

Preparation of anchored ceramic coatings on metal substrates: a modified sol-gel technique using colloidal silica sol

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A single-step dip-coating technique was developed to produce stable films or washcoats of controlled thickness, surface area and pore-size distribution on alumina whisker-covered metal substrates (both flat plates and monoliths). Dip-coating slurries were prepared by dispersing fine porous powder in a colloidal silica sol. The method provided control over coating thickness and coating properties, such as pore-size distribution and surface area. The coating thickness could be varied between approximately 2 and 40 μm by selecting slurry composition and withdrawal speed in the dipping procedure. The pore-size distribution and surface area could be varied by changing type and amount of porous filler material in the dipping slurry. Uniform and bimodal pore-size distributions were obtained using silica and ZSM-5 molecular sieves, respectively, yielding coatings with surface areas between 60 and 400 m^2g^{-1} .

1. Introduction

Ceramic coatings on various substrate materials have become increasingly important for many applications, which often require highly precise procedures for deposition of the films. These applications may be categorized as follows [1]:

- (a) protective – corrosion and abrasion resistance [2, 3];
- (b) optical – reflectance and transmittance properties [4];
- (c) electrical – low-permittivity material in integrated circuits packaging [5];
- (d) porous – ultrafiltration, membranes, catalysis [3], and insulation [6].

One of the applications of thin ceramic coatings that has been developed and commercialized during recent decades is the use as catalyst support. Here, a porous ceramic coating is applied on a honeycomb support consisting of a large number of parallel channels. The porous coating is deposited on the channel walls and acts to increase the surface area of the support. The most important application of this type of catalyst system is as a three-way car exhaust catalyst [7]; other applications have also received considerable interest during recent years. The reader is referred to the extensive reviews by Irandoust and Andersson [8] and Cybulski and Moulijn [9] for more detailed discussions of honeycomb catalysts.

Ceramic coatings can be obtained using a number of high-temperature techniques, such as chemical va-

pour deposition (CVD) and spray-coating. Application of coatings from a liquid phase is an option that offers advantages such as simplicity and low cost [10]. Ceramic coatings may be deposited from a powder slurry or by using sol-gel techniques. The slurry method is often used in the preparation of honeycomb catalysts.

Sol-gel techniques may be based on either alkoxide precursor solutions or colloidal solutions. In both cases, gelation is achieved, upon which a rigid gel is obtained with controllable porosity and surface area. This gel can be converted to a solid oxide material by calcination, yielding monoliths, fibres, foams or coatings [11]. Alkoxide-based methods have received most attention, because they allow for mixing on an atomic scale in the preparation of multi-component gels. Preparation based on colloidal sols, on the other hand, offers advantages such as simplicity, non-hazardous starting materials and easier industrial handling.

Application of sol-gel coatings can be done by one of the following techniques; dip-coating, spin-coating or spraying. The use of spin-coating is restricted to circular substrates whereas flat substrates are usually required for the spraying technique. Dip-coating is commonly used for deposition of ceramic porous washcoats on honeycomb substrates. Although dip-coating of honeycomb substrates is applied widely, relatively little has been published on the fundamentals of this process [12]. Furthermore, the use of

sol-gel methods has not received much attention for this application.

Application of ceramic coatings may be the most advantageous application of sol-gel technology. This has induced large research and development efforts, which have led to a number of commercial applications. The most widely investigated material is silica, due to the application in optical and electrical systems, as well as the availability of alkoxide and colloidal precursors.

A modified sol-gel coating method based on colloidal silica sols is reported here. Coatings were applied on metal substrates from precursor slurries containing colloidal silica sol, water glass and porous filler powder, such as silica and zeolite. The use of water glass in the sol-gel preparation of porous silica from colloidal sols has been reported to facilitate drying and sol-gel transition [13]. Addition of water glass leads to larger pores, which reduces stress caused by surface tension, during evaporation of the solvent. The addition of porous filler material, demonstrated by us, allows thick coatings to be deposited in one step. Furthermore, this work shows that control over the coating thickness is achieved. Silica, prepared from a colloidal sol, was chosen as a filler in order to obtain a material with a homogeneous pore structure. In addition, redispersion of silica aggregates was shown to reduce stress in silica gels during gelation [14, 15]. A zeolite was chosen as filler material because of the interest in zeolites for various catalytic processes that may use honeycomb catalysts, such as abatement of nitrogen oxide emissions [16]. Some interesting aspects of the zeolite-silica sol system are discussed in this paper.

