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CATALYST CHARACTERIZATION: SILICA OVERLAYERS ON TRANSITION METALS

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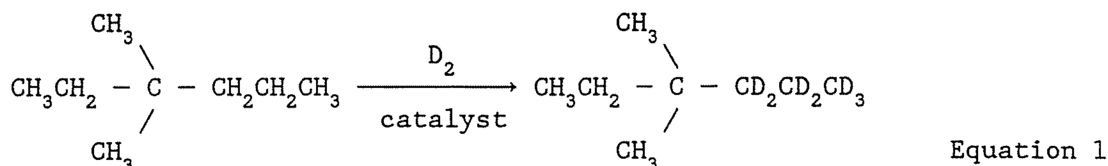
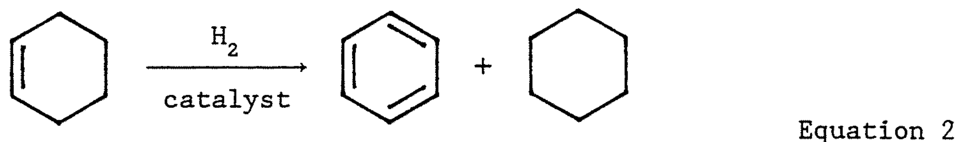
Thin silica films (200 to 23,000 Å) over metal underlayers of Rh, Pd, or Pt are active catalysts for heterogeneous hydrogenation/dehydrogenation reactions [1] and for C-H bond activation in hydrogen/deuterium exchange reactions [2]. These unique catalysts typically consist of 200 Å transition metal films deposited onto polished silicon wafers and covered with varying thicknesses of SiO_2. The dihydrogen migrates through the SiO_2 layer, is activated by the transition metal underlayer, and subsequently migrates back to the SiO_2 surface where it reacts with the carbon containing substrate. Carbon or other materials capable of poisoning the transition metal underlayer do not diffuse through the SiO_2 overlayer. Unusual hydrogenation catalysts can potentially be produced by modifying the outer surface of the SiO_2 layer.

Two examples of the reactions that have been studied are shown in Equations 1 and 2. The catalysts must be activated by



Equation 1



Equation 2

heating to ~250° C in the presence of H_2, and the reactions require an H_2 atmosphere. The general mechanism for hydrogenation reactions involves two processes: Dihydrogen activation by adsorption onto the metal surface with subsequent formation of two H-metal surface bonds, and hydrogen transfer to carbon by adsorption of the carbon containing substrate onto the catalyst surface followed by transfer of hydrogen from the metal to carbon and desorption of the product. Starting with C-H activation, dehydrogenation proceeds along the reverse reaction pathway, and Equations 1 and 2 involve components of both hydrogenation and dehydrogenation. The catalysts are prepared on polished silicon wafers by electron beam evaporation of a layer of Pt, Pd or Rh followed by a capping layer of SiO_2. Supports such as tungsten foils have been used, but the flat wafers

facilitate catalyst characterization. This paper describes the characterization of these new catalysts.

The general structure of the catalysts is confirmed by Rutherford backscattering spectrometry (RBS), sputtered neutral mass spectrometry (SNMS), and secondary ion mass spectrometry (SIMS). Figure 1 shows the RBS spectrum of a used Pd catalyst with 2.3 μm of overlayer SiO_2, and the inset shows the high energy portion of the spectrum expanded by a factor of 250 to indicate the presence of trace levels of impurities (masses ~40 and ~55) near the outer surface of the SiO_2 overlayer. It is important to note that Pd is below the RBS detection limits at the outer surface. Therefore, dihydrogen activation must be occurring after diffusion to the Pd inner layer. In contrast to Auger or SIMS depth profiling techniques, RBS analysis is unaffected by the insulating properties of the thick SiO_2 overlayer.

