CH 6231 - Operando XRD analysis of novel zeolite-based methanol-to-olefins catalysts

A) Overview

During these experiments we studied a series of zeolite catalysts modified with Na^{+}, Ca^{2+} and Sr^{2+} cations, active for methanol conversion to olefins (MTO), with operando XRD. The results showed how the unit cell of zeolite catalyst changes during the reaction.

B) Quality of measurement/data

The experiments were successful and the data quality was acceptable.

C) Status and progress of evaluation

The data have been fully analyzed and we are working on including them in a publication.

D) Results

With the aid of operando XRD study, we elucidated the difference in the zeolite cell size and a- and b-unit cell parameters upon the MTO reaction over HZSM-5, Ca/ZSM-5, Sr/ZSM-5 and Na/ZSM-5 catalysts and correlated the change with gradual increase of hydrocarbons retained. First, we acquired the diffractogram arrays upon the working catalyst from five different positions along the bed (Fig.1).

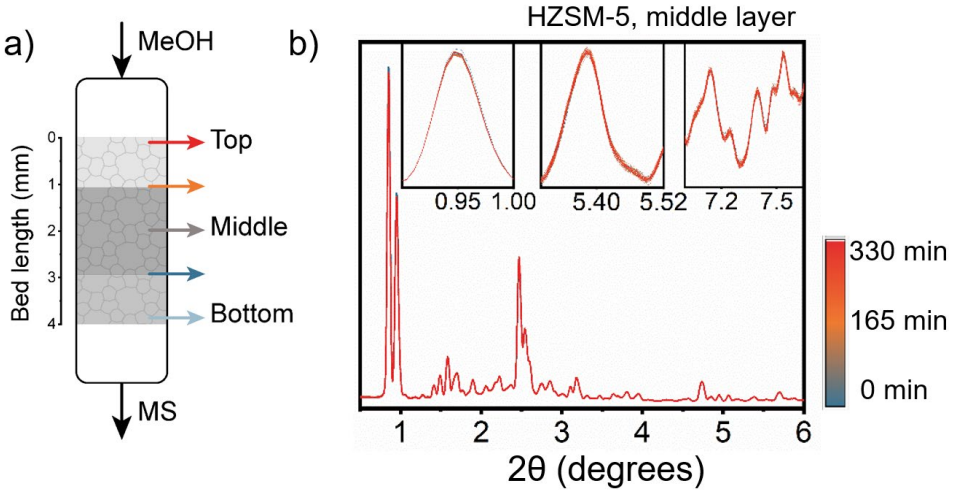

Figure 1. a) Positions within the catalyst bed where the XRD data were acquired; b) XRD patterns of HZSM-5 catalyst recorded in the middle of the catalyst during 5.5 h of an operando experiment with methanol was switched on at t = 10 min.

We carried out Rietveld refinement and extracted unit cell parameters such as volume and (a-b) difference which were linked with the presence of hydrocarbons and other adsorbates such as oxygenates and water over the unit cell of the zeolite.[1,2,3,4] Figure 2 represents the change of the volume of elementary cell combined with subsequent MS tracing. The presence of MS signals belonging to hydrocarbons (27, 56, 92 and 106) indicate that the hydrocarbon pool was built up and catalytic reaction took place. During the primary stage of the MTO reaction for HZSM-5 and Na/ZSM-5 we observe fast expansion of the unit cell reaction with subsequent monotonous growth of the cell volume when the reaction proceeds toward the steady state (Figs. 2a,b). After the methanol switched off, we observed the contraction of the cell (t = 300 – 330 min) for both catalysts. At the same time, Ca/ZSM-5 and Sr/ZSM-5 catalysts demonstrated different dynamics of the pore

expansion and contraction – steep increase of the cell volume during all five hours on stream indicates that more adsorbates were retained in the presence of Ca^{2+} and Sr^{2+} cations (Fig. 2c,d). However, we did not observe any cell contraction after switching off the methanol, supporting the trends for stronger retention of adsorbates over Ca and Sr-modified catalysts.

