Electronic Supplementary Information

Recent Advances in Secondary Ion Mass Spectrometry of Solid Acid Catalysts: Large Zeolite Crystals under Bombardment

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1 ToF-SIMS

The instrument used for the experiments presented in this article is a ToF-SIMS 5 machine (IONTOF GmbH, Münster, Germany). The machine is equipped with a 25 keV Bi-cluster primary ion gun, 2 keV Cs- and O_2-guns for sputtering. The crystals were transferred into the UHV chamber of the ToF-SIMS machine without further preparation. For fixation crystals were sprinkled on conductive 0.2 mm thick polycarbonate stickers with graphite powder mixed in the adhesive as commonly used for scanning electron microscopy (Plano GmbH, Wetzlar, Germany). An alternative fixation of pristine could be achieved by glueing the crystals on oxidized and hydroxylated Si(100) wafers. Therefore, crystals are sprinkled onto a wafer, covered with a droplet of MilliQ water and subsequently heated on a hotplate to 120 °C to evaporate the water. During heating, hydroxyl groups on both surfaces of the wafer and the zeolite crystals condense resulting in robust adhesion of the crystals on the wafer. The advantage of the latter method is that less organic species – originating from the carbon sticker – are present in the background gas during ToF-SIMS analysis. The standard instrument handling requires flat samples with a minimum size of about 1 x 1 mm². The investigated crystals in this paper are definitely smaller and the orientation of the crystals is random. The crystals cannot be focused completely in the video camera image. Therefore we scanned the carbon sticker area by area by the total secondary ion intensity raster and searched for crystals lying in suitable orientation flat on the tape. Focusing and adjustment of the reflectron is done roughly via the total ion image. As analysis species (primary ions) mainly Bi_3^{++} is used. To obtain the highest possible mass resolution for the identification of carbon fragments, the primary ion gun was operated in the high current bunched mode. For images with high lateral resolution the burst alignment mode with Bi^+ as primary ions was used. Sputtering for depth profiling was done either by 1 keV O_2^+ or 1 kV Cs^+ ions.

2 Large zeolite ZSM-5 crystals

Large coffin-shaped zeolite H-ZSM-5 crystallites (100×20×20 μm^3) were provided by ExxonMobil (Machelen, Belgium). The Si/Al ratio of these crystals was ~ 17 as determined by the synthesis protocol and SEM-EDX measurements. The preparation method and basic characterization details of these micron-sized zeolites can be found in references [S1-S5]. Zeolite ZSM-5 samples were further treated as reported e.g. in [S6]: The as-prepared zeolite ZSM-5 crystals were calcined, first preheating them at 120 °C (30 min, 2 °C/min) and then increasing the temperature to 550 °C (360 min, 10 °C/min). This was followed by a triple ion exchange with a 10 wt% ammonium nitrate (Acros Organic, 99+%) solution at 80 °C. Subsequently, a second calcination was performed to obtain the ZSM-5-P sample. Before starting the hydrothermal treatment ZSM-5-P was preheated to 120 °C (30 min, 2 °C/min) in a quartz tubular oven (Thermoline 79300). Afterwards, steaming was performed during 300 min at 500 °C (ZSM-5-MT) and 700 °C (ZSM-5-ST) via saturation of a nitrogen flow (180 ml/min) with boiling water. Subsequent to the hydrothermal treatment the zeolite crystals were calcined following the above mentioned procedure.

Methanol-to-hydrocarbons reactions were performed in a Linkam FTIR 600 in-situ cell equipped with temperature controller (Linkam TMS93), as reported in [S7]. For activation, the zeolite crystals were heated to 500 °C at a rate of 10 °C/min and kept at this temperature under inert atmosphere for 1 h. Then the temperature was brought to the desired reaction temperature (350 °C or 500 °C) with a rate of 10 °C/min. Subsequently, the N_2 flow (70 ml/min) was diverted through a bubbler containing the methanol thereby acting as a carrier gas. The methanol saturator was kept at room temperature throughout the experiment. Methanol (99 %, Antonides Interchema) was used as received. Ageing of the sample H-ZSM-5-P-350 was performed at 350 °C under pure N_2 flow (70 ml/min) for 14 h resulting in sample H-ZSM-5-P-350-aged.

3 Example ToF-SIMS spectrum of a H-ZSM-5 sample for demonstration of mass resolution

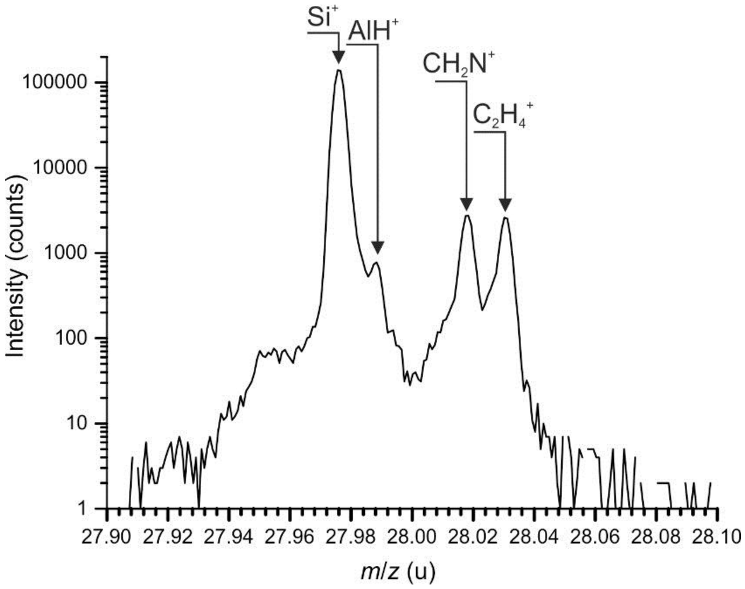

Figure S1. ToF-SIMS spectrum (high current bunch mode, 25 keV Bi^+) of a zeolite H-ZSM-5 powder pellet showing the m/z = 28 region. Si^+ and AlH^+ are resolved. The mass resolutions of the signals are $m/\Delta m(Si^+)$ = 8340 and $m/\Delta m(AlH^+)$ = 7960.

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