What makes Au an active catalyst: facts and speculation

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Since the discovery in the eighties by Haruta[1] that the oxidation of carbon monoxide may occur under sub-ambient temperatures over certain gold-supported catalysts the number of scientific papers on this and other reactions has grown exponentially. A variety of explanations for the unprecedented catalytic activity has been forwarded without any one of these being accepted as of general validity alone. The various views will be summarized and critical questions asked in relation to claims that emphasize the importance of specific charge states (cationic vs. neutral vs. anionic gold) and effects of the particle size or choice of the support material. The influence of low-coordinated step sites on Au particle surfaces (in the absence of ceramic support) will be demonstrated by video-Field Ion Microscopy (FIM). This technique allows applying electric fields from the onset of electron emission to the onset of gold ionisation at reversed polarity thus simulation charged surfaces. In this manner we have shown that carbon monoxide binds to step sites at 300 K and that the binding increases in the presence of a positive electric field. $Au(CO)_2^+$ species are formed in steps and induce surface mobility. The occurrence of a moving reaction front of $Au(CO)_2^+$ is imaged by video-FIM with nano-scale resolution, and the chemical nature of these species is confirmed by local chemical probing using single-ion time-of-flight mass spectrometry. Different from CO, oxygen molecules are adsorbed only with very short surface lifetimes at 300 K. In particular, no dissociation is seen on low-coordinated Au steps. Density Functional Theory (DFT) has demonstrated that the activation barrier in the presence of a positive field increases; i.e. under conditions of positively charged surfaces no O-O dissociation is seen by both DFT and FIM. It follows that the CO oxidation does not occur over flat and stepped surfaces of bulk gold surfaces either neutral or positively charged. Interestingly, DFT calculations show that the situation in the presence of a negative field is reversed as compared to a positive field. This has led us to prepare supported Au-based catalysts in which the electric field is produced by (ionic) alkali adsorption. It will be shown that the CO conversion in the CO/O_2 reaction is very low on pure Au/TiO_2 catalysts while it increases dramatically in the presence of Na.

[1] M. Haruta, T. Kobayashi, N. Yamada, Chem. Lett. 2 (1987) 405