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Effect of ageing time on chemical and rheological evolution in γ-Al_2O_3 slurries for dip-coating

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Abstract

The evolution during ageing time of a suspension of a submicronic γ-Al_2O_3 powder with $HNO_3/Al_2O_3 = 2.16$ mmol/g and $H_2O/Al_2O_3 = 3.2$ ml/g has been studied. The physico-chemical and rheological evolution has been followed up to 48 h of ageing. Surface charging and dissolution reactions are fast and proceed with comparable rates in the first 5 h to reach a stable pH 3.5 that corresponds to maximum surface charging and maximum Al^{3+}. Surface charging is responsible for the formation of the colloidal particles that aggregates to form the physic-type gel phase (weak gel). Gel formation is a slow process and is completed within 20 h of ageing. The suspensions present a non-Newtonian pseudoplastic behaviour; at shear = 10 s^{-1} viscosities between 0.03 and 0.5 Pa s are measured. Viscosity is strongly time dependent and shows a maximum about 27 h of ageing. This behaviour has been related to the presence of modification of the suspension composition during ageing: viscosity increases due to the increasing amounts of gel, the increasing of gel strength and flocks formation, while the viscosity decreases due to both decrease of gel strength and flocks re-dispersion. Well adherent coating layers characterised by loadings between 1.1–2.2 mg/cm^2 and thickness of 10–20 μm have been obtained upon dip-coating deposition.

Keywords: Rheological evolution; Dip-coating; Ageing; Time

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1. Introduction

The properties of concentrated alumina suspensions are of interest in many industrial applications. For example, they are used in ceramic forming process, in the production of catalyst supports, and in the preparation of structured catalysts, such as catalytic mufflers, monoliths for SCR of NO*x* and catalytic combustion process [1]. The structured catalysts consist of metallic or ceramic structures in the form of honeycombs, plates or foams, coated with layers of catalytically active materials (washcoat). Dip-coating is widely used to deposit the washcoat material since it allows to obtain uniform coating on complex-structured substrates [1,2]. In dip-coating, the support is immersed into a suspension with appropriate rheology and then it is withdrawn at a constant rate. The deposited wet film, upon drying and calcining, transforms in a solid one adherent to the support. The properties of the final coating films are primarily determined by the composition parameters of the suspension, such as pH, solid content and particle size distribution [3–11]. Data on the preparation of stable suspensions for dip-coating application for catalytic purposes are reported either on patents literature or on scientific literature where operating conditions far from those of application interest are used [5,12–22].

In previous works the effect of the preparative variables, such as HNO_3, powder and water content on the obtainment of homogeneous and well adherent alumina coatings onto metallic slabs and ceramic tubes have been reported [23,24]. A submicronic γ-Al_2O_3 powder has been used to avoid the use of a ball milling. An optimal composition has been found that corresponds to $HNO_3/Al_2O_3 = 2.16$ mmol/g and $H_2O/Al_2O_3 = 3.2$ g/g. Using this composition and a fixed ageing time of 24 h, well adherent coating layers, characterised by loads of about 2.3 mg/cm^2 and thickness of 25 μm, have been obtained. These layers preserve the morphological and structural properties of the original alumina powder and,

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upon impregnation with Pd ions, they are active in catalytic combustion of CH_4 and CO oxidation [23,24]. In this work the study of the effect of the ageing time between 1 and 48 h on the rheological properties of the alumina suspension at above is reported. The physico-chemical modification, with particular attention to the reactions occurring during ageing, have been studied and related to the final rheological properties of the suspension. The final goal of the work is to deep inside the fundamental aspects on preparation parameters, and rheological behaviour of suspensions with compositions close to those of application interest. The results of this study could give guidelines for the rational selection of the preparation method with respect to the desired features of the final coating layers.

2. Experimental

A commercial submicronic γ-Al_2O_3 powder (AKP-G015 from Sumitomo) was used characterised by a surface area of 140 m^2/g, a pore volume of 0.6 cm^3/g and a bimodal granulometric distribution with maxima centred at 2.2 and 0.2 μm and relative amounts of the two peaks of about 90 and 10% (v/v), respectively.

