Ceramics International **21** (1995) 43–49

Influence of Some Precursors on the Physico-Chemical Characteristics of Transition Aluminas for the Preparation of Ceramic Catalytic Filters

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(Received 1 August 1994; accepted 29 August 1994)

Abstract: This work deals with the development of a new type of product, a *catalytic filter*, which could be used for treating flue gases, coupling particulate filtration and catalytic abatement of noxious gases. The first step of this project concerned the coating of the pore walls of a ceramic candle filter (made of α Al_2O_3) with a high specific surface area phase (i.e. a transition alumina). This layer will act as a catalyst support. The coating was obtained by impregnation of the porous support and subsequent calcination, using three different precursors. An alumina sol (A), an aluminium nitrate solution (B) and an urea + aluminium nitrate solution (C) were compared as regards the thermal stability and surface characteristics of the transition aluminas produced. The transition aluminas were investigated in the operation temperature range which can be of potential interest for the foreseen application (400°–800°C). Both physico-chemical and surface characterization results indicated precursors A and C as the most promising. Preliminary coating tests have demonstrated the feasibility of a continuous, homogeneously distributed layer of transition alumina on the pore walls of the support, enabling further development of the manufacture by deposition of specific catalytic principles.

1 INTRODUCTION

The study of catalytic porous barriers has been a relevant research topic for materials and catalysts scientists, as well as for chemical engineers, in the last decade.[1] These barriers allow the coupling of two functions (e.g. separation and reaction) in a single unit.

According to one of the potential applications, the porous barrier could remove particulate from gas streams with simultaneous catalytic abatement of some gaseous pollutants. This rather new concept, which could be referred to as *catalytic filtration*, might be used for treating flue gases generated by combustion processes[2] (e.g. waste incinerators, diesel engines, fluidized-bed coal combustors, boilers) or, more widely accepted, whenever gaseous streams need to be purified from both particulate (fly-ashes, soot) and noxious gases (NO_x, volatile organic compounds, etc.).

The catalytic processes generally require temperatures ranging from 200°C to 600°C, which the widely used polymeric filters cannot withstand. Therefore, these filters require a preliminary cooling down of hot flue gases to lower temperatures (100–150°C) and subsequent reheating up to temperatures suitable for catalytic abatement. This energy consuming cycle and the separation in two units (filtration and catalytic abatement) could be by-passed if the filter is designed with thermally resistant materials (such as metals or ceramics) and activated with suitable catalysts. Most of the catalyst supports are ceramic (e.g. transition phases of alumina, silica, titania, mixed oxides):

Ceramics International 0272-8842/95/$9.50

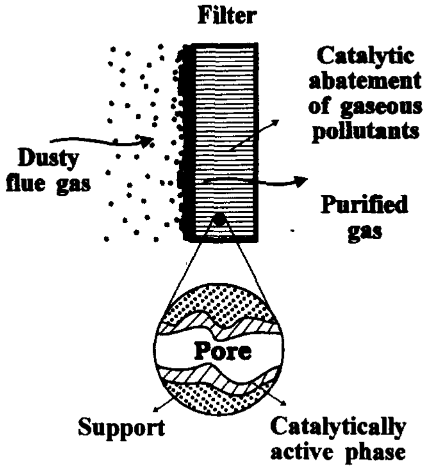

Fig. 1. The catalytic filter concept.

these catalysts supports have limited cohesion and mechanical resistance and, therefore, need to be placed on a pre-shaped structural support for the above considered applications. From this viewpoint, the use of ceramic components is preferable to metal ones, since they allow limited thermal expansion mismatch with the catalyst support phase.

Ceramic filters for high temperature application are developing fast,[3–5] but only a little effort has been devoted to the coupling of filtration and catalytic abatement in one single module.[2]

A scheme of a catalytic filter is shown in Fig. 1: a dusty flue gas is filtered by the ceramic barrier (generally made by mullite, cordierite, α alumina, silicon carbide) and a dust cake forms; gaseous pollutants are reacted away throughout the ceramic matrix, owing to the action of the catalyst placed on the filter pore walls.

