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Preparation and characterization of extruded monolithic ceramic catalysts

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Abstract

The rheological characterization of ceramic pastes is illustrated as an advantageous tool in the development of easily extrudable materials. Then each step of the extrusion process of monolithic ceramic catalysts is discussed, and the relation between the nature and amount of the raw materials, the rheological characteristics of the resulting paste, and the morphological and mechanical properties of the final material are discussed. This matter is illustrated with selected examples taken from the literature and from our experience in the preparation of TiO_2-based monolithic honeycomb catalysts. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Extruded monolithic ceramic catalysts are widely used in automotive and stationary NO_x emission control reactors [1,2]. They are also considered in other applications including catalytic combustion, chemical processing industries and others [3].

The extruded monolithic ceramic honeycomb used for automotive emission control is based on synthetic cordierite $2MgO*2Al_2O_3*5SiO_2$. The fabrication of cordierite includes the following basic steps: (i) mixing of the raw oxides to favour complete solid state reactions during thermal heating; (ii) plasticizing with water and other organic additives; (iii) extrusion of the resulting ceramic paste through appropriate dies; (iv) careful drying to drive out moisture without cracking; and (v) firing at 1450°C to transform the raw materials into the cordierite monolithic substrate. Cordierite substrates are coated with a mixture of high surface area oxides which directly supports noble and base metal catalysts.

Extruded monolith for the control of NO_x emissions from stationary sources consist of homogeneous mixtures of anatase TiO_2 as high surface area support, of WO_3 (or MoO_3) and V_2O_5 as active components, and of silico-aluminates and glass fibres as mechanical promoters. In this case the high surface area support material represents the major component of the monolith instead of being applied as a washcoat. These monolithic catalysts are fabricated according to the following basic steps: (i) dry mixing of the solid raw materials; (ii) wet mixing and plasticizing with water and organic additives; (iii) extrusion of the monolith honeycomb; (iv) drying uniformly; and (v) calcining at about 500–600°C. In some cases vanadia is not

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added in the dry mixing stage but is impregnated on the extruded monolith after calcining.

High surface area monoliths based on oxides or zeolites and with the same characteristics of washcoats and traditional extrudates can also be fabricated directly. After drying these materials are generally fired at temperatures in the range 500–800°C to prevent appreciable sintering and loss of surface area. The active catalyst components can be added in the mixing stage or after forming and heat treatment.

Each of the production steps in the extrusion process does influence the quality of the final material. Therefore, it is important to know the correlations between process parameters and the relevant properties of the catalysts or of the catalyst substrates. This is particularly true for extruded monolithic ceramic catalysts considering that the precision demanded for these materials may be in the range of microns and is much higher than that of traditional items that are also formed by extrusion of ceramic pastes such as bricks and pipes.

In the following we shall address first the rheological characterization of ceramic pastes. Then we shall discuss each step of the extrusion process of monolithic ceramic catalysts (mixing and plasticizing of the raw materials, extrusion, drying and calcining), the relation between the nature and amount of the raw materials, the rheological characteristics of the resulting paste, and the morphological and mechanical properties of the final material.

2. Rheological characterization of ceramic pastes

2.1. Analysis of paste flow

We recall that the extrusion process is generally accomplished in a screw extruder consisting of a feed port, a screw rotating in a barrel and an extrusion die. The ceramic paste is fed through the port, is pumped through the barrel at a desired flow rate of material Q (while the pressure build up necessary for the extrusion step is generated) and is finally forced through the forming die. Screw extruders are well suited to continuous operation for making large batches while the outlet pressure is generally not such high. The pressure developed in the screw extruder as the paste moves towards the die is affected by the screw geometry and the paste rheology.

Considering that extrusion can be envisaged as an ordinary flow process, it is useful to use rheological methods to investigate the formability behaviour of ceramic pastes [4]. The capillary rheometer is generally employed for this purpose in view of its correspondence to the extrusion machines and the slit capillary devise is preferred to the road capillary one since its geometry makes it possible to analyse a range of shear rate values (from 0 to 100 s^{-1}) that compares well with those estimated inside the honeycomb die land during the extrusion process.

