

FORMATION OF ZEOLITE Ti-BETA INVESTIGATED BY ²⁹Si NMR AND X-RAY ABSORPTION SPECTROSCOPY

Mojca Rangus¹, Matjaž Mazaj¹, Gregor Mali^{1,2}, Iztok Arčon^{3,4}, Venčeslav Kaučič¹

¹National Institute of Chemistry, Hajdrihova 19, SI-1000 Ljubljana, Slovenia

²EN→FIST Centre of Excellence, Dunajska 156, SI-1000 Ljubljana, Slovenia

³University of Nova Gorica, Vipavska 13, SI-5000 Nova Gorica, Slovenia

⁴Institute Jožef Stefan, Jamova 39, SI-1000 Ljubljana, Slovenia

E-mail: mojca.rangus@ki.si

ABSTRACT

We used spectroscopic techniques such as liquid and solid-state nuclear magnetic resonance (NMR) and X-ray absorption near edge structure (XANES) to monitor the formation of aluminium-free Beta zeolite functionalized with titanium (Ti-Beta) from the initial gel through the colloidal solution containing nanosized zeolitic crystals to the final product with fully formed zeolitic framework.

Keywords: NMR spectroscopy, XANES, colloidal precursors, nanosized particles.

INTRODUCTION

Nanosized zeolitic particles have attracted considerable attention because of the improved catalytic performance which is due to the increased external surface and decreased channel lengths compared to the conventional zeolitic materials [1]. For the use in the catalytic processes, which involve large molecules, micro/mesoporous composite materials which combine properties of both, microporous and mesoporous materials, are particularly convenient [2]. In these types of materials nanosized microporous particles are deposited into the pores or incorporated in the walls of the mesoporous matrix. In order to obtain zeolitic particles that are sufficiently small to be successfully incorporated in the mesoporous material, the crystallization process must be stopped at the right stage of the synthesis. Therefore, understanding of the crystallization process of the zeolitic phase is of high importance. Here we report on the systematic study of formation and growth process of Ti-modified zeolite Beta under hydrothermal conditions investigated by NMR and XAS techniques.

EXPERIMENTAL

Ti-Beta zeolitic material was hydrothermally synthesised from a reaction gel which was prepared by dissolving tetraethylorthotitanate in tetramethylammonium hydroxide prior to the addition of silicic acid. Gel with molar ratios of reaction components 0.025 TiO₂ : SiO₂ : 0.55 TEAOH : 8.8 H₂O was treated in autoclaves at 403 K. For monitoring the crystallization of Ti-Beta zeolite, hydrothermal treatment was stopped at different times and the gels were subjected to liquid-state ²⁹Si NMR measurements. Afterwards, the gels were dried at ambient temperature and analyzed again using solid-state ²⁹Si NMR spectroscopy and X-ray absorption spectroscopy. The times, at which the hydrothermal treatment was stopped, are denoted in the sample names. After 72 hours of synthesis time, the final Ti-Beta product was obtained.

Liquid and solid-state ²⁹Si NMR spectra were recorded on a 600 MHz (14.1 T) Varian VNMRs spectrometer using a Varian 5 mm broadband liquids probe and Varian 3.2 mm MAS solids probe, respectively. Solid samples were spun with the spinning rate of 10 kHz. Liquid and solid-state spectra were recorded using a single-pulse excitation, 20 s (for liquids) or 50 s (for solids) repetition delay, and accumulation number of 1200.

X-ray absorption spectra of the samples and Ti reference compounds were measured in the energy region of the Ti K-edge in transmission detection mode at beamline C of HASYLAB synchrotron facility at DESY in Hamburg. A Si(111) double crystal monochromator was used with the energy resolution of about 1 eV at the Ti K-edge (4966 eV). The intensity of the monochromatic X-ray beam was measured by three consecutive ionization chambers filled with 600 mbar N₂, 160 mbar Ar and 220 mbar Ar for the first, second and third ionization chamber, respectively. The dried gel samples were prepared as homogeneous self-supporting pellets with the total absorption thickness (μ d) of about 2.5 above the Ti K-edge.

