

Active sites for photocatalytic CO₂ reduction in meso- and microporous oxide materials

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For the photocatalytic reduction of CO₂, many research efforts are directed towards crystalline TiO₂ and isolated titanate species on silica [1]. While both systems are well known as active photocatalysts for the reaction, the mode of action of the photocatalysts and the reaction mechanism are still mostly unknown to date, impairing a directed improvement of the photocatalytic activity of those systems.

This talk will highlight our progress towards the understanding and improvement of photocatalyst systems based on isolated titanate species for photocatalytic CO₂ reduction in the gas phase. All studies were conducted in a high-purity photoreactor with trace gas analysis [2]. Self-made systems from an organometallic grafting procedure were compared to commercial TS-1 material. On all studied systems, methane was the main product, but the formation of CO, H₂ and some longer chain hydrocarbons was also observed. A low water contents in the reaction mixture was found to be beneficial to achieve high methane yields, but at the same time the yields of CO slightly decrease. This might be due to an unfavorable influence of a photoreforming reaction at high water levels [3], and/or the preferential adsorption of water compared to CO₂. However, an improvement of CO₂ adsorption by addition of Zn to TiO_x/SBA-15 did not significantly increase methane yields. Methane yields can be improved by the photodeposition of gold or silver nanoparticles onto TiO_x/SiO₂ [2]. When starting from isolated titanate on SBA-15, gold photodeposition leads to the formation of a titanium-rich shell around the gold nanoparticles. This shell was found to improve electron transfer over the interface [4]. On TS-1, silver nanoparticles lead to an even stronger enhancement of photocatalytic activity than gold nanoparticles.

Mechanistically, our results indicate that a direct hydrogenation of CO₂ running over C₁ intermediates (CO, CH₂O, HCOOH) is unfavorable, because those species are oxidized much faster than they are further hydrogenated. Instead, it appears that the formation of a C-C bond has to take place in the reaction mechanism, giving access to intermediates such as acetaldehyde or acetic acid.

References

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