In this work a porous candle filter made of α Al_2O_3 was considered, though due to its low specific surface area (SSA < 1 m^2/g), it is a poor catalyst support. To overcome this hurdle, preformed catalyst particles could be coupled with the filter, but the small pore size would hamper their direct intrusion. For this reason, in order to increase its active area, the pore walls of the ceramic matrix must be covered with a homogeneous coating of a higher SSA phase, such as transition alumina. The well stuck and crack-free layer will be the real support for the catalyst (e.g. V_2O_5 for NO_x reduction with ammonia). Much care must be taken in obtaining this coating and controlling its thickness and distribution in order to avoid excessive decrease of the mean pore size, and pore plugging. The coating was obtained by impregnation of the α Al_2O_3 support with suitable precursors followed by promoted *in situ* formation/deposition of aluminium hydroxydes, which were then thermally transformed into transition aluminas.

This paper focuses on the synthesis and the characterization of different transition aluminas in order to choose the best one for use as catalyst-support phase in a catalytic ceramic filter. Three different precursors were considered (i.e. an alumina sol, a concentrated aluminium nitrate solution, a solution of urea and aluminium nitrate) and compared on the basis of the physicochemical characteristics of the transition aluminas obtained. Some results of the impregnation tests of the α Al_2O_3 tube with the best precursors are also reported.

2 MATERIALS AND METHODS

2.1 Ceramic support

Porous α Al_2O_3 tubes (250 mm length, 10 mm external diameter, 1·5 mm thickness) were used as structural ceramic support (SCT, Societé des Céramiques Techniques, Bazet, France). They showed a SSA of 0·25 m^2/g, an open porosity of 24·5% with a mean pore size of about 15 μm, that allows successful particulate filtration from flue gases and negligible dust penetration into the bulk matrix.[3]

2.2 Transition alumina precursors

Three different precursors were investigated. For the sake of clarity, they will be denoted by A, B and C:

(A) A stable colloidal dispersion (sol) obtained by 0·1N HCl peptization of an aluminium hydroxyde gel (0·038 Cl^-/Al^{3+} molar ratio). The gel was precipitated by adding 4N NH_4OH to 0·6M aqueous solution of $AlCl_3 . 6H_2O$ up to a final pH of 9; after several washings to eliminate precipitation by-products, the gel was peptized by HCl addition at 80°C for 48 h in closed vessels.[6]

(B) An aluminium nitrate saturated aqueous solution, obtained by dissolution of $Al(NO_3)_3 . 9H_2O$ at 75°C. Drying and calcination yield nitrate decomposition.

(C) An aluminium nitrate and urea aqueous solution prepared by dissolving at 50°C 750 g/litre of $Al(NO_3)_3 . 9H_2O$ (close to solubility limit) and adding urea up to a nitrate/urea weight ratio of about 2/1. The precipitation of aluminium hydroxyde was due to nitrate hydrolysis induced by the presence of ammonia, arising from urea thermal decomposition.[7]

2.3 Characterization of the transition aluminas

A physico-chemical characterization of the products was performed on powdered samples before the impregnation tests, in order to verify which of these precursors yields the transition alumina having higher SSA and thermal stability (properties of major importance for catalyst activity and durability).

The comparatively low amount of γ Al_2O_3 deposited on the pore walls during the impregnation steps and the strong matrix effect due to the α Al_2O_3 support would make *in situ* characterization of the transition alumina very difficult. It was reasonably assumed that unsupported alumina powders showed similar surface and bulk characteristics to the supported ones, on condition that preparation methodology and the thermal treatments had been retained. The powders obtained from A, B and C precursors, after calcination at 400°C for 1 min, were divided into small samples of about 1·5 g each and heat treated at different temperatures (400°, 500°, 600° and 800°C) for different times (1, 24 and 72 h), to follow phase development and SSA changes.

