

# The Role of Subnanosized Gold Clusters in Photocatalytic CH<sub>4</sub> Transformation and CO<sub>2</sub> Hydrogenation on Titania and Titanate Nanotubes

János Kiss

Department of Applied and Environmental Chemistry, MTA-SZTE Reaction Kinetics and Surface Chemistry Research Group, University of Szeged, Hungary

Gold nanoclusters (AuNCs) formed on oxide supports have been found to be catalytically active depending on the number of atoms forming the clusters. The catalytic properties depend on the Au-Au distance, the coordination number and the electronic structure of the cluster. It is considered that small clusters (< 2-3 nm) lose their bulk-like electronic properties (e.g. no Fermi level); for example, they no longer support the plasmonic excitation characteristic of relatively large metal nanocrystals (3-50 nm). Due to the large amount of defects, titanate nanotubes (TNT) can stabilize sub-nanosized gold clusters, presumably in Au<sub>25</sub>. On the other hand, ion exchange allows titanate nanostructures to incorporate metal adatoms in their framework [1]. The Au<sub>25</sub> clusters may be directly involved in the photo-induced reactions, namely in the direct activation of the methane/Au<sub>25</sub><sup>δ+</sup> complex during irradiation [2,3]. Gold nanoparticles supported on titanate nanotubes exhibited high catalytic activity in CO<sub>2</sub> hydrogenation. Our results revealed fundamental differences in the reaction schemes as the products of the two routes are CO (thermal process) and CH<sub>4</sub> (photocatalytic route), indicating the importance of photogenerated electron-hole pairs in the reaction. The presence of gold nanoparticles on the surface has been found to have multiple roles. On the one hand, gold in nano and sub-nano sizes promotes the adsorption and scission of reactants, important for both types of reactions. On the other hand, the gold-support interface forms a rectifying Schottky contact that helps in the separation of photogenerated carriers, thus improving the utilization of electrons and holes in the reduction and oxidation steps, respectively. Furthermore, gold ions (Au<sup>+</sup>), in the cationic sites of the titanate lattice promote the photocatalytic transformation of formate (which is one of the intermediates), thus advancing the reaction further towards the fully reduced product.

## References:

- [1] Á. Kukovecz, K. Kordás, J. Kiss, Z. Kónya: *Surface Science Reports*, 71 (2016) 473-546.
- [2] B. László, K. Baán, A. Oszkó, A. Erdőhelyi, J. Kiss, Z. Kónya: *Topics in Catalysis*, 61 (2018) 875-888.
- [3] J. Kiss, Á. Kukovecz, Z. Kónya: *Catalysis Letters*, 149, (2019) 1441-1454.