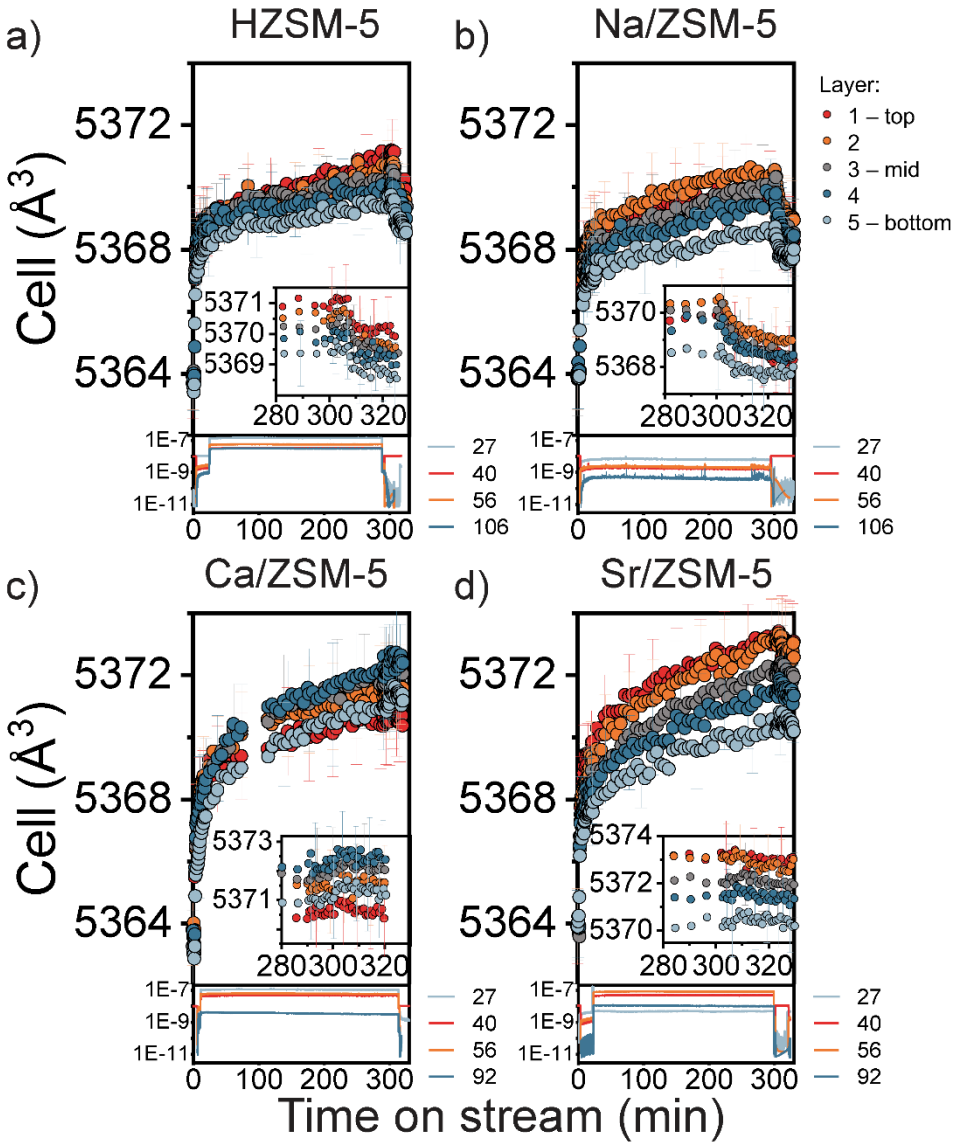

Figure 2. Unit cell volumes derived from Rietveld refinement of operando XRD data for HZSM-5, Ca/ZSM-5, Sr/ZSM-5 and Na/ZSM-5 catalysts and after 5 h on stream and subsequent switch off the methanol for 30 min; MS spectra of the reaction are attached below. Conditions: 400 °C; carrier – 50 mL^{-1}·min He; 20 mg of catalyst; 13 kPa of MeOH.

We extracted (a-b) parameter being instrumental to ascribe the changes upon the filling the pores with aromatic adsorbates as well (Fig. 3). In all cases after the methanol was fed, we observed monotonous decrease in (a-b) parameter pointing out the advancing deactivation of the catalysts over time on stream. After the methanol was switched off, we observed no changes for HZSM-5 and Na/ZSM-5 but relaxation of (a-b) parameter to the initial numbers for Ca/ZSM-5 and Sr/ZSM-5, particularly caused by the sudden increase of the a-parameter. We suggest that relaxation of a-parameter is caused by instantaneous removal of products of methanol decomposition and instable aliphatic intermediates which are mostly present in Ca/ZSM-5 and Sr/ZSM-5 pores.

