DRIFTS and XPS *operando* Studies of a CuO-CeO_2 WGS Catalyst

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Introduction and Objectives

Copper-cerium oxide catalysts constitute an interesting, cheaper alternative to precious metals-based systems for the preferential CO oxidation (CO-PROX) and water gas shift (WGS) processes used in hydrogen production from fossil fuels or biomass feedstocks. It is normally assumed that CO is activated on Cu sites and extract oxygen from the Ce oxide, which is then reoxidized by O_2 or water in a Mars-van Krevelen mechanism; but some aspects of the redox changes and adsorption-desorption steps remain unclarified.

Here we study WGS-related reactions on a catalyst having inverse configuration (CeO_2 on CuO), which has shown good performance in previous works of ours [1]. *Operando*-DRIFTS experiments as well as SSITKA-DRIFTS tests exchanging ^{12}CO and ^{13}CO were performed under WGS conditions in order to get insights into mechanistic details. In turn, such results were complemented by XPS data taken at the ISISS station of BESSY synchrotron in Berlin, under either vacuum or 0.5 mbar of flowing gas containing 7% CO and/or 20% H_2O (He balance) while monitoring gas composition with MS.

Results and Discussion

DRIFTS results display the formation under WGS reaction conditions of Cu^+-carbonyl species as well as hydroxyls and various carbonate-type and/or formate species at T < ca 523 K while above such temperature a new carbonyl at ca. 2010 cm^{-1} (most likely related to a metallic copper carbonyl in a particularly stable geometrical configuration [2]) starts to be formed and grows with the reaction temperature. In turn, SSITKA-DRIFTS experiments show important changes in the region related to carbonate-type and/or formate species although in principle analysis of $^{12}CO_2$ vs. $^{13}CO_2$ gas evolutions do not point towards active involvement of such species as reaction intermediates, at least at practical relatively high reaction temperature.

XPS and Cu Auger spectra show that both Cu and Ce are partially reduced to Cu^+ and Ce^{3+} already upon contact with CO at 295 K; at 473 K, under CO, surface Cu is almost totally Cu^+ and larger amount of Ce^{3+} is formed (Fig. 1a). Adding H_2O at 473 K (Fig. 1b) starts to form Cu^0 (Auger peak at 918.6 eV) and increases the amount of Ce^{3+} (XPS peak at 894 eV). Thus the initial effect of H_2O interaction appears not to be a reoxidation one,

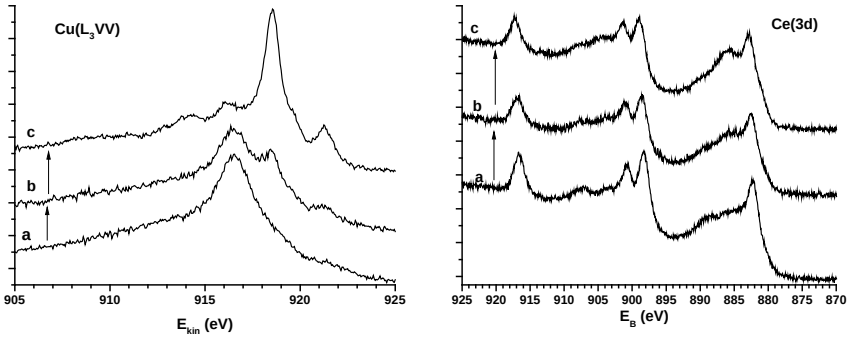

Fig. 1 Cu Auger and Ce XPS spectra of $CuCeO_x$ catalyst a) at 473 K under CO, b) after adding H_2O at 473 K and c) raising temperature to 523 K under both gases

but maybe it facilitates reduction by H_2, which begins to appear as shown by MS, and the ensuing nucleation of Cu^0 particles. Other possible effects can be related on the one hand to stabilization of reduced states of cerium in the presence of hydroxyl species (considering the higher thermodynamical stability of Ce^{3+} hydroxide) as well as possible electron transfer processes between copper and cerium oxide. Correlation with bulk results obtained in previous work by XRD and XANES will be also used to analyse the possibility of surface-bulk oxygen transport effects under reaction conditions. In turn, at 523 K (Fig. 1c) extensive reduction of Cu to Cu^0 and increase in the amount of Ce^{3+} occur under WGS reactant mixture.

Conclusions

Mechanistic details for WGS reaction over an inverse CeO_2/CuO (initial form according to previous characterization by XRD, XANES and HRTEM) have been analysed by DRIFTS and SSITKA-DRIFTS as well as XPS. The results suggest the absence of direct involvement of carbonates and/or formate species as reaction intermediates at practical relatively high temperature thus suggesting a redox mechanism could rather be the operative one. Nevertheless, details achieved by XPS suggest redox processes of a complex nature must be taken into account to explain the WGS activity of this type of systems.

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References

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