The powders were characterized by DTA-TG analysis (Netzsch STA; heating rate of 10°C/min), thermal desorption analysis coupled with mass spectrometry of the emitted gases (Balzers QDP 101; heating rate of 10°C/min), BET measurements of SSA (Sorptomatic 1800, Carlo Erba Instruments) and XRD after calcination at different temperatures for different times (Philips 1710 diffractometer with CuKα radiation).

In order to get further information about the surface status of the transition aluminas, some surface activity tests were performed on unsupported powders, calcined at different temperatures (from 400° to 800°C), using isopropanol dehydration as a model reaction, in a batch-operated differential recycle reactor, described elsewhere.[8] This reaction was chosen since it is catalyzed by the transition alumina itself thanks to its acidic sites.[9]

As long as the reaction proceeds, the variation of the overall conversion ζ in the batch volume was monitored as a function of time by gaschromatographic analysis (Hewlett Packard HP 5890 Series II, equipped with Porapack Q column and TCD detector).

From the slope of such curves estimates of the intrinsic reaction rate R ($mol . g^{-1} . s^{-1}$) were drawn.

2.4 Support impregnation tests

After ultrasonic washing in acetone and drying at 80°C for 30 min, the virgin supports were placed in a glass cell under vacuum ($\cong 10^{-2}$ bar). The cell was then filled with precursors A, B or C, and the liquid penetration into the porous matrix was then facilitated by increasing the operating pressure up to atmospheric level. The supports impregnated with precursor C were kept in an oven overnight at 95°C to allow urea decomposition. All the supports impregnated with precursors A, B or C were then dried and calcined, in order to develop a transition alumina phase and induce adhesion of the layer. A controlled thermal cycle (drying at 105°C for 4 h; heating up to 230°C at 2°C/min; 1 h stay at 230°C; heating up to 400°C at 2°C/min; 3 days stay at 400°C; cooling down to room temperature at 2°C/min) was followed in order to limit the residual stresses and the occurrence of diffuse cracks on the deposited layers. The impregnation cycles were repeated up to a maximum of 5 times.

In the case of precursor A, the sol viscosity was considered as a critical parameter for optimizing the coating: for this reason, three viscosities were tested (2·7, 3·65 and 5·05 mPa·s).

All the impregnated samples were characterized by weight-increase measurements after each impregnation cycle, SEM observations (Hitachi S-2300), Hg porosimetry (Porosimeter 2000, Carlo Erba Instruments) and BET determination of SSA.

3 RESULTS AND DISCUSSION

After drying at 105°C, powders A, B and C were analyzed by DTA-TG [Fig. 2 (a), (b) and (c)]. Large weight losses, coupled with endothermic peaks, were recorded in the temperature range between 80°C and 400°C, due to the elimination of physisorbed and chemisorbed water, as well as of reaction by-products (i.e. NO_x, NH_4OH). No weight losses were detected at temperatures higher than 600°C for powders B and C, while they continued, even if very poor, up to about 900°C for powder A. An exothermic peak, due to α Al_2O_3 crystallization, was noticed at about 1120°C for powders B and C and at about 1270°C for powder A.

These results are in agreement with those obtained by thermal desorption analysis [(Fig. 3(a), (b) and (c)]. The surfaces of samples B and C, both produced after starting with aluminium nitrate, were strongly polluted by adsorbed nitrate groups. However, nitrogen oxides were totally eliminated from the surface of sample C in the temperature range 350–500°C.

On the contrary, some nitrate groups persisted on the surface of sample B up to about 800°C. In sample A, the precursor salt and the peptization process led to a severe pollution by chloride ions which diminished only at temperatures higher than 600°C.

