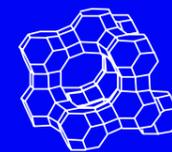




# Formation and Decomposition of Surface Ethoxy Species on Acidic Zeolite Y Studied by the *In Situ* MAS NMR-UV/Vis Spectroscopy



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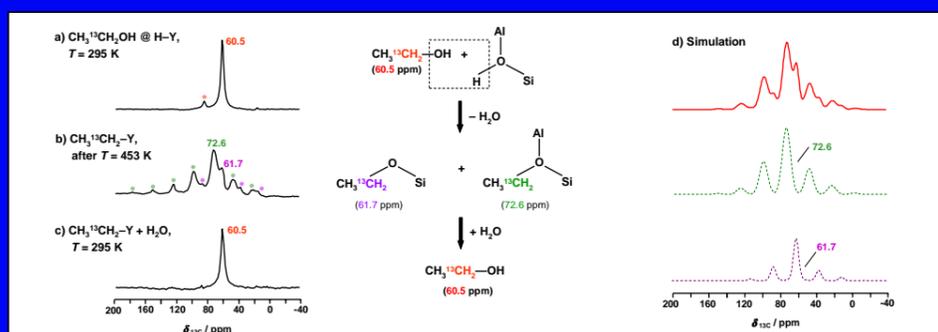
## INTRODUCTION

On the basis of *in situ* MAS NMR technique under flow conditions,<sup>1-4</sup> the combined *in situ* MAS NMR-UV/Vis spectroscopy<sup>5</sup> has recently been developed to obtain complimentary information on solid catalysts and, therefore, to better elucidate the mechanism involved in heterogeneous catalysis. While NMR spectroscopy allows the identification of species on the working catalyst in more detail, UV/Vis spectroscopy offers the high sensitivity for detecting the formation of aromatic compounds and unsaturated carbenium ions. In this contribution, the first solid-state <sup>13</sup>C MAS NMR evidence is presented for the existence of surface ethoxy species on acidic zeolites. Moreover, the further decomposition of these surface ethoxy species to hydrocarbons and carbenium cations was studied by the combined *in situ* MAS NMR-UV/Vis spectroscopy at elevated reaction temperatures.

## RESULTS AND DISCUSSION

### I. Formation of Surface Ethoxy Species on Acidic Zeolite Y

- After purging the CH<sub>3</sub><sup>13</sup>CH<sub>2</sub>OH-loaded zeolite H-Y with dry nitrogen at 453 K to remove water and physisorbed ethanol, the <sup>13</sup>C CP/MAS NMR spectrum is dominated by a signal at 72.6 ppm with spinning sidebands characteristic for strongly bound surface species (Fig. 1b).
- The signal at 72.6 ppm was assigned to surface ethoxy species [SiO(<sup>13</sup>CH<sub>2</sub>CH<sub>3</sub>)Al], while the signal at 61.7 ppm was due to terminal ethoxy species [SiO(<sup>13</sup>CH<sub>2</sub>CH<sub>3</sub>)] and/or strongly bonded ethanol.
- After water was deliberately loaded onto the catalyst at 295 K (Fig. 1c), the reoccurrence of the ethanol signal at 60.5 ppm confirms the former formation of surface ethoxy species.



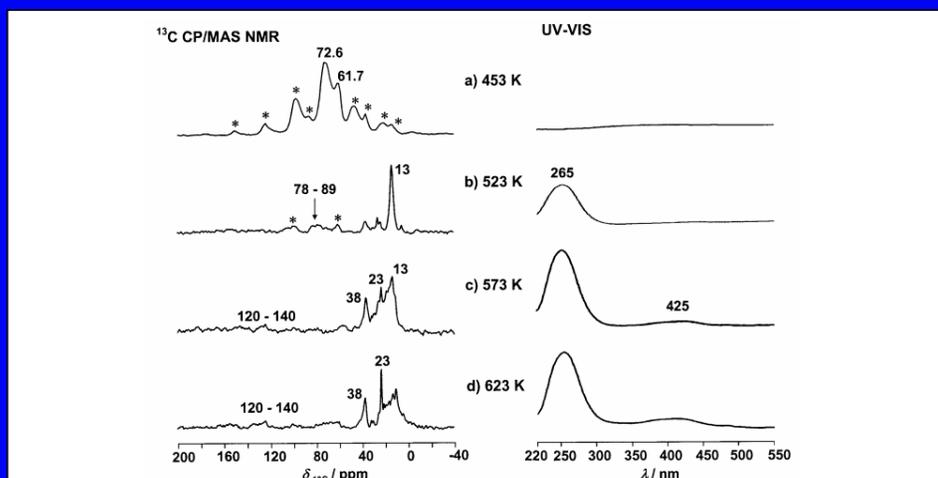
**Fig. 1** <sup>13</sup>C CP/MAS NMR spectra of zeolite H-Y recorded after a continuous injection of CH<sub>3</sub><sup>13</sup>CH<sub>2</sub>OH into the MAS NMR rotor reactor at 295 K and a subsequent purging with dry nitrogen at 295 K (a), after a subsequent purging with dry nitrogen at 453 K (b), and after water was injected into the MAS NMR rotor reactor at 295 K (c). Figure (d) shows the deconvolution and simulation of the <sup>13</sup>C CP/MAS NMR spectrum (b) performed using the Bruker software WINFIT.