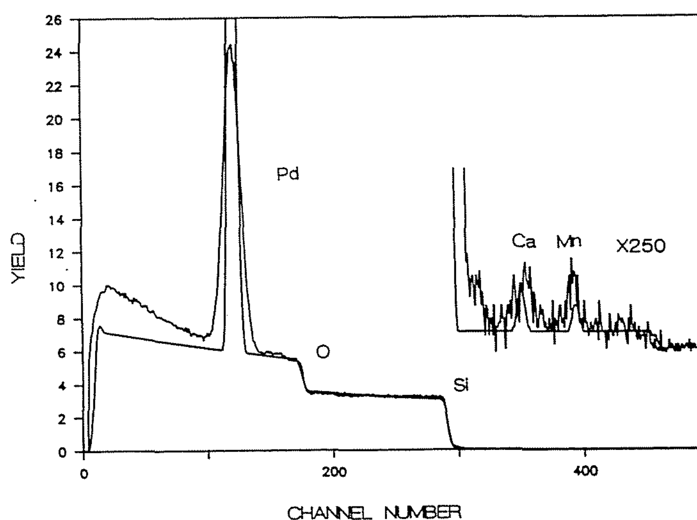


Figure 1. RBS spectrum of a used Pd catalyst. Expanded inset shows near surface trace elements.

The SNMS depth profile of a used Pt catalyst with a thinner SiO_2 overlayer is shown in Figure 2. SNMS is largely unaffected by sample charging, and it shows the general catalyst structure with good depth resolution of the inner metallic layer.

The negative ion Cs^+ bombardment SIMS depth profile of a used Pt catalyst with a 830 Å SiO_2 overlayer is shown in Figure 3. This SiO_2 thickness causes severe sample charging problems that were overcome by gold coating the sample surface and by the use of autovolting to automatically provide a compensatory offset to the mass spectrometer accelerating voltage. The depth scale is calibrated using the RBS measured SiO_2 thickness (which was in good agreement with the thickness measured by quartz crystal thickness monitoring at deposition). The indicated outer surface concentration of Pt is ~1 ppm which is near the detection limit for this SIMS method.

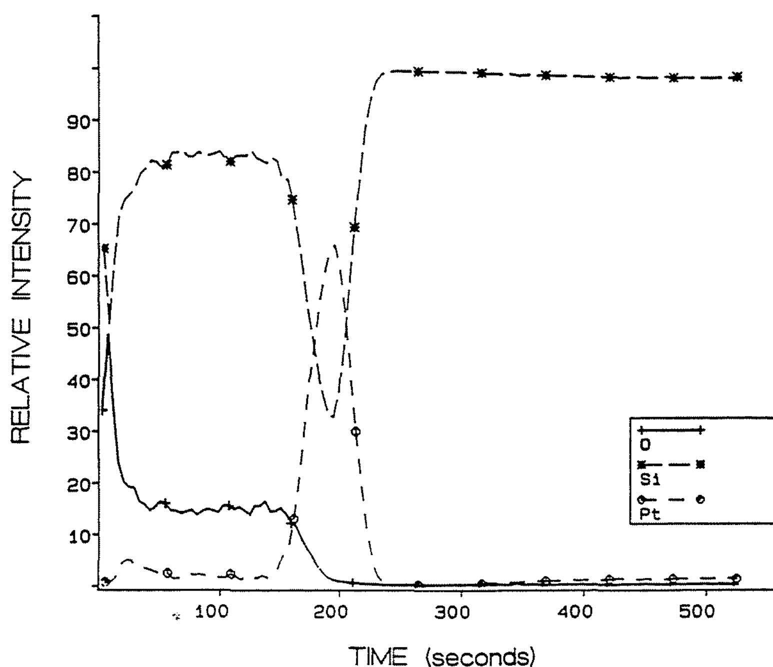


Figure 2. SNMS depth profile of a used Pt catalyst.

In addition to general catalyst characterization, two specific analytical questions provide insight into catalyst behavior: Is sufficient Pt present at the outer SiO_2 surface to catalyze the hydrogenation/dehydrogenation reactions, and do carbon compounds migrate into the transition metal-SiO_2 interface? To answer the first question a 8.9 x 10^{11} atom/cm^2 Pt layer was deposited onto the outside of a 250 Å SiO_2 layer which had been deposited on a silicon wafer. Both SIMS and RBS detected the Pt and indicated that it had migrated into the SiO_2 layer. This sample produced no catalytic activity although samples with 100 times more Pt did produce detectable activity. This sample was used to calibrate the concentration scale in Figure 3.

