

The Effect of Plastic Deformation and Thermal Annealing of the Copper Substrate on the Zeolite Film Formation

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The influence of thermal annealing and plastic deformation of the copper substrate on the zeolite film formation is investigated; the crystal imperfections in the subsurface layer are potential sites for zeolite nucleation.

Zeolite molecular sieves play an important role in industrial catalysis, ion exchange and gas separation. During the last few years a large number of articles and patents have been published on the preparation of composite materials containing continuous zeolite films.¹⁻⁴ *In situ* crystallization on different types of metal substrates or microporous metal modules is commonly used for preparing thin zeolite films. The growth of thin films of zeolite Y⁵ and ZSM-5⁶ on different metal substrates has been shown to be very sensitive to the type of the metal, to the conditions of preparation, to the position of the substrate in the reactor, *etc.* There have been, however, no systematic studies on the effect of the substrate surface structure and defects on the zeolite film properties. It is well known that the thermal and plastic treatment of metals and alloys leads to significant changes in their structure.^{7,8}

The aim of this paper is to investigate these effects for the case of thin Y zeolite films on copper substrates.

The experiments on zeolite film growth were carried out on copper substrates of 99.99% purity. The substrates were heated for 4 h at 700 °C, and then cooled to room temp. in the furnace. The substrates were then cleaned with 24% sulfuric acid (Merck) before use. In another experiment copper plates

of a thickness of 5 mm and surface area of 10 × 200 mm were subjected to plastic deformation by rolling at room temp. to reach half of the initial thickness. These copper supports were vertically immersed in a gel which yielded zeolite Y after 40 h at 90 °C. The gel was prepared by mixing silica sol (Merck), sodium hydroxide (Merck), aluminium hydroxide (Merck) and distilled water and aged for 24 h at room temp. The type of the zeolite synthesized was confirmed by X-ray powder diffraction using a Philips APD 5 diffractometer with Cu-K α radiation. The surface morphology and the thickness of the zeolite film was studied by scanning electron microscopy (SEM Philips 515).

Fig. 1(a,b) shows metal plates on which the zeolite film is mechanically destroyed. The zeolite film deposited on a support not treated thermally sticks only slightly to the surface and can be removed easily from a large area under mechanical treatment [Fig. 1(a)]. In contrast, on a thermally treated support the zeolite film is destroyed only within the area of the mechanical impact [Fig. 1(b)]. Another difference in the zeolite coating in both cases is the size of the zeolite crystals. The size of the crystals deposited on plates not treated thermally is 2–3 μ m, while after thermal treatment of

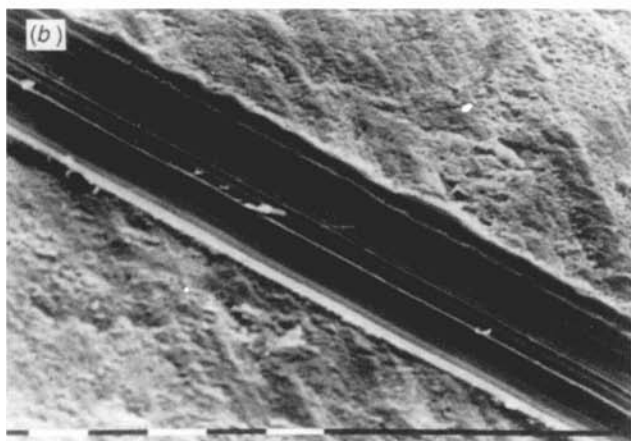
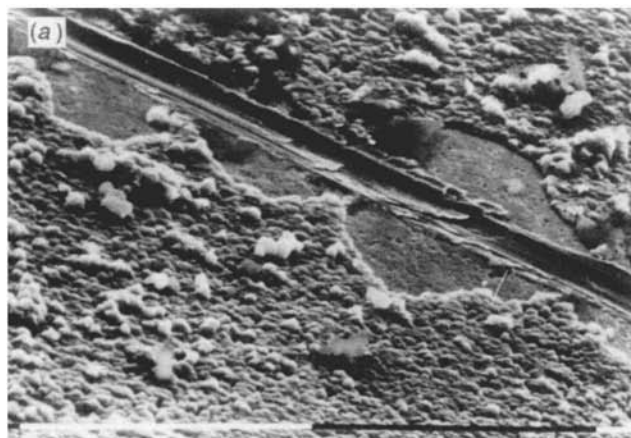


