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C. R. Chimie 8 (2005) 341–352

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Synthesis of ITQ-7 with a new template molecule and its crystal structure analysis in the as synthesized form

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Received 28 June 2004; accepted after revision 22 October 2004

Abstract

Using a new template, 1,3,3-trimethylspiro[6-azoniabicyclo[3.2.1]]octane-6,1′-piperidinium fluoride, an efficient synthesis of the 12 membered ring zeolite ITQ-7 has been discovered. The zeolite has been characterized using DTA, TG, and solid-state NMR spectroscopy. In order to elucidate the host–guest interaction, the crystal structure analysis of the as synthesized form has been carried out using a Rietveld refinement of X-ray powder diffraction data. The influence of the cotemplate F^- on the silicate condensation was studied with ^{19}F MAS NMR, observing the sample during the synthesis procedure. The analyses show clearly the unspecified templating role of the organic structure directing agent for the ITQ-7 pore system and the interaction of the F^--ion with double-4-ring silicate species in the early process of the formation of the silica framework. ***To cite this article: J.Q. Song et al., C. R. Chimie 8 (2005).***

Résumé

En utilisant le fluorure de 1,3,3-triméthylspiro[6-azoniabicyclo[3.2.1]]octane-6,1′-pipéridinium comme agent structurant, une voie de synthèse efficace de la zéolithe ITQ-7, dont les ouvertures sont délimitées par des cycles à 12 côtés, a été découverte. Cette zéolithe a été caractérisée par ATD, TG et résonance magnétique nucléaire du solide. Dans le but de comprendre les interactions structurant organique–charpente minérale, la détermination de la structure de cette zéolithe a été réalisée par affinement Rietveld à partir du diffractogramme de poudre. L'influence du co-structurant F^- sur la condensation des espèces silicates a été étudiée par RMN du fluor 19 au cours de la formation du matériau. Les analyses montrent clairement le rôle non spécifique de la molécule organique pour le système de pores du solide ITQ-7 et l'interaction des ions F^- avec les espèces silicates de type double cycle à quatre tétraèdres dès les premières étapes de formation de la charpente silicate. ***Pour citer cet article : J.Q. Song et al., C. R. Chimie 8 (2005).***

Keywords: Zeolite ITQ-7; ISV; ^{19}F and ^{29}Si MAS NMR; Synthesis; Rietveld structure refinement

Mots clés : Zéolithe ITQ-7 ; ISV ; RMN du solide ; Affinement Rietveld

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doi:10.1016/j.crci.2004.10.029

1. Introduction

New high-silica zeolite framework types with 10–12-membered-ring (MR) pores are still of key interest in petroleum and chemical industry for separation and catalysis since the pore size and shape influences significantly the selectivity in educt uptake and product release in catalytic processes. A careful study of the reasons crucial for the specific catalytic properties of microporous materials showed that the pore size of the pore opening and the curvature of the internal oxide surface play a fundamental role in the catalytic activity and the shape selectivity of microporous zeolite catalysts [1]. It was concluded that 8–12 MR zeolite frameworks are most effective. Smaller pores can not be entered by organic molecules, larger ring size allows bigger molecules to selectively enter pore space, but product formation becomes more and more equivalent to reactions with flat, amorphous oxide surfaces. ITQ-7 is a very interesting new member of the family of high silica 12 MR zeolites. It is structurally closely related to zeolite beta which has a disordered framework structure. As zeolite beta, ITQ-7 also has a 3-dimensional (3D) channel system made of intersecting 12 MR pores whose pore diameters are almost similar (5.9–6.5 Å diameter). In contrast to beta, however, this material can be obtained with a highly ordered silicate framework structure. It is typically synthesized with a specific structure directing agent (SDA), 1,3,3-trimethylspiro[6-azoniabicyclo [3.2.1]]octane-6,1′-pyrrolidine (TAD), in a narrow synthesis field using the fluoride route [2]. The crystal structure of the calcined material (zeolite framework type ISV [3]) has been reported recently by Villaescusa et al. [2]. In successive papers very interesting catalytic properties have been reported [4–6]. In addition, the substitution of Si by Ge has been studied [7–9]. Of particular interest for the basic understanding of the formation is the selective occupation of T-sites by Ge, in particular in the D4R and the Ge-induced reduction of the synthesis time by two orders of magnitude to 12 h. Although the general features of the crystal structure are known, there is no detailed information on the host guest interaction in the as synthesized material which might be important for the efficiency of the SDA. Here we report on the synthesis of pure silica ITQ-7 with a new, modified SDA and on the structural characterization with solid state NMR and powder XRD. Particular attention has been paid to in situ studies of the synthesis with ^{19}F solid state NMR and on the crystal structure analysis of the as synthesized form using the Rietveld technique.

2. Experimental

ITQ-7 was synthesized from quasi-dry gel preparations in the temperature range 150–170 °C with a starting gel composition of $SiO_2/SDA/H_2O$ = 1:0.5:2.97–15.90 (Table 1). 1,3,3trimethylspiro[6-azoniabicyclo[3.2.1]]octane-6,1′-piperidinium fluoride (TAT) was used as new SDA for ITQ-7 type materials (Fig. 1). The starting material was transferred into a Teflon lined steel autoclave and kept for 5–10 d in an oven at synthesis temperature.

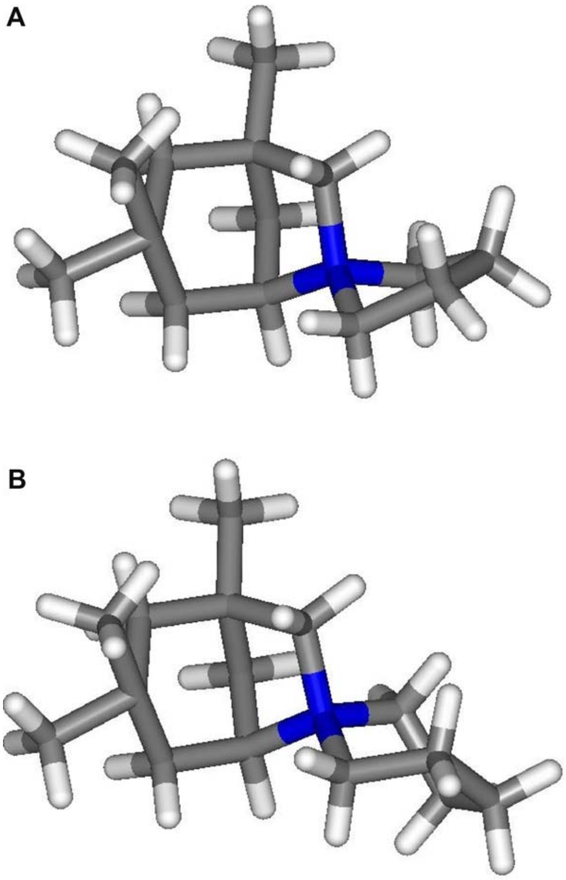

Fig. 1. The known (**A**) and the new (**B**) SDA used for the synthesis of ISV-type material. (**A**) 1,3,3-Trimethylspiro[6-azoniabicyclo[3.2.1]]-octane-6,1′-pyrrolidinium cation. (**B**) 1,3,3-Trimethylspiro[6-azonia-bicyclo[3.2.1]]octane-6,1′-piperidinium cation.