Figure 3 indicates the presence of slightly more than background levels of carbon at the SiO_2 interface. To evaluate the significance of the carbon level we prepared a Pt catalyst with no SiO_2 overlayer and used it to catalyze the reaction in Equation 2. Carbon containing materials rapidly covered the Pt surface during catalysis. The catalyst was recovered and coated with SiO_2 to produce an overlayer catalyst that was still active and which produced the SIMS profile in Figure 4 showing carbon at the SiO_2-Pt interface. The carbon accumulation at an exposed Pt catalyst surface is much greater than carbon detected occasionally at the SiO_2-Pt interfaces of new and used overlayer catalysts.

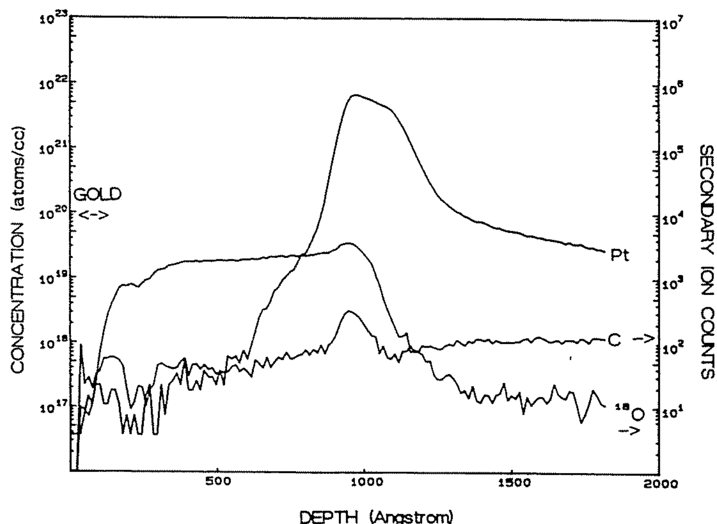


Figure 3. SIMS depth profile of Pt catalyst. Element symbols with arrows use right side scale.

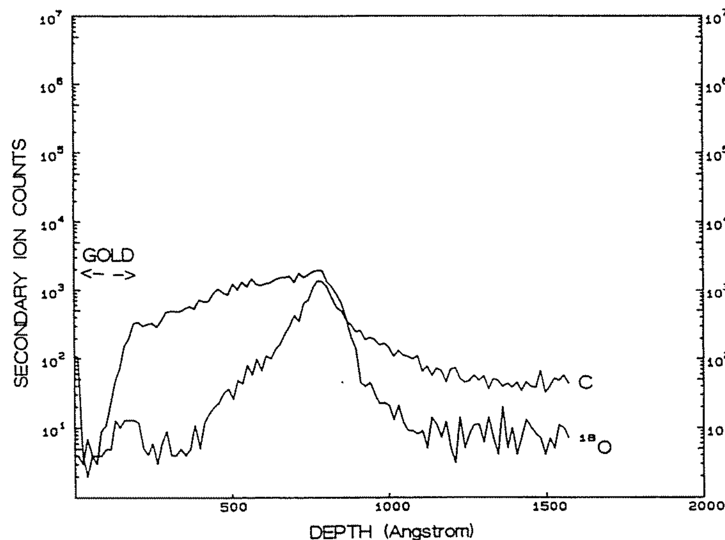


Figure 4. SIMS depth profile of catalyst with overlayer applied after catalyst use.

We conclude that the activity of these catalysts requires a group eight transition metal underlayer. Although there might be concentrations of the metals as high as 1 ppm (detection limit) at the outer surface of the SiO_2 layer this is insufficient to explain the observed catalytic activity. Further work is under way to measure and control an observed slow transition metal migration into the SiO_2 layer and to determine whether it has a role such as transporting the activated hydrogen back to the outer surface.

1. A.B. McEwen, W.F. Maier, R.H. Fleming and S.M. Baumann, Nature, in press, 1987.
2. J.M. Cogen, K. Ezaz-Nikpay, W.F. Maier, R.H. Fleming and S.M. Baumann, Angew. Chem., Int. Ed. Eng., in press, 1987.