

Combined X-ray absorption, X-ray powder diffraction and Raman study on cluster formation in zeolites; effect of pore geometry.

Karina Mathisen, Department of Chemistry, Norwegian University of Science and Technology, N-7491 Trondheim, Norway.

Adding hydrogen to the selective catalytic reduction (SCR) hydrocarbons (HC) deNO_x process over silver systems leads to enhanced activity. This has been ascribed to the formation of silver nano clusters. Subsequent treatment in NO disperses the metal clusters through oxidation to silver(I). We believe that the silver(I) are redispersed to their original protonic sites in within the pores. The reversibility of the valence states with the formation of clusters in both systems is significant part of the overall mechanism for reducing NO_x (Fig. 1).

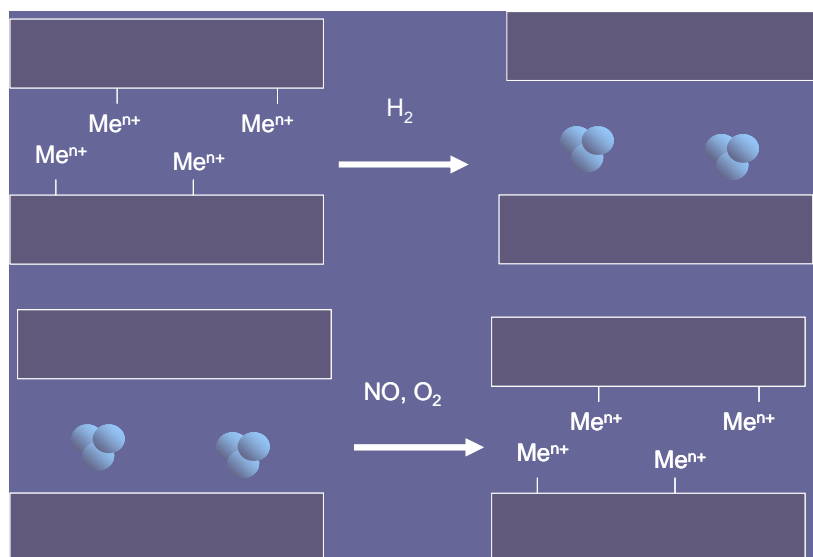


Fig.1 Proposed mechanism for the reduction of NO_x over metal nano clusters.

The silver environments in the two microporous systems Ag:ZSM-5 and Ag:Y have been studied by *in situ* X-ray Absorption spectroscopy (XAS) at the Ag K-edge. Samples were heated stepwise in hydrogen while collecting Extended X-ray Absorption Fine Structure (EXAFS), powder diffraction (XRD) and Raman spectroscopy to determine the cluster size as a function of temperature. The EXAFS yields information about the local environment of silver such as bond distances and number of neighbours. Silver(I) is reduced to form clusters of metallic silver by hydrogen, but the degree of reduction depends on the parent zeolite. The reduction starts below 100°C for both zeolites and is complete at 350°C. This is seen by the decreased contribution from the Ag-O bond and subsequent formation of an Ag-Ag bond in the Fourier Transform of Ag:Y in Fig. 2.

