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Supporting Information

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**Formation and Decomposition of Surface Ethoxy Species
on Acidic Zeolite Y**

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Materials. Zeolite Na-Y ($n_{\text{Si}}/n_{\text{Al}} = 2.7$) was purchased from Degussa AG, Hanau, Germany. Zeolite NH₄-Y was prepared by a fourfold ion exchange of zeolite Na-Y at 353 K in a 1.0 M aqueous solution of NH₄NO₃. After an ion-exchange degree of 90% was reached, the material was washed in demineralized water and dried at room temperature. Subsequently, zeolite NH₄-Y was heated in vacuum with a rate of 20 K/h up to the final temperature of 723 K. There, the material was calcined at a pressure below 10⁻² Pa for 12 h leading to zeolite H-Y.^[1] The catalyst was characterized by AES-ICP, XRD and solid-state ¹H, ²⁷Al, and ²⁹Si MAS NMR spectroscopy, indicating that the material obtained after cation exchange and calcination was neither damaged nor dealuminated. ¹³C-1-enriched ethanol, CH₃¹³CH₂OH (¹³C-enrichment of 99%), was purchased from ISOTECH.

In situ MAS NMR and UV/Vis spectroscopy. The detailed description of the experimental set-up used for the *in situ* stopped-flow protocol was described elsewhere.^[2] Prior to the *in situ* MAS NMR experiments, ca. 200 mg dehydrated solid catalysts were filled

into a 7 mm MAS NMR rotor under dry nitrogen in a glove box and pressed to a cylindrical catalyst bed. After transferring the rotor into the modified DSI-740 7 mm STD MAS NB NMR probe of Doty Scientific Instruments,^[3] a second dehydration was performed at 673 K for 1 h under flowing nitrogen (30 ml/min). Subsequently, ¹³C CP/MAS NMR spectroscopy was applied to monitor the *in situ* formation of surface ethoxy species during the stopped-flow experiment consisting of a continuous injection of ¹³C-1-enriched ethanol, CH₃¹³CH₂OH, into the MAS NMR rotor reactor at 295 K for 10 min (modified residence time of $W/F = 100 \text{ g}\cdot\text{h/mol}$) in the first step. In the second step, a purging with dry nitrogen (200 ml/min) was performed at 295 to 453 K. This treatment leads to a conversion of ethanol to ethoxy species and a desorption of water as well as of physically adsorbed ethanol. In some experiments, water was deliberately injected into the MAS NMR rotor reactor again after the formation of surface ethoxy groups.

For preparation of surface ethoxy species under vacuum conditions, the following procedure was applied. Upon calcination of zeolite H-Y under vacuum at 723 K for 12 h, ¹³C-1-enriched ethanol was loaded at 295 K under a vapor pressure of 72 mbar until saturation was reached. Then, the catalyst was evacuated at 453 K for 24 h. Thereafter, the ethylated catalyst was filled into an MAS NMR insert (Wilmad) and sealed. Prior to the ¹³C MAS NMR measurements, the sealed samples were heated at reaction temperature for 20 min.

All ¹³C MAS NMR studies of the formation of surface ethoxy species were performed on a Bruker MSL-400 spectrometer at a

resonance frequency of 100.6 MHz. *In situ* ^{13}C CP/MAS NMR investigations using the modified DSI-740 7 mm STD MAS NB NMR probe of Doty Scientific Instruments^[3] were performed applying a contact time of 5 ms and a sample spinning rate of ca. 2.2 kHz. ^{13}C CP/MAS NMR investigations of the decomposition of surface ethoxy species on zeolite Y were performed with the sample spinning rate of ca. 2.5 kHz using a modified 7 mm Bruker MAS NMR-UV/Vis probe^[4] at 295 K. A contact time of 5 ms and a repetition time of 5 s were used. Simultaneously, UV/Vis spectra were recorded applying an AvaSpec-2048 Fiber Optic spectrometer, an AvaLight-DH-S deuterium light source, and a glass fiber reflection probe FCR-7UV20-3-SR-S1 by Avantes.

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