In a standard rheological measurement the paste is forced to flow at a definite flow rate Q through the capillary. The resulting pressure drop between two pressure sensors placed at a given distance along the slit capillary axis and where the entrance effects are negligible are used to calculate the apparent shear stress at the wall ($\tau_w = \mathrm{d}P^*H/2L$ where L and H are the length and the height of the slit capillary). When a Newtonian fluid of viscosity η deforms, the shear is uniform throughout its volume and the viscosity is defined as the ratio of shear stress to the shear rate $\mathrm{d}\gamma/\mathrm{d}t = \gamma'$. That is

$$\eta = \tau/\gamma'. \qquad (1)$$

In the case of non-Newtonian fluid η is not independent of τ and γ'. To correlate experimental shear stress and true shear rate values for a non-Newtonian fluid such as ceramic pastes a simple power law function can be used in line with the literature approach for plastic extrusion [5]. Accordingly

$$\eta = \eta_0 \gamma' n - 1_t \qquad (2)$$

and thus,

$$\tau = K\gamma' n_t. \qquad (3)$$

Alternatively a Bingham's law can be used, since there is evidence that ceramic bodies can be ideally represented as two-phase media for which shear flow occurs only when τ exceeds a characteristic yield stress τ_0 [6]:

$$\tau = \tau_0 + \eta\gamma'_t. \qquad (4)$$

The true shear rate γ'_t of a non-Newtonian fluid is obtained from experimental data by correcting the apparent shear rate γ'_N valid for a Newtonian fluid, which depends on the flow rate Q, by the Rabinowitsch equation [7]. That is to say:

$$\gamma'_{\mathrm{N}}(\text{at}\,H/2,\ \text{corresponding to}\ \tau_{\mathrm{w}}) = 6Q/(WH^2), \quad (5)$$

$$\gamma'_{\mathrm{t}} = \frac{\gamma'_{\mathrm{N}}}{3}\left[2+\frac{\mathrm{d}\log\gamma'_{\mathrm{N}}}{\mathrm{d}\log\tau_{\mathrm{W}}}\right] = \frac{\gamma'_{\mathrm{N}}}{3}(2+S). \quad (6)$$

Since ceramic pastes are pseudoplastic fluids, S values are well above unit and thus $\gamma'_{\mathrm{t}} > \gamma'_{\mathrm{N}}$

The rheological parameters in the power low (K and n) and in the Bingham equation (τ_0 and η) can be estimated by fitting the characteristic equation of a slit die to the experimental data of flow rate and pressure buildup. The characteristic equation of a slit die for the power law model (Eq. (7)) and for the Bingham model (Eq. (8)) are given in the following [6]:

$$Q = \frac{nWH^2}{2(1+2n)}\left(\frac{H\,\mathrm{d}P}{2KL}\right)^{1/n}, \quad (7)$$

$$Q = \frac{\mathrm{d}P\,WH^3}{12\eta L}\left(1-\frac{3\tau_0 L}{H\,\mathrm{d}P}+\frac{4\tau_0^3}{H^3\,\mathrm{d}P^3}\right). \quad (8)$$

A critical assumption of the flow analysis described above is that of fluid adhesion to the wall. Experimental methods have been developed to separate the effect of slip at the wall based on rheological measurements performed with different capillaries [8].

2.2. *Examples*

Fig. 1 shows the shear stress functions $\tau(\gamma')$ of two ceramic pastes [4,9,10].

The paste of curve A consists of natural clay and is characterized by a flat shear stress function with a smoothly increasing shear stress for increasing shear rate. This is the typical rheological curve for a material with good extrudability due to a plug-like velocity profile in the capillary, with most of the deformation occurring in a thin layer near the wall. Accordingly most of the volume of the flowing materials remains almost undeformed and a better recombination of the paste flows is thus allowed in the die land to form the honeycomb matrix.

The paste of curve B consists of a catalyst carrier material called Pural SB with Luviskol as plasticizer in the liquid phase. A step increase of shear stress with a broad range of scattering was observed at high shear rates. This effect is caused by a layer of hardened dry material that forms near the wall where the highest shear stress exists. The extrusion of a regularly shaped honeycomb catalyst is not possible in this case and remarkable surface defects are present in the extrudate that showed a Christmas-tree shaped body instead of the intended monolith honeycomb.