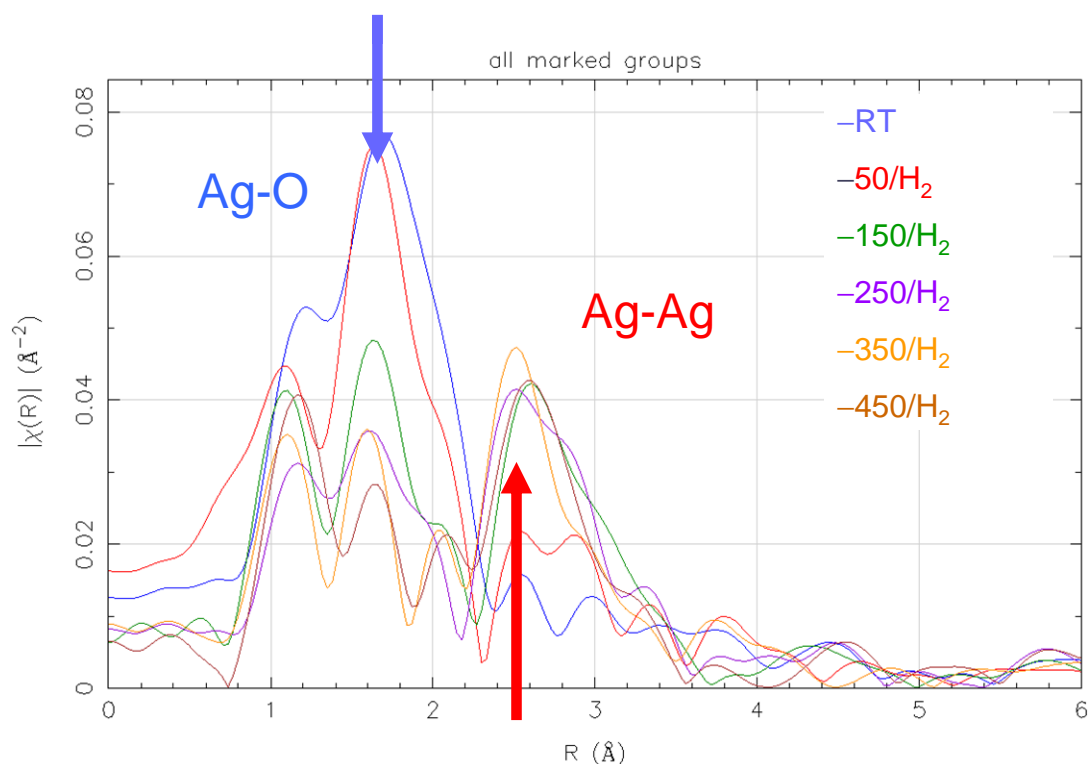


Fig. 2 Fourier Transforms of ion exchanged Ag:Y heated in hydrogen.

The coordination numbers of the Ag-Ag neighbouring shell are shown in Fig. 3. Silver metal with its fcc structure has a coordination number of 12 in the bulk form, and coordination numbers of 2-3 are generally expected for nano clusters. It is clear from the EXAFS that nanoclusters are formed in both zeolites at temperatures between 150 and 250°C.

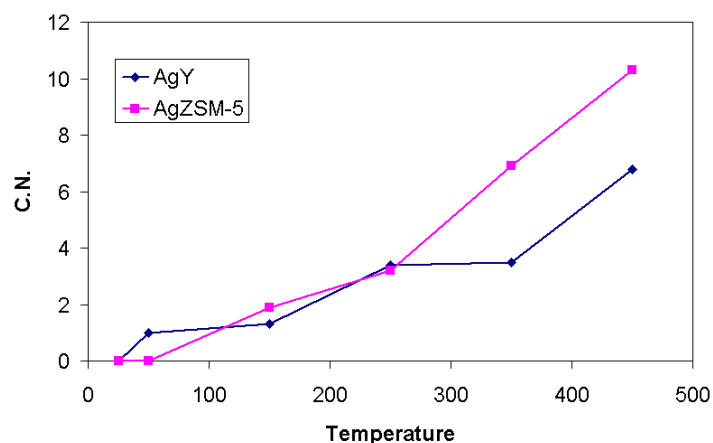


Fig. 3 Coordination number of silver clusters in zeolites Y and ZSM-5 from EXAFS analysis.

The results are consistent with powder diffraction data (Fig. 4) which for ZSM-5 contains peaks stemming from silver clusters that appear from 350°C. The size of clusters are 60-100 Å (the shift in position is due to the large thermal expansion coefficient of silver). The silver

peak is only barely visible for zeolite Y, and only at the highest temperature of 450°C, thus confirming that clusters size is limited by pore geometry. It is also clear that the nanoclusters formed between 150°C and 250°C are too small to be detected by XRD. The parent material is unaffected by the heating and formation of silver clusters. We believe that small clusters are initially formed inside the pores of both zeolite systems, which then sinter upon further heating. For ZSM-5 the larger clusters are allowed to disperse out of the pores, forming larger nanoclusters on the external surface. This is attributed to the zig-zag structure of ZSM-5 formed by interconnecting 10-rings. In zeolite Y the clusters are trapped in the supercages thus limiting the size of the clusters.

