

Preparation of thin zeolite films on porous titania-stainless steel composite substrates

Mikihiro Nomura, Leszek Gora*, Thomas Maschmeyer*, Ben Meester*
Joop Schoonman*, Freek Kapteijn* and Jacob A. Moulijn*

Department of Chemical System Engineering, Faculty of Engineering, University of Tokyo
Hongo 7-3-1, Bunkyo-ku, Tokyo, 113-8656, JAPAN,

Fax: 81-3-5841-7346, e-mail: Lscathy@chemsys.t.u-tokyo.ac.jp

*DelftChemTech, Delft University of Technology, Julianalaan 136, 2628 BL, Delft, The Netherlands

Thin ZSM-5 zeolite films were prepared on porous titania-stainless steel substrates using a hydrothermal synthesis method. Titania-stainless steel substrates were made by an electrostatic sol-spray deposition (ESSD) method. The titania layer deposited on stainless steel substrate by ESSD was stable against thermal shock (200 K/min) by aging the parent sol more than 5 h. Deposition temperature was one of the key factors to prepare fine porous structures on a porous stainless steel substrate. Uniform pores of a few micrometer in size were obtained at 533 K on dense stainless steel, while similar structures were obtained at 493 K on porous stainless substrate. The porous titania layer was stable against calcination at 873 K by mixing fresh sol and aged sol. However, the obtained titania surface was not smooth when the ratio of fresh sol was up to 33.3 vol%. Many titania aggregates of ca. 10 μm were observed on the surface. Next, zeolite was crystallized on these titania-stainless steel substrates. Smooth zeolite layer was found on the smooth titania layer (12.5 vol% of fresh sol). But, the zeolite layer consisted of many domes of 10 μm on the titania aggregates (33.3 vol% of fresh sol). In order to obtain a smooth zeolite layer on a thermostable titania layer, 12.5 vol% of fresh sol in the titania precursor was optimal.

Key words: ZSM-5 film, titania film, porous stainless steel substrate, electrostatic sol-spray deposition, heat exchange (HEX) reactor

1. INTRODUCTION

A composite material of a (non)porous metal substrate and a thin porous ceramic film can be solutions for a heat exchange (HEX) or membrane reactor. Thermal conductivity of a metal film is usually higher than that of an inorganic catalyst support. The temperature profile of a ceramic layer could become uniform by the aid of a metal support. In order to obtain a composite material of a dense stainless steel substrate and thin titania film, an application electrostatic sol-spray (ESSD) method has been studied [1]. Uniform porous titania layers without cracks were prepared on dense stainless steel substrates by using the mixtures of aged titania sol and fresh titania sol as a precursor. This titania layer was stable against calcination at 1273 K. Recently, a new type of composite membrane reactor was proposed [2]. This membrane reactor consists of three layers (separation layer, catalyst layer, metal support). Diffusion resistance between a separation layer and a catalyst layer could be decreased by coupling these layers. Furthermore, dense zeolite membranes were successfully prepared on porous titania substrates [3].

In this article, preparation of a titania layer on a porous stainless steel substrate by an ESSD method was investigated. Effects of deposition temperature and type of substrates were studied. Next, MFI zeolite was crystallized on a porous titania-stainless steel composite.

Surface morphologies of the titania layers were investigated to obtain a smooth zeolite layer.

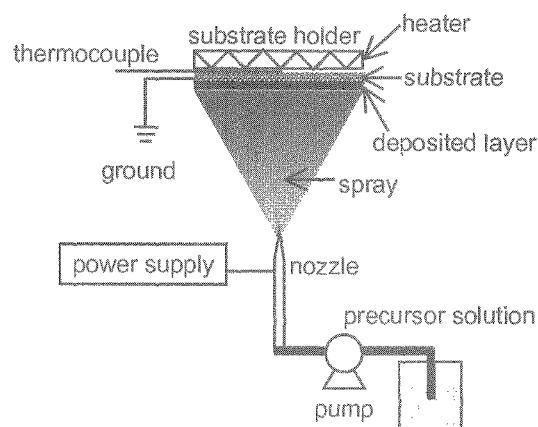


Fig. 1 Schematic diagram of ESSD apparatus

2. EXPERIMENTAL

Fig. 1 shows the schematic diagram of an ESSD. Porous stainless steel disks having 2-5 μm pores were provided by Trumem and Alltech. The diameters of the disks were $\phi 12.7$ or 15 mm. Deposition temperature was controlled by the thermocouple in the substrate holder. ESSD was carried out at 493 K – 533

