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ELECTRONIC INTERACTION IN Rh/TiO_2 SYSTEMS INVESTIGATED BY ELECTRON AND X-RAY SPECTROSCOPIC TECHNIQUES

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ELECTRONIC INTERACTION IN Rh/TiO_2 SYSTEMS INVESTIGATED BY ELECTRON AND X-RAY SPECTROSCOPIC TECHNIQUES

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Several spectroscopies (Auger, XPS, UPS, and ELS) as well as LEED and work function measurements have been used to study charge transfer of Rh films on $TiO_2(110)$. A comparable charge transfer study of very highly dispersed Rh/TiO_2 catalysts prepared by ion exchange has been studied by NEXAFS and EXAFS of the Rh K edge.

In order to avoid the morphological changes and encapsulation that occur when catalysts are reduced at high temperatures to induce SMSI, $TiO_2(110)$ substrates have been reduced by inert gas ion bombardment prior to Rh deposition. Comparison of model catalysts prepared on reduced supports with those prepared on fully oxidized supports indicate that electronic charge is transferred from reduced Ti cations to Rh particles, resulting in a partially ionic Rh-Ti bond. The Rh-Ti bonding may provide a driving force for encapsulation of the Rh but does not lead to a large scale suppression of the capacity of the Rh to chemisorb CO.

Previous theoretical and experimental investigation of Ni_3Ti (1) and Pt_3Ti (2) have established charge transfer from Ti to the group 10 metal. We have used NEXAFS (white line) of Rh foil, Rh_3Ti and RhTi to demonstrate a systematic increase in the electron occupancy of the valence band of Rh as the Ti/Rh ratio is changed from 0 to 1. The white line of the Rh K edge in the oxidized Rh/TiO_2 catalyst decreases dramatically as the reduction is initiated and monotonically as the reduction temperature is increased from 473 to 773K. The EXAFS analysis of same X-ray absorption spectra show a monotonic increase in the average coordination of Rh around Rh (particle size growth) reduction temperature and the formation of a Rh-Ti bond at reduction temperatures above 623K (3). The Rh-Ti bond length is shorter than that in the intermetallic RhTi and is consistent with cationic character of the Ti. Both the UPS of the model Rh/TiO_2 and the NEXAFS of the high area Rh/TiO_2 provide direct evidence for modification of the valence levels of the Rh due to the presence of the encapsulating Ti suboxide moieties during SMSI.

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