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Karina Mathisen and David G. Nicholson

In-situ X-ray absorption studies on the changes in copper valence state following treatments in the component gases for SCR-HC deNO_x process.

We report here on an XAS in-situ study on hydrothermally and conventionally ion exchanged Cu:ZSM-5. The samples were heated to 500°C in He to remove water from the pores and clear the inner surfaces while collecting XANES spectra. Activation was carried out in an 2% O₂/He mixture at 500°C for 30 mins, before switching to the reactant gas mixture of 0.2 %NO, 0.12% propene, 2% O₂ with balance helium for a total flow of 15ml/min. The sample was then cooled to room temperature in the reactant gas mixture while collecting XANES spectra at selected intervals. The initial idea was to monitor the copper valence state while imitating the catalytic procedure, meaning subjecting the samples to the reaction gas mixture at varying temperatures. This would in the case of a red-ox mechanism as previously proposed not show any changes as we would only see the end point in any case. But it could give crucial information regarding the possible formation of oxide species or clusters at elevated temperatures under real conditions. Secondly we also wanted to verify the ability of reducing copper(II) in a mixture of C₃H₆ (0.12%) and O₂ (2%) at temperatures up to 500°C, and subsequently switching to the NO(0.2%) and O₂ (2%) while cooling. The first step involves the competing components propene and oxygen where reduction and oxidation is favoured at different temperatures. The sample was initially heated to 150°C in He to remove any water from the pores.

Heating Cu:ZSM-5 in helium to 500°C leads to the formation of copper(I) by autoreduction, the reduction Cu(II) → Cu(I) is not complete (Fig. 1). The activation step in O₂ leads to some of the copper(I) being reoxidised to copper(II) and as verified by EXAFS some oxide species are formed, clearly seen in the Fourier Transform as the second Cu...Cu peak around 2.8Å (Fig.

2). This peak is sustained also in the reaction mixture (0.2%NO + 0.12% propene + 2% O₂) at 500° and down to 200°C where copper(I) is formed.(Fig.3-4)

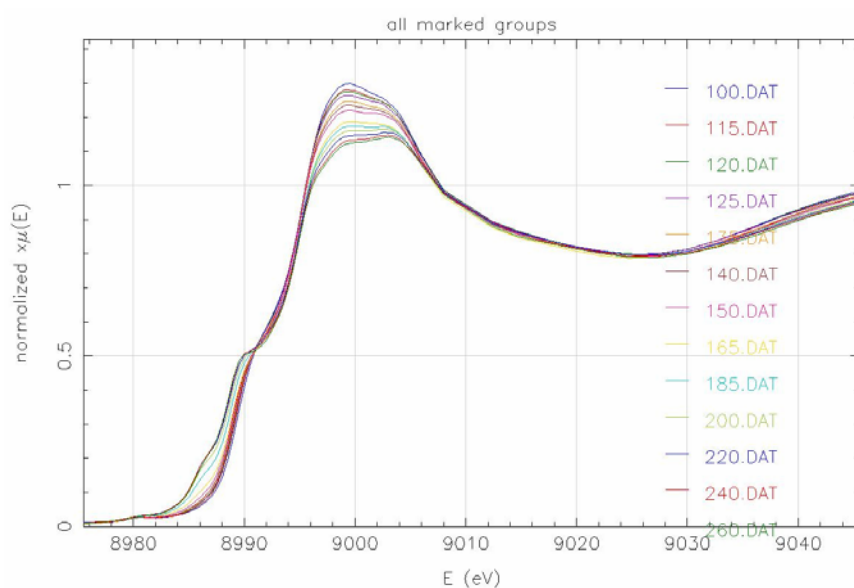


Fig. 1 Autoreduction in CuZSM-5/HT heated in He to 260°C.