RESULTS AND DISCUSSION

With liquid-state ²⁹Si NMR we observed that silicate species start to interconnect (oligomerize) immediately after the preparation of the initial gel (Fig. 1a). In the spectrum of the 0.5 h sample (sample that was hydrothermally treated for 30 minutes) the signals of Si dimers at -81.0 ppm and cyclic trimers at -83.0 ppm and -83.2 ppm become more pronounced and the signals belonging to the rudiments of double trirings (-91.0 ppm) start to appear. A peak at -72.9 ppm, which corresponds to Si monomers (Q⁰), is also present in the spectrum. Simple building units start to connect into more complex silicon oligomers after approximately an hour of hydrothermal synthesis. After three hours of the synthesis a wide range of signals with different chemical shifts appear, indicating the existence of a large variety of building units. The signals can be divided into four different regions: Q¹ (from -80 ppm to -82 ppm), Q² (from -82 ppm to -90 ppm), Q³ (from -90 ppm to -104 ppm) and Q⁴ (signals beyond -104 ppm). Here Qⁿ we denote a silicon environment with *n* Si-O-Si bonds. After approximately 3 hours of hydrothermal treatment the liquid ²⁹Si NMR spectrum becomes comprised of narrow as well as broad signals. This suggests that after few hours of the synthesis individual oligomers start to connect or aggregate into bigger clusters – nanoparticles. The formation and growth of nanoparticles results in the broadening of the signals in the liquid-state NMR spectra, because such nanoparticles are much less mobile than the oligomers. We can see that in the first six hours of the synthesis the fraction of nanoparticles extremely quickly increases on the expense of the fraction of oligomers. Afterwards the changes are slowed down and after 24 hours of hydrothermal synthesis the majority of oligomers already aggregate into nanoparticles and almost only broad signals are detected in the spectra of 24 h, 38 h, and 72 h samples.

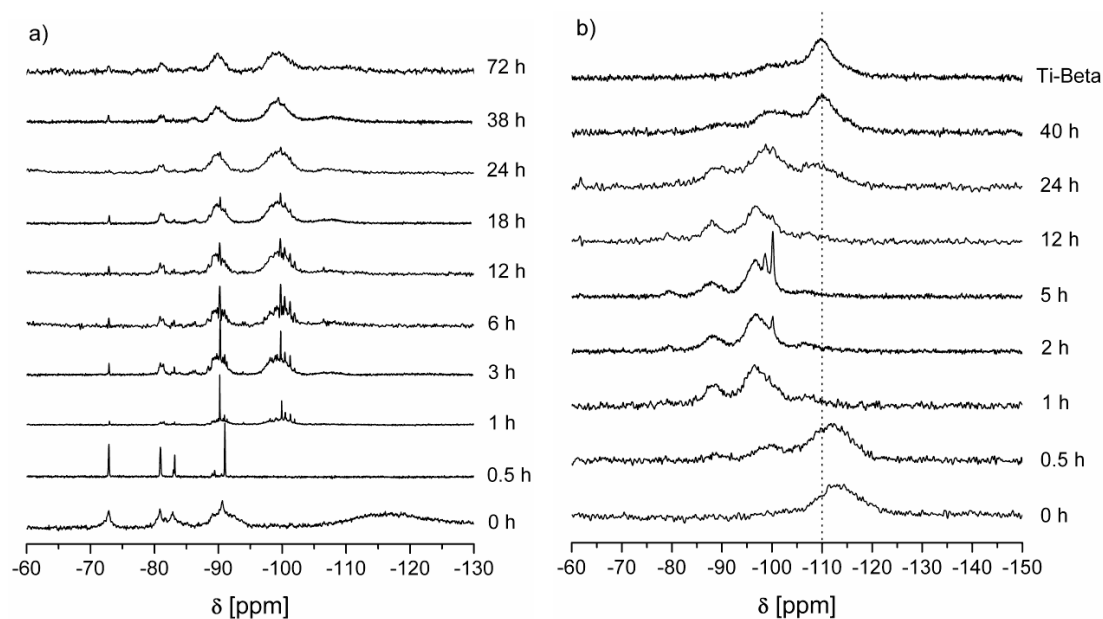


Figure 1. Liquid (a) and solid-state (b) ²⁹Si NMR spectra of Ti-Beta gels and the reference Ti-Beta product.