Slabs of Fecralloy® were used as support. To favour the adhesion of the ceramic layers at the slabs, the Fecralloy® was previously calcined at 900 °C for 10 h, to cause surface segregation of α-Al_2O_3 whiskers, and then coated with a layer of boehmite primer [23,24].

The alumina suspension was prepared using a commercial solution of HNO_3 (J.T. Backer 65% w/w, $d = 1.4$ g/cm^3, $M = 14.44$ mol/l), with acid amount to obtain the ratio $HNO_3/Al_2O_3 = 2.16$ mmol/g and a water amount to obtain the ratio $H_2O/Al_2O_3 = 3.2$ ml/g. In previous works such suspension had been found as the optimal composition for our application purposes [23,24].

In a typical preparation, the required acid and water amounts were stirred in a jacket reactor at a constant temperature of 20 °C. The alumina powder was thus added to the solution. The obtained suspension was aged, under stirring, for 48 h. The acid consumption was followed by measuring the pH by using a pH-meter (Titrino 719 S, Metrohm) with a combined glass electrode specific for slurries measurements (Unitrode, Metrohm).

The composition and the rheological behaviour of the suspension was determined on aliquots of the suspension taken from the reactor at different time of ageing in the range 2–48 h.

To separate the constituent phases, the suspension was ultra-centrifuged (HEMRLE, Z 323 K) at 1.3×10^4 rpm for 1 h: a liquid (sol), a translucent solid (gel) and a white solid (powder) were thus obtained. The amounts of each phase were quantified by weighing the obtained separated phases after calcination at 700 °C in a ventilated oven (heating and cooling ramp 1 °C/min, hold at temperature 10 h).

Part of the sol was also ultra-filtered to separate the dissolved Al^{3+} ions from colloidal particles using a FILMTECH BW30 (Dow Chemie) membrane in a pressure filter (Millipore) (operating pressure from 2 to 6 bar). The ultra-filtered liquid was analysed by atomic absorption using a Varian AA 110 instrument.

To determine the rheological properties a rotational stress controlled rheometer (STRESSTECH 500 from Reologica) was used.

Viscosity of the suspension was determined at $T = 20$ °C using flat plates (diameter = 40 mm).

The linear viscoelastic properties of the gels were determined in the oscillatory mode [25]. In a typical experiment the upper plate performs dynamic oscillations at a given frequency (1 Hz) and the applied stress is varied between 0.01 and 10 kPa. The results were analyzed according to the Maxwell model that describes the response of linear viscoelastic materials to a small-amplitude oscillatory shear [26].

The coating deposition was performed by dipping the metallic slabs into the dispersion and by removing them at constant speed of 3 cm/min. On the deposited coatings a flash-heating procedures at 280 °C for 5 min has been applied. This procedure results in a fast evaporation of the solvent that guarantees the adhesion of the layers. Details have already been reported elsewhere [23,24].

After flash-heating the coated slabs were calcined up to 700 °C in a ventilated oven (heating and cooling ramp 1 °C/min, hold at temperature 10 h).

The coating amount after calcination at 700 °C was determined by weighting.

The adherence of the coating was evaluated in terms of weight loss after exposure to ultrasounds: the calcined coated slabs were immersed in petroleum ether, inside a sealed beaker, and then treated in an ultrasound bath (Starsonic 90) for 30 min.

3. Results and discussion

3.1. Chemistry of the suspension

The pH evolution has been followed up to 48 h of ageing time and results are shown in Fig. 1a. The pH increases very fast in the first hours of ageing, and it approaches, within 5 h, the asymptotic value of 3.5. This plateau value is close to that of 3.4 reported in the literature for similar alumina suspensions [15,19]. This behaviour is better detailed plotting acid consumption as function of ageing time (Fig. 1b) It is evident that, immediately after the contact of the powder with the acid solution, a marked acid consumption is observed in the first couple of hours. Then it slows down and, after 4–5 h of ageing and acid consumption is no longer observed thus a stable pH is reached.

