Preparation of titanium-silicate Ti-SBA-15 catalyst

Edyta MAKUCH, Agnieszka WRÓBLEWSKA – Faculty of Chemical Engineering, West Pomeranian University of Technology, Szczecin

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Introduction:

Titanium-silicate mesoporous materials, such as Ti-MCM-41, Ti-MCM-48 or Ti-SBA-15, are currently of great interest. They are obtained by a direct method based on introducing titanium source into crystallisation gel. By using this method, titanium is incorporated into silica structure. At high content of titanium in crystallisation gel, not only Ti can be incorporated into silica structure, but also titanium dioxide (anatase) can precipitate, which is an unfavourable effect. An amount of titanium incorporated into the catalyst structure, below which anatase precipitation does not occur, depends on titanium-silicate catalyst and amounts to a few % of moles for TS-1, e.g. 2% of mole, Nowadays, particular attention is paid to Ti-SBA-15. This is caused by its structure which is more durable than in case of Ti-MCM-41 and Ti-MCM-48, which were obtained much earlier (it can be employed in industrial processes for longer time). Moreover, its synthesis is much more friendly to the natural environment as this process takes places without involving any ammonium compounds, only in the presence of ethylene oxide-propylene oxide copolymer (Pluronic P123) – lower odour noxiousness to the natural environment. Titanium-silicate catalysts are mainly applied in the oxidation processes of olefinic compounds or in hydroxylation of aromatic compounds.

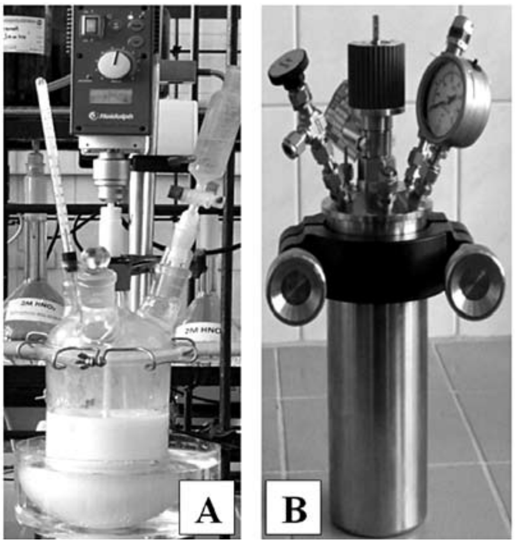

Fig. 1. Apparatus for the synthesis of Ti-SBA-15 catalyst: A – glass reactor, B – autoclave

The objective of this work was to prepare Ti-SBA-15 materials with different content of titanium and to characterise them using various instrumental methods. Those materials will be later used in tests during epoxidation processes, and their results will be presented in further papers.

Synthesis of Ti-SBA-15 catalyst

Ti-SBA-15 catalysts were obtained by the direct method described by Berube and his co-workers [1]. The following raw materials were used in that method: Pluronic P123 (Aldrich, MW = 5800) as template, tetraethyl o-silicate (TEOS, 98%, Aldrich) as silica source, and tetraisopropyl o-titanate (TiPOT, >98%, Merc) as titanium source. 18 g of Pluronic P123 was dissolved in the mixture of 140 g of deionized water and 10.5 g of hydrochloric acid (HCl, 37%, Hartim) at 35°C, Then, the mixture of TEOS and TiPOT was added very slowly (dropwise addition) to that solution (amounts of TEOS and TiPOT were selected to maintain Si/Ti molar ratio equal to 20, 40 and 60 respectively). The mixture prepared as described above was stirred for 24 hours at 35°C, and then transferred into an autoclave in which it was kept for the next 24 hours at 35°C (without stirring). The obtained sediment was filtrated, rinsed and dried at 100°C for 24 hours, and then calcinated at 550°C for 3 hours. For comparison, SBA-15 material was obtained by the same method, but without using titanium source.