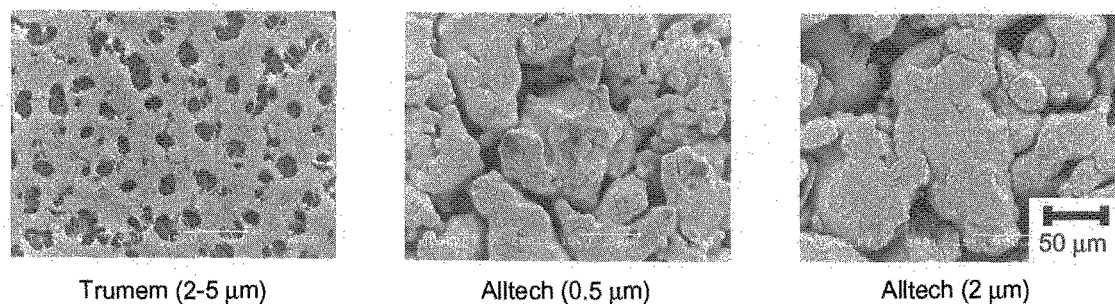


Fig. 2 SEM images of surface views of titania layer on various stainless steel substrate at 493 K

K for 15 min. Flow rate of titania sol was set at 1.6 ml min^{-1} by the syringe pump. Titanium tetraisopropoxide was used for titania precursor at 0.006 M in ethanol, butyl carbitol (BC) and acetic acid (AA) solution. Ratio of the solution was fixed at 16.7: 16.7: 66.6 vol % for ethanol, BC and AA, respectively. Aging of titania sol was carried out at room temperature for more than 5 h. Electric field strength was set between 3.5-4.5 kV to keep a Taylor cone at the top of the nozzle. After the deposition of a titania layer, hydrothermal synthesis was employed for preparation of zeolite layer. The molar sol composition was set at 100SiO_2 : 123 Tetrpropilammonium⁺: 63.7 OH⁻: 14200 H₂O. Aging was conducted for 5 h at room temperature. Crystallization was carried out at 453 K for 1-17 h in an autoclave. Calcination was carried out using an air oven (VULCAN 3-550). SEM pictures were made using a JEOL JSM-5800LV.

3. RESULTS & DISCUSSION

3.1 Titania deposition on porous stainless steel substrate

Titania layers were deposited on porous substrates at 533 K. The condition to obtain uniform $5 \mu\text{m}$ pores on dense substrate [1]. Fig.2 shows the SEM images of the surface views after the deposition on various porous

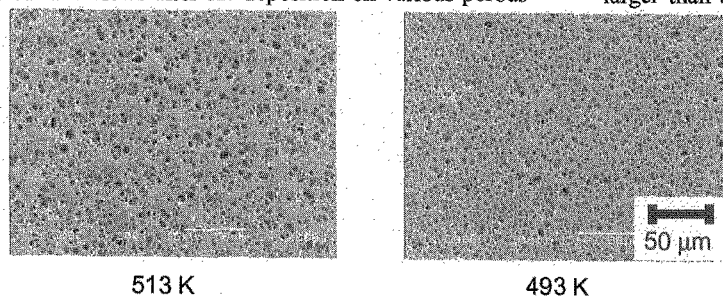
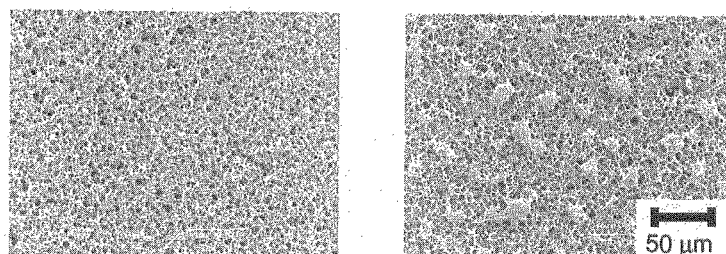