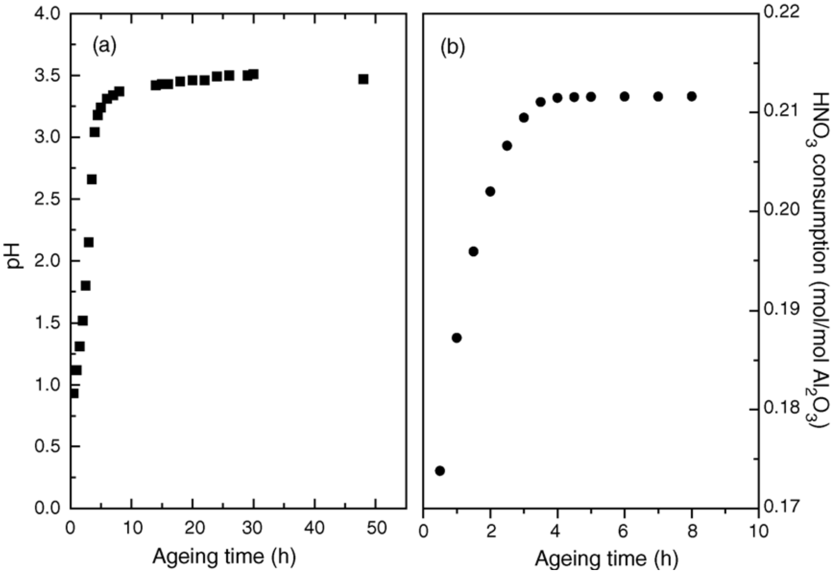

Fig. 1. (a) pH evolution of the suspension as function of the ageing time under stirring; (b) total acid consumption between 1 and 10 h of ageing calculated from pH.

When alumina powder is contacted with of a strong acid, two different processes, implying acid consumption, could take place: surface charging and dissolution, for these processes the following reactions have been proposed [15–20]:

$$\text{bulk} - \text{AlOH}_{\text{surf.}} + \text{H}^+ \rightarrow \text{bulk} - \text{AlOH}^+_{2\,\text{surf}} \quad (1)$$

$$\text{Al}_2\text{O}_3 + 6\text{H}^+ \rightarrow 2\text{Al}^{3+} + 6\text{H}_2\text{O} \quad (2)$$

The acid consumption due to dissolution ($H^+_{\text{dissolution}}$) can be calculated by evaluating the amount of Al^{3+} formed during ageing. Al^{3+} can be estimated by atomic absorption after separation by ultra-filtration [15,19,21]:

$$H^+_{\text{dissolution}} = 3\text{Al}^{3+}_{\text{measured}} \quad (3)$$

The acid consumption associated with surface charging ($H^+_{\text{surface charging}}$) cannot be directly measured, but it can be calculated according to the following relation:

$$H^+_{\text{surface charging}} = H^+_{\text{initial}} - H^+_{\text{dissolution}} - H^+_{\text{final}} \quad (4)$$

where H^+_{initial} corresponds to the initial amount of acid in the suspension, $H^+_{\text{dissolution}}$ corresponds to the Al^{3+} present after ageing (determined by chemical analysis on the ultrafiltered sol) and H^+_{final} is calculated by the final pH.

The suspensions at different ageing time have been analysed to determine the contribution of charging and dissolution reactions to the total acid consumption.

The results are shown in Fig. 2. It is evident that both surface charging and Al^{3+} dissolution reactions are fast and they are almost concluded in a couple of hours of ageing. The Al^{3+} dissolution is responsible for the main acid consumption (80–90%), however the amount of dissolved alumina is quite negligible being the dissolved powder less than 1% of the total.

The amount of acid due to the surface charging process is small if compared to dissolution. An asymptotic value for the surface site densities of about 1.6 sites/nm^2 is reached within 8 h. This value is in good agreement with that of 1.03 sites/nm^2 reported in the literature as the maximum surface charging observed for the same submicronic alumina [19].

