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## Changes in ion exchanger catalysts after more than 10 year time-on-stream

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In this contribution will be reported results of examination of a series of industrial ion exchanger catalysts samples exposed to the environment of catalytic reactor in process of esterification of acrylic acid with methanol for more than 10 years. There was evaluated their acid capacity, swelling and using inverse steric exclusion chromatography (ISEC) also their morphology in water-swollen state. For comparison, similarly were evaluated also reference samples of the same but virgin ion exchangers.

Before examination the samples were exhaustively washed with methanol and water for to purify them from remnants of the reaction components. For the exchange capacity determination the samples were additionally washed with diluted hydrochloric acid and then by deionized water.

There was found that in comparison with the virgin materials, after the long-term stay in the reactor the catalysts exhibited similar or slightly increased swelling but only 10 – 20 % of the original exchange capacity. ISEC examination of their swollen-state morphology shown that while the virgin catalysts contains only water-swellaable polymer matrix, in the “used” materials were detected also some non-polar domains swelling in tetrahydrofuran. Evidently, some parts of the polymer skeleton were desulfonated. The remaining polar regions swelling in water shown better swelling than the virgin polymers, like if their crossliking was significantly reduced. It appears that during the long term exposition of the ion exchangers to the reaction environment of acrylic acid esterification with methanol there occurs splitting of both C – C and C – S bonds, most probably due to presence of traces peroxidic compounds in the reaction environment.

Better expansion of the polymer matrix promotes catalytic activity of sulfonic groups located in these region, which to some extend could compensate the depletion of the acidic centers due to the desulfonation process. It may explain why these effects and mechanisms of ion exchanger catalysts deterioration were not yet reported.