Fig. 3 SEM images of the surface views on Trumem



Aged titania sol: fresh titania sol=
87.5: 12.5 66.7: 33.3

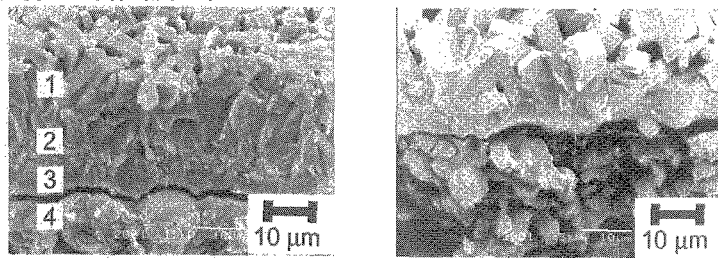
Fig. 4 SEM images of the surface views from the mixture of titania precursor

stainless steel substrates. A Trumem substrate has a smooth surface compared with Alltech substrate before the deposition of titania. Fibrous titania depositions were observed on all the substrates. A continuous titania layer was found on a Trumem substrate. The surfaces were partially covered for Alltech substrates. It is difficult to prepare a continuous layer on such rough surfaces like Alltech substrates using an ESSD technique. For the deposition on Trumem, there was many big pores of about $10 \mu\text{m}$ found on the substrate. The surface big pores looks similar to that deposited at higher temperature on dense substrates. Therefore, lower deposition temperatures were studied.

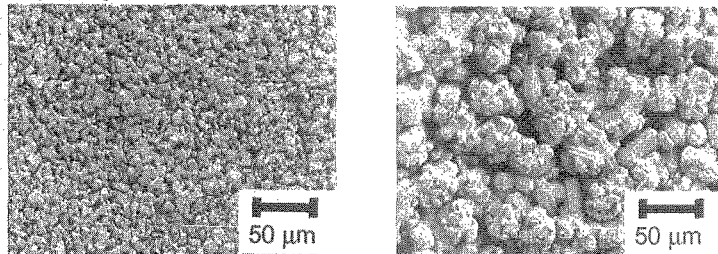
Fig.3 shows the surface images at 513 K and 493 K on Trumem substrates. The morphology at 533 K was shown in Fig.2 (left). The size of the big pores decreased with decreasing the deposition temperature. Uniform structures were observed at 493 K. Pore size of this titania structure was ca. $5 \mu\text{m}$. This can be explained by the surface area difference between a porous substrate and a dense substrate. The pore size of deposited layers is the result of a balance of supply rate of titania precursor and evaporation rate of solutions on substrates [2]. Surface area of a porous substrate is larger than that of a dense substrate. The evaporation rate of the solution should be faster for a larger surface area substrate, because the supply rate of the precursor by ESSD is the same. Thus, the lower deposition temperature compared with a dense substrate was suitable to obtain a porous titania layer on a porous substrate. The samples shown in Fig.3 were removed directly from the sample holders after the deposition. The sample temperature decreased to room temperature within a minute. The porous structures look uniform indicating that the deposited titania layers are stable for thermal shock. This property is similar to the titania layers on dense stainless steel substrates [1]. There were no significant peaks related to the titania crystals found by XRD measurements for the sample deposited at 493 K. This shows that the obtained titania layers were amorphous after the ESSD at 493 K.

Next, surface morphologies of mixing of the precursor were studied.