A ceramic paste with advantageous extrusion properties based on the same material Pural SB can be obtained by the use of a suitable plasticizer. A more flat shear stress function and a flow pattern with rather good extrusion properties were measured in this case and nice extruded honeycomb catalyst carriers were obtained from this paste; also in this case the velocity profile is

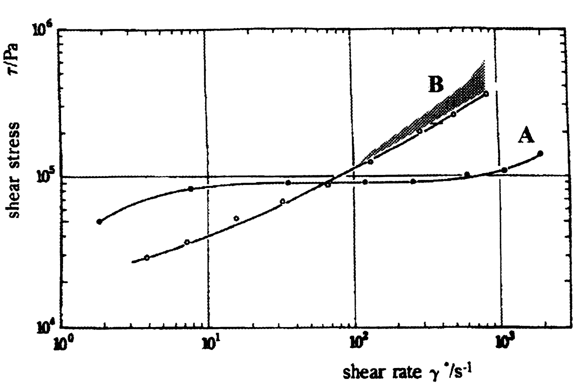

Fig. 1. Shear stress functions of ceramic pastes: (A) clay; (B) Pural SB (a catalyst carrier) + Luviskol (a plasticizer) (adapted from [4]).

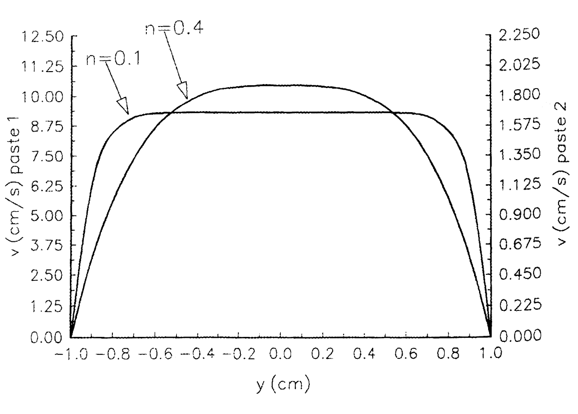

Fig. 2. Velocity profiles inside the slit capillary for pastes with good (n=0.1, paste 2) and poor (n=0.4, paste 1) extrudability.

plug-like, and most of the deformation occurs near the wall.

It is worth noting that curves A and B of Fig. 1 can be fitted by a power law function with low and high n values, respectively (see Eq. (3)). Lower n values are associated to a more flat velocity profile inside the capillary (see Fig. 2 [11]) and thus to a more favourable conditions for extrusion with lower or no tendency to generate lamination defects. Indeed lamination defects are generally associated with the inadequate joining of two adjacent layers of the paste in the bulk of the material. Lamination is reduced if the cross-section of the die is reduced after the streams are brought together.

3. Mixing and plasticizing

The solid powders are first dry mixed to ensure a uniform distribution of all the solid components. Extrusion aids and binders can also be added at this stage as solid components. Indeed when added as liquid these components are usually very viscous and can be very difficult to mix uniformly with powders.

The process of wet mixing follows until the liquid is distributed uniformly, namely until a liquid layer or film is formed covering the whole surface of each solid particles. The liquid need to be very mobile initially to favour its incorporation into the paste while a high viscosity is preferred in the final stages of mixing so that the high shear forces are transmitted through the bulk of the paste to obtain good and uniform packing of the particles and to ensure stable extrusion. During this stage the mixing of the solid components also continues.

High shear mixing is required in some applications to break down the large particles present in the starting solid powder and those formed during mixing and to ensure that the powder is in a consistent stage of close packing.

Parameters that are of relevance in the mixing and plasticizing stage include the geometry of the kneading chamber and of the blades, and time. It is also important to control the concentration of water and of organic additives to ensure the appropriate rheology of the liquid phase during mixing, since if the viscosity is too high the mixer may be ineffective.

4. Paste composition

The relation between the nature and amount of the raw materials, the rheological characteristics of the resulting paste, and the morphological and mechanical properties of the final material will be discussed with reference to the preparation of TiO_2-based monolithic honeycomb that is presently under study in our labs [12].

