



## Shape-selective organic–inorganic zeolitic catalysts prepared via interlayer expansion



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### ABSTRACT

Interlayer expansion of layered zeolite precursors is achieved via the insertion of an additional T-atom in between the layers, typically by means of a silylating agent as source of the T-atom. (3-Mercaptopropyl)methyltrimethoxysilane was used as Si-source in the interlayer expansion of the layered zeolite precursors RUB-36 and RUB-39. The structure expansion was confirmed with PXRD. The incorporation of the silylating agent was followed with <sup>29</sup>Si MAS NMR, <sup>13</sup>C CP MAS NMR and thermogravimetric analysis. The incorporated thiol groups were oxidized with H<sub>2</sub>O<sub>2</sub> to obtain sulfonic acid groups in between the layers. <sup>13</sup>C CP MAS NMR was used to characterize the organic species and monitor the conversion of thiol to propylsulfonic groups. The shape-selective properties of the obtained materials were investigated in acid-catalyzed tetrahydropyranylation reactions.

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### 1. Introduction

Layered zeolite precursors are versatile building blocks for the synthesis of zeolitic catalysts. Besides their transformation into fully three-dimensionally connected zeolite frameworks by topotactic condensation of the silicate sheets, the layers can be rearranged in a variety of ways. Examples are interlayer expansion by placing an additional T-atom in between the layers, or swelling followed by pillaring, delamination or recombination of the sheets [1–8]. The resulting materials differ from their corresponding zeolite condensation products in pore size and shape, accessibility of active sites in the layers, sorption characteristics and other physicochemical and catalytic properties. In the case of interlayer expansion, typically a silylating agent containing two methyl- and two leaving groups (chloro-, ethoxy-) is used to link the opposite layers of the precursor instead of directly connecting those layers. This is illustrated in Fig. 1 for RUB-36, the layered zeolite precursor consisting of the ferrierite-type layer, which can be

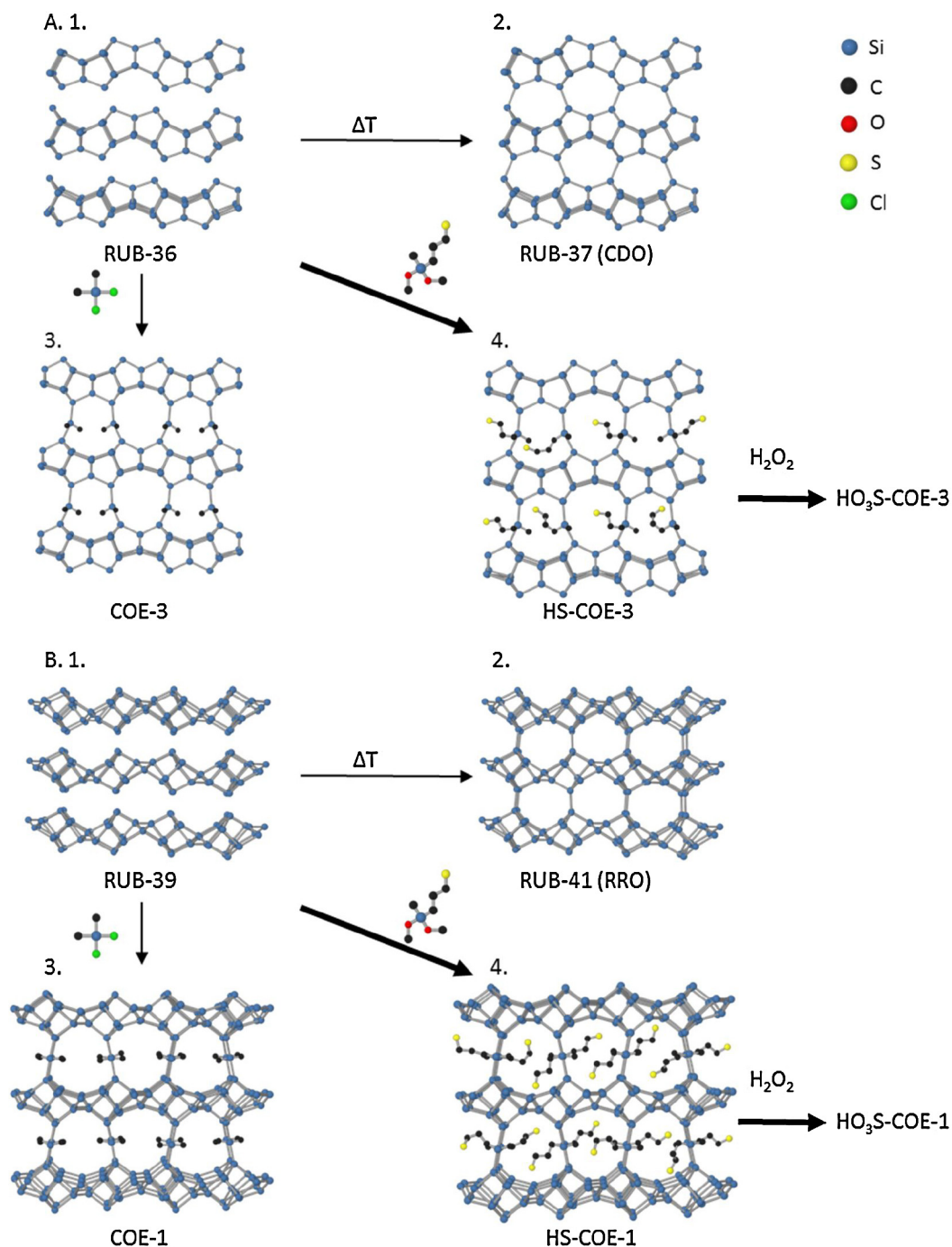
condensed to the three-dimensionally connected zeolite RUB-37 (CDO topology) or interlayer expanded with dichlorodimethylsilane (DCDMS) to the methyl group-containing, hydrophobic COE-3 [9]. As another example, the layered silicate RUB-39, which consists of heulandite-type layers, can be condensed to RUB-41 (RRO topology) or interlayer expanded to COE-1 [10,11].