2. Experimental procedure

2.1. Materials

A commercially available colloidal silica sol, Bindzil 30/80 (Eka Nobel, Sweden), was used in all experiments. The silica content of the sodium-stabilized sol was 30 wt% and the sodium content was 0.13 wt% as Na₂O. The average particle diameter of the silica particles was 40 nm, which gave them a surface area of approximately 80 m² g⁻¹. A 40 wt% potassium water glass with K₂O:SiO₂ = 1:3 (Eka Nobel, Sweden) was used. ZSM-5 (Eka Nobel, Sweden) was used in the zeolite coatings. The SiO₂:Al₂O₃ ratio was 53, the sodium content was 0.027 wt% (as Na₂O) and the surface area was 414 m² g⁻¹. All data given are the supplier's specifications.

The metallic substrate used was OC 404, an iron-chrome-aluminium alloy (Sandvik Steel AB, Sweden). The metal was obtained as 0.17 mm foil and was pretreated to give a surface covered with alumina whiskers. This material has received considerable interest for application in three-way catalysts.

2.2. Coating procedure and characterization

The preparation of silica powder from colloidal silica sol is described in detail elsewhere [17]. The colloidal sol was evaporated to dryness at 75 °C, after which

alkali ions were removed using a washing procedure similar to that reported by Cao *et al.* [13]. Subsequently, the gel was dried at 75 °C, followed by calcination at 500 °C for 4 h. The material thus obtained was ground in a ball mill and sieved. ZSM-5 was used as-received after sieving. In all cases, the fraction smaller than 63 μm was used. Nearly all particles were between 1 and 40 μm, as determined by a sedimentation-centrifugation method (Brookhaven Instruments XDC particle sizer).

Dipping slurries were prepared by addition of small amounts (2.5 wt% total silica) of water glass to colloidal sol, acting as a dispersion agent. Fine silica or ZSM-5 powder was added slowly to the colloidal sol-water glass mixture whilst stirring. The amount of dry substance was varied by changing the amount of powder added to the mixture. The mixture was covered and kept at room temperature under vigorous stirring for at least 30 min. Some experiments were carried out with colloidal sol only, for comparison.

Flat metal-substrate samples were then rapidly immersed in the dipping slurry. Subsequently, they were withdrawn at uniform controlled speed, using a homemade device. The withdrawal speed could be varied over a wide range. Part of the slurry was saved for characterization. The coated samples and saved slurry were dried at 75 °C, followed by calcination at 500–600 °C. The all-silica samples were washed once more, following the same procedure as for the silica powder, as described elsewhere [17].

The coated samples were analysed using a scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectrometry (EDS) unit (Zeiss DSM 940 with Link QX2000). The thicknesses of the coatings were determined by an electro-magnetic method (Fischer Deltascope MP3). X-ray diffraction was used to study the sol-gel mixtures of ZSM-5 and silica (Siemens Diffraktometer 5000). Surface area and pore-size distribution (PSD) were determined using nitrogen adsorption (Micromeritics ASAP 2000).

3. Results and discussion

Fig. 1 shows a scanning electron micrograph of the whisker-covered metal substrate. Clearly visible are the alumina whiskers, which can anchor the coating to be deposited on them. EDS and X-ray photoelectron spectroscopy (XPS) showed that the whiskers contained only alumina, whereas the bulk composition of the steel was roughly Fe:Cr:Al = 75:20:5 by weight [17].

