had been characterised, they were used to washcoat Fecralloy monoliths. The use of binders in slurries is a very widespread method that favours the adherence between a catalyst and a structural support. Since we wanted to support a siliceous material on Fecralloy, protected by an alumina scale, two types of colloids could be considered: silica such as SBA-15 or alumina like the Fecralloy scale. Preliminary tests with colloidal alumina,

the usual choice for Fecralloy, did not produce significant improvements to the slurry without additives. Therefore, it was decided to use AS30 as a binder that is a commercial colloidal silica. Fig. 11a shows that the effect of the binder was very important in the first two washcoatings, as the loading using the slurry with 16% AS30 as binder was 2.6 times greater than that obtained using the slurry without a binder. No improvement was observed when additional washcoatings were carried out, as a result of the presence of colloidal silica in the formulation. The binder seemed to favour the chemical compatibility between SBA-15 and Fecralloy. To confirm this point, adherence tests were carried out and the results are shown in Fig. 11b. It can be inferred that the binder improves the adherence significantly.

5. Conclusions

The main target of this study was to washcoat Fecralloy monoliths with SBA-15. The amount loaded and the adherence of the coatings depended on whether the silica binder was used in the formulation of the slurry. The most homogeneous and adherent coatings were obtained when AS30 was used. The coating kept the textural properties of the parent SBA-15 almost unchanged, although its macroscopic aspect evolved noticeably. The suspensions required 2–4 days under magnetic stirring to become stable and acquire an adequate viscosity to perform the washcoatings. During ageing, the viscosity of the SBA-15 slurries decreased against the established trends due to a change in particle size and morphology. The parent SBA-15 presented the typical wheat-like morphology, but under magnetic stirring the big aggregates were broken down into rod-shaped units that became more and more irregular and spherical, making the slurry less viscous.

Acknowledgements

The authors appreciate the financial support provided for this study by UPV/EHU (GIU07/63), the Spanish Educational Ministry (MAT2006-12386 and the Juan de la Cierva contract for P. Navarro), and UJAT-PROMEP-México (Pre-doctoral grant for H. Pérez).