Fig. 1 Mechanically destroyed zeolite films on untreated ($M = 100 \mu\text{m}$) (a) and thermally annealed ($M = 10 \mu\text{m}$) (b) copper substrates

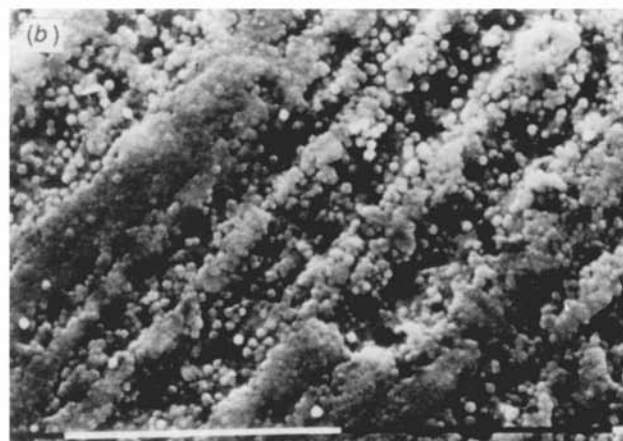
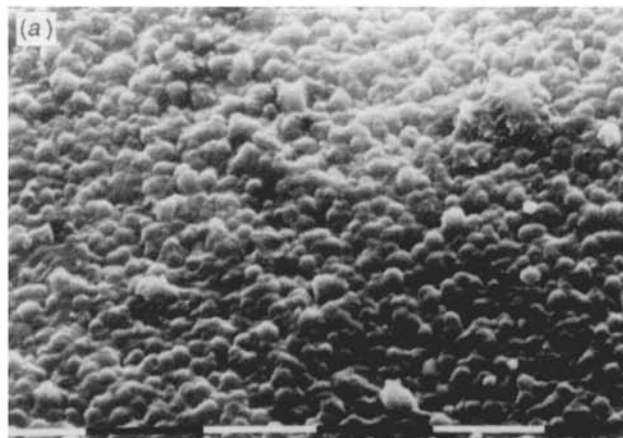


Fig. 2 Zeolite films deposited on untreated ($M = 10 \mu\text{m}$) (a) and plastically treated ($M = 10 \mu\text{m}$) (b) substrates

the substrate a homogeneous film of fine zeolite crystals of a size below the SEM resolution forms on the surface. The thermal treatment of the support leads to migration of defects from the bulk to the surface, to an increase of the surface energy and to stabilization of the structure in the bulk. The concentration of crystal defects on the metal surface obviously influences directly the process of zeolite nucleation. The formation of the films of fine sized zeolite crystals on thermally treated substrates indicates that a large amount of zeolite nuclei is formed and grown simultaneously. The thermally induced structural modification of the copper supports provokes both morphological changes in the zeolite film and another stronger sticking interaction between the film and metal surface.

The plastic deformation of the substrates, besides transporting vacancies and dislocations from bulk towards the metal surface, produces new surface defects. This type of treatment changes the specimen crystal structure and leads to an apparent modification of the metal surface consisting of the appearance of parallel relief lines. Figs. 2(a) and (b) show SEM micrographs of zeolite films deposited on untreated and plastically treated substrates, respectively. While in the former case the plate is homogeneously coated by zeolite crystals and no relief patterns or density fluctuations are seen [Fig. 2(a)], the film on the plastically deformed plate replicates the substrate and a marked densification of the film due to the growth of more zeolite crystals in the relief zones is observed [Fig. 2(b)]. The formation of a greater amount of seeds in the regions characterized with maximum plastic deformations

reveals the effect of the metal substrate structure on the process of zeolite nucleation.

The results obtained show that the structural modification of the copper supports influences considerably the zeolite film growth. The crystal imperfections produced by the thermal and plastic treatment in the subsurface layer become potential sites for zeolite nucleation. Thus, the high density of defects in the near surface region promotes the formation of fine sized, homogeneous and well adhesive zeolite films.

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