Cross-sectional view



Surface view



Aged titania sol: fresh titania sol=

87.5: 12.5

66.7: 33.3

Fig. 5 SEM images after the deposition of zeolite layer

Mixing of a fresh sol and an aged sol for a titania precursor was important to obtain a stable titania layer for calcination above 873 K [1]. Fibrous titania structures are formed by an aging procedure, and fresh titania sol works as a glue between fibrous structures to obtain stable layers. Fig.4 shows the surface images after the depositions at 493 K of the parent sol prepared by mixing of the fresh sol and the aged sol. The ratios of the mixture are described in the figure. The surface morphology by mixing 12.5 vol% of fresh sol looks similar to that without mixing (Fig.3, right). On the other hand, lumps having about 10 μm diameters were found for the precursor containing 33.3 vol% of fresh sol. The fraction of fresh sol was too high to obtain a smooth surface. The titania layer from 12.5 vol% kept its structure after calcination at 873 K to obtain anatase titania. This is the same result for that on the dense stainless steel substrate [1].

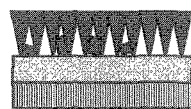
3.2 Preparation of zeolite layer on titania-stainless steel composite material

Synthesis of a zeolite layer on a porous titania-stainless steel composite material is investigated. Fig.5 shows the surface and cross-sectional images after zeolite synthesis on the porous titania layers shown in

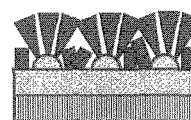
Smooth surface



Zeolite growth



Rough surface



zeolite layer
titania layer
stainless steel substrate

Fig. 6 Growth mechanism of zeolite layer on a smooth and a rough surface

Table 1 Atomic ratio of the samples

	Si	Ti	Fe
1	99.0	0.0	1.0
2	98.6	0.7	0.7
3	84.4	3.4	12.2
4	17.2	0.0	82.8

[atom%]

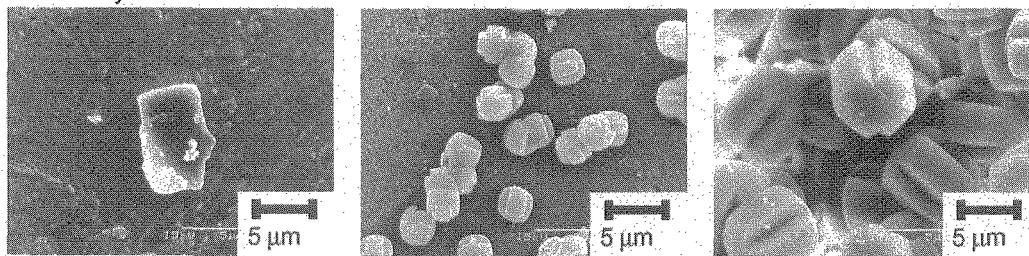
Fig.4. The deposited layers were confirmed as MFI zeolite by XRD measurements. The surface image on smooth titania layer (12.5 vol%) appears as intergrown MFI crystals. MFI crystals are coffin shape with ca. 10 μm for the longer side. These crystals look vertically crystallized on the substrate. The atomic ratio was measured using EDX. Table 1 shows the ratio of Si, Ti and Fe at the points shown in Fig. 5. From the point 1 to 2, the main content was Si indicating that this part mainly consisted of MFI zeolite. The SEM image at this point also exhibits zeolite crystals. At the point 3, Ti was found

by the measurement, and the ratio of Fe was 12.2 atom%. Titania layer should be stable during the synthesis procedures. However, the titania layer was too thin to be measured by this apparatus. The main content was Fe at point 4. It is obvious that this is the porous stainless steel layer in Fig. 5. The surface appears smooth for 12.5 vol% of fresh sol, while the surface for the 33.3 vol% mixture was rough. Aggregates of about 20 μm of zeolite crystals were found on the surface. The zeolite crystals must start to grow from the surface, and half-sphere shapes were obtained on the surface.