The solid components employed in the manufacture consist of tungsta/titania (90% w/w), clays (~6.5% w/w) and glass fibres (3.5% w/w). Water with small amounts of methyl-hydroxy-ethyl-cellulose (MHEC) and poly-ethylen-glycol (PEG) are added to impart plasticity and to provide effective lubrication during extrusion.

4.1. *Water content*

The water content in the kneading mixture influences the quality of the plastic mixture and its extrudability and it is also directly correlated to relevant characteristics of the final product.

Fig. 3 shows the shear stress function $\tau(\gamma')$ of two TiO_2 based ceramic pastes with different water contents. The data in Fig. 1 are well fitted by power law functions with appropriate values of the parameters K and n (Eq. (3)). Good formability with no surface defects were observed for the paste of curve A that is characterized by high shear stress ($K=\lim \tau$ (for $n\rightarrow 0)=3.5\times 10^4$ Pa) and a flat rheological curve ($n=0.1$). In the case of curve B the paste is characterized by much lower shear stress values ($K=2.5\times 10^3$ Pa) and a higher value of the power law coefficient ($n=0.4$).

Lamination defects and a tendency to collapse were observed for the extruded material with the high water content. The lamination defects originate from the flow pattern with a more extended deformation region whereas the tendency to collapse is associated to the presence of excess liquid between the particles which accounts for the low viscosity and makes the material too soft to retain its shape. Lamination defects are favoured by fast heat treatments.

A direct correlation can be found between the water content and the morphological and mechanical characteristics of the extruded monolithic honeycombs as reported in Table 1. A marked drop in the crushing

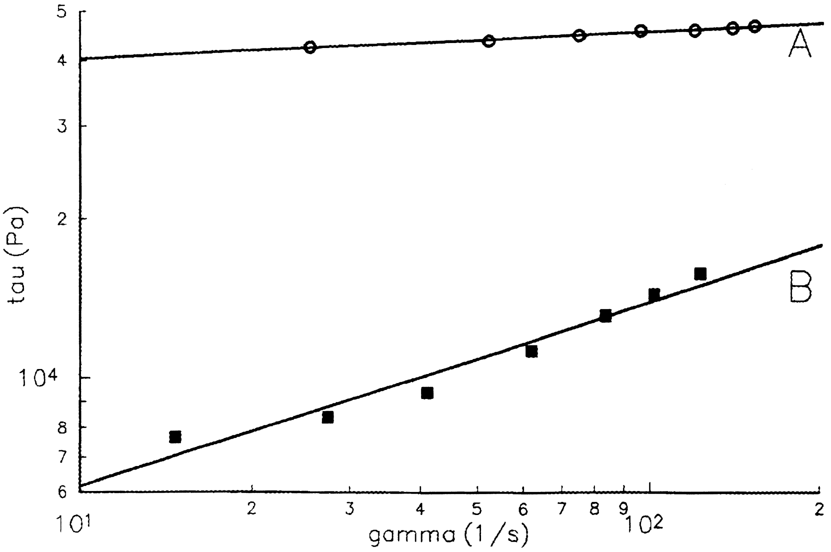

Fig. 3. Shear stress curves of TiO_2-based ceramic pastes with water content of 30% (w/w) (A) and 40% (w/w) (B).

Table 1
Effect of water content on the morphological and mechanical characteristics of monolithic TiO_2-based honeycomb catalysts.

Water content (% w/w)	30	40
Mean radius of micropores (Å)	80	80
Volume of micropores (cm^3/g)	0.20	0.22
Mean radius of mesopores (Å)	700	1400
Volume of mesopores (cm^3/g)	0.1	0.3
Crushing Strength (kg/cm^2)	22	3

strength and a corresponding increase in the volume of mesopores is measured on increasing the water content. Noticeably a bimodal pore size distribution was always determined with micropores of ~100 Å, in line with the crystal dimensions of TiO_2 as derived from XRD analysis, and mesopores of ~1000 Å, in line with the dimensions of the powder aggregates determined by granulometry measurements. The diameter and the volume of the micropores were not affected by the water content.

