

## Influence of Reactive Radicals in Cellulose Fibres on the Formation of Zeolite Coatings

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The effect of the chemical composition and structure of vegetal fibres on the formation of zeolite coatings is investigated; it is shown that hydroxyl groups in cellulose fibres intensify the zeolite nucleation.

Membrane separation has proved to be an important technology in the chemical industry. That is why the design of zeolite membranes in the form of molecular sieves has received much attention during the last decade.<sup>1-3</sup> A simple and widespread method for preparing zeolite-containing membranes on metal or Teflon modules is by *in situ* crystallization.<sup>4-6</sup> Sano *et al.*<sup>7-8</sup> have considered OH groups in cellulose as favourable sites for zeolite crystallization. These authors have used cellulose moulding for preparing self-bounded zeolite films. To prepare pure zeolite membranes the composite was calcined by burning for 24 hours at 500 °C. There are a large number of patents concerning the preparation of various types of paper by embedding zeolite crystals with added adhesive substances in the cellulose matrix.<sup>9-11</sup>

In this communication we report data on the *in situ* synthesis of zeolite A on cellulose fibres.

Throughout this study we used as cellulose membranes the following materials: softwood CTMP fluff (Folla AS, Norway), softwood kraft pulp (Cellhard Co., Bulgaria), and hardwood sulfate pulp which was subsequently bleached (Svilozha Co., Bulgaria). The three materials used differ from

each other in the content of lignin: the CTMP fluff contains 28% lignin as determined by the standard ISO 3260-1982, the kraft pulp contains 6% lignin, determined according to the standard SCAN-C 1 : 77, while the sulfate pulp of a brightness of 90% ISO contains less than 0.1% lignin. These three pulps were beaten by a Rapid Kotten apparatus to 30° SR (Shopper Riegler) in order to produce sheets of a weight of 60 g cm<sup>-2</sup>. Small cuts of the obtained sheets were covered with zeolite A by immersing in a gel which led to zeolite crystallization after 4.5 hours at 90 °C. The initial aluminosilicate gel was prepared from waterglass (Merck), sodium aluminate (Fisons) and distilled water. The nature of the crystallized zeolite was determined by X-ray powder diffraction using a Philips APD 15 diffractometer with Cu-K $\alpha$  radiation. The distribution of the zeolite particles in the sheet was determined by scanning electron microscopy (SEM Philips 515).

Fig. 1 shows the surfaces of the three cellulose fibres after the crystallization of zeolite A. As seen in Fig. 1(a), only a few loosely attached zeolite crystals were formed on the fibre surface in the case of CTMP. For the kraft pulp two types of fibres are present, the first type, which is densely coated by



Fig. 1 SEM photographs of zeolite A coatings: on (a) CTMP, (b) kraft pulp, (c) crystals formed in the bulk of sulfate cellulose fibres and (d) on the surface of sulfate cellulose

zeolite crystals, are elongated and thin, whereas the other fibres, without any zeolite coverage, are short and thick [Fig. 1(b)]. As Fig. 1 indicates, the homogeneous coverage of the sulfate cellulose fibres by zeolite A proceeds in two stages. At the first stage of crystallization (3.5–4.5 hours) crystals were formed in the bulk of the cellulose fibre [Fig. 1(c)], while during the second stage (5–7 hours) the fibre surface was coated by a dense zeolite film [Fig. 1(d)].

Significant differences were thus observed in the process of crystallization of zeolite A on different fibres. The results indicate that an increase in the content of lignin limits the crystallization of zeolite A on fibre surfaces. Lignin is a high-molecular-weight compound built of phenylpropane units connected by various radicals (CO, OH, C<sub>2</sub>O, OCH<sub>3</sub>).<sup>13</sup> The structural units of lignin interact with each other as well as with active radicals in cellulose forming a three-dimensional disordered network of low chemical reactivity, which explains the low degree of coverage of the fibres with zeolite A. In contrast to lignin, cellulose is a crystalline compound containing a small amount of an amorphous phase.<sup>14,15</sup> Cellulose can be considered as a polyvalent alcohol since each structural unit contains three unbound OH groups of different chemical activity which form hydrogen bonds between the cellulose chains. Hydroxy ions in the aluminosilicate gel can destroy the hydrogen bonds in cellulose, increasing their reactivity and intensifying the zeolite nucleation. This result confirms the suggestion of Sano *et al.*<sup>7,8</sup> that the hydroxy groups in cellulose provide favourable sites for zeolite nucleation.

The study of the crystallization of zeolite crystals on vegetal fibres shows that the structure and the chemical composition of the fibres determine their capacity to interact with aluminosilicate precursors. Lignin turns out to be very inert in the process of zeolite crystallization, preventing the formation

of zeolite crystals. The high activity of cellulose in the zeolite crystallization is due to the high abundance of reactive hydroxyl groups which interact with the aluminosilicate species and thus promote the formation of zeolite nuclei.

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