Role of Cu dopant in H_2 dissociation on Cu:CeO_2 surface

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The search for innovative materials alternative to noble metals in H_2 based devices has increased the interest towards metal oxides systems with high reducibility and high versatility. One of these intriguing materials is CeO_2, that has demonstrated a strong ability in forming and transporting oxygen vacancies [1]. When low-valence metal cations are substituted to some Ce, the H_2 dissociation barrier is strongly reduced [2]. Nevertheless, this effect strongly depends on the dopant oxidation state and on charge redistributions that increase the ability to exchange oxygen and electrons with the environment. Previous results report that Cu inclusion improves ceria reducibility and activity towards H_2 dissociation [3]. It is thus important to clarify the electronic modifications at the atomic level in the ceria matrix and in the dopant to understand the role of the metal atom in the catalytic reaction.

In this work we have investigated the modifications of the Ce and Cu oxidation states during H_2 exposure at ambient pressure (1 bar) by means of near edge x-ray absorption fine structure (NEXAFS). Films of 5 nm CeO_2 doped with a variable amount of Cu have been grown by thermal evaporation and transferred to ELETTRA where the Ce $M_{4,5}$ and Cu $L_{2,3}$ edges have been acquired in an ambient pressure reaction cell, in flow of H_2/He at increasing temperature between RT and 620 K [4]. We have observed a progressive reduction of Ce^{4+} to Ce^{3+}, the presence of Cu in the 1+ state and an increasing reduction of Cu^{2+} to Cu^{1+} up to 500K (Fig.1). The presence of Cu^{1+} during the whole process supports the strong activity in H_2 dissociation. Besides, the system is fully reversible to the initial state both for Ce and Cu when the dopant concentration is around 5 at%.

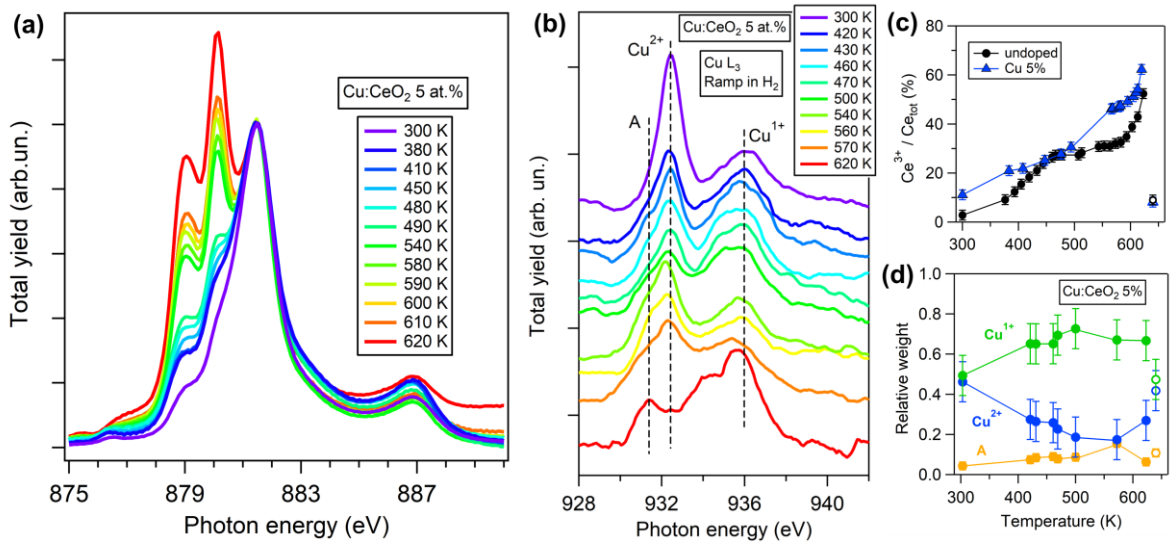

Fig. 1. NEXAFS (a) Ce M_5 and (b) Cu L_3; (c) Ce^{3+} and (d) Cu components as a function of temperature in H_2 flow.

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