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ATOMIC LAYER DEPOSITION OF REVERSE MODEL CATALYST: FeO/Pt(111) FOR BOUNDARY INTERFACE MEDIATED CATALYTIC ACTIVITY

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ABSTRACT

The importance of a monolayer-catalyst and its support-layer such as metal oxide/metal catalyst layers lay in the formation and activity of the boundary interface between a metal-catalyst and a support that could be crucial for understanding the working mechanism of a catalyst. These studies can be addressed through designing a reverse catalyst, which is basically an oxide particle or thin film deposited on the surface of a bulk metal catalytic support. The reverse catalysts approach allows researchers to overcome technical problems such as sample conductivity and sensitivity, which are typical for regular catalysts where small boundary interface between metal-catalyst and oxide support could hardly be detected.

Pt catalysts promoted by Fe demonstrated the superior results for water gas shift reaction better than just supported platinum. The adjacent Pt and Fe atoms could form an active site of reaction. To understand the interaction between iron and platinum during a catalytic process, we used a reverse model catalyst: FeO on Pt(111). The novel preparation of reverse catalyst based on decomposition of organometallic precursor, ferrocene ($\text{Fe}(\text{Cp})_2$), was proposed.

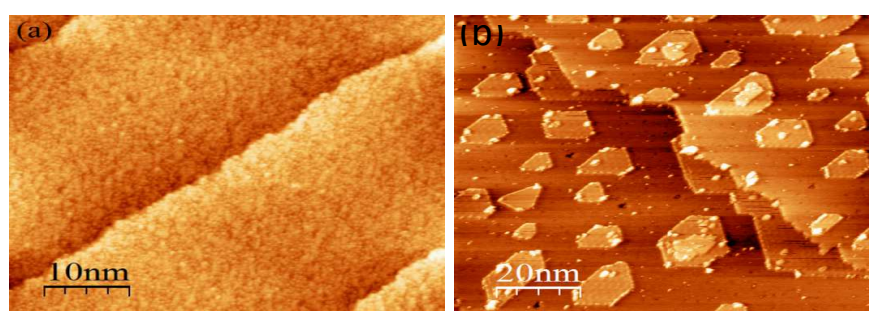


Figure 1. STM images of (a) ferrocene molecules adsorbed on Pt(111) and (b) FeO islands on Pt (111) observed after 3 cycles of ferrocene adsorption/oxidation.

Reverse model catalyst FeO/Pt(111) was prepared on the surface of a Pt(111) single crystal (MaTeck GmbH, $< 0.5^\circ$) by adsorption of ferrocene, $\text{Fe}(\text{Cp})_2$, (Sigma Aldrich, 99%) followed by oxidation in 10^{-6} mbar O_2 at 625 K. Sample was characterized by X-ray Photoelectron Spectroscopy (XPS), Low Energy Electron Diffraction (LEED), High Resolution Electron Energy Loss Spectroscopy (HREELS), Scanning tunneling microscopy (STM) in one μ -metal chamber (base pressure of 5×10^{-11} mbar).

ABSTRACT

Ferrocene was found to adsorb dissociatively at low exposures. Single cyclopentadienyl rings covered the Pt(111) terraces, while $\text{Fe}(\text{Cp})_2$ species agglomerated by the Pt steps. At high exposures, molecularly adsorbed $\text{Fe}(\text{Cp})_2$ species dominated on the surface. These surface transformations were monitored by STM and HREELS. Figure 1(a) shows the STM image obtained after adsorption of 90 L $\text{Fe}(\text{Cp})_2$ on Pt(111) at 300 K. Ferrocene desorbed and dissociated at a temperature between 475 and 575 K. Heating of the saturated $\text{Fe}(\text{Cp})_2$ adlayer in O_2 at 625 K resulted in the formation of the one-layer-thick iron oxide islands with thickness of nearly 0.15 nm. According to XPS, iron was in the form of FeO and carbon was below the XPS detection limit. The coverage/size of the FeO islands can be precisely controlled through the number of $\text{Fe}(\text{Cp})_2$ adsorption/oxidation cycles. Figure 1(b) shows FeO islands obtained after 3 cycles of $\text{Fe}(\text{Cp})_2$ adsorption/oxidation.

HREELS data demonstrated that the presence of FeO and Pt(111) was crucial for CO and H_2O adsorption. Water was found to dissociate on the FeO islands, whereas CO adsorbed only on the Pt(111) surface. The CO_{ads} species in a bridge adsorption configuration was altered in the vicinity of the FeO islands. The saturated CO_{ads} was titrated by O_2 at 300 K on FeO/Pt(111) surface. This was not possible to achieve on Pt(111) (without iron) under the same conditions. The developed procedure of a novel reverse catalyst preparation provides the precise control of chemical composition and morphology of reverse catalyst having. Application of such models in fundamental research allows studying the ample scope of aspects of catalysts behavior.

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