AB INITIO STUDIES OF DIRECT PROPENE EPOXIDATION AT OXIDE-SUPPORTED GOLD CLUSTERS AND NANOPARTICLES

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Gold nanocatalysts have recently attracted a great deal of interest due to their novel applications, one of the most interesting ones being the direct formation of propene oxide (C_3H_6O) from propene, oxygen and hydrogen at TiO_2-supported gold nanoparticles. When these particles have a diameter of around 3-4 nm, they become active and extremely selective [1]; such selectivity is extremely sensitive to the degree of dispersion of the catalysts, and particles only slightly smaller (~2 nm) mainly produce propane. The reasons for such complex behaviour, as well as the detailed reaction mechanisms that take place, are to a large extent unknown. In this presentation, we will report the results obtained in an extensive ab initio DFT study of the reaction at the Au/TiO_2 interfacial region, since recent experimental results by Nijhuis *et al.* [2] suggest that the active reaction sites are located there.

Figure 1 shows the base model system built for the simulations, where a thin Au rod is placed on top of the anatase-TiO_2(101) surface. Then, the main stages of the epoxidation reaction were simulated, starting with the dissociation of H_2, coadsorption of O_2 at a partially hydroxylated surface, and the interaction of propene with the catalyst in the presence of various co-adsorbates. The results are in agreement with the experimental findings by Nijhuis et al., which suggest an easy formation of a strongly bound propene oxide species at the Au/TiO_2 interface. We find an easy reaction of propene with co-adsorbed peroxo (-OOH) species, leading to formation of metallocycle-like propene oxides species at the TiO_2 substrate in the neighbourhood of the Au nanoparticle, which catalyzes the reaction. Finally, preliminary results from simulations of the analogous process at similar catalysts (with gold supported at a different oxide material) will be presented, showing that the activity of gold for propene epoxidation is not specific to a particular oxide.

References:

[1] A. K. Sinha, S. Seelan, S. Tsubota and M. Haruta, Topics in Catal., **29** (2004) 95.

[2] T. A. Nijhuis, T. Visser and B. M. Weckhuysen, Angew. Chem. Int. Ed., **44** (2005) 1115.

Figures:

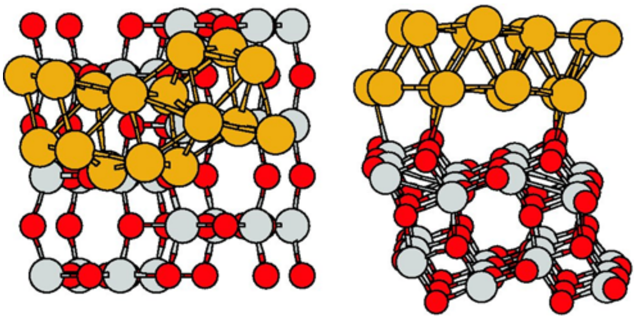

Figure 1: Model of the Au/TiO2 perimeter interface for propene epoxidation catalysts