

Report Beamtime CH-2205

DUBBLE BM26A

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The reversibility of the silver valence state in ion exchanged Ag:ZSM-5 compared to Ag:SAPO-5. Silver nano-clusters as active sites in the SCR deNO_x process.

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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 which act as active sites for removing NO_x. The silver environments in two microporous systems (Ag:ZSM-5 and Ag:SAPO-5) have been studied. Silver was conventionally and hydrothermally ion exchanged.¹ Samples were placed inside the cell and heated stepwisely in helium then hydrogen (5% in helium) and finally NO (0.6% in helium). A flow rate of 5 ml per minute was applied and the samples were ramped at 2°C/min while collecting XANES. EXAFS data were collected at end points. The formation of a black line in the beam's point of impact, indicative of the photoreduction of Ag^I→Ag⁰ was not accompanied by changes in the XANES or EXAFS. The fraction reduced is very low, and thus will not affect the XAS data as the sum will consist mainly of the silver(I) state. In contrast to previous reports about the thermal instability of silver we have found that ion-exchange of H-ZSM-5 with silver nitrate solution (AgNO₃) at room-temperature results in a Ag:ZSM-5 material in which silver(I) is stabilised within the matrix. Heating the material up to 500°C in air lead to no apparent changes in the EXAFS compared to the as-prepared material. XANES also show no indication to the formation of metallic silver.

During the SCR deNO_x process the redox behaviour of the metal in hydrogen and its subsequent reversibility was monitored in both systems by means of XAS measured in an *in situ* cell at the Ag K-edge. The silver valence state as function of temperature during treatments in helium, hydrogen and NO was monitored using an in-situ cell made of pressed boron nitride components. During heating in helium few changes are apparent in the xanes spectra (Fig. 1). Shift in edge position to lower energies indicate reduction of small amounts of silver(I) to silver metal.

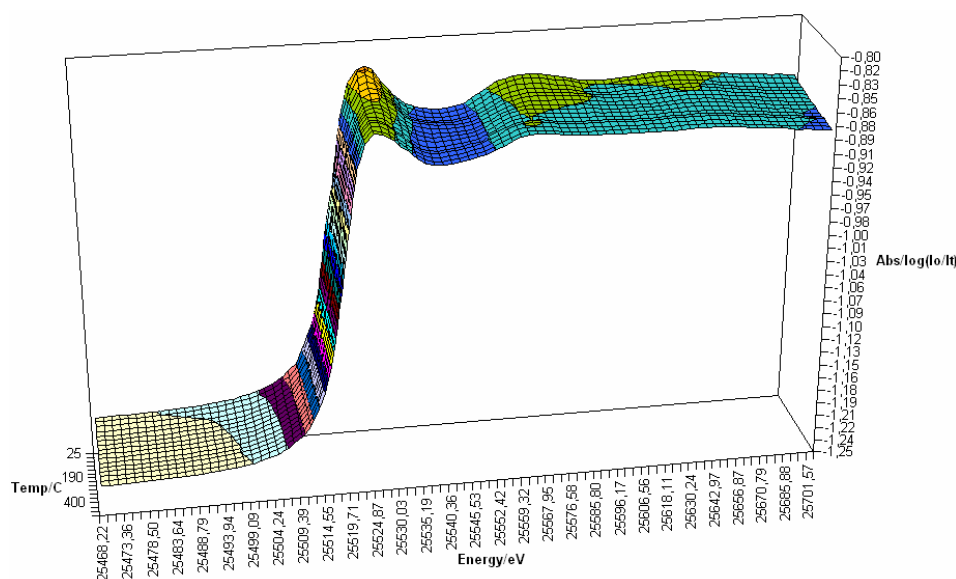


Fig. 1 XANES spectra of Ag:ZSM-5/HT heated in helium.

Silver(I) is completely reduced to form clusters of metallic silver by hydrogen reduction by hydrogen (Fig. 2). The clusters formed up to 500°C are large, indicated by a multiplicity (N1) of 9-10 for the Ag...Ag shell. The reduction process of silver(I) to silver metal starts below 100°C and is complete at 350°C. We believe that small clusters are initially formed inside the pores, which then disperse out of the pores, forming larger nanoclusters on the external surface. Subsequent treatment in NO disperses the metal clusters through oxidation to silver(I) thereby verifying the assumption that 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. 3). We believe that the silver(I) are redispersed to their original protonic sites in within the pores.