Fig. 2 shows a scanning electron micrograph and an EDS spectrum of the metal substrate covered with silica obtained by dipping once in the colloidal silica sol. It is obvious that the silica completely covers the textured surface, yielding a very smooth surface. The intensity of the peaks in the EDS spectrum, related to the metal substrate components are very low. The thickness of the film was 1–2 μm. The coatings did not show any tendency to peel after calcination up to 600 °C. This good adherence may be ascribed to the anchoring effect of the alumina whiskers. A parallel experiment was performed in which a coating was

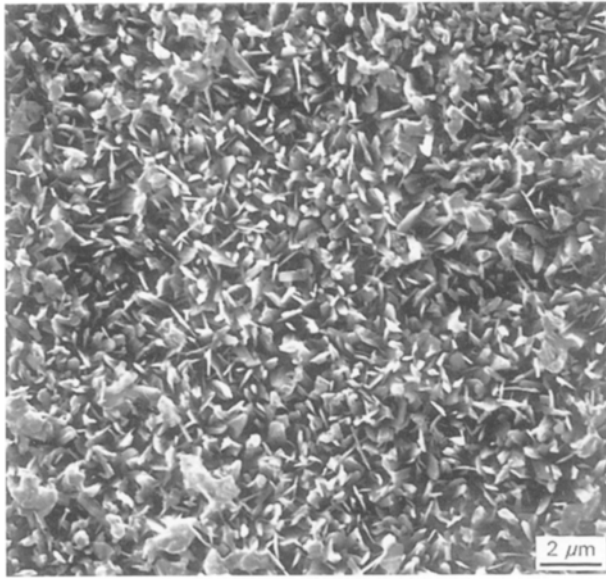


Figure 1 Scanning electron micrograph of the whisker-covered metal surface.

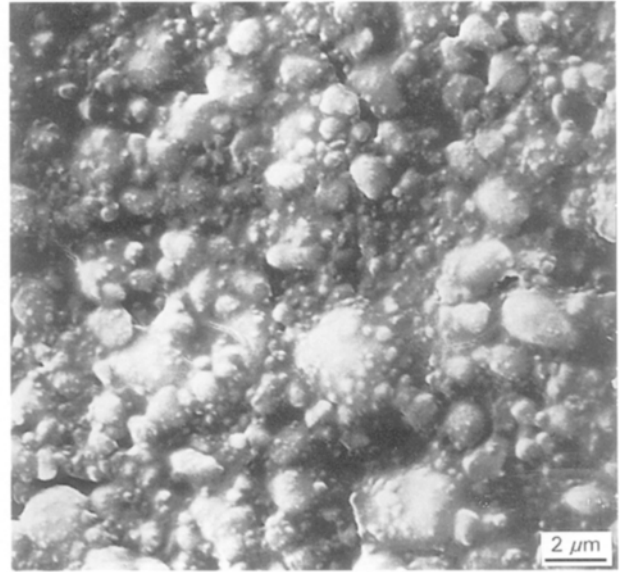
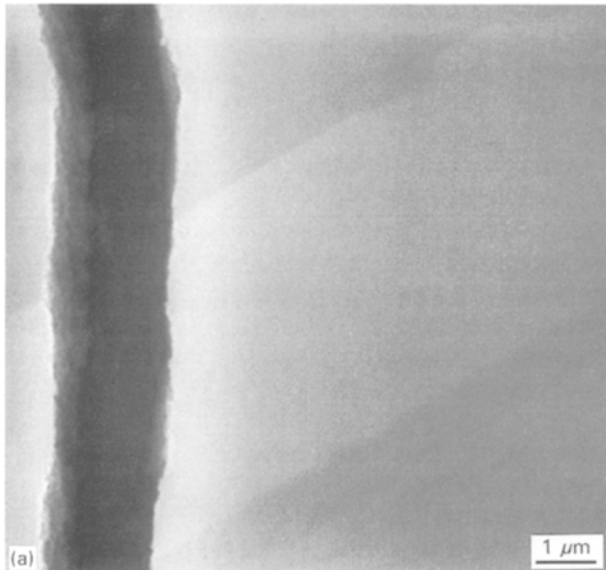
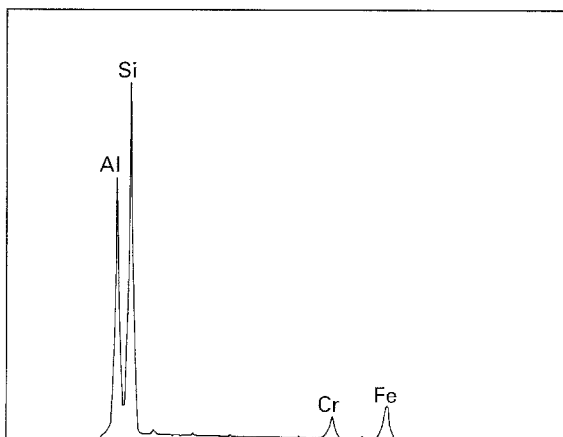


