

## Size Dependence To The Metal-Support Interaction: Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> Catalysts

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Supported palladium (Pd) catalysts are among the most intensively studied catalyst systems for their application to many industrial processes.[1] For a full understanding of the catalytic performance of these systems, it is desirable to know the morphology, distribution, size and oxidation state of the Pd species and perhaps most importantly, whether or not any metal-support interaction (MSI) exists. Although significant research efforts have been devoted to the study of the Pd-alumina system, a full understanding of the MSI has not yet been reached. Early studies indicated  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> to be inert with Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts showing either no MSI or only a weak MSI.[2] Recent experiments, however, have shown that there exists an appreciable degree of interaction between Pd and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>,[3,4] which is either attributed to the formation of Pd-Al alloys or to the charge transfer between Pd and alumina.

In general, the MSI phenomenon is described as either a “geometric” encapsulation or decoration of the metal species by the support oxide or by an “electronic” charge transfer between metal particles and the support.[5] Since the metal particles are usually of nanometer size, we need to use imaging and spectroscopy techniques to extract both morphological and electronic structure information on the metal-support interface on an atomic scale. Atomic resolution electron energy-loss spectroscopy (EELS) and Z-contrast imaging, which can be performed simultaneously in a scanning transmission electron microscope (STEM),[6] are techniques that can be used to determine changes of the valence and oxidation states of the metal particles, the support, and the metal-support interface at an atomic level.

In this study, Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts with 2.0 wt.% Pd loading, reduced in 4% H<sub>2</sub>/Ar at 523, 773 and 1073 K, respectively, were studied using the STEM techniques with a probe size of 0.2 nm and an energy resolution of 1.2 eV for the EEL spectrum. Figure 1 shows Z-contrast images taken from the catalyst reduced at 523, 773 and 1073 K. Figure 1 (d) shows the size distribution of the particles formed at these different reduction temperatures (200 particles from each sample were measured). At reduction temperatures lower than 773 K most particles are in a range of 3-5 nm while at 1073 K most particles are larger than 10 nm. EELS analysis indicates that all the Pd particles in these reduced catalysts are metallic.

Interestingly, negative chemical shifts in oxygen K edges from the metal-support interfaces are observed for particles > 5 nm (Figure 2a). EEL spectra acquired from the specific sites marked in Fig. 2 (a) are shown in Fig. 2 (b) which contain Pd:M<sub>4,5</sub> (335 eV) and Pd:M<sub>2,3</sub> (532.3 eV) edges (spectra 1, 2 and 3) and oxygen K edge (532 eV) (spectra 4, and 5). The oxygen K edge of the interface spectrum 4 show a negative shift of about 3.6 eV to that of the alumina spectrum 5. This indicates the existence of interaction between the metallic Pd particle and the alumina support. By comparing the shape of the oxygen K edge spectra obtained from the Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> interface, alumina and PdO (shown in Fig. 2 (c)), we concluded that the origin of the observed MSI may not be caused

by the Pd-O bonding since the fine structure of the interface spectrum is not consistent with the bulk PdO reference spectrum. Instead, the interaction may be attributed as arising from charge transfer between Al and Pd atoms to form Al-Pd-O bonding at the interface, similar to the case of the Fe-Al-O system.[7] Since we have not observed this interaction in smaller particles, there may be a size-dependence to the onset of the MSI (the origin of which is as yet unknown). These results can be correlated directly with the CO dissociation behavior on Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts as a function of reduction temperature.[4]

## References

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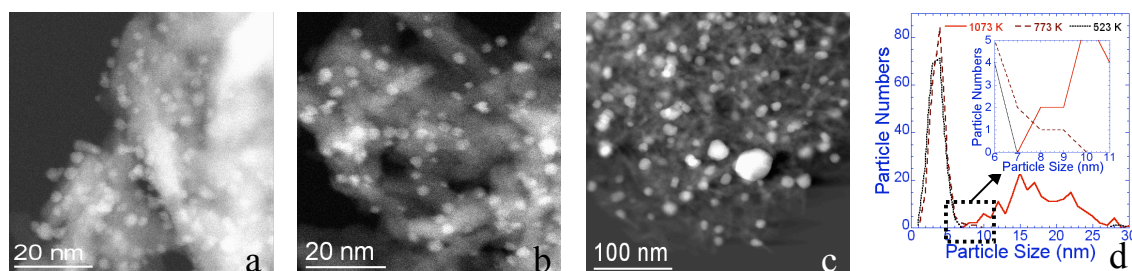


FIG. 1. (a), (b) and (c) are Z-contrast images taken from the Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst reduced at 523, 773 and 1073 K, respectively; (d) the corresponding Pd particle size distributions.

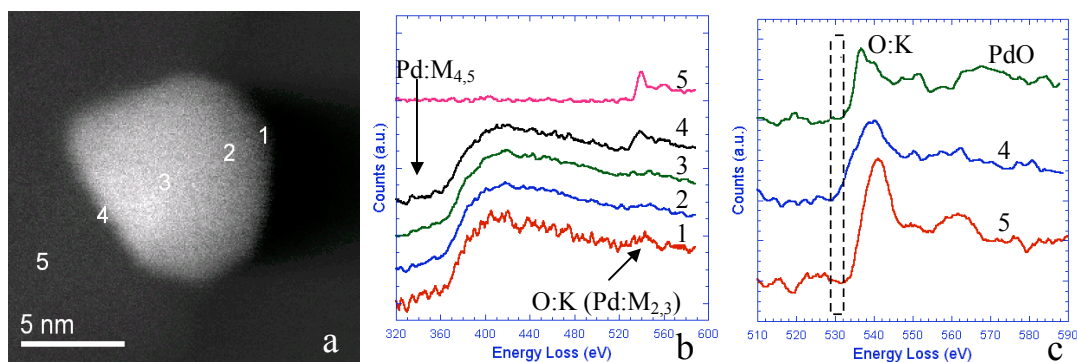


FIG. 2. (a) Z-contrast image showing the locations of (b) EEL spectra acquired from a Pd particle in the Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst reduced at 1073 K; (c) Oxygen K edges of the interface spectrum 4, the support spectrum 5 and a spectrum acquired from PdO powders.