The obtained samples of Ti-SBA-15 catalyst (and also SBA-15 material) were instrumentally tested. The tests were performed by XRD (spectroscopy technique of X-ray diffraction) method to confirm the structure of those materials. The tests were conducted on the XPERT PRO diffractometer within the range of 2-Theta angle from 0 to 5°using a copper lamp with a wavelength of 0.154 nm. UV-vis (spectroscopy in the UV and visible light) method was used in tests to confirm Ti incorporation into SBA-15 structure. SPECORD M40 apparatus was used in those tests. Also infrared ray (IR) spectroscopy was employed in testing Ti-SBA-15 catalysts to confirm titanium incorporation into the mesoporous structure of silica. JASCO FT/IR-430 apparatus was used in the tests conducted by that method. Morphology of Ti-SBA-15 catalysts was determined using scanning electron microscopy (SEM). The tests were conducted on JOEL JSM-610 apparatus.

Test results and their review

Figure 2 presents the XRD pattern of the SBA-15 material obtained after its drying at 100°C for 24 hours and its calcination at 550°C for 3 hours.

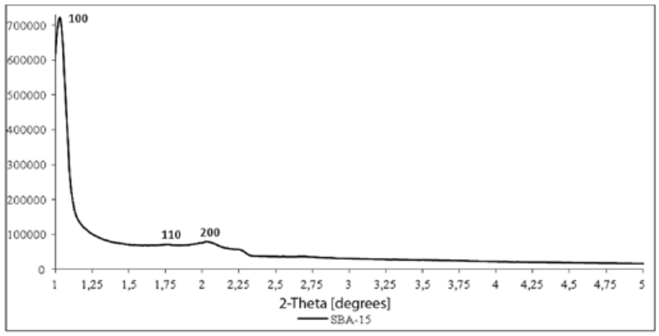

Fig. 2. The XRD pattern of the obtained SBA-15 material

Using X-ray diffraction (XRD) the obtained structure of material was identified as SBA-15. XRD spectrum depicted in Figure 2 shows one very intense diffraction peak at ca, 1° of 2-Theta angle (100) and two weak diffraction peaks at ca. 1.75° and 2.05° of 2-Theta angle (110 and 200). Those peaks comply with literature data [2] and they are typical for 2-D hexagonal structure (p6mm) [3].

Figure 3 illustrates the XRD pattern of Ti-SBA-15 catalysts having the moral ratio Si/Ti equal to 20, 40 and 60 respectively. XRD patterns depicted in Figure 3 show that reduction in titanium content in particular samples of the catalyst results in a shift of typical diffraction peaks (100, 110, 200) towards lower values of 2-Theta angle. This effect directly confirms that titanium content in the mesoporous structure of silica is decreasing.