Figure 3 Scanning electron micrograph of the metal substrate covered with a coating from a silica-water glass-colloidal silica sol mixture.



(a)



(b)

Figure 2 (a) Scanning electron micrograph of the metal surface covered with a coating from colloidal silica sol. The crack seen on the left-hand side is due to the electron beam in the electron microscope. (b) EDS spectrum of the surface.

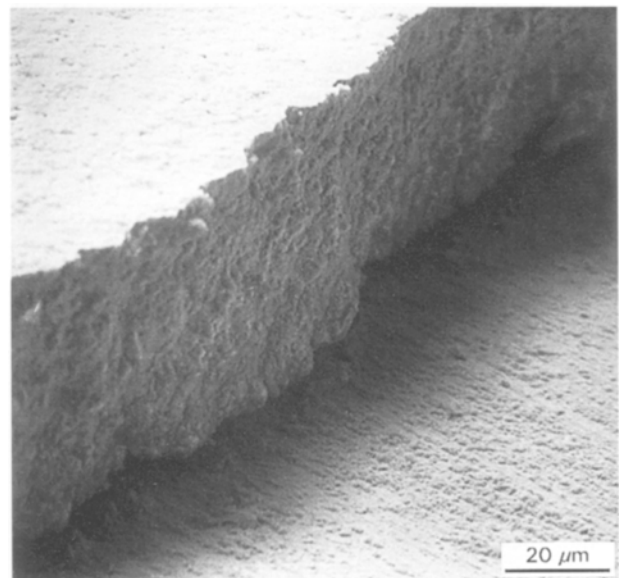


Figure 4 Scanning electron micrograph of a cross-cut of a silica-based coating.

applied to a metal substrate without whiskers. The coating exfoliated readily upon drying at room temperature.

A coating thickness of a few micrometres is not sufficient for applications such as in catalytic reactors. In such cases a few tens of micrometres are desirable. This would require a number of dipping steps [3, 18]. This is circumvented by the method presented here, which will be shown below.

A coating based on a silica-colloidal sol-water glass mixture is shown in Fig. 3. The presence of particulate material in the coating is obvious. The thickness of this coating is approximately 40 μm. This is clearly seen in Fig. 4, showing a cross-section of the coating. The coating is seen on the left-hand side, whereas remainders of the coating appear on the right-hand side. EDS showed that only silica is present

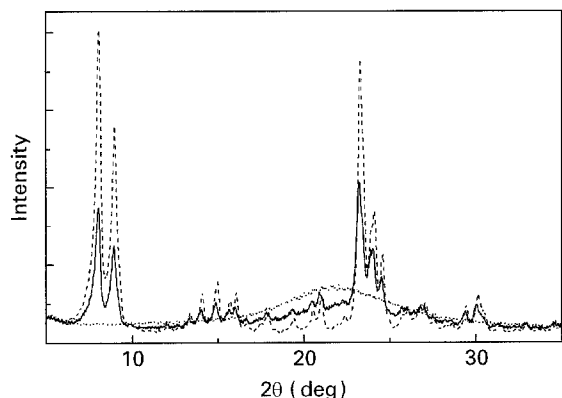


Figure 5 XRD patterns of a mixture of ZSM-5 and silica and of both components alone. ZSM-5: SiO₂ weight ratios: (---) 100:0, (—) 50:50, and (-·-) 0.100. All samples calcined at 500 °C.

in the coating, together with trace amounts of alkali from the sol and the water glass. The surface area and pore volume of the coating after calcination at 600 °C were 60 m² g⁻¹ and 0.23 cm³ g⁻¹, respectively. These values did not vary more than 10% when the ratio of silica powder:silica sol was varied between approximately 2:1 and 3:1 (silica weight basis). The thickness and surface area make such coatings interesting for catalytic applications, as demonstrated elsewhere [17]. It was also shown that the porous properties can be tailored by using different types of colloidal sols.