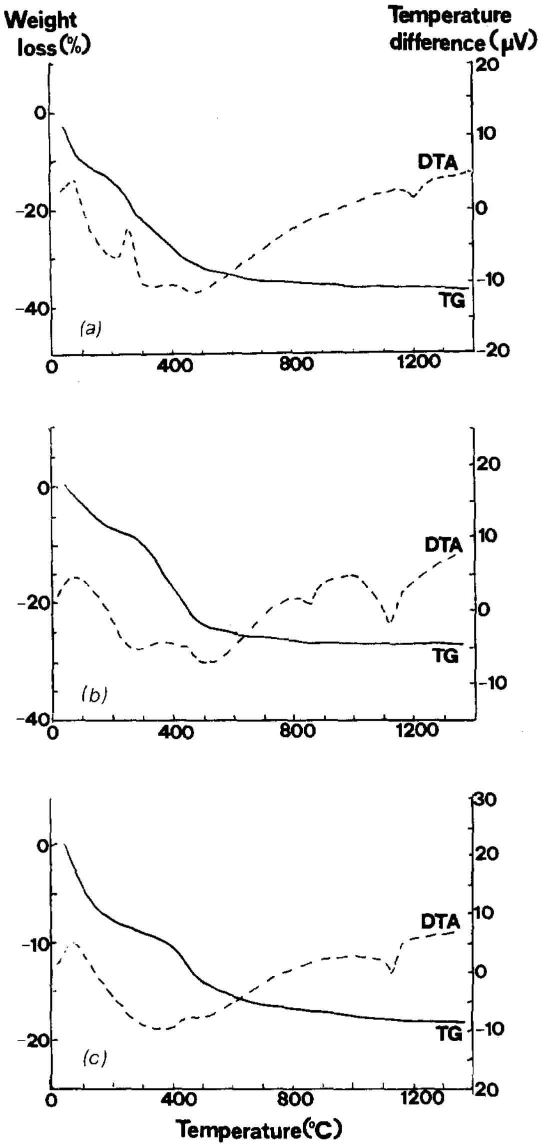

Fig. 2. DTA-TG curves of the powders obtained from precursors A (a), B (b) and C (c).

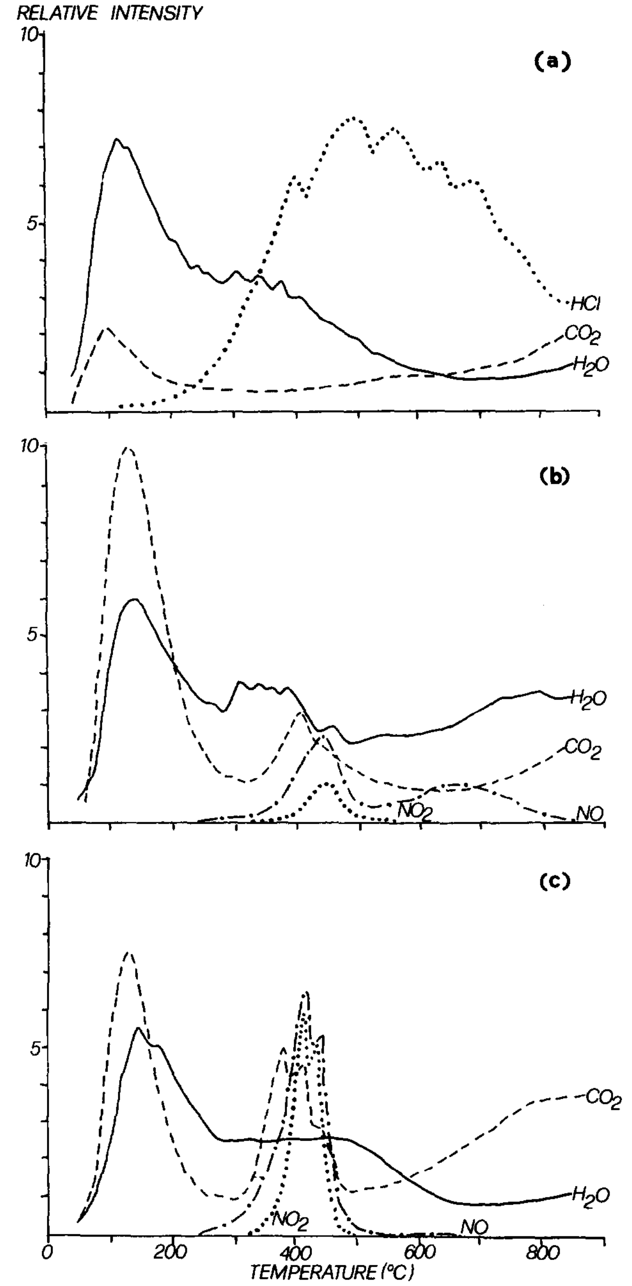

Fig. 3. Thermal desorption curves of precursors A (a), B (b) and C (c).