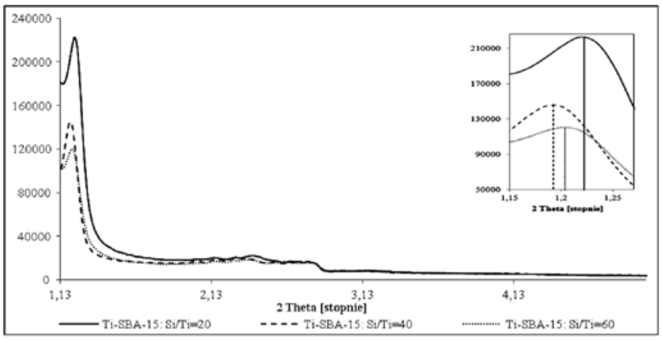

Fig. 3. XRD patterns of Ti-SBA-15 catalyst having different Si/Ti molar ratio

UV-vis spectra of all tested samples of Ti-SBA-15 catalyst demonstrated very intense absorption band at the wavelength of ca. 210 nm (Fig. 4) associated with titanium ($Ti^{+4)}$ incorporated into the mesoporous structure of silica [4, 5]. The band intensity was increasing as titanium content increased. UV-vis spectrum of all tested samples of Ti-SBA-15 catalyst also showed very weak absorption band at the wavelength of 290 nm, which was associated with titanium present in Ti^{+5} or Ti^{+6} coordination [4, 5]. For all samples of Ti-SBA-15 catalyst which were dried, and then calcinated, no absorption band at the wavelength of 330 nm was observed. It indicated that TiO_2 in the anatase form is not present in the synthesised material after its drying and calcination [4, 5]. UV-vis spectroscopy was used to describe the coordination of titanium atoms in the analysed samples of Ti-SBA-15 catalyst and confirmed that atoms of that transition metal were incorporated into the mesoporous structure of silica. For comparison, the UV-vis spectrum of SBA-15 material is illustrated in Figure 5. No visible bands related to the presence of Ti atoms in the structure were observed there.

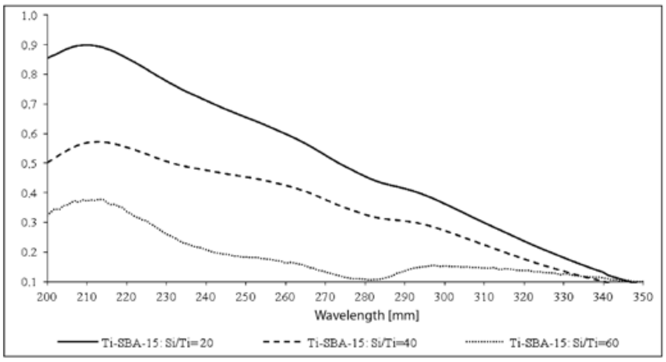

Fig. 4. UV–vis spectrum of the Ti-SBA-15 catalyst having different Si/Ti molar ratio

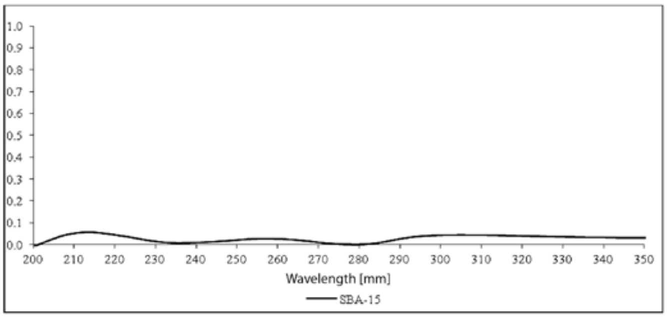

Fig. 5. The UV–vis spectrum of the obtained SBA-15 material Si/Ti

The IR spectrum of the Ti-SBA-15 catalyst (for all tested samples) had a typical absorption band at the wavelength of 968 cm^{-1}. The presence of that band confirmed titanium incorporation into the mesoporous structure of silica, and its intensity was increasing with an increasing titanium content (Fig. 6). The band appearing at 968 $cm-^{1}$ was associated with stresses of Si-O-Ti polar bonds or the presence of titanyl group (>T=O). However, the band at 560 cm^{-1} was not reported in any tested sample of Ti-SBA-15 catalyst. It indicated that TiO2 in the anatase form was not present in the synthesised material [6].

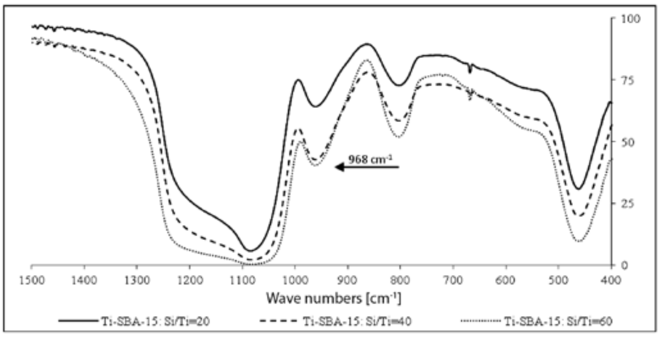

Fig. 6. The IR spectrum of the Ti-SBA-15 catalyst having different Si/Ti molar ratio

Figure 7 illustrates IR spectrum of the pure SBA-15 material. After the calcination phase, the absorption band at 955 cm^{-1} was observed in that spectrum. As titanium was not present in the structure, this band was associated with water molecules adsorbed on the catalyst surface [7].