One way of introducing catalytic activity into the materials derived from layered, siliceous zeolite precursors is the isomorphous substitution of Al or other heteroatoms in the silicate layer [4,5,12–15]. Alternatively, the layers themselves can also serve as a support for catalytic sites through e.g. grafting of a metal precursor, or by creating hybrid organic–inorganic materials using organosilanes [16–18]. One interesting possibility is selectively placing the active sites in between the layers. Corma and co-workers used for instance 1,4-bis(triethoxysilyl)benzene as organic linking group between the layers of Al-containing MCM-22. Subsequent amination of the organic linkers introduced basic functionalities in close proximity of the layer-associated acid sites, resulting in a bifunctional catalyst [19].

In previous reports on the interlayer expansion of RUB-36 and RUB-39, the possibility of introducing reactive functional groups via interlayer expansion has been suggested [9,11]. In this contribution, we demonstrate one of these possibilities by altering the interlayer expansion protocol to introduce sulfonic

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**Fig. 1.** Materials derived from layered zeolite precursors RUB-36 (A) and RUB-39 (B). Displayed are the layered precursors (1) and the products of topotactic condensation (2) and interlayer expansion with DCDMS (3) or with 3-MPS (4) followed by oxidation with H<sub>2</sub>O<sub>2</sub>. Framework O-atoms and the organic SDAs in the layered precursors are omitted for clarity. In the case of RUB-39, two linking sites eclipsing each other are shown.

acid sites in between the layers, consequently obtaining a hybrid catalyst with acid sites placed selectively inside the interlayer gallery of the inorganic zeolite. Similar types of organic–inorganic hybrid catalysts containing propylsulfonic groups have been used in *e.g.* tetrahydropyranylations for the protection of alcohols, in bisphenol A synthesis, acetalizations, condensation of acetone and 2-methylfuran and esterifications [20–25]. We have modified the interlayer expansion by using a silylating agent containing besides two leaving groups also one methyl group and an alkylthiol group, which can be oxidized to a sulfonic acid group. The appropriate conditions for this oxidative transformation have been investigated. Finally, the acid and shape-selective properties of the

functionalized catalysts in the protection of alcohols *via* tetrahydropyranylation were explored.

## 2. Experimental

### 2.1. Catalyst synthesis

#### 2.1.1. Synthesis of the layered precursors

Purely siliceous RUB-36 and RUB-39 were synthesized according to Refs. [9,10] using the respective organic structure directing agents (SDA) diethyldimethyl ammonium hydroxide and dimethyldipropyl ammonium hydroxide. After drying the

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