

Project report for DUBBLE BM26a

CH-1959

May 2005

In situ XAS measurements on silver substituted zeotypes

Karina Mathisen and David G. Nicholson

It has recently been found that silver-containing systems, and especially Ag/Al₂O₃ reduce NO_x under realistic conditions using hydrocarbons as the reductant.¹⁻³ These studies show that addition of H₂ to the reactant gas mixture greatly enhances the catalytic activity towards NO_x reduction at lower temperatures. This has been ascribed to the reduction of Ag⁺ to small Ag-clusters which promote the reaction, although the mechanism is not yet fully understood.

The oxidation state of silver-substituted silico aluminium phosphate AgSAPO-5 for the reduction of NO_x with different reductants has been monitored using in-situ XAS. The material was heated in helium and then reacted with hydrogen and NO sequentially to verify changes in the silver oxidation state during the different stages of reaction. The process was then repeated but using propene as a reductant to establish the role of hydrogen vs. hydrocarbons in the catalytic reduction of NO_x. It was also of interest to verify the formation of silver clusters and if these are reoxidised in NO making the red-ox mechanism a possible route for the reduction of NO_x over AgSAPO-5.

XANES spectra (Fig. 1) show that in AgSAPO-5 silver is present as Ag⁺ in the as-synthesised and calcined samples, with few changes visible upon heating the sample in helium. Reacting the sample with H₂, led to silver being reduced to metallic silver, Ag⁰. The size of these clusters was verified by EXAFS refinements to be in the nano-size range. During the final treatment in NO the silver clusters are redispersed and reoxidised to the Ag⁺ state. This establishes the reversible oxidation states as a possible mechanism for the reduction of NO_x by hydrogen on AgSAPO-5.

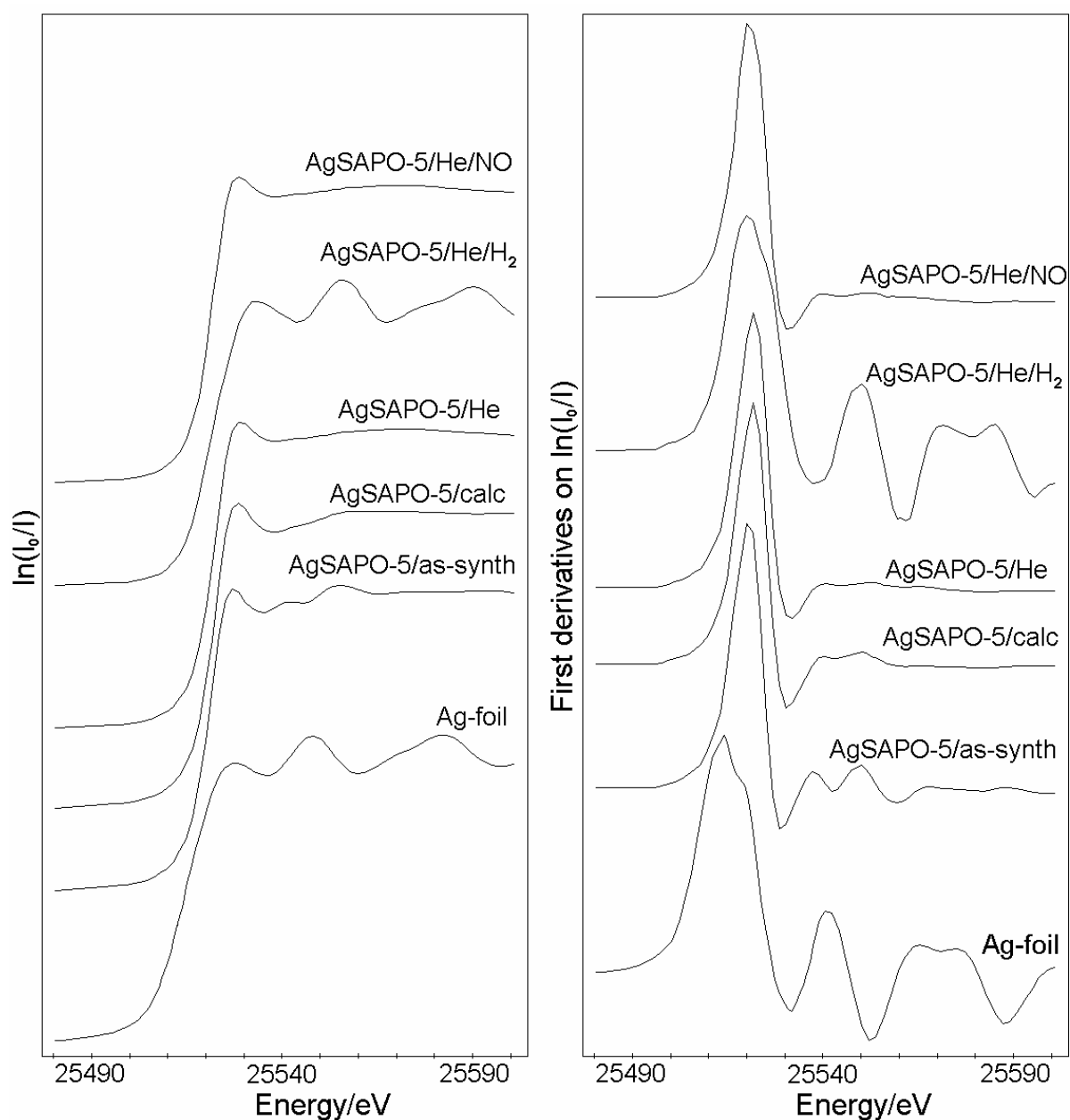


Figure 1 Normalised Ag K-edge XANES of AgSAPO-5 during different stages of reactions; as-synthesised, calcined, heated in helium, treated in H₂ and finally NO_x.

References

1. P. Burch, J. P. Breen, C. J. Hill, B. Krutzsch, B. Konrad, E. Jobson, L. Cider, K. Eränen, F. Klingstedt and L. E. Lindfors, Topics in Catalysis, 2004, 30/31, 19.
2. J. Shibata, Y. Takada, A. Shichi, S. Satokawa, A. Satsuma and T. Hattori, Journ. of Catal., 2004, 222, 368.
3. U. Bentrup, M. Richter and R. Fricke, Appl. Catal. B: Env., 2005, 55, 213.