

The electronic and atomic structure of active single Pt site for water gas shift reaction

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Single atom catalysts (SACs) were reported to show enhanced catalytic activity in selective oxidation, hydrogenation, and water gas shift reactions over their counterparts with nano-sized metal loading, and thus have attracted much attention. However, without systematic studies, a general conclusion that SACs are good catalysts could not be made. The supported single atoms could aggregate into small clusters due to high temperature treatment usually required for the activation and/or reaction processes. Therefore, in many cases, it is the supported clusters, rather than SACs, that are actually working. The thermal stability of SACs is determined by atom-support interaction. The latter can be inhomogeneous since single metal atoms could reside on surface, subsurface, or inner of the support. The differences in atom-support interaction cause differences in the electronic structure of metal atoms, and in turn, in interactions between atoms and adsorbates, and, hence, the catalytic behaviors. The goals of this work are 1) to investigate the stability of SACs at elevated temperatures (“the temperature effect”) and in different environment (“the adsorbate effect”), and 2) to determine the electronic and atomic configurations of the active metal site, and track their changes in reaction conditions for understanding the working mechanism.

To achieve those goals, ceria supported Pt SAC was prepared and confirmed by scanning transmission electron microscopy (STEM), energy dispersive spectroscopy (EDS), and X-ray absorption spectroscopy (XAS). The electronic/atomic structures of the catalyst were tracked by ambient-pressure X-ray photoelectron spectroscopy (AP-XPS) and *operando* XAS.

In the reduction condition, this catalyst is quite stable at temperatures below 250°C. On the other hand, the temperature-programmed activity test for water gas shift reaction (WGS) shows the catalyst starts to exhibit activity at 150°C and the products reach complete conversion at about 230°C. Within this temperature range ($\leq 230^\circ\text{C}$), Pt atoms keep singly dispersed. The Pt SAC is thus active catalyst for WGS reaction. The evolution of electronic and atomic structure of Pt single active site were then determined and monitored by AP-XPS and *operando* XAS.

In conclusion, the atom-support interaction plays the key role in determining the electronic and atomic configuration of atomically dispersed Pt atoms. In the as-prepared sample, there are two Pt configurations with Pt in 2+ and 4+. The Pt²⁺ is in majority in the as-prepared sample and more stable than Pt⁴⁺, which transforms into 2+ and 0 at elevated temperatures. By tracking the structural changes of these two species in *operando* conditions, the activity site and working mechanism were revealed.

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