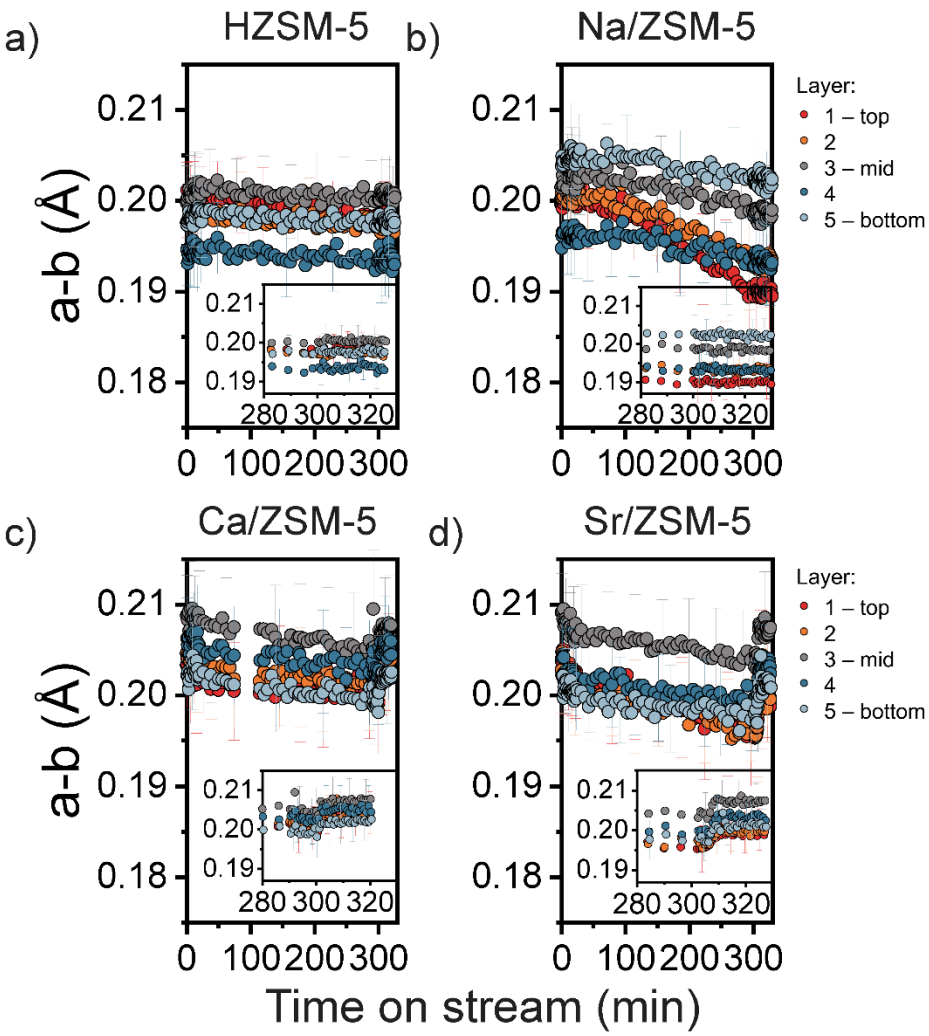

Figure 3. Difference of unit cell vectors a and b derived from Rietveld refinement of operando XRD data for HZSM-5, Ca/ZSM-5, Sr/ZSM-5 and Na/ZSM-5 catalysts and after 5 h on stream and subsequent switch off the methanol for 30 min; MS spectra of the reaction are attached below. Conditions: 400 °C; carrier – 50 mL^{-1}·min He; 20 mg of catalyst; 13 kPa of MeOH.

To summarize, using operando XRD analysis we compared dynamics of unit cell expansion for zeolite catalysts upon MTO reaction. We found that in the presence Ca^{2+} and Sr^{2+} cations zeolites retain more adsorbates in an irreversible manner. Altogether, the experiments help to link the hydrocarbons evolution to the structural properties of the zeolite catalyst and explain unusual olefin selectivity in the presence of alkali earth cations.

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4. Wragg, D. S., Johnsen, R. E., Norby, P. & Fjellvåg, H. The adsorption of methanol and water on SAPO-34: in situ and ex situ X-ray diffraction studies. *Microporous mesoporous Mater.* **134**, 210–215 (2010).