The BET and XRD results referred to powders A, B and C calcined at different temperatures for different times are reported in Fig. 4.

Sample A had already crystallized as γ Al_2O_3 after 1 min at 400°C and remained stable at all the temperatures and times investigated. On the contrary, sample B crystallized only after 72 h at 600°C or at the higher temperature tested: this behaviour is probably due to severe surface pollution by nitrate groups,[10] as confirmed by thermal desorption data. Sample C, which presented the maximum of NO_x desorption at about 400°C, crystallized as γ Al_2O_3 at all temperatures and times tested. However, in both samples B and C, detectable amounts of α Al_2O_3 were already present after 72 h at 800°C.

The SSA evolution was in agreement with the XRD and thermal desorption data. For all the samples, the SSA became almost constant after 72 h of calcination: measurements performed on samples calcined at 400°C for about 200 h confirmed this trend.

Samples A and C presented very similar behaviours (with slightly higher values for sample C) and their SSA values were always markedly higher than those of sample B.

The above-reported results underline that the different precursors yielded three transition aluminas, different in crystallinity, phase stability, SSA and surface pollution. In order to better understand the influence of the precursor salt and of the preparation procedure on the surface status of these transition aluminas, their catalytic response towards isopropanol dehydration was assessed.

Figure 5 reports the initial-time intrinsic reaction rate (R_0) for the different calcined powders.

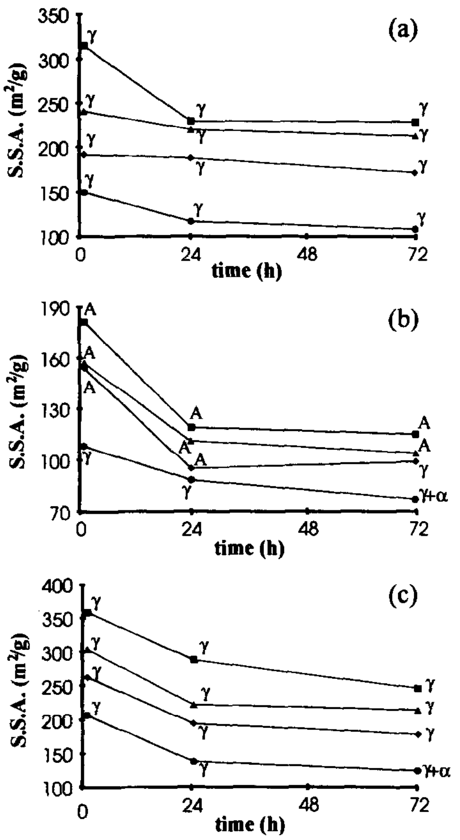

Fig. 4. Evolution of phases and SSA of the transition aluminas obtained starting from precursors A (a), B (b) and C (c), as a function of calcination temperature and time (■ 400°C; ▲ 500°C; ◆ 600°C; ● 800°C; A = amorphous; γ = transition alumina; α = α Al_2O_3).

These data can be properly employed for a comparison of the surface activity of the different powders since the relative ratio of the reaction rates remains almost unaffected as long as the reaction proceeds. This can be easily deduced from the variation of ζ as a function of run time as reported, for instance, in Fig. 6, where the behaviours of the powders calcined at 500°C and of a commercial transition alumina (Ketjen alumina grade 001-1,5E- AKZO Chemie, Deventer, Holland) are compared.