It is reported in the literature that surface charging is faster than dissolution. In fact, when alumina is contacted with solutions at low acid content (i.e., pH 4–5) protons are adsorbed at the surface and the rate of this reaction progressively decreases on increasing the surface charging. At this medium pH value, the acid consumption is due only to surface charging and this process goes on up to a plateau that corresponds to the surface sites saturation, and the plateau is observed around pH 3.4 [15,18,19]. If more acid is added, the alumina dissolution occurs, and, below pH 3.4, dissolution becomes the main reaction. Therefore, in strong

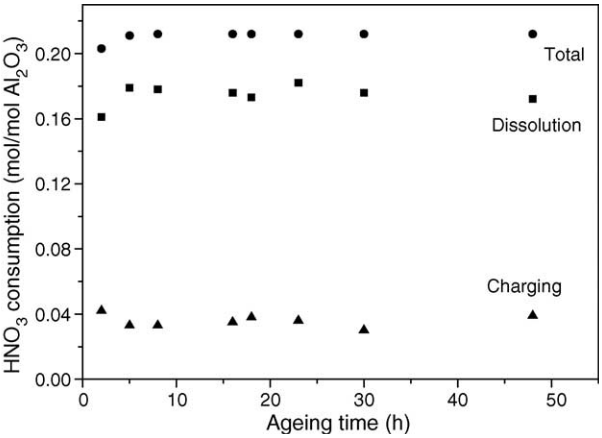

Fig. 2. Acid consumption for surface charging and dissolution as function of the ageing time under stirring.

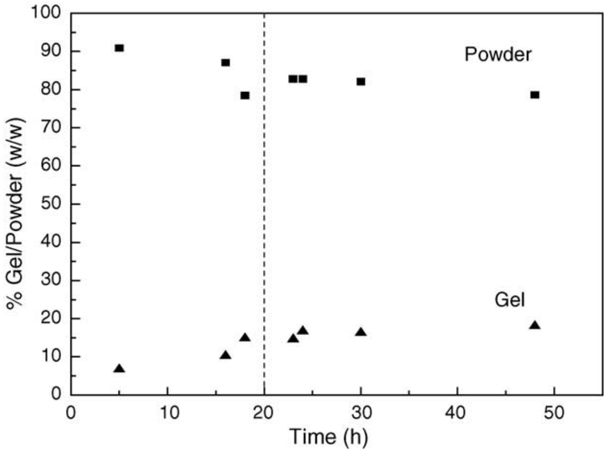

Fig. 3. Weight percentages of gel (triangles) and unreacted powder (squares), determined upon ultracentrifugation at 1.3×10^4 rpm and calcination at 700 °C, as function of the ageing time.

acid conditions similar to these here reported, the charging and the dissolution process occur simultaneously [15,18,19].

Accordingly, the strong acid consumption observed in the first hours of ageing is due both to the surface charging and to the dissolution processes that, in view of the high acid content, go on with similar rates at the plateau.

Furthermore, the constant concentration of dissolved Al^{3+} after 8 h of ageing is in line with the plateau in the solubility curve of Al^{3+} between pH 1 and 4. This behaviour has been explained considering that the progressive decline in the soluble species contrasts the higher solubility due to the lower pH values [17].

3.2. Sol–gel transformations

The amounts of gel and powder, separated by ultracentrifugation at 1.3×10^4 pm, are plotted in Fig. 3 as a function of the ageing time. The amounts of the different phases have been quoted in terms of weight percentage of the original powder. The gel amount progressively increases up to 20 h then it sets at a constant final value of 15–20% (w/w), while the powder amount decreases to 75–80% (w/w) with a parallel trend. Constant sol amounts of about 6% (w/w) are measured in all the investigated range of ageing time.

For highly dispersible alumina, the literature reports that surface charging is necessary to obtain the deaggregation of the large powder aggregates in order to give colloidal particles (sol) [21,27]. The gel formation consists in the aggregation of the charged colloidal particles to form a continuous network [3,28].