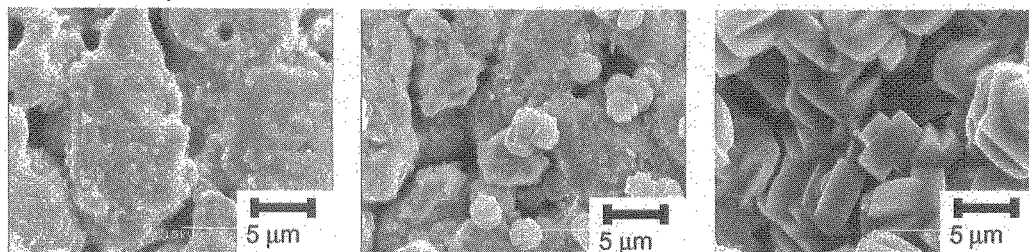
Fig.6 shows the schematic diagram of the growth mechanism. This mechanism is based on 3 assumptions. One is that the titania layer is stable during zeolite synthesis procedure. Second is that zeolite crystals start to grow from the surface of titania layer, and there are no accumulations of crystals from the solutions. Third is that the growth rate of zeolite is proportional to the length of the final length of each axis. The longer axis side can grow faster than the shorter axis side. At the start of zeolite growth, the direction of the growth is randomly. If the longer axis starts to grow vertically, the growth rate must be fastest. The crystals for other direction should be interfered by the crystals grown vertically (Fig.6, above). Thus, only the longer

axis side can survive at the top of the zeolite layer on a smooth surface [4]. On the other hand, the zeolite layer consisted of half-spherical shapes for the rough surface according to the

On titania layer



Without titania layer



Crystallization period

1 h

2 h

3 h

Fig. 7 SEM images for early stage observation of zeolite synthesis on Trumem with or without titania layer

same mechanism show in the figure (Fig.6, below). The roughness of zeolite layer should be the same as that for titania layer. In order to confirm the assumptions of the mechanism, we investigated the early stage observation of zeolite growth on the substrates with titania layer and without titania layer.

Fig.7 shows the surface images for crystallization times of 1 to 4 h with or without titania layer on the substrates. Upper images were surface images on Trumem (stainless steel with titania layer), and lower images were on Trumem without titania layer (porous stainless steel substrate). Silicalite crystals grew with increasing crystallization time. There were no crystals found after 1 h crystallization on substrates with or without titania layer. The lump shown in Fig.7 (left, above) might be amorphous structures from the shape in the figure. After 2 h crystallization (Fig.7, center), about 3 μm sized crystals were found on both substrates. The sizes of the crystals with and without titania layer look similar. This indicates that the difference in substrate has little effect on the nucleation of zeolite crystals for this synthesis conditions. The sizes of the crystals increased to more than 5 μm at 3 h. The deposition directions were random for both substrates. The crystal sizes for both samples were also similar. This indicates that the nucleation finished between 1 h to 2 h of crystallization, and zeolite crystals grow after 2 h of crystallization. This is an indication for the second assumption of Fig.6 (zeolite starts to grow from the surface of substrate) The growth rates on stainless steel and on titania layer were similar from the early stage observation. The fact that nucleation and growth rate were not influenced by the surface difference supports the first assumption shown in Fig.6 (titania layer is stable.).

4. Conclusions

Porous titania layers were successfully deposited on porous stainless steel substrate by using electrostatic sol-spray deposition method. The optimum deposition temperature was 493 K. This is 40 K lower than for a dense stainless steel substrate. This difference was explained by surface area difference between dense and porous substrates. Zeolite layers were crystallized on porous titania layer deposited by ESSD method. The surface smoothness of the titania layer was important to obtain smooth zeolite layer. Titania layer had little effects on crystallization of zeolite by early stage observations of zeolite synthesis.

5. References

- [1] M. Nomura, B. Meester, J. Schoonman, F. Kapteijn, J. A. Moulijn, *Chem. Mater.* **15**(6), 1283-1288 (2003)
- [2] M. Nomura, B. Meester, J. Schoonman, F. Kapteijn, J. A. Moulijn, *Sep. Pur. Tech.* **32**, 387-395 (2003)
- [3] L. Gora, N. Nishiyama, J.C. Jansen, F. Kapteijn, V. Teplyakov, and T. Maschmeyer, *Sep. Pur. Tech.*, **22-23**, 223(2001).
- [4] G. Bonilla, D. G. Vlachos, M. Tsapatsis, *Micropor. Mesopor. Mater.*, **42**, 191(2000)

(Received October 13 2003; Accepted March 31, 2004)