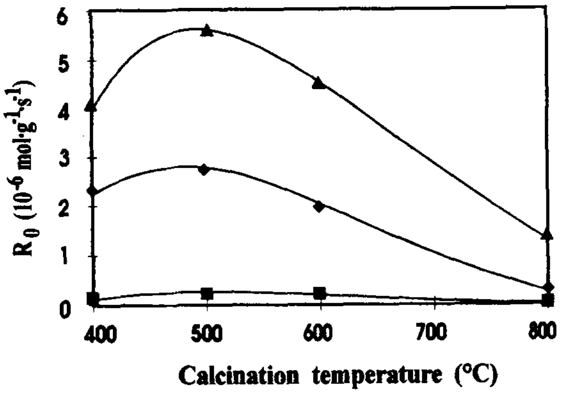

Fig. 5. Initial-time intrinsic reaction rate R_0 as a function of the calcination temperature of the transition aluminas prepared from precursors A (▲), B (■) and C (◆) (catalyst amount: 0·1 g; reaction temperature: 200°C; batch volume: 1100 cc; isopropanol initial partial pressure: 15 mbar).

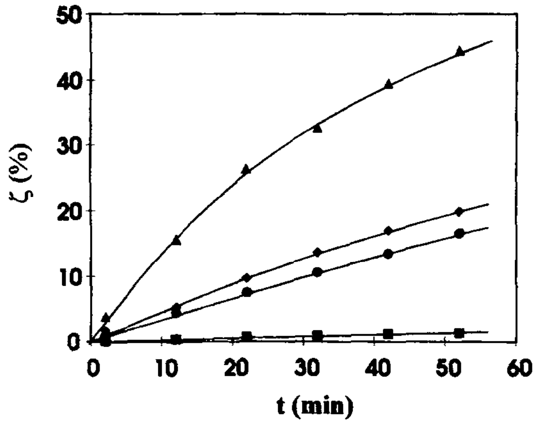

Fig. 6. Per-cent conversion (ζ) curves for transition aluminas A (▲), B (■) and C (◆) calcined at 500°C and for a commercial product (●) (same operating conditions listed in Fig. 5).

From the above data the following information can be drawn:

- —each powder performs at its best in the calcination temperature range from 400°C to 600°C (an optimum activity is detected at about 500°C);
- —the powders calcined at 800°C presented a much lower surface activity, owing to the relevant lowering of the SSA;
- —the surface activity of the sol–gel derived powders is higher than that of sample C, while that of sample B is extremely low;
- —sample C after calcination at 500°C behaves very similarly to the commercial transition alumina.

An explanation of these results can be attempted. Powder B probably owes its poor activity to its comparatively low SSA and to its amorphous state. The higher activity of powder A compared with powder C can be at least in part due to the presence of surface chloride ions.[11]

On the basis of these preliminary physico-chemical and surface characterizations, precursors A and C were chosen for further investigation, concerning the impregnation of α alumina tubes. Some explorative deposition cycles performed with precursor B led to disappointing results: instead of getting a homogeneous layer on the pore walls all over the manufact, almost all the deposit remained localized at the filter external surfaces, causing extensive pore blocking. This is a likely consequence of salt precipitation due to evaporative concentration during the drying step.

The impregnation tests were carried out with three sols (precursor A) having different viscosities and concentrations (30 mg Al_2O_3/cm^3 sol for η = 2·7 mPa . s; 45 mg Al_2O_3/cm^3 sol for η = 3·65 mPa . s, 53 mg Al_2O_3 sol for η = 5·05 mPa . s), and a concentrated solution C having a viscosity of 15 mPa . s at 25°C.

Table 1. Cumulative per-cent weight gain of the α Al_2O_3 supports after each impregnation

Type of precursor	Number of impregnations				
	1	2	3	4	5
A(η = 2·70 mPa . s)	0·55%	1·10%	1·80%	2·10%	2·75%
A(η = 3·65 mPa . s)	1·05%	1·90%	2·85%	3·70%	4·40%
A(η = 5·05 mPa . s)	1·15%	2·10%	3·20%	4·10%	4·68%
C	1·47%	2·77%	4·19%	5·04%	5·95%

In Table 1 the cumulative weight gain of the supports after each impregnation cycle and after calcination at 400°C is reported: at an equivalent number of impregnations, precursor C led to a more important weight gain and to an earlier occurrence of pore plugging than precursor A.