Accordingly, the small amount of gel formed in our dispersion can be due to the low surface charging. It is interesting to notice that, although the surface charging is already completed within 8 h of ageing, the gel formation proceeds until 24 h indicating that the rate of this process is low.

3.3. Rheological behaviour

The flow curves of the suspension at different ageing times are plotted in Fig. 4a and b. A non-Newtonian behaviour is evident for all the investigated ageing times: as a matter of fact, a strong shear dependence is observed. Viscosity decreases on increasing the shear rate from 10 to 100 s^{-1}, thus confirming the pseudoplastic behaviour of the suspensions. At a shear of 10 s^{-1}, the value of interest for dip-coating application, viscosities between 0.03 and 0.5 Pa s are measured. Also a strong dependence with the ageing time is present: viscosity increases up to 27 h, and then it decreases.

For boehmite systems the literature reports that the viscosity of the dispersion is influenced not only by

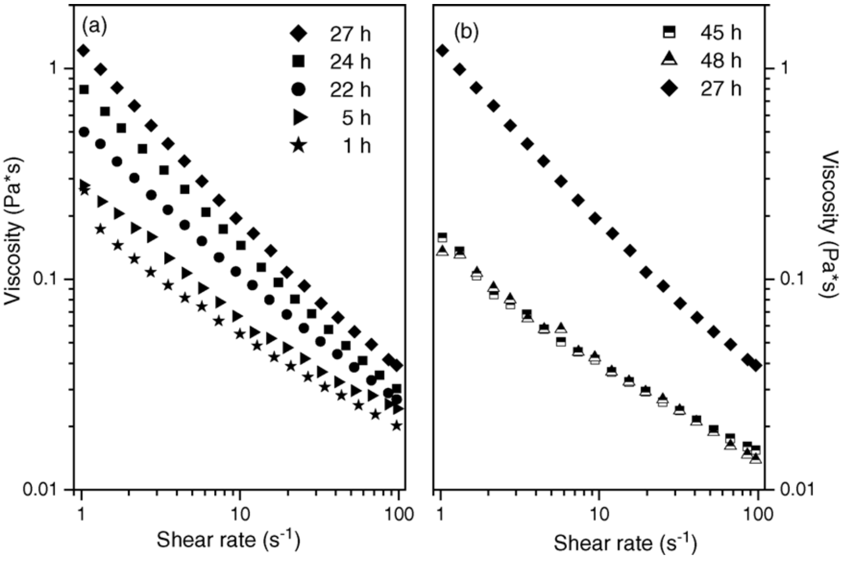

Fig. 4. Flow curves of the suspensions aged between: (a) 1 and 27 h; and (b) 45 and 48 h (measurements performed at 20 °C, using flat plates of diameter = 40 mm).

the amount but also by the nature of the gel phase present in the suspension [22,25,29–31]. In particular, viscosity is reported to increase on increasing the gel strength, i.e., the degree of interaction in the gel network.

The gel strength can be assessed by evaluating the viscoelastic properties measured by rehological tests in oscillatory mode [25]. Mechanically, a gel can be defined as a soft material having both solid- and liquid-like properties [3]. Gels are viscoelastic in nature [3] and the application of oscillating small strains to these materials provides information on their elastic or viscous behaviour [26]. Experimental results of oscillating tests can be mathematically analyzed according to the ''Maxwell model'' [26]. The response of the material to an imposed force is expressed by a vector which modulus is the complex number $G^* = G' + iG''$, where the dynamic moduli G′ (the storage modulus) and G″ (the loss modulus) represent a measure of the elasticity and of the viscosity at a given frequency of oscillation [26]. Accordingly, G′ is associated with the solid-like behaviour of the gel, i.e., to the gel strength, and G″ is associated with its liquid-like behaviour. It is reported that the higher is G′ compared to G″, the greater is the solid-like behaviour thus the greater is the degree of interaction in the gel network [25,26,30].

