Composition-Driven Differences in Active Site Speciation and Behavior in Methane to Methanol Oxidation of Copper Exchanged Chabazite

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Introduction. The wasteful handling of natural gas in the oil and gas sector in combination with the strive for resource efficiency has animated research efforts to identify effective methods to convert retained CH_4 into high-value commodity chemicals such as CH_3OH. [1,2] Direct, low-temperature CH_4 oxidation by Cu exchanged zeolites via chemical looping has proven to be a particularly promising technology as a result of its scale flexibility and exceptional CH_3OH selectivity. Among the different zeolite topologies, Cu exchanged chabazite (Cu-CHA) is of special interest due to its superior CH_3OH yield. [3] However, attempts at industrial implementation are impaired by the lack of knowledge regarding the influence of the Si/Al ratio and the Cu-loading on the Cu active site speciation governing the redox behavior and CH_3OH selectivity of the material. This is further aggravated by the fact that information about the site-specific kinetic properties is missing. The present work aims at identifying the composition dependent Cu speciation by determining characteristic spectroscopic fingerprints and at elucidating their distinct kinetic behavior. Structure-activity relationships are established by correlating these results to the redox activity and CH_3OH selectivity of the bulk material.

Experimental/methodology. Four Cu-CHA materials differing in Cu speciation were prepared by deliberately varying the Si/Al ratio and Cu-loading. The results of plug flow reactor (PFR) reactivity tests were correlated to *in situ* X-ray absorption near edge structure (XANES) and *in situ* Fourier-transform infrared (FTIR) spectroscopy experiments. The observed differences in redox behavior and CH_3OH selectivity of the samples were linked to the variation in Cu speciation, which was established by means of *in situ* FTIR of adsorbed NO as well as *ex situ* Raman, *ex situ* photoluminescence (PL), *operando* ultraviolet-visible diffuse reflectance (UV-Vis), and *operando* electron paramagnetic resonance (EPR) spectroscopy.

Results and discussion. Samples exhibiting a low Si/Al ratio and Cu content predominantly host monomeric Cu^{2+} species such as bare Cu^{2+} ions or $[CuOH]^+$ sites. At high Si/Al ratio and/or Cu-loading, oxygenated multinuclear Cu centers including $[Cu_2(\mu\text{-}O)]^{2+}$ and $[Cu(\mu\text{-}1,2\text{-}O_2)]^{2+}$ species are formed. Compared to dimeric Cu-Oxo compounds, materials containing predominantly monomeric Cu^{2+} active sites are characterized by a slower reaction rate as well as a shift of the redox activity profile to higher reaction temperatures. Simultaneously, these active centers feature a higher CH_3OH-based Cu efficiency and CH_3OH selectivity than their multinuclear counterparts. This indicates that the high activity of $[Cu_2(\mu\text{-}O)]^{2+}$ and $[Cu(\mu\text{-}1,2\text{-}O_2)]^{2+}$ moieties comes at the expense of material selectivity. These findings highlight the influence of the composition on Cu active site speciation, which ultimately determines the material's redox properties and behavior in CH_4 oxidation.

Acknowledgmentes

Funding for this work was provided by the ETH Research Grant ETH-48 21-1.

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