The pH of silica sol is between 9 and 10, whereas the pH of the water glass, used in this study, is higher than 10. In the experiments with ZSM-5, a strongly acidic oxide, it was necessary to add ammonia simultaneously to the addition of the zeolite. This was done to prevent the pH from dropping below 5. If the ammonia addition was omitted when adding the zeolite, the pH decreased to a value between 3 and 4 which caused rapid gelation of the silica sol. Hence, the viscosity of the mixture increased and coating was impossible. When the pH was kept above 5, coatings containing ZSM-5, silica sol, and water glass could be applied, having the same appearance as in Fig. 3.

X-ray diffraction was used to study the influence of the silica sol on ZSM-5 during mixing and application of the coating. Fig. 5 shows the XRD patterns of ZSM-5, silica prepared from silica sol, and a 50:50 mixture (weight basis) of ZSM-5 and silica prepared by mixing the zeolite with colloidal silica sol. The pattern of ZSM-5 confirms literature data (e.g. [19]). Silica exhibits a very diffuse XRD pattern, as expected from its amorphous structure. The most interesting aspect in Fig. 5 is the fact that the mixture of ZSM-5 and silica appears to behave as a mechanical mixture. Apparently, the sol, containing silica particles and free silicate ions, does not influence the crystal structure of the zeolite. The sol particles are more than an order of magnitude larger than the pore size of the zeolite and hence cannot enter or block the zeolite pores. Hence, a coating with a bimodal PSD is obtained, which is shown in Fig. 6.

The PSD of ZSM-5 shows a maximum below 1.7 nm, the lower limit of the equipment used, whereas

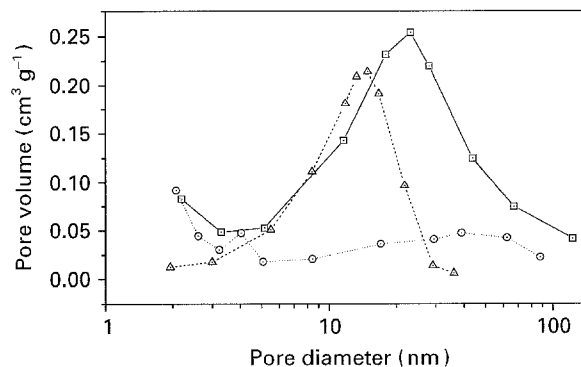


Figure 6 Pore-size distributions of a mixture of ZSM-5 and silica and of both components alone. ZSM-5: SiO₂ weight ratios: (○) 100:0, (◻) 50:50, and (△) 0.100. All samples calcined at 500 °C.

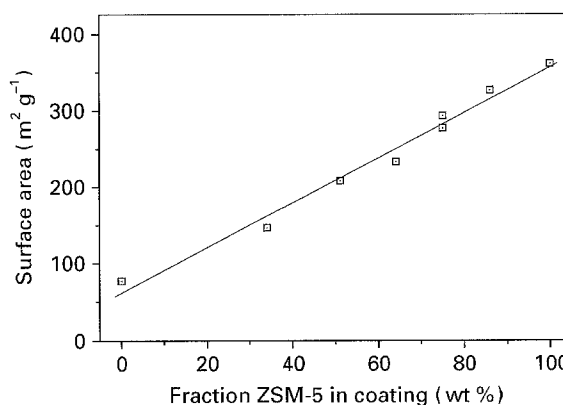


Figure 7 Coating surface area after calcination at 500 °C versus the fraction of ZSM-5 in the washcoat. The balance is silica.

the maximum for silica is found at 150 nm. The mixture of the two exhibits peaks of both components. Note that, the absolute values of graphs of the single components are divided by a factor of 2, in order to facilitate comparison. The fact that the silica-related peak is shifted to a larger pore size may be due to a certain degree of gelation in the mixture. Furthermore, the presence of water glass also increases the pore size. This was validated by a separate experiment in which the PSD of dried and calcined silica sol was compared to the PSD of a silica sol to which a small amount, 2.5 wt% silica base, was added. The mixture had a peak in the PSD at approximately 10% larger pore size. The silicate ions in the water glass are deposited on the sol particles during drying, leading to an increase in particle size, and hence pore size. Mixing of ZSM-5 with colloidal silica sol thus provides a method to prepare coatings with both mesopores and micropores.

