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Selective functionalization of the external surface of zeolite L

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Abstract

Methods for the functionalization of the external surface of zeolites are discussed with emphasis on zeolite L. Concepts are presented which allow for assigning functionalities to the whole external surface or selectively to the regions of the external surface where the channel entrances are located. This latter principle implies the development of so-called stopcocks. Stopcock molecules are designed to provide the possibility to reversibly or irreversibly plug the entrances of zeolite channels and assign functionalities to those parts of the external surface where the pore openings are located. Examples are presented in which the functionalization of the external zeolite surface is applied to define and optimize the interface between guest molecules in the channels of the zeolite and external species. **To cite this article G. Calzaferri and al, C. R. Chimie 8 (2005).**

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Résumé

Les méthodes de fonctionnalisation de la surface externe des zéolithes sont discutées en mettant l'accent sur la zéolithe L. Des concepts qui permettent d'attribuer des fonctionnalités à l'ensemble de la surface externe ou sélectivement aux régions correspondant à l'entrée des canaux sont présentés. Ce dernier principe implique le développement de ce que l'on appelle communément des obturateurs. Les molécules obturatrices sont conçues de façon à permettre la possibilité de fermer réversiblement ou irréversiblement l'entrée des canaux des zéolithes et de conférer des fonctionnalités aux zones de la surface externe où se trouvent les ouvertures des pores. Des exemples dans lesquels la fonctionnalisation de la surface externe de la zéolithe est utilisée pour définir et optimiser l'interface entre les molécules hôtes présentes dans les canaux de la zéolithe et les espèces externes sont présentés. **Pour citer cet article G. Calzaferri et al, C. R. Chimie 8 (2005).**

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1. Introduction

1.1. Scope of the article

The defined pore structures of molecular sieves are ideal for obtaining organized arrangements of a large variety of guest species [1]. In order to fully exploit the potential of these host–guest systems it is essential to control the interaction of a given molecular sieve particle with its environment. This article discusses methods for the functionalization of the external crystal surface of zeolites; thereby focusing on our research on zeolite L. Concepts are presented which allow for assigning functionalities to the whole external surface or selectively to the regions of the external surface where the channel entrances are located.

1.2. Zeolite L

Zeolite L is a crystalline aluminosilicate featuring hexagonal symmetry [2–4]. The crystals consist of cancrinite cages linked by double six-membered rings, thereby forming columns in the *c*-direction. Connection of these columns gives rise to 12-membered rings with a free diameter of 7.1 Å. As a consequence, zeolite L possesses one-dimensional channels running parallel to the *c*-direction through the entire crystal. The

free diameter varies from 7.1 Å (narrowest part) to 12.6 Å (widest part). The main channels are linked via non planar eight-membered rings forming an additional two-dimensional channel system with openings of about 1.5 Å. As can be seen from the scanning electron microscopy image shown in Fig. 1, the morphology of the crystals can be approximated by a cylinder, with the entrances of the main channels located at the base. The number of channels is equal to $0.265(d_c)^2$, where d_c is the diameter of the cylinder in nanometers. A crystal with a diameter of 550 nm, therefore, consists of about 8×10^4 parallel channels.

The substitution of Si^{4+} by Al^{3+} creates an anionic framework. Charge compensation is accomplished by additional cations (usually Na^+ and K^+). The stoichiometry of zeolite L containing monovalent cations M is $\text{M}_9[\text{Al}_9\text{Si}_{27}\text{O}_{72}] \cdot n\text{H}_2\text{O}$, where n is 21 in the fully hydrated state, and 16 at about 20% relative humidity. The water molecules in the large cavities of zeolite L have been reported to behave like an intracrystalline liquid, whereas they seem to build clusters around the cations in the smaller pores [5].

1.3. Dye–zeolite composites

The inclusion of cationic or neutral dye molecules into the one-dimensional channels of zeolite L yields

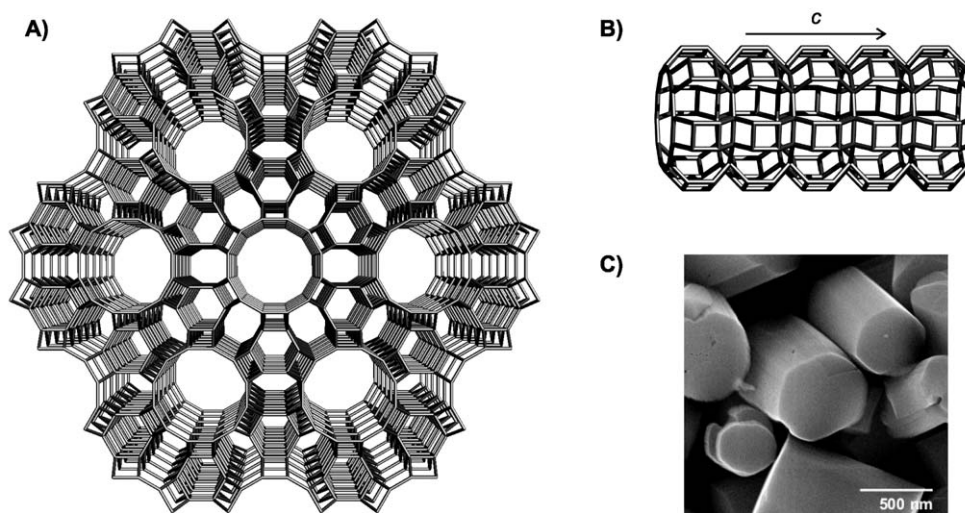


Fig. 1. Framework and morphology of zeolite L. (A) Framework viewed along the *c* axis, (B) side view of the main channel, (C) scanning electron microscopy image of zeolite L crystals.

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