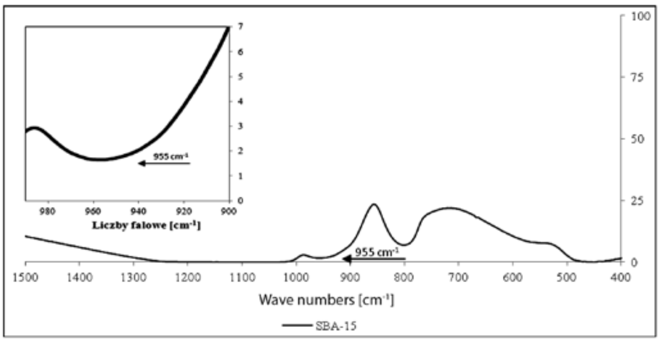

Fig. 7. The IR spectrum of the obtained SBA-15 material

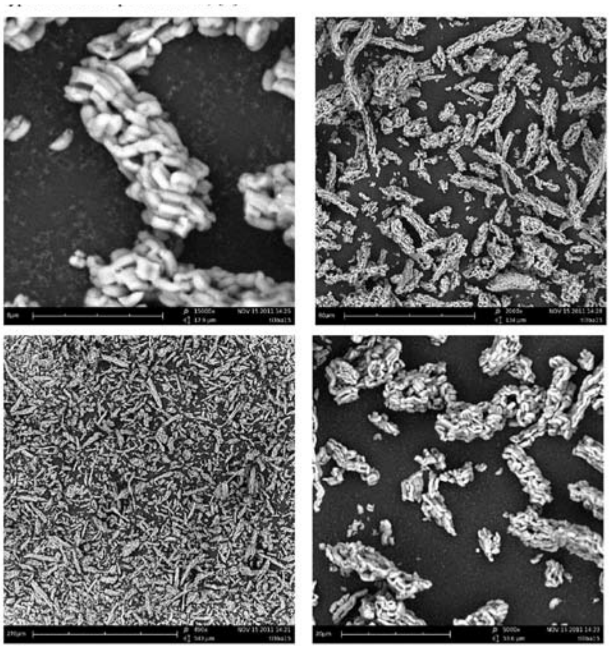

Fig. 8. SEM micrographs of Ti-SBA-15 catalyst obtained at Si/Ti molar ratio = 40

Figure 8 illustrates the SEM micrographs of TI-SBA-15 catalyst obtained at Si/Ti molar ratio = 40. At the same time, the samples of Ti-SBA-15 catalyst obtained at two other Si/Ti molar ratios were characterised by very similar molecular morphology, similarly as the sample of SBA-15 material. For all tested samples of the catalyst, particles of relatively uniform structure were observed that were well shaped and whose appearance resembled rice grains having the size of ca. 0.7 x 3 m. They joined together and formed particles similar to a woven cord having the size of 4 x 9 m (which is typical for mesoporous silica) [8].

Summary and conclusions

The tests (IR spectrum) demonstrated that the highest content of titanium was obtained for the catalyst synthesised at Si/Ti molar ratio =20 (the most intense band at $960\ cm^{-1}$). UV-vis spectra showed that titanium in the anatase form was not present in any obtained material. Regardless of Si/Ti molar ratio, Ti-SBA-15 catalyst particles were very similar in appearance and size. They were uniform and well shaped particles resembling rice grains, which joined together forming particles similar to the woven cord.