The surface area of such a coating is strongly dependent on the fraction of ZSM-5 in the washcoat, as is shown in Fig. 7. This graph shows the surface area of ZSM-5-based washcoats with varying amounts of zeolite. There is a near-linear relationship between the surface area and the fraction of ZSM-5 in the washcoat. This suggests that there is no detrimental influence, such as pore blockage, of the colloidal sol on the zeolite pore structure.

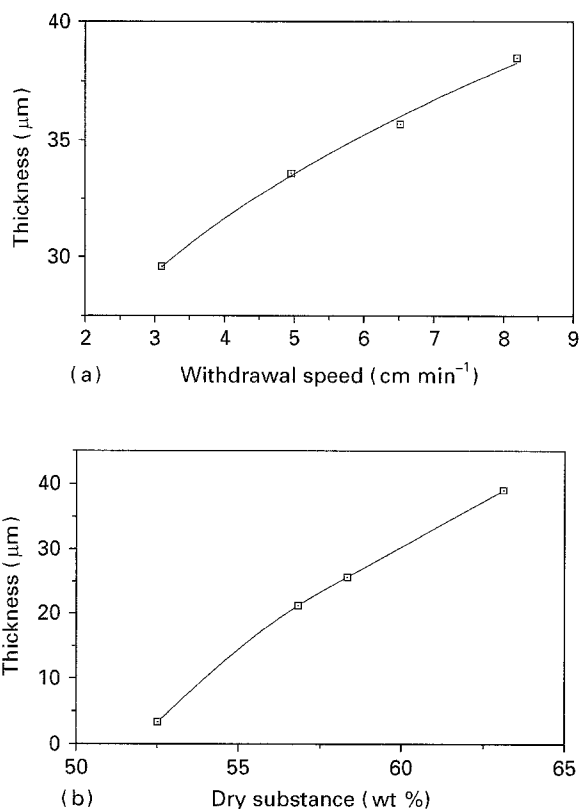


Figure 8 Silica coating thickness versus (a) withdrawal speed at 63.1 wt% dry substance; and (b) slurry dry substance at 5 cm min⁻¹ withdrawal speed.

Variation of the amount of porous zeolite powder in the dipping slurry influences the surface area for the zeolite-colloidal sol system. On the other hand, the surface area of the silica powder-based washcoats was not very dependent on the ratio silica powder:colloidal sol, as mentioned previously. Thus, the silica powder and the colloidal sol appear not to influence each other significantly.

The thickness of the coating may be controlled by both the withdrawal speed and the dry substance in the slurry. The almost linear increase of the coating thickness with the withdrawal speed is shown in Fig. 8a and that with the dry substance in the slurry in Fig. 8b. The results shown in Fig. 7 were obtained with silica powder as porous filler material. Similar results were obtained with the zeolite-based coatings. Thus excellent control over the coating thickness over a wide range can be achieved using the presented technique.

4. Conclusion

A novel modified sol-gel coating method has been developed to bring a ceramic coating, strongly anchored on to a metallic substrate. It is a dip-coating technique in which a mixture of porous powder and colloidal silica sol is used as a coating precursor slurry. It is applicable to metal substrates with various shapes, such as flat, tubular or honeycomb-type.

This method allows good control and tailoring of coating properties, such as surface area, pore-size distribution and coating thickness. The thickness can be varied over a wide range, 1–40 μm, in a single-step procedure. This possibility to tailor the properties of ceramic coatings or washcoats on metal substrates opens up interesting opportunities for, amongst others, catalytic applications.

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