**Tab. 1** Isotropic chemical shifts  $\delta$ , chemical shift anisotropies  $\Delta\sigma$ , asymmetry parameters  $\eta$ , and relative intensities  $I$  of the simulated <sup>13</sup>C MAS NMR signals in Figure 1d.

Isotropic Chemical Shift, $\delta$	Chemical Shift Anisotropy, $\Delta\sigma$	Asymmetry Parameter, $\eta$	Relative Intensity, $I$
72.6 ppm	-52 ppm	0.75	81%
61.7 ppm	-43 ppm	0.70	19%

### II. Decomposition of Surface Ethoxy Species on Acidic Zeolite Y

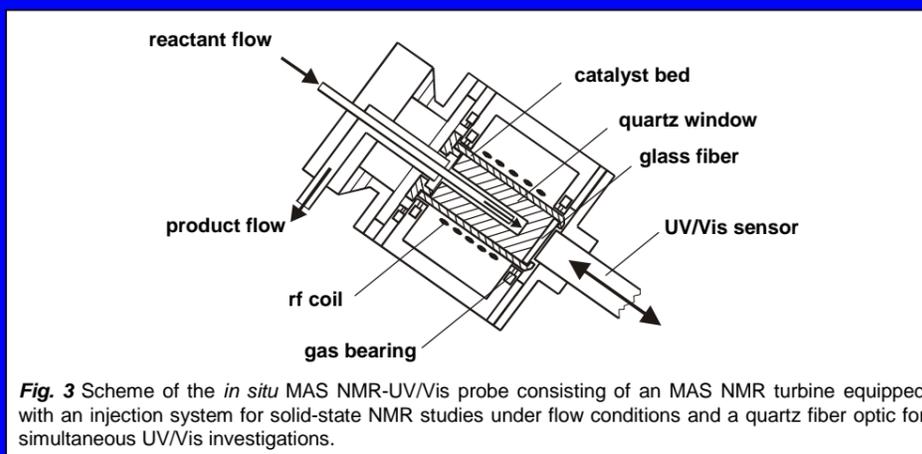
- Upon a thermal treatment at 523 K, the <sup>13</sup>C CP/MAS NMR spectrum (Fig. 2b, left) indicates that the decomposition of surface ethoxy species occurs. The broad signals at 78 to 89 ppm are due to oligomeric alkoxy species.
- No UV/Vis band occurs in the spectrum recorded after adsorption of CH<sub>3</sub><sup>13</sup>CH<sub>2</sub>OH and evacuation at 453 K (Fig. 2a, right). The spectra obtained at 523 to 623 K contain, however, UV/Vis bands at ca. 265 and 425 nm (Figs. 2b to 2d, right). The band at 265 nm is caused by the formation of cyclohexadiene and neutral aromatics, while the broad bands at ca. 425 nm are due to polyaromatics and unsaturated carbenium cations, such as, dienyllic, trienyllic carbenium or alkyl-substituted benzenium cations.<sup>6,7</sup>



**Fig. 2** <sup>13</sup>C CP/MAS NMR (left) and UV/Vis (right) spectra of ethylated zeolite Y (CH<sub>3</sub><sup>13</sup>CH<sub>2</sub>-Y) recorded at 295 K after thermal treatments at 453 K (a) to 623 K (d).

## EXPERIMENTAL

All <sup>13</sup>C MAS NMR studies of the formation and decomposition of surface ethoxy species were performed on a Bruker MSL-400 spectrometer at a resonance frequency of 100.6 MHz. *In situ* <sup>13</sup>C CP/MAS NMR investigations of the formation of surface ethoxy species using the modified DSI-740 7 mm STD MAS NB NMR probe of Doty Scientific Instruments<sup>2</sup> were performed applying a contact time of 5 ms and a sample spinning rate of ca. 2.2 kHz. <sup>13</sup>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 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.<sup>5</sup> The modified *in situ* MAS NMR-UV/Vis probe is shown schematically in Figure 3.



**Fig. 3** Scheme of the *in situ* MAS NMR-UV/Vis probe consisting of an MAS NMR turbine equipped with an injection system for solid-state NMR studies under flow conditions and a quartz fiber optic for simultaneous UV/Vis investigations.

## SUMMARY

- For the first time, the formation and decomposition of ethoxy species on an acidic zeolite catalyst could be investigated by the combined *in situ* <sup>13</sup>C MAS NMR-UV/Vis technique.
- The formation of surface ethoxy species was confirmed by an analysis and discussion of the chemical shielding tensor and by the reaction of these species with water to ethanol.
- At temperatures of  $T \geq 523$  K, decomposition of surface ethoxy species occurs leading to the formation of ethylene, followed by fast oligomerization and formation of hydrocarbons and carbenium cations.

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