The results obtained on a selected representative sample are shown in Fig. 5a where the curves of the elastic and viscous moduli are plotted as a function of the applied stress. The gel shows a solid-like behaviour up to 0.8 kPa: that is $G' > G''$ throughout the applied stress range. At 0.8 kPa a sharp crossover between the viscous and the elastic moduli is observed. This indicates that, at such stress value, the gel structure collapses and the two moduli have the same value. When the gels are of physic-type (weak gel), the following peculiar characteristics are observed in the oscillatory measurements: (a) values of $\tan\delta = G''/G' > 0.1$; (b) frequency dependence of the moduli; (c) the capability of the fluid to flow under large deformation without rupture due to the absence of permanent cross-linking [32]. For the gel samples of this work tanδ in the range 0.11–0.9 has been calculated throughout the applied stress range, a slight frequency dependence of G′ and G″ has been observed and high values of the crossover point have been found. Thus, it is concluded that the separated gels are of physic-type (weak gels).

In Fig. 5b the G′ storage moduli of gels, of comparable humidity, obtained at different ageing time are plotted. For samples aged up to 18 h, increasing G′ values are found, while lower and comparable G′ values are measured for the samples aged at 24 and 48 h. Accordingly, a maximum of the gel strength in between 18 and 24 h of ageing can be evinced.

The maximum of viscosity observed during ageing (see Fig. 4) could be explained as follows. On increasing the ageing time, viscosity increases due to the increasing amount of gel (up to 20 h), to the increasing gel strength (up to 18 h) and to flocks formation (up to 5 h to reach pH 3.5). The maximum at 24–27 h could results from the balance of all these processes. Furthermore, the observed decrease of viscosity could be due both to the decrease of the gel strength and the re-dispersion of the flocks.

In fact, as reported in the literature, in alumina suspensions prepared via peptization reaction, the formation of colloidal gels is accompanied by the formation of reversible flocks, particularly in powder with a low particle size and a low surface charge density [27]. The flocks formation results in a higher viscosity of the

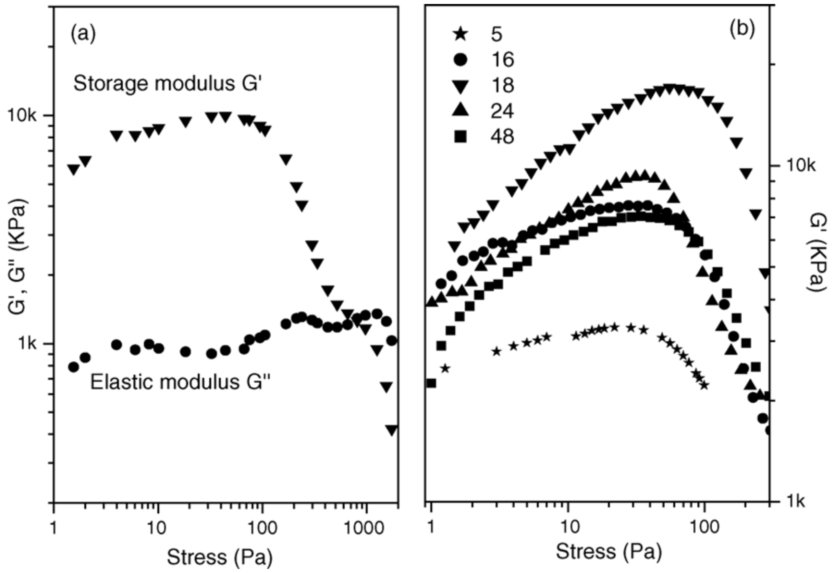

Fig. 5. (a) Storage G′ (triangles) and elastic G″(circles) moduli of the gel separated after 24 h of ageing determined in oscillatory mode (Dynamic oscillations = 1 Hz, applied stress between 0.01 and 10 kPa), (b) G′ storage moduli of gels separated at different ageing time (gels are of comparable humidity content, dynamic oscillations = 1 Hz, applied stress between 0.01 and 10 kPa).

suspension. However, in the pH range 3.5–5, the formation of polynuclear aluminium species (e.g., $[AlO_4Al_{12}(OH)_{24}(OH_2)_{12}]^{7+}$ [21]) occurs at the expense of the dissolved Al^{3+} ions. The polynuclear species adsorb on the flocculated particles thus charging their surface and inducing the re-dispersion of the flocks. This process lowers the viscosity of the suspension [27].

