

# Isolated Ag Cations Interacting with Luminescent Ag Clusters Confined in FAU Zeolites Identified as Highly Active Sites for CO Oxidation By a Combination of XEOL-XAFS, DRIFT and PL Spectroscopy

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## Introduction

Ag exchanged FAU zeolites AgX and AgY, exhibiting unique photoluminescence properties<sup>1, 2</sup> due to the presence of few-atom silver clusters (AgCLs) confined in their sodalite cages, have also demonstrated unprecedented catalytic properties in the CO oxidation reaction after a proper activation treatment.<sup>1, 3, 4</sup> Although, isolated single Ag cations and AgCLs confined in ZSM-5 zeolites were already envisaged as possible active sites for the CO oxidation reaction,<sup>5</sup> no clear picture of the active structure has emerged yet. This is partly due to the complexity of the FAU topology that can accommodate extra-framework cations in five different sites and additionally host few-atom clusters as well as to the susceptibility of the Ag-based functional structures towards highly energetic beam probes.<sup>6</sup> Moreover the fact that AgX and AgY only differ by their framework Si/Al ratio show opposite catalytic behaviors suggests that beside the geometrical confinement, the electronic state of the silver species is also playing a very important role in their catalytic properties. To achieve a full understanding of the location and the electronic properties of the silver species at the origin of their luminescent and catalytic properties, we have applied a unique combination of XEOL and transmission detected XAFS, DRIFT and PL spectroscopies under various environments.

## Experimental methods

Fully silver exchanged Faujasite zeolites AgX (Si/Al=1.3) and AgY (Si/Al=2.7) were investigated at the Ag K-edge with XEOL-XAFS at LISA-BM08 beamline, in situ under CO oxidation with transmission detected XAFS at DUBBLE, BM26A beamline of the The European Synchrotron (ESRF). In parallel, their PL was investigated under different environments by using a steady state and time-resolved optical spectroscopy. CO probe were investigated using a mixture of CO+O<sub>2</sub> in He as the probe gas using a Vertex 70 infrared spectrometer (Brüker Optics) equipped with a DRIFTS cell (Praying Mantis, Harrick) and connected to an online mass spectrometer (Omnistar, Pfeiffer).

## Results and discussion

Although the structures of both Ag FAU zeolites seem very similar, AgX catalyst is significantly more active ( $T_{100} = 240^\circ\text{C}$ ) than AgY ( $T_{50} = 330^\circ\text{C}$ ) under CO oxidation. Combination of XEOL and transmission detected XAFS shows that in the as-prepared hydrated state, luminescent  $\text{Ag}_4(\text{H}_2\text{O})_{3-4}$  clusters are confined in the center of sodalite cages and surrounded with Ag cations residing in the center of the six membered rings ( $\text{Ag}_R$ ) in the supercage and in the prisms ( $\text{Ag}_P$ ) in both systems. Under CO oxidation condition,  $\text{Ag}_4(\text{H}_2\text{O})_{3-4}$  clusters lose their water ligands and are transformed into oxygenated AgCLs ( $\text{Ag}_{2/4}\text{O}_2$ ) that strongly interacting with the surrounding  $\text{Ag}_R$  cations. In situ EXAFS and DRIFT have allowed the identification of  $\text{Ag}_R$  interacting with AgCLs in AgX as low oxidation state isolated  $\text{Ag}^{\delta+}$  sites that possess strong redox properties and a very high activity while in contrast, the equivalent  $\text{Ag}^{\delta+}$  sites in the AgY show no activity. The different level of interaction of AgCLs with isolated  $\text{Ag}_R$  cations that may explain these results is reflected in the lower PL intensity of AgCLs in AgX compared to that of the AgCLs in AgY.

## Conclusion

The combination of XEOL-XAFS, DRIFT and PL spectroscopies allowed the identification of  $\text{Ag}^{\delta+}$  interacting with AgCLs in AgX as the most active sites in the CO oxidation reaction due to their facile redox properties. This indicates that the optimization of both geometrical and electronic confinements of the Ag active sites are essentials for an efficient catalytic activity in the oxidation of CO.

## Acknowledgements

The authors gratefully acknowledge financial support from the Research Foundation Flanders (FWO) grants (G0990.11, G.0197.11, G.0962.13), the European Union's Seventh Framework Programme (FP7/2007-2013 under grant agreements no. 310651 SACS, the Flemish government in the form of long-term structural funding "Methusalem" grant METH/15/04 CASAS2, the Hercules foundation (HER/11/14), the "Strategisch Initiatief Materialen" SoPPoM program. Access to DUBBLE was arranged through the general support of the FWO for the use of central facilities. The authors thank the ESRF for providing beamtime at LISA-BM08 (CH-4818) and the staff of LISA-BM08 and DUBBLE-BM26A beamlines of the ESRF for their assistance and technical support.

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