The total porosity decreased from 24·5% (mean pore diameter = 15 μm) of the virgin support to about 10·5% (mean pore diameter = 4·8 μm) after 5 impregnations with the sol having η = 2·7 mPa . s; to about 14·7% (mean pore diameter = 3·8 μm) with the sol having η = 3·65 mPa . s; to about 17·2% (mean pore diameter = 3·8 m) with the more viscous sol. In the case of precursor C, the porosity decrease was more important: after just 2 impregnation cycles the total porosity was only 14·4% (mean pore diameter = 3·1 μm), a value comparable to those obtained after 5 impregnations with sols.

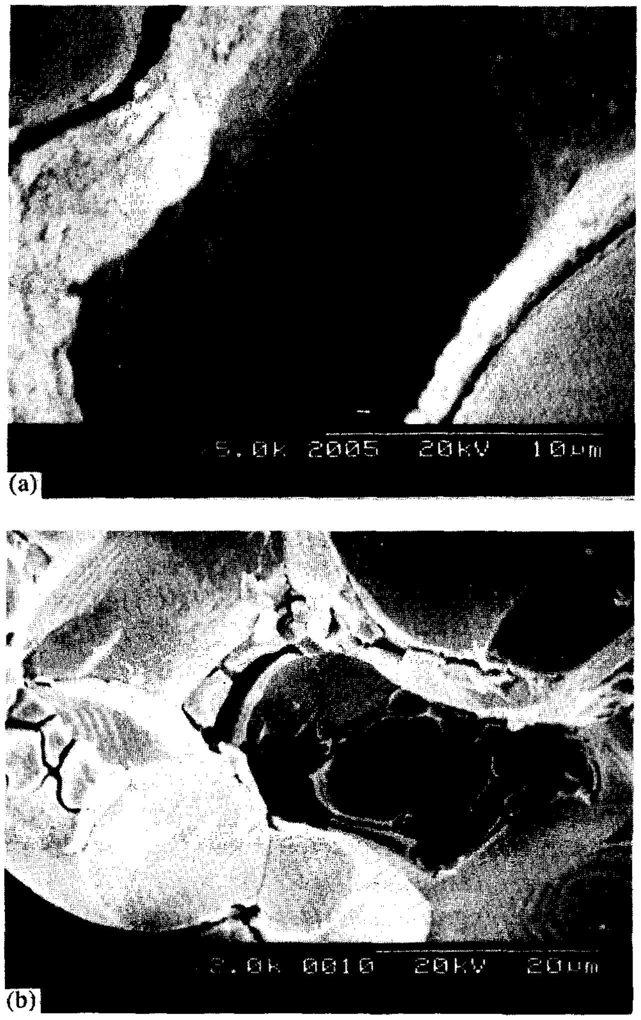

Fig. 7. SEM micrographs of the transition alumina coating in the α Al_2O_3 filter: (a) example of layer obtained by sol–gel impregnation technique; (b) pore plugging after three impregnations with precursor C.

In the absence of pore plugging the maximum value of the total SSA of the impregnated α Al_2O_3 support reached about 7–9 m^2/g after repeated impregnations with the sols and about 9–11 mg^2/g with precursor C.

The quality, distribution and thickness of the layers were determined by SEM observations (Fig. 7). It was confirmed that a number of impregnations higher than two with precursor C led to diffuse pore plugging. Moreover, the layers obtained by the three sols after four to five impregnations and by precursor C after two impregnations are similar to one another.

The layer is continuous, with a thickness ranging from about 0·5 to 2 μm; some cracks are present, especially in the layer obtained from precursor C.

4 CONCLUSIONS

The following conclusions can be drawn from the above results. The nature of the precursors has a fundamental influence on the physico-chemical characteristics of the transition aluminas prepared.

