Reaction conditions determine the structure of active Cu sites

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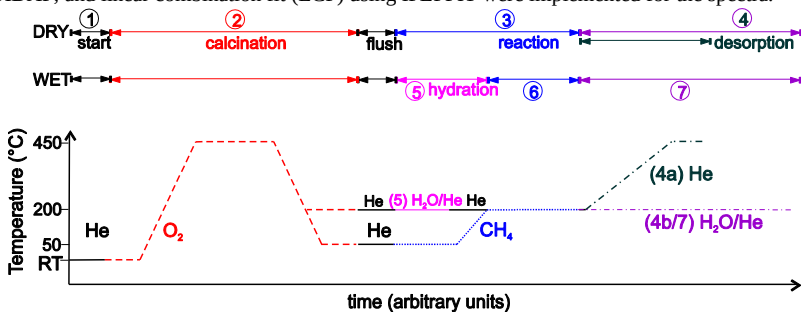
Introduction

A low temperature route for utilizing natural gas as feedstock for chemical synthesis remains elusive. Copper exchanged zeolites can convert methane to methanol with high selectivity; however, a true catalytic operation to date is not yet achieved. Understanding the identity and structure of the active sites is crucial in the development of a catalytic process.

Materials and Methods

The Cu-mordenite catalyst was prepared by aqueous ion exchange of copper acetate and Na-mordenite at room temperature. It was subjected to dry and wet treatments according to Scheme 1 [1]. In situ QuickXAS measurements at the Cu K edge were performed at the SuperXAS beamline of the Swiss Light Source and standard data reduction procedures using XDAP, and linear combination fit (LCF) using IFEFFIT were implemented for the spectra.



Results and Discussion

Cu-MOR after aqueous ion exchange (1) was composed of hydrated Cu^{II} sites. Thermal treatment in (dry) oxygen (2) formed the water-sensitive dicopper active sites. Reaction with methane (3) reduced a significant fraction of the copper sites and formed the sorbed reaction intermediate, which was removed by heating (4a) as CO_2 or by water-assisted desorption (4b) as MeOH. Figure 1 shows the mass spectrometer traces of water, MeOH, and CO_2 during interaction with a wet stream of helium at 200°C directly after methane interaction, and the corresponding structural components of the Cu species determined by LCF of the XAS spectra. The amount of MeOH was about one-tenth for the wet pretreatment compared to the dry. In both cases, the amount of Cu^{I} component decreased while the fraction of Cu^{II} oxide increased, suggesting that the methane conversion intermediate is associated with a Cu^{I} species. Reactivity data and XAS analysis further showed that treatment of oxygen-activated Cu-MOR with water (5) left a water stable Cu^{II} oxide species that was able to activate methane (6-7).

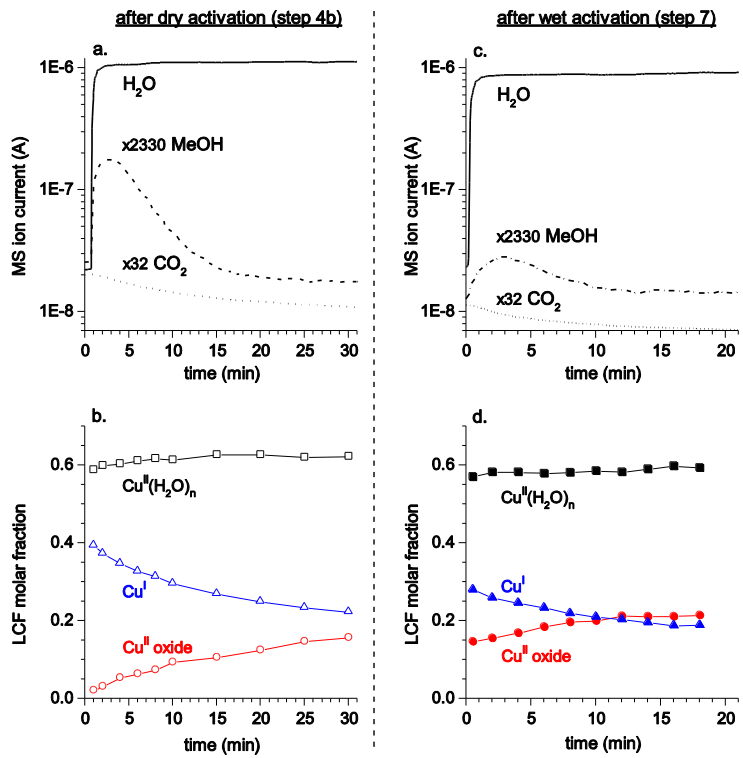


Figure 1. (top) MS profiles of water, MeOH, and CO_2 recorded during interaction with a wet stream of helium at 200°C after methane interaction (step 4b or step 7); (bottom) the structural components: $Cu^{II}(H_2O)$, Cu^{I}, and Cu^{II}oxide from the LCF of the XAS spectra recorded at the same time

Significance

In a dry environment, the Cu sites took the form of dehydrated oxygenated copper species, characterized in literature as the mono(μ-oxo) and bis(μ-oxo) dicopper species. At wet conditions, they destabilized to a hydrated Cu^{II} species, but a fraction that resisted full hydration and converted methane to MeOH. This is important, given that a feasible catalytic cycle has to operate in a hydrated environment because of the necessity to desorb the intermediate.

References

1. Alayon, E.M.C.; Nachtegaal, M.; Bodi, A.; van Bokhoven, J.A.; *ACS Catalysis* **2014,** *4*, 16.