4.2. Organic additives

MHEC content. When the MHEC content was increased lower and more steep shear stress functions were measured, which implies lower K values (i.e. lower viscosity) and higher n values (i.e. more pronounced velocity profile in the capillary), respectively. Upon the addition of MHEC the volume and the mean diameter of the mesopores decreases significantly. Thus it was concluded that MHEC acts as organic binder by lowering the viscosity of the paste and by favouring the compacting of the solid particles in the final material. Indeed MHEC polymers are soluble in water and reduce the surface tension of aqueous solutions, which favours improved wetting of the surface of solid powders.

PEG content. The shear stress rheological functions of pastes with increasing PEG content are characterized by lower shear stresses and with almost constant and low n values. This indicated that PEG acts primarily as a lubricating agent thus ensuring lower operating pressure and more flat velocity profiles in the die land during extrusion. Still the content of PEG must be carefully chosen since at high PEG content a dramatic increase in the diameter and volume of the mesopores and a drop in the crushing strength of the monolithic honeycomb were observed.

4.3. Inorganic additives

Clays (bentonite) and glass fibres were used as inorganic additives. The results obtained with and without these additives indicated that clays improve the mechanical strength of the monolithic honeycomb and that fibres are oriented in the direction of the extrusion, thus ensuring good radial crushing properties to the monoliths.

The presence of clays also affects the viscosity of the ceramic paste, since higher shear stresses with a maximum at pH=6–7 were measured in this case. These clays posses a layered structure with platelets negatively charged (due to the substitution of Al^{3+} cations by Fe^{2+} or Mg^{2+}) separated by layers of hydrated exchangeable cations such as Na^+, Ca^{2+} and Mg^{2+} to counterbalance the weak negative charge in the structure. Since the natural pH of bentonite is 9, the particles experience lower repulsive forces for pH=6–7 which results in higher viscosity or become more positively or more negatively charged when the pH is varied from the neutral value into the acidic range or into the basic range. Accordingly pH can be used as a rheological control agent in this specific case.

4.4. *Packing of solid particles*

The packing density of a bed made of non-porous particles differing significantly in size has been addressed by many authors. The concept underlying these approaches is that particles of small diameter can be introduced between particles of large diameter to give closer packing.

When applying these concepts in paste extrusion, it must be remembered that they refer to packing without surface effects. It has been shown that the packing of the particles affects the rheology of the paste. The particle size distribution also affects sintering during heat treatment and the pore size distribution of the final product. Besides the high shear mixing used to prepare extrudable pastes typically results in closer packing than predicted on a pure geometrical basis.

This matter is illustrated by the examples shown in Fig. 4 where mixture of solids with different pore size distribution (P) are contrasted with the corresponding distributions of the dried (D) and fired (F) extrudates [6,13]. The powder shown in Fig. 4(a) is characterized by a narrow pore size distribution and accordingly it does not pack closely. On the contrary the powder of Fig. 4(b) is made of a fraction with a larger mean particle diameter and a fraction of a smaller mean particle diameter and the pores of the dried and fired sample are dominated by the smaller fraction and accordingly are much smaller.

The mesoporosity may also be created by using organic additives in the liquid phase that must be burned off completely with no residues such as carbon

