

## A novel and practical method for the preparation of a porous coating on the internal and external surfaces of catalyst particles.

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### Introduction

The preparation of porous films directly deposited onto the surface of catalyst particles is attracting increasing attention [1-4]. This type of composite materials displayed unusual activity and selectivity patterns in a number of reactions of academic and industrial interest, e.g., amine [1] and maleic anhydride [2] syntheses, selective hydrogenation reactions [3] and Fischer-Tropsch synthesis [4]. Some of us have shown that it is possible to prepare Na-A zeolite-coated catalysts that are active for the selective oxidation of CO in the presence of butane [2]. The methods reported so far are complex, e.g. requires the use of autoclaves to carry out the hydrothermal synthesis, and sometimes the coating step needs to be repeated a number of times to achieve a satisfactory coating of the sample surface [3].

We report here for the first time a method that can be carried out in ambient air for the preparation of porous films deposited over a Pt-based oxidation catalyst. An advanced characterisation of this open-air (OA) sample, and that of a material (AU) made using an autoclave-based method as reported in reference [2], will be presented.

### Materials and Methods

The oxidation catalyst was 5% Pt-0.5% Fe supported on 3 mm-size spherical macroporous silica beads. Prior to the formation of the coating layer, the surface of the sample was impregnated with a cationic acrylamide copolymer, which led to a positive surface charge in spite of the basic nature of the solutions used for zeolite synthesis [2]. The beads were subsequently soaked in a gel of composition 3.6 Na<sub>2</sub>O: Al<sub>2</sub>O<sub>3</sub>: 2.6 SiO<sub>2</sub>: 223 H<sub>2</sub>O and heated either in an autoclave at 100 °C for 18 h (AU sample) or in open-air (OA sample) at 105 °C in a glass beaker covered with a watch glass (the water level was maintained by adding boiling water). The samples were characterised by BET, XRD, SEM, FIB-TEM and <sup>27</sup>Al-MAS-NMR.

### Results and Discussion

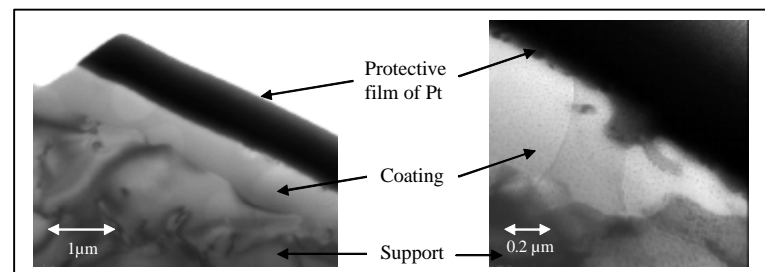
The AU and OA catalysts exhibited a similar activity for the selective oxidation of CO in the presence of butane. As compared to the non-coated material, the temperature for butane light-off was shifted to a higher value by more than 200°C, while that of CO was essentially unchanged. SEM pictures were taken of the macropores present in the volume of the particles of the AU and OA samples. The OA catalyst showed no evidence of the presence of any zeolite microcrystal, as opposed to the case of the AU catalyst. In fact, the internal surface of the OA sample appeared to be covered by a smooth homogeneous film. A FIB-TEM analysis of the OA internal surface showed that the coating was closely adhering to the surface and was ca. 500 nm thick [Fig. 1]. Some material loosely bound to the catalyst observed during the sample preparation for the TEM analysis appeared to be poorly crystallized LTA-type

solid. The <sup>27</sup>Al-MAS-NMR signal of the OA sample showed that the tetrahedral Al signal was very broad, and a calibration curve made using NMR and XRD data revealed that the sample crystallinity was merely 5%. A study based on the specific surface area of the OA sample and that of pure LTA crystal powder (LTA crystals were formed alongside the beads being coated during the synthesis) led to a similarly low crystallinity (13%). The structural differences between the AU and OA will be discussed in terms of LTA crystallization stages [6].

The effect of the constituent of the zeolite gel on the sample catalytic activity was also investigated. It was shown that the mere exposure of the sample to the gel was sufficient to shift the butane light-off, although significantly less than that obtained during the OA synthesis. Nonetheless, these data show that the modification of the catalytic activity can originate from various effects, e.g. modified reactant diffusivity due to the formation of the porous coating and also some electronic effect of the gel constituents on the Pt metal.

### Significance

This work shows that it is possible to prepare a homogeneous porous coating deep into the bulk of 3 mm-large catalyst beads by a simple aqueous method not requiring the use of autoclaves. Applications in shape/size/polarity-selective catalysis are vast, and the possibility to use this technique to prepare a protection layer against mechanical attrition is also to be considered.



**Figure 1.** TEM pictures of a FIB-milled cross-section of the surface of an internal macropore of the OA sample (two different magnifications are shown). The Pt film over-layer was used to protect the section of interest during the milling of the surface with Ga ions.

### References

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