The sol–gel precursor (A) yielded a high-SSA product, polluted by chloride ions. The thermal stability of this transition alumina is excellent in all the temperature and time ranges tested. This γ Al_2O_3 showed the highest surface activity towards isopropanol dehydration, a likely consequence of the presence of surface chloride ions.

The thermal decomposition of aluminium nitrate (precursor B) led to an amorphous product, with a surface strongly polluted by nitrate groups; this transition alumina also presented particularly low SSA. In addition, its intrinsic surface activity is really poor and its thermal stability is limited (a slight conversion to α Al_2O_3 was already noticed at 800°C).

The urea+aluminium nitrate precursor (C) yielded the transition alumina with the highest SSA, a good surface activity comparable with that of a commercial product, but its crystallisation in the α phase has already started after a long stay at 800°C.

Precursors A (as sols at different viscosities) and C have been successfully used for impregnating porous α Al_2O_3 filters: a well-distributed and stuck layer on the pore walls of the filter was obtained in all cases, leading to a 40-fold increase of the total SSA of the product (from 0·25 to about 10 m^2/g).

The next step in the development of this new catalytic filter will be the deposition of a catalytic principle on the transition alumina coating. Some efforts could be also made in further improving the thickness homogeneity and adhesion of this coating.

The influence of the nature of the precursors, especially of the anion of the starting salt, on the surface characteristics of the powders has been underlined. If, during the further development of the product, it will be verified that the obtained surface characteristics may negatively affect the deposition and performance of supported catalytically active principles, modified procedures for the synthesis of transition aluminas will be investigated. For instance, as concerns the sol–gel method, transition aluminas could be prepared either purer (e.g. starting from alkoxydes) or polluted by different anions (e.g. using other precursor salts or peptizing agents).

ACKNOWLEDGEMENTS

The authors would like to thank the Ecole Nationale Supérieure des Mines of St. Etienne, France (Dept Chimie Physique des Processus Industriels) for the thermal desorption analyses performed.

REFERENCES

1. SARACCO, G. & SPECCHIA, V., Catalytic inorganic membrane reactors: present experience and future opportunities. *Catal. Rev. Sci. Eng.*, **36** (1994) 304–83.
2. KUDLAC, G. A., FARTHING, G. A., SYZMANSKY, T. & CORBETT, R., SNRB catalytic baghouse laboratory pilot testing. *Environ. Prog.*, **11** (1992) 33–38.
3. ZIEVERS, J. F., EGGERSTEDT, P. & ZIEVERS, E. C., Porous ceramics for gas filtration. *Ceram. Bull.*, **70** (1991) 108–11.
4. ALVIN, M. A., LIPPERT, T. E. & LANE, J. A., Assessment of porous ceramic materials for hot gas filtration applications. *Ceram. Bull.*, **70** (1991) 1491–8.
5. CLIFT, R. & SEVILLE, J. P. K. eds., *Gas Cleaning at High Temperatures.* Chapman & Hall, London, 1993.
6. MONTANARO, L. & GUILHOT, B., Preparation of microspheres from an alumina–zirconia sol. *Ceram. Bull.*, **68**(5) (1989) 1017–20.
7. SHAW, W. H. R. & BORDEAUX, J. J., The decomposition of Urea of aqueous media. *J. Am. Ceram. Soc.*, **77** (1955) 4729–33.
8. SARACCO, G. & MONTANARO, L., Catalytic ceramic filters for flue gas cleaning. I. Preparation and characterization. *Ind. & Eng. Chem. Res.* (in press).
9. YOSHIDA, S., Quantum-chemical studies of the acidity and basicity of alumina. In *Theoretical Aspects of Heterogeneous Catalysis*, ed. J. B. Moffat, van Nostrand, New York, 1988, pp. 506–29.
10. MATHIEU, M. V., Contribution à l'étude des gels d'alumine désorganisée, Ph.D. thesis, p. 31. University of Lyon, France, 1956.
11. LIPPENS, B. S., Active alumina in Physical and Chemical Aspects of Adsorbents in Catalysis. Lippens, B. C. & Steggerda, J. J. eds. pp. 171–211. Academic Press, London, 1970.