The picture describing formation of nanoparticles can be supplemented by solid-state NMR measurements (Fig. 1b). In the spectrum of the initial gel only a broad signal at -113 ppm, which corresponds to the amorphous form of the silicon, is present. In the spectra of other samples there are signals at -80 ppm, -88 ppm, -99 ppm, and -110 ppm, which can be assigned to Q¹, Q², Q³, and Q⁴ silicon species, respectively. Apart from two minor exceptions, all these signals are broad and belong to nanoparticles obtained during the synthesis of zeolite Beta. We can notice that in the solid-state spectra of 24, 40 or 72 h samples, the contributions of Q⁴ silicon species are much more pronounced than in the corresponding liquid-state spectra. The reason for weaker Q⁴ signals in the latter case is in the fact that liquid-state NMR simply could not detect particles with dimensions of several tens or even hundreds of nanometers. We expect that in the solid-state NMR spectra all nanoparticle populations are detected. During the first 24 hours of synthesis the composition of nanoparticles is almost constant. Afterwards the fraction of Q⁴ species in dried gels starts to drastically increase on the expense of the Q³ species. Both liquid and solid-state NMR measurements suggest that nanoparticles larger than 2 nm start to form after 24 hours of synthesis and that they are already very abundant after 38 hours of the synthesis. Since bigger nanoparticles contain a very large fraction of Q⁴ units, they probably already have a zeolitic character and can in high enough concentrations act as seeds for the growth of zeolite Beta crystallites. The concentration of the larger nanoparticles is increased with the time of hydrothermal treatment and probably also by a drying procedure. Indeed, after 72 hours of synthesis the Q⁴/Q³ fraction of particles within the dried gel increases even further and reaches the value that is typical for the as-synthesised zeolite Beta.

Information on the valence state and coordination of Ti atoms was obtained by XANES. The energy position of the Ti K absorption edge is shifted to higher energies with the increasing oxidation state of the investigated atoms [3]. By comparing the Ti K-edge position of our samples to the edge positions of TiO₂ rutile and anatase reference compounds we determined the valence state to be 4+ for all our samples (Fig. 2).

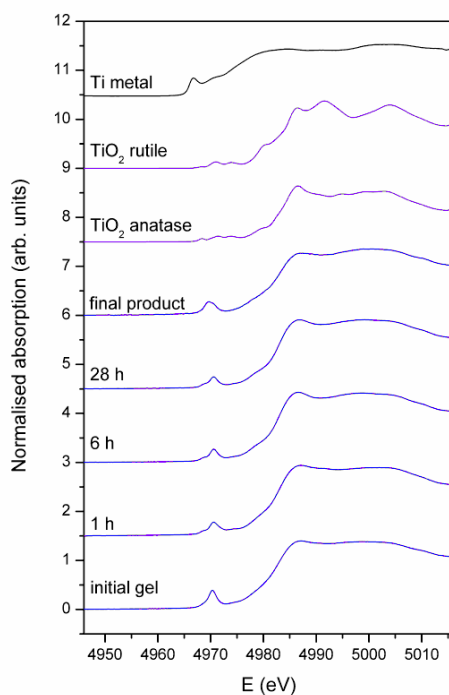


Figure 2. XANES spectra of the samples along with the reference compounds (Ti metal, rutile and anatase).

The position, shape and intensity of the pre-edge resonance can also give us information about the coordination of Ti atoms [4]. In octahedrally coordinated Ti, as for example in rutile or anatase, three low-intensity pre-edge resonances are detected [4]. Tetrahedrally and five-fold coordinated titanium, lacking a centre of inversion, gives rise to a single high intensity pre-edge peak [4,5]. The XANES spectra of all our samples exhibit single pre-edge peaks, which are positioned at 4970 eV and have 30% of the intensity of the edge jump. Such pre-edge resonances are in zeolitic materials characteristic for framework Ti coordinated with additional water molecules or OH groups [6-8]. XANES spectra of our samples also show slight differences in the shape of the pre-edge resonances between Ti-Beta gels and the final product. This suggests that there is a minor difference in the local surroundings of Ti atoms between the fully formed and still growing framework. A similar difference was reported between Al-free Ti-Beta zeolite and Ti-Beta/SBA-15 composite with Ti-Beta nanoparticles deposited in the SBA-15 pores [9].

CONCLUSION

Liquid and solid-state NMR enabled us to gain an atomic-scale insight in the formation of zeolite Beta and thus monitor the crystallization process. Our measurements show that the synthesis of zeolite Beta starts with a quick desolvation of the silicate source and with a quick formation of oligomers. The oligomers aggregate into smaller nanoparticles with the diameter of 2 nm, which after 24 h of the synthesis start to aggregate in larger crystalline nanoparticles. Studies of formation of the silicate framework were complemented with XANES providing the information on incorporation of Ti into zeolite Beta. The results show that Ti incorporates into silicate clusters as early as after an hour of the hydrothermal treatment.

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