

The role of supported metal clusters and ions in thermal and photo induced catalytic reactions

János Kiss,

MTA-SZTE Reaction Kinetics and Surface Chemistry Research Group, Department of Applied and Environmental Chemistry, University of Szeged, Rerrich B tér 1., Szeged H-6720, Hungary
e-mail: jkiss@chem.u-szeged.hu

Great efforts are currently made to produce hydrogen, for example for fuel cell applications by heterogeneous catalytic processes. This demand inspired studies of the dehydrogenation of oxygenated hydrocarbons and methane. In particular, the light alcohol ethanol is an important candidate as a chemical hydrogen carrier. Noble metals, especially Rh, proved to be excellent catalysts for the dehydrogenation reaction, but their price is prohibitively high. As an alternative, the less expensive transition metal Co is considered a promising catalyst for the reforming of ethanol and methane [1]. The addition of a small amount of Rh as a promoter to the Co containing catalyst resulted in a significant increase in hydrogen selectivity. Metallic Rh and Co sites are responsible for C-C bond rupture at higher temperatures, but Co^{2+} is also necessary for the low temperature reaction of ethanol, probably because of its dehydrogenation activity in which the aldehyde is the main reaction product.

In the present work, our aim is to find a correlation between the surface properties of supported Co catalysts (such as acid-base character or reducibility with and without Rh loading) and their catalytic activity in ethanol steam reforming. On Co on the acidic Al_2O_3 support ethylene formation was the dominant, although on the basic CeO_2 support a significant amount of hydrogen was formed.

The importance of the size and the shape of metal nanoparticles supported on different oxides is in the focus of thermal- and photo-induced catalytic processes. Gold is usually an inert, poorly active catalyst. Most of the important reactions cannot be catalyzed by gold. It was found recently that when dispersed ultrafine particles are supported on a metal oxide like titania, Au showed an outstanding effect for several catalytic reactions. The presence of Au clusters manifests as a marked increase in the reaction rate as the diameter of the Au clusters decreases below ~ 3.5 nm in CO_2 hydrogenation on titania and titanates.

It was demonstrated in the present study that titanate nanotubes have numerous advantageous properties that play an important role in the investigated reactions. It's well known that larger amount of defect sites (Ti^{3+} and oxygen vacancy) compared to pristine TiO_2 produces more donor levels thus make the titanates more active in the photocatalysis of methane transformation [2]. Surface defect sites can stabilize nearly atomic sized gold clusters and the titanate framework stabilizes Au^+ in ion exchange position, as we pointed out recently [3]. We verified that the activity of gold in adsorbing molecules is strongly depending on the size of the particles. Even the second step of the photocatalytic reaction, namely the electron transfer, can occur on the gold particles due to the plasmon excitation or the molecular-like electron transitions and Au^+ ions may also participate in photo induced methane activation and in CO_2 hydrogenation.

References:

- [1] Zs. Ferencz, A. Erdőhelyi, K. Baán, A. Oszkó, Z. Kónya, C. Papp, H.-P. Steinrück, J. Kiss, ACS Catal. **4**, 1205 (2014).
- [2] B. László, K. Baán, E. Varga, A. Oszkó, A. Erdőhelyi, Z. Kónya, J. Kiss, Appl. Catal. B: Environmental **199**, 473 (2016).
- [3] Á. Kukovecz, K. Kordás, J. Kiss, Z. Kónya, Surf. Sci. Rep. **71**, 473 (2016).