Metal-Support Effects in Pd and Ni Model Catalysts

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Introduction

The term "strong metal support interaction" or SMSI was coined in the late 70's to describe the interaction between a reducible oxide support and a Gr. VIII metal [1]. This so-called SMSI, extensively studied during the last several decades [1-9], leads to suppression of CO and H_2 adsorption [1,2] and to significantly altered catalytic properties [1-5]. Despite intensive research efforts, the origin of the SMSI state is still in question. Frequently the effect has been attributed in part to either partial [6] or complete encapsulation [7-9] of the metal by the oxide support. In the present study the surface composition of Pd and Ni model catalysts has been characterized using low energy ion scattering spectroscopy (LEIS). The catalysts consist of: (a) a so-called 'inverted or reverse catalyst' made of a TiO_x film deposited on Pd(110); and (b) Pd or Ni evaporated onto a Mo(112)-(8x2)-TiO_x support. LEIS was used to access the surface composition of these model catalysts after various treatments sufficient to induce the SMSI state.

Materials and Methods

An ultrahigh vacuum chamber equipped with LEIS, a quadrupole mass spectrometer for temperature programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS), and low energy electron diffraction (LEED) was used in this study. The metals (Pd, Ti and Ni) were deposited from the corresponding metal wrapped around a tungsten wire. The evaporation rate was calibrated using LEIS, XPS and TPD. The Pd(110) and Mo(112) substrates were cleaned by Ar^+ sputtering followed by an anneal at 1300 K for Pd(110) and an e-beam treatment to 2200 K for Mo(112). An ordered thin TiO_x film was prepared using a previously published method [10]. The LEIS measurements were carried out utilizing He^+ ions of 1 keV in combination with Ne^+ or Ar^+ sputtering.

Results and Discussion

It was found that the Pd LEIS intensity is reduced significantly when the Pd/TiO_x/Mo(112) is heated to 900 K (Fig. 1a-1c). For Ni/TiO_x/Mo(112), the Ni LEIS intensity decreases significantly even at lower temperature, i.e., 600 K (Fig 2a-2c). Ni apparently more easily diffuses through the TiO_x thin layer during annealing. These data show that Pd supported on TiO_x undergoes essentially complete coverage by TiO_x. A depth profile of the SMSI surface was then carried out by acquisition of LEIS data as a function of sputtering time. Depth profiles of all systems studied show that the oxide covers the metal after an anneal in vacuum. TPD data also show that the CO adsorption capacity of Pd in the SMSI state is significantly reduced. These findings agree with previous SMSI observations on realistic supported catalysts [1-5]. Studies currently underway to investigate the properties of these well-defined SMSI model catalysts toward CO hydrogenation will also be discussed.

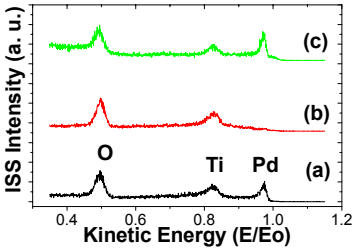

Figure 1. LEISS data for 1 ML Pd/TiOx/Mo(112): (a) as deposited; (b) annealed at 900 K (note TiO_x covering the Pd); and (c) annealed to 900 K for 5 minutes then LEIS acquired at 600K. (Note appearance of Pd.)

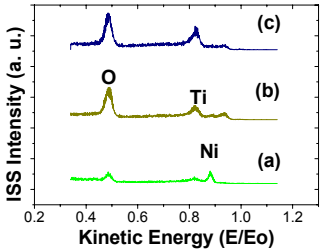

Figure 2. LEISS data for Ni deposited on TiOx/Mo(112) system (a) 2 ML Ni/TiOx/Mo(112) as deposited, (b) annealed to 600 K, (c) annealed to 900 K.

Significance

These studies show that Pd and Ni catalysts prepared on a reduced TiO_x surface are excellent models of the more realistic supported catalysts yet are amenable to investigation with modern surface techniques. These findings are directly relevant to understanding the long-standing questions regarding the SMSI state of supported metal catalysts.

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