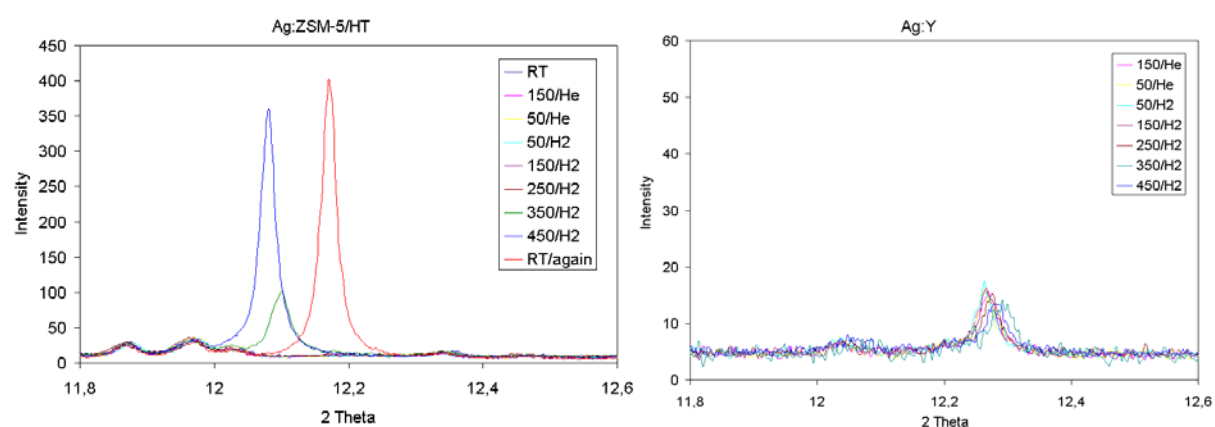


Fig. 4 Powder diffractograms displaying the (111) reflection of silver appearing during heating in hydrogen for the two zeolite systems.

This study also included Raman spectroscopy to possibly detect the formation of surface species, or new phases not detectable by XAS or XRD. We encountered several problems with the zeolites materials, the most noticeable is the increased background when heating the samples due to fluorescence from the sample (Fig. 6) The Raman spectra of zeolite Y during dehydration in helium by ramping to 150°C clearly shows the peak attributed to the O-H stretching mode at 3700 cm^{-1} . This arises from water in the system but also protonic sites in the zeolites. The intensity of this peak is clearly reduced during removal of water. The peaks between 1150-1650 cm^{-1} are ascribed to vibrational and stretching modes of the zeolite lattice.

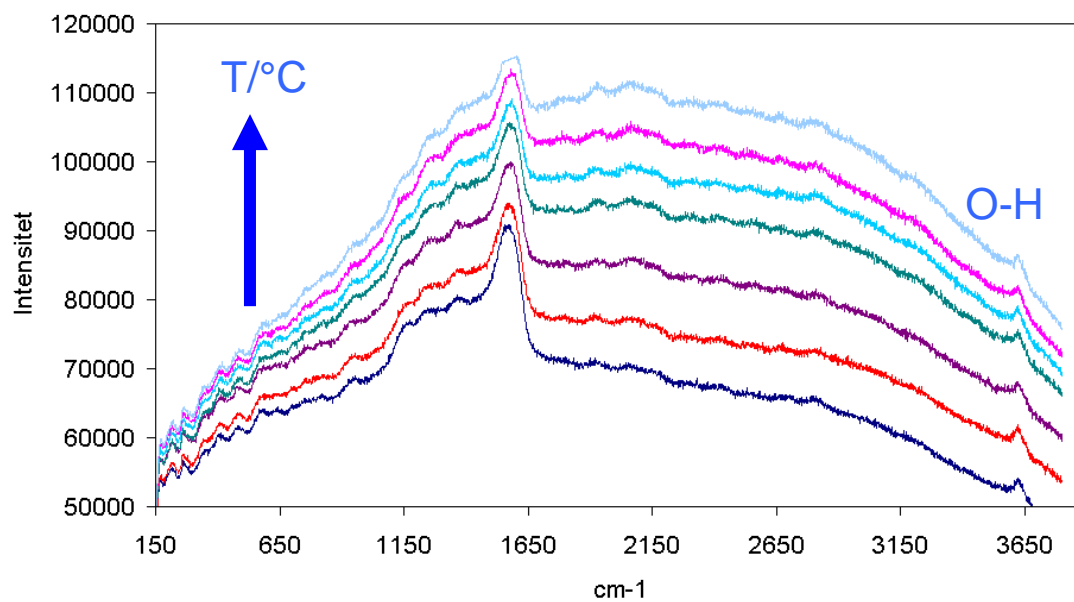


Fig. 6 Raman spectra of dehydration of Ag:Y to 150°C in helium.

References

J. P. Breen and R. Burch, *Topics in catalysis*, 2006, **39(1-2)**, 53.

K. Shimizu, K. Sugino, K. Kato, S. Yokota, K. Okumura and A. Satsuma, *J. Phys. Chem. C*, 2007, **111**, 6481.