Literature

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9. Preparation of titanium-silicate Ti-SBA-15 catalyst

Edyta MAKUCH – M.Sc., graduated from the Faculty of Chemical Engineering at the West Pomeranian University of Technology in Szczecin (former Szczecin University of Technology) in 2010. At the same year, she started the post-graduate (doctoral) studies at the Institute of Organic Chemistry Technology at the West Pomeranian University of Technology in Szczecin, under the supervision of Sc.D.,(Eng) Agnieszka Wróblewska the Professor at the West Pomeranian University of Technology in Szczecin. The research works performed during her post-graduate doctoral studies are financed by the Ministry of Science and Higher Education as part of the research project and by the Provincial Labour Office in Szczecin (scholarships for PhD students "Investing in knowledge as a driving force for developing regional innovation – 2nd edition"). Research interests: safe and non-waste technologies for obtaining epoxy compounds on titanium-silicate compounds and using hydrogen peroxide as an oxidising agent. She is co-author of 2 patent applications, 3 chapters in monographs, 5 papers published in scientific and technical journals with outstanding IF rating, 7 multipage articles, 19 papers and posters presented at national and internaltional conferences.

e-mail: editamakuch@wp.pl

Agnieszka WRÓBLEWSKA – Sc.D., (Eng), graduated from the Faculty of Chemical Engineering at the Szczecin University of Technology in 1994. In 1998, she received the academic degree of doctor at that university. She did her habilitation at the Faculty of Chemical Engineering at the West Pomeranian University of Technology in Szczecin (former Szczecin University of Technology) in 2009. She is currently working as an associate professor at the Institute of Organic Chemistry Technology at the West Pomeranian University of Technology in Szczecin. Research interests: oxidation processes employing titanium-silicate catalysts, including epoxidation of allylic compounds and hydroxylation of aromatic compounds using hydrogen peroxide as an oxidising agent; synthesis of new titanium-silicate catalysts, low-waste technologies; nanotechnologies; biologically active compounds of natural origin. She is the author and co-author of 6 monographs, 64 scientific and technical papers, 22 Polish patents and 3 patent applications as well as about 100 papers and posters presented at national and international conferences.

e-mail: Agnieszka.Wroblewska@zut.edu.pl

New coating turns ordinary glass into super glass

A new transparent, bioinspired coating makes ordinary glass tough, self-cleaning and incredibly slippery.

The new coating could be used to create durable, scratch-resistant lenses for eyeglasses, self-cleaning windows, improved solar panels and new medical diagnostic devices.

The new coating builds on an award-winning technology, called Slippery Liquid-Infused Porous Surfaces (SLIPS), is the slipperiest synthetic surface known. The new coating is equally slippery, but much more durable and fully transparent. Together these advances solve longstanding challenges in creating commercially useful materials that repel almost everything.

SLIPS was inspired by the slick strategy of the carnivorous pitcher plant, which lures insects onto the ultraslippery surface of its leaves, where they slide to their doom. Unlike earlier water-repelling materials, SLIPS repels oil and sticky liquids like honey, and it resists ice formation and bacterial biofilms as well.

To create a SLIPS-like coating, the researchers corral a collection of tiny spherical particles of polystyrene, the main ingredient of Styrofoam, on a flat glass surface. They pour liquid glass on them until they are more than half buried in glass. After the glass solidifies, they burn away the beads, leaving a network of craters that resembles a honeycomb. They then coat that honeycomb with the same liquid lubricant used in SLIPS to create a tough but slippery coating.

By adjusting the width of the honeycomb cells to make them much smaller in diameter than the wavelength of visible light, the researchers kept the coating from reflecting light. This made a glass slide with the coating completely transparent.

The team is now honing its method to better coat curved pieces of glass as well as clear plastics such as Plexiglas, and to adapt the method for the rigors of manufacturing.

(Source: http://www.chemistrytimes.com/research/New_coating_turns_ordinary_glass_into_super_glass.asp, 18.08.2013)