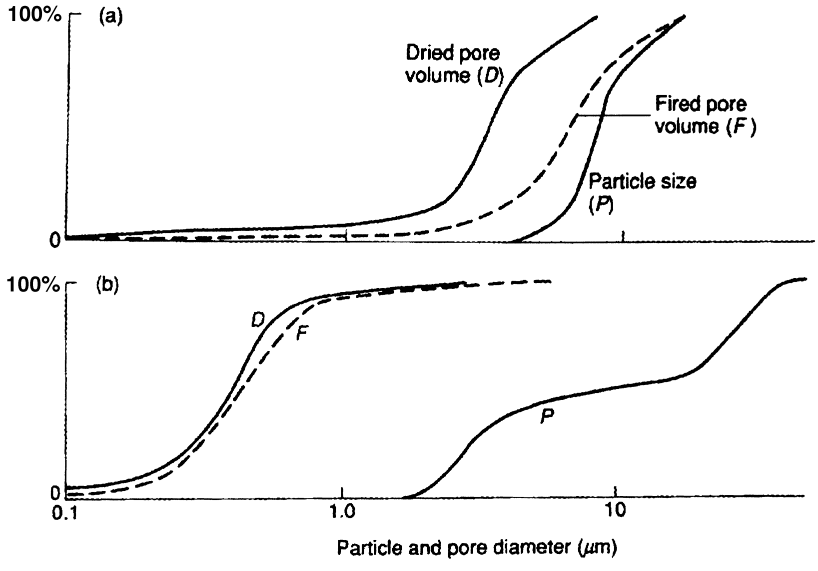

Fig. 4. Particle size distribution of α-alumina particles and pore size distribution of the dried (D) and fired (F) product made by extrusion (adapted from [6]).

that could adversely affect the properties of the extrudate.

5. Drying and calcining

During drying the liquid is driven off and the extruded green body shrinks. This step requires a careful control of temperature and moisture and must be slow enough to prevent ruptures and cracks.

The final step in the preparation of monolithic honeycomb is calcination. The changes that take place during calcination can be investigated by performing DTA-TG analysis of the dried sample. This is shown in Fig. 5 where the TG and DSC curves obtained for a dried P25-TiO_2 green body are presented [14].

The endothermic desorption of water at 100°C and the exothermic burn off of organic additives (cellulose and poly-ethyleneoxide) at 200°C and 360°C are evident. During burn off the heating rate and the air flow must be controlled to avoid hot spots. The broad exothermic effect measured between 700°C and 800°C is associated with the phase transformation from anatase into rutile TiO_2.

6. Conclusion

In this paper we have attempted to provide a critical survey of the extrusion of monoliths ceramic catalysts that are extensively used in automotive and stationary emission control and are being considered for many other applications as well.

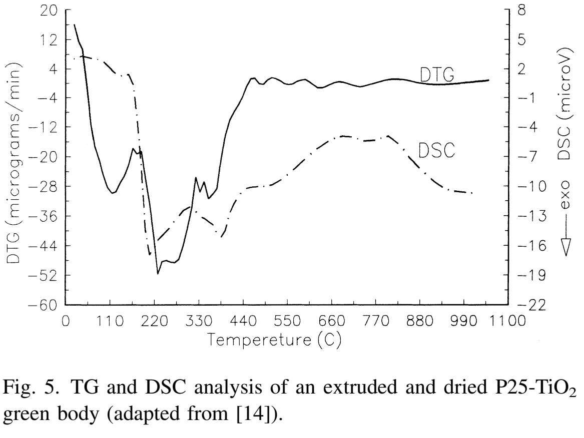

Fig. 5. TG and DSC analysis of an extruded and dried P25-TiO_2 green body (adapted from [14]).

Since plastic ceramic materials can be treated as ordinary concentrated suspensions, rheometric methods are especially suitable for testing these materials. In particular it has been shown that, in spite of the complexities associated with flow processes of ceramic pastes, capillary rheometry when critically applied is a useful tool to foresee the extrudability of ceramic pastes.

The fundamental steps of the extrusion process of ceramic pastes, namely mixing and plasticizing of the raw materials, extrusion, drying and calcining, have been illustrated with the aim to correlate the process parameters and the relevant properties of the catalysts or of the catalyst substrates. In particular the effects of the paste composition (water content, organic additives, inorganic additives, size distribution of the solid powder) on the rheology of the paste and on the morphological and mechanical characteristics of the final product have been discussed and mutually correlated. In particular it has been shown that:

1. a narrow water content must be identified as most appropriate for extrusion;
2. organic additives are used to lower the viscosity of the paste, and act as binders and lubricating agents;
3. the nature and content of organic additives influence the morphology of the final product;
4. inorganic additives act as mechanical promoters to increase the strength of the final material but are also used as binders;
5. drying must be performed under a careful control of temperature and moisture and at an appropriate rate to prevent ruptures and cracks;
6. calcining up to selected temperatures allows burn off of the organic additives and sometimes solid state reactions of the raw materials to form the structure of the final product.

Acknowledgements

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