References

[1] R.M. Heck, S. Gulati, R.J. Farrauto, Chem. Eng. J. 82 (2001) 149.
[2] P. Avila, M. Montes, E.E. Miró, Chem. Eng. J. 109 (2005) 11.
[3] M. Valentini, G. Groppi, C. Cristiani, M. Levi, E. Tronconi, P. Forzatti, Catal. Today 69 (2001) 307.
[4] C. Agrafiotis, A. Tsetsekou, J. Mater. Sci. 35 (2000) 951.
[5] V. Blachou, D. Goula, C. Philippopoulos, Ind. Eng. Chem. Res. 31 (1992) 364.
[6] T. Shimrock, R.D. Taylor, J. Collins, Eur. Patent 0,157,651 (1985).
[7] C. Agrafiotis, A. Tsetsekou, J. Eur. Ceram. Soc. 20 (2000) 815.
[8] R.M. Heck, R.J. Farrauto, Catalytic Air Pollution Control-Commercial Technology, Van Rostrand Reinhold, New York, 1995.
[9] J.W. Geus, J.C. van Giezen, Catal. Today 47 (1999) 169.
[10] E. DeLiso, W.R. Cannon, A.S. Rao, Dispersion of alumina–zirconia powder suspensions', in: S. Somiya, N. Yamamoto, H. Yanagida (Eds.), Advances in Ceramics, vol. 24, Science and Technology of Zirconia III, American Ceramic Society, Westerville, OH, 1988, pp. 335–341.
[11] J. Cesarano, I.A. Aksay, A. Bleier, J. Am. Ceram. Soc. 71 (1988) 250.
[12] P. Cini, S.R. Blaha, M.P. Harold, V. Venkataraman, J. Membr. Sci. 55 (1991) 199.
[13] G. Tari, J.M.F. Ferreira, A.T. Fonseca, O. Lyckfeldt, J. Eur. Ceram. Soc. 18 (1988) 249.
[14] I.I.M. Tijburg, J.W. Geus, H.W. Zandbergen, J. Mater. Sci. 26 (1991) 6479.
[15] C. Agrafiotis, A. Tsetsekou, C.J. Stournaras, A. Julbe, L. Dalmazio, C. Guizard, J. Eur. Ceram. Soc. 22 (2002) 15.
[16] C. Agrafiotis, A. Tsetsekou, C.J. Stournaras, A. Julbe, L. Dalmazio, C. Guizard, G. Boretto, M. Debenedetti, F. Parussa, Appl. Catal. B: Env. 34 (2001) 149.
[17] C. Agrafiotis, A. Tsetsekoua, C.J. Stournaras, A. Julbe, L. Dalmazio, C. Guizard, Solid State Ionics 136/137 (2000) 1301.
[18] C. Agrafiotis, A. Tsetsekou, A. Ekonomakou, J. Mater. Sci. Lett. 18 (1999) 1421.
[19] C. Agrafiotis, A. Tsetsekou, J. Eur. Ceram. Soc. 20 (2000) 825.
[20] C. Agrafiotis, A. Tsetsekou, I. Leon, J. Am. Ceram. Soc. 83 (2000) 1033.
[21] D. Zhao, J. Feng, Q. Huo, N. Melosh, G.H. Fredrickson, B.F. Chmelka, G.D. Stucky, Science 279 (1998) 548.
[22] D. Zhao, Q. Huo, J. Feng, B.F. Chmelka, G.D. Stucky, J. Am. Chem. Soc. 120 (1998) 6024.
[23] W.W. Lukens Jr., P. Schmidt-Winkel, D. Zhao, J. Feng, G.D. Stucky, Langmuir 15 (1999) 5403.
[24] M. Kruk, M. Jaroniec, C.H. Ko, R. Ryoo, Chem. Mater. 12 (2000) 1961.
[25] B.L. Newalkar, N.V. Choudary, P. Kumar, S. Komarneni, T.S.G. Bhat, Chem. Mater. 14 (2002) 304.
[26] S.W. Kim, S.U. Son, S.I. Lee, T. Hyeon, Y.K. Chung, J. Am. Chem. Soc. 122 (2000) 1550.
[27] X.Q. Wang, H.L. Ge, H.X. Jin, Y.J. Cui, Micropor. Mesopor. Mater. 86 (2005) 335.
[28] Z. Zhang, S. Dai, D.A. Blom, J. Shen, Chem. Mater. 14 (2002) 965.
[29] V. Escax, M. Impéror-Clerc, D. Bazin, A. Davidson, C. R. Chim. 8 (2005) 663.
[30] S. Jun, S. Hoon Joo, R. Ryoo, M. Kruk, M. Jaroniec, Z. Liu, T. Ohsuna, O. Terasaki, J. Am. Chem. Soc. 122 (2000) 10712.
[31] J.M. Kim, G.D. Stucky, Chem. Commun. 13 (2000) 1159.
[32] S.S. Kim, A. Karkamkar, T.J. Pinnavaia, M. Kruk, M. Jaroniec, J. Phys. Chem. B 105 (2001) 7663.
[33] K. Flodström, V. Alfredsson, Micropor. Mesopor. Mater. 59 (2003) 167.
[34] S. Yasaki, Y. Yoshino, K. Ohkubo, US Patent 5,208,206 (1993).
[35] M. Kosmulski, J. Colloid Interface Sci. 275 (2004) 214–224.
[36] T.A. Nijhuis, A.E.W. Beers, T. Vergunst, I. Hoek, F. Kapteijn, J.A. Moulijn, Catal. Today 43 (2001) 345.
[37] T. Tao, J.M. Torns, B.P. Usiak, US Patent 6,903,051 B2 (2005).
[38] S. Vallar, D. Houivet, J. El Fallah, D. Kervadec, J.M. Haussonne, J. Eur. Ceram. Soc. 19 (1999) 1017.
[39] A. Einstein, Ann. Phys. 19 (1906) 289.
[40] A. Einstein, Ann. Phys. 34 (1911) 591.
[41] G.K. Batchelor, J. Fluid Mech. 83 (1977) 97.
[42] I.M. Krieger, T.J. Dougherty, Trans. Soc. Rheol. 3 (1959) 137.
[43] R. Wakeman, Powder Technol. 11 (1975) 297.
[44] R.J. Farris, Trans. Soc. Rheol. 12 (1968) 281.
[45] B. Clarke, Trans. Inst. Chem. Eng. 45 (1967) 251.
[46] H. Giesekus, in: R. Jowitt (Ed.), Physical Properties of Foods, Applied Science Publishers, 1983 (chapter 13).
[47] C. Logos, Q.D. Nguyen, Power Technol. 88 (1996) 55.
[48] H.G. Yang, C.Z. Li, H.C. Gu, T.N. Fang, J. Colloid Interface Sci. 236 (2001) 96.