



Abstracts: Surface reactions and catalysis

reactivity. Nevertheless, our study strongly suggests that the Pd metal is the most active phase for the full oxidation of methane.

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 [2] R.F. Hicks, H.H. Qi, M.L. Young, R.G. Lee, *J. Catal.* 122 (1990) 280.
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 [4] S. Oh, P.J. Mitchell, R. Siewert, *J. Catal.* 123 (1991) 287.
 [5] J.G. McCarthy, *Catalysis Today* 26 (1995) 283.

Contributed Room D-2, Wed 14:50–15:10

Spectro-microscopic study of ceria-copper based water-gas shift catalysts

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The use of CeO₂-based materials in catalysis has attracted considerable attention in recent years. Ceria has shown potential as a novel reducible oxide support with excellent stability and unique oxygen storage capacity (OSC) [1]. The formation of well-ordered CeO₂ films is a prerequisite to minimize substrate effects in the surface chemistry of ceria. An earlier successful approach to this problem involved growth of ceria films on Ru(0001) [2]. More recently, CeO₂(111) was grown on Cu(111) [3]. High activity of ceria-based model catalysts was demonstrated on inverse catalyst [4,5] with ceria nanoparticles supported on noble metals. However, there is still little known about the mechanism for the growth of ceria film on metal surfaces, its resulting structure and stoichiometry and the influence of catalyst structure on the observed chemistry.

In the present work the growth of ceria films on Cu(111) has been investigated in-situ by means of low-energy electron microscopy (LEEM). Ce was deposited onto Cu(111) under O₂ atmosphere. Real-time observation of the film growth revealed that at relatively high substrate temperature (above 800 K), a highly crystalline, epitaxial CeO_x(111) film has been formed. Control of the oxidation state of ceria, i.e. CeO₂/CeO_x ratio, has been achieved by adjusting the growth temperature and the initial oxidation state of the Cu(111) surface. Following the growth of CeO_x films, the reaction of the CeO₂-Cu(111) surface in the CO oxidation reaction (CO(g) + O(l) → CO₂(g)) was observed in situ in LEEM.

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Contributed Room D-2, Wed 15:10–15:30

Laterally-resolved reaction kinetics by PEEM

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To describe the behavior of a heterogeneous catalyst, laterally-resolved studies of reaction kinetics are necessary. Up to date, experi-

mental kinetic studies of heterogeneous surfaces were mainly performed by mass spectroscopy (MS) and suffer from spatial averaging over the whole catalyst.

A certain improvement can be achieved by "scanning-MS" using gas sampling via a capillary leak (with a lateral resolution of about 0.2 mm [1]). Nevertheless, as with every scanning procedure, a real *parallel* measurement on different grains or facets is not possible within such an approach. In turn, microscopies such as LEEM or PEEM, which are based on the parallel imaging principle, provide the laterally-resolved information from the entire sample surface.

Recently, we have demonstrated for the first time that information about local reaction kinetics for individual grains of a polycrystalline Pt foil can be obtained by PEEM [2]. By processing the video-PEEM data obtained during catalytic CO oxidation, we were able to construct the kinetic phase diagrams for the individual differently oriented domains. Such domains provide interesting mesoscopic model systems which exhibit well-defined single crystal structures, but are confined in a heterogeneous environment, differing from one grain to another. We extend the above approach to the individual grains of a polycrystalline Pd foil and discuss the differences between the Pt and Pd domains of the same orientation with respect to CO oxidation as well the effects of reaction-coupling between the domains.

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Contributed Room D-2, Wed 15:30–15:50

Role of molecule-surface and molecule-molecule interactions in the on-surface polymerization of a graphene nanoribbon

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We present a density-functional theory study elucidating some of the reaction mechanisms enabling – as well as limiting – the formation of a graphene nanoribbon on the Au(111) surface. Cai and co-workers recently reported [1] on the polymerization of a bianthryl derivative into poly-anthryl chains. The poly-anthryl subsequently undergoes a cyclodehydrogenation, resulting in graphene nanoribbon with a width of 7 carbon atoms. Here we investigate the second mechanism, namely the cyclodehydrogenation, discussing the role of the molecule-surface as well as molecule-molecule interactions.

By comparing the cyclodehydrogenation of oligo-anthryls into polycyclic aromatic hydrocarbons (PAHs) of various sizes, it is concluded that the process is less favorable for larger oligomers than for smaller ones. This is explained by the removal of hydrogen atoms, as these are shown to have a large impact on the overall adsorption of a PAH on Au(111). Furthermore, the molecule-molecule interactions also have an important impact on the cyclodehydrogenation. It is shown that, due to steric hindrance between adjacent phenyl groups, the cyclodehydrogenation begins in one end of the poly-anthryl and then propagates, with a domino effect, step-wise throughout the polymer. Finally, we discuss the catalytic role of the Au(111) surface, illustrating the reaction pathways of the cyclodehydrogenation from transition state calculations.

- [1] J. Cai et al., *Nature* 466 (2010) 470.

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