Carbon (e.g., carbon nanotube and graphene) supported metal nano-structured catalysts with superior performance has drawn considerable attentions in heterogeneous catalysis.[1] However, “metal-carbon support interaction” is much less understood. For instance, it is not clear how to tune metal-carbon support interaction for preparing the supported metal nanoparticles with optimal morphologies and structures, stabilizing the chemical environment in interfacial area of metal and supports, and keeping the catalytic performance in severe conditions. Advanced techniques in transmission electron microscopy (TEM) are powerful research tools for probing the metal-carbon support interaction. It can provide the fine surface/interface structures at atomic and sub-electron-volt level, such as defects, location of doped atoms, coordination state, functional group species and electronic structures.[2-3] Here, selected several examples will be demonstrated in this presentation. Figure 1 shows typical high angle annular dark field-scanning TEM (HAADF-STEM) image of Pd rings on oxygen functionalized carbon nanotube (O-CNT) and the schematic representation of the formation of Pd rings on O-CNT. Metal-support interactions between Pd nanoparticles (NPs) and functionalized CNTs were established for controlling the metal-size distribution. Thermal detrapping permits nanosized Pd to possess similar dynamics as generated carbonaceous species under electron irradiation and results in a carbon metal hybrid structure with Pd rings on the edges of the nanobead.[4] Figure 2 shows the surface/interface changes of Pd supported on L-CNT (a) and H-CNT (b) after one hour of Suzuki-Miyaura reactions. Corresponding to the commonly reported high reactivity in homogeneous catalysis, carbon–carbon couplings with high efficiency can be achieved on supported Pd NPs by improving surface functionalization and the dispersibility of the catalyst. Such a system offers opportunities for characterizing surface catalysis with atomic precision, which is crucial for detecting dynamic changes on catalytically active species and understanding catalysis pathways.[5]

Reference

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Fig. 1: a) HAADF-STEM image of Pd rings/O-CNT. Schematic representation of the formation of Pd rings on O-CNT: b) Morphology of Pd/O-CNT in the initial stage. c) Coupled with heating (red ribbons, bottom), the electron-beam induces a significant rearrangement in the Pd NPs. The Pd rings are formed at the borders of the irradiated areas.\cite{4}

Fig. 2: HRTEM images after 1 hour catalysis of: a) a Pd NP on L-CNTs, b) a Pd NP on H-CNTs. CNTs annealed at 700 °C have more defects than CNTs annealed at 1500 °C. HNO₃ treatment introduced a high functionalization (H-CNTs) on defective CNTs and a low functionalization (L-CNTs) on graphitized CNTs.\cite{5}