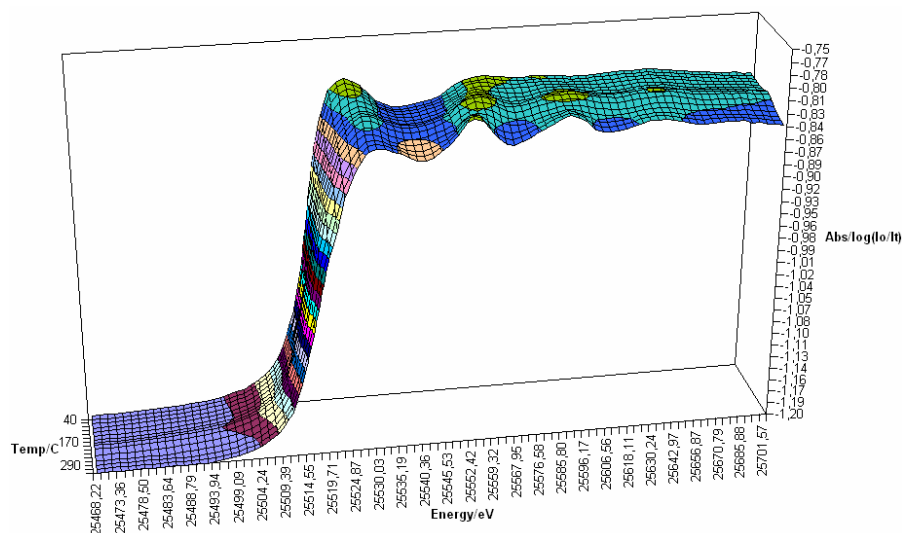


Fig. 2 XANES spectra of Ag:ZSM-5/HT heated in H₂.

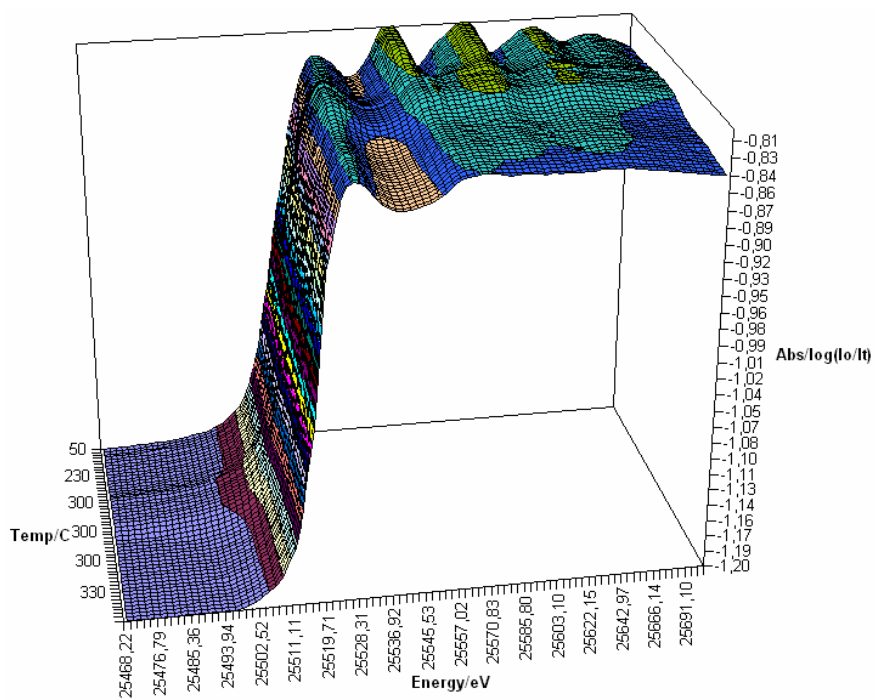


Fig. 3 XANES spectra of Ag:ZSM-5/HT heated in NO after treatment in H₂.

References

1. *A New Experimental Cell for in situ and Operando X-ray Absorption Measurements in Heterogeneous Catalysis*, J. S. Girardon, A. Y. Khodakov, M. Capron, S. Cristol, C. Dujardin, F. Dhainaut, S. Nikitenko, F. Meneau, W. Bras, and E. Payen, *J. of Synchrotron Radiation*, 2005 **12**, 680.