It should be pointed out that an ageing time of 24 h was found to be the optimal time to obtain a stable slurry that leads to uniform and well adherent alumina layers [23,24].

3.4. Dip-coating

Metal slabs of Fecralloy® were dip-coated with the alumina suspension aged at different times. In Fig. 6, the coating load and the adhesion as a function of the ageing time are reported. The coating load increases on increasing ageing time due to the increasing viscosity of the suspensions [23,24]. A constant loading of about 1.1 mg/cm^2 is obtained for the suspensions aged from 2 to 6 h that have evidenced very close viscosities, while a coating load of about 2.2 mg/cm^2 is obtained for the suspension aged up to 24 h that has shown the maximum degree of viscosity. Due to the lower viscosity of the suspension, a coating load of 1.4 mg/cm^{2}has been obtained for the suspension aged for 48 h. Such coating loads correspond to a thickness of 10–20 μm. The adhesion of the layers, also in view of the relative low thickness and despite of large amount of water in the wet layers, is always good being zero or negligible for all the samples.

This coating procedure allowed us to prepare active catalytic coatings on ceramic and metallic slabs, tubes and foams. The obtained structured catalysts have been tested on both catalytic combustion of CH_4 and CO oxidation showing good activity and stability [23,24,33–35].

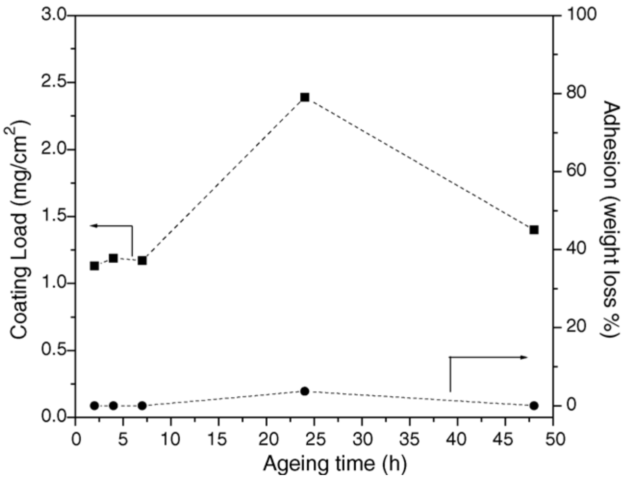

Fig. 6. Coating load and adhesion of the deposited layers using suspensions at different ageing time (withdrawal velocity = 3 cm/min).

4. Conclusions

The following main conclusions can be drawn:

1. Two reactions are involved in the acid consumption: dissolution and surface charging. The largest part of the total acid consumption is due to dissolution, although only 1% of the total alumina powder is dissolved. The reactions are fast and proceed with comparable rates in the first 5 h of ageing to reach a stable pH that corresponds to maximum surface charging and maximum Al^{3+} dissolution in the adopted experimental condition.
2. Gels of physic-type are formed. Gel formation continues to increase until 20 h of ageing and final gel amounts about 15–20% (w/w) are formed. Gel formation is a slow process that is completed within 20 h of ageing, a far longer time than that required for surface charging and colloid formation (5 h).
3. For all the investigated range of ageing time, non-Newtonian pseudoplastic behaviour of viscosity is found. At shear = 10 s^{-1}, viscosities between 0.03 and 0.5 (Pa s) are measured.
4. Viscosity is strongly time-dependent showing a maximum at 27 h of ageing. The viscosity increases up to the maximum level due to the growing amounts of gel, to the increase of the gel strength and to the formation of the flocks. The decrease of viscosity is due both to the decrease of gel strength and to the re-dispersion of the flocks. Depending on the ageing time well adherent layers characterised by loadings between 1.1 and 2.2 mg/cm^2 and thickness of 10–20 μm are obtained.

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