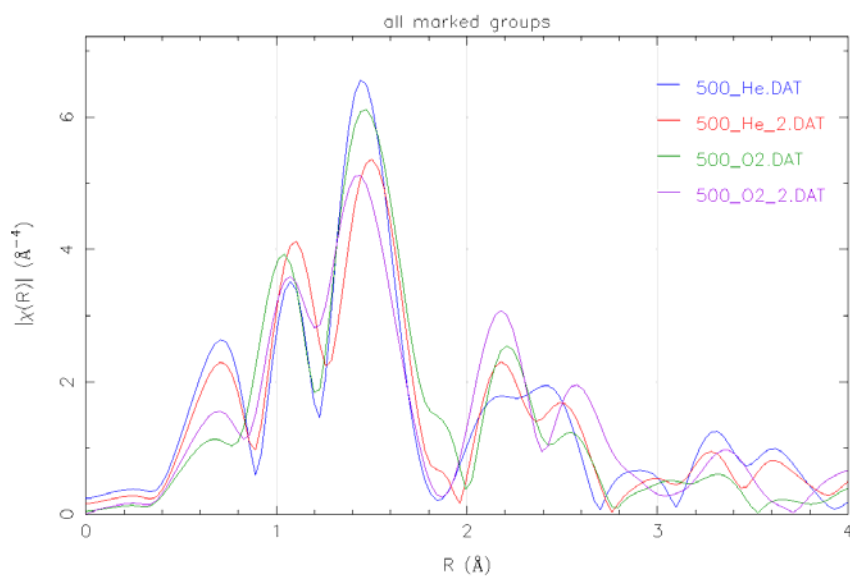


Fig 2. Formation of copper(II) oxide in Cu:ZSM-5/HT during activation in O₂ (5% in He) at 500°C.

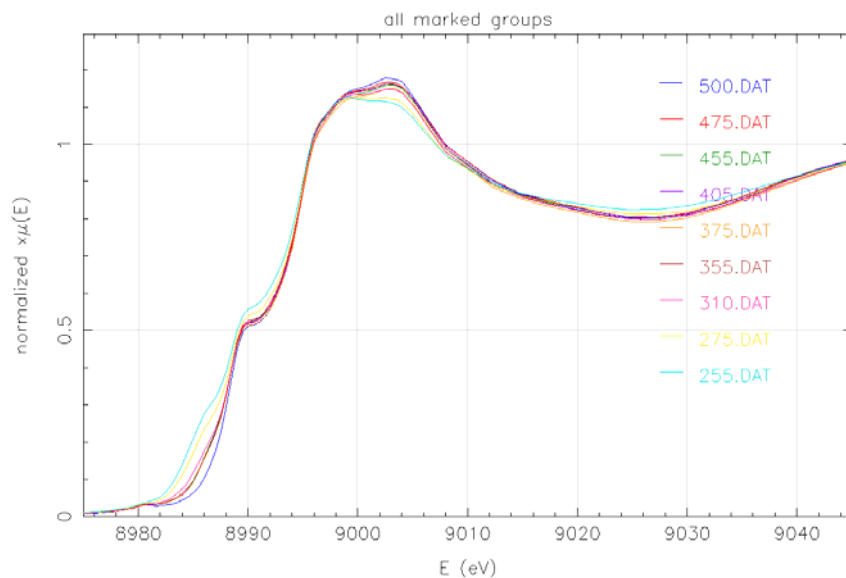


Fig. 3 CuZSM-5 cooled in reaction gas mixture (NO + propene + O₂ + He) after activation in O₂ at 500°C from 500-250°C.

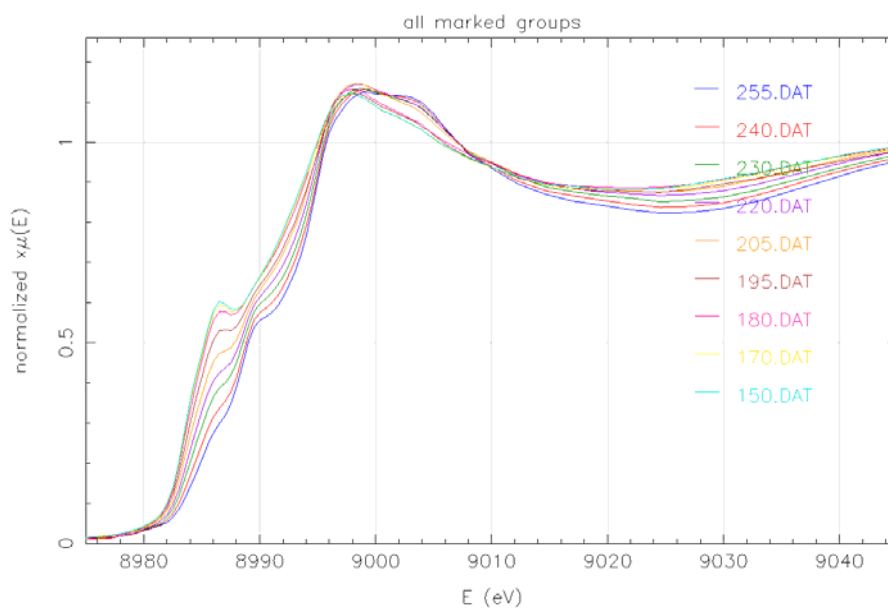


Fig. 4 CuZSM-5 cooled in reaction gas mixture (NO + propene + O₂ + He) after activation in O₂ at 500°C from 250-150°C.

Clearly, few changes occur in the XANES spectra from 500 to 250°C while cooling in the reaction gas mixture. Several features are present, indicating presence of oxide species seen by the shoulder halfway up the edge, from 250°C copper(I) starts forming, reaching a maximum fraction at 150°C before oxidation again occurs.