

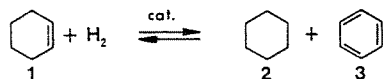
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Catalytic Dehydrogenation of Cyclohexene on Silica Overlayer Films**

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Heterogeneous dehydrogenation of cyclohexene **1** to benzene **3** has received attention as a model reaction for dehydrogenation processes.^[1] This reaction is not stoichiometric (see temperature dependence of the product distribution in Fig. 3) and requires the presence of dihydrogen.



The reaction is not only catalyzed by noble metals, but also by spillover hydrogen^[2] as well as on carbonaceous overlayers on Pt.^[3,4] Chemically bound hydrogen atoms on Te were proposed as active sites for cyclohexene dehydrogenation in Te-NaX zeolites.^[5] The reaction also occurs on gold covered Pt^[6] and may be due to active spillover hydrogen on the Au surface.^[7] These studies indicate that an exposed transition metal surface may not be necessary to catalyze this reaction.

To test the importance of an exposed transition metal surface the catalytic properties of Pt films supported on Si wafers with and without silica overlayers were compared (see Fig. 1). It was hoped that dihydrogen would diffuse readily through the overlayer to become activated (dissociated) at the underlayer. This activated hydrogen could then migrate back to the oxide surface and was expected to

exhibit catalytic reactivity different from that of the exposed transition metal surface.

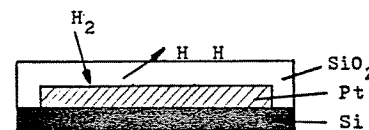


Fig. 1. Schematic representation of the overlayer catalysts.

The film catalysts were prepared by deposition of 10 ± 1.5 nm of Pt by electron beam evaporation at 10^{-7} torr onto polished silicon single-crystal wafers. Overlayers were deposited at a rate of 30–40 nm/min by electron beam evaporation of SiO₂ (from quartz) and the thickness was followed by a quartz crystal thickness monitor. The films were then transferred to a gas-phase flow reactor to test the catalytic activity at atmospheric pressure with dihydrogen or dideuterium as carrier gas. These SiO₂/Pt/Si films catalyze the hydrogenation and dehydrogenation of cyclohexene, while in control experiments SiO₂/Si proved to be catalytically inert.

The effect of the silica overlayer thickness on the rate of conversion of **1** to **2** and **3** at 250 °C was studied for SiO₂/Pt/Si.^[8] The reaction rate per unit of geometric surface area drops exponentially with increasing overlayer thickness up to about 30 nm after which the rate stabilizes at about 1/100 (3 orders of magnitude above the background) of the activity of exposed metal and becomes nearly independent of thickness (overlayer thicknesses up to 2200 nm were investigated). During this study we noted that the activity decreases with decreasing deposition rate of the SiO₂ overlayer. Annealing of the overlayer catalyst prior to the reaction also results in a reduction of activity. These data suggest that catalytic activity requires defects in the overlayer film which can serve as carriers of the dissociated hydrogen and/or dihydrogen.

To exclude edge effects the Pt was deposited through a window leaving an outer frame (2 mm) of uncovered silicon so that the subsequent SiO₂ deposition completely covered the edges of the Pt film. On such films the masked (Pt-free) area showed no catalytic activity providing evidence against lateral Pt diffusion. As expected from the low concentration (based on simple geometrical estimates) of exposed edge platinum on unmasked films there was no detectable difference in the activity of masked and unmasked overlayer films. Scanning electron microscopy (SEM) of new and used overlayer catalysts gave no evidence for cracks or pores in the overlayer. Subsequent deposition of silica or gold onto used overlayer films (to fill any cracks or pores) did not decrease catalytic activity. Relative rates of deuteration of *n*-hexane and *n*-octane (first order in hydrocarbon) on overlayer catalysts correlate with boiling point (as with Pt^[9]) and not with hydrocarbon diffusion rates. These experiments are evidence against cracks or pores as carriers of catalytic activity.

The dependence of catalytic activity on SiO₂ overlayer thickness is most likely due to hydrogen recombination processes. However, due to analytical limitations we can not rule out partial accessibility of the Pt films with thin silica overlayers. For this reason subsequent experiments were conducted on thicker (>60 nm) SiO₂ overlayers for which possible exposure of Pt could be addressed.

Auger electron spectra (AES) and thickness profiles of such films are very clean and no transition metal diffusion into the overlayer or to the surface has been detected.^[10]

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However, the rather low sensitivity of AES (about 0.5% for Pt) is not suitable for trace analysis. The most sensitive method for trace analysis of such layered thin films is secondary ion mass spectrometry (SIMS, sensitivity limit < 0.0005 atom-% for Pt),^[11] which was used to analyze representative thin film catalysts before and after use. Rutherford back scattering spectrometry (RBS, sensitivity limit ≈ 0.005 atom-% for Pt)^[12] was also used for chemical analysis and thickness measurements of the overlayer films. SIMS depth-profiling is based on sputtering which leads to unavoidable tailing of one layer into the next, while RBS is nondestructive and provides a much better depth resolution and accuracy. The RBS data confirmed film thicknesses in all cases. RBS and SIMS (see Figure 2) gave no evidence for Pt at or near the oxide surface. The RBS profiles show that the thickness of the films is homogeneous and that the surface of the SiO₂ is continuous and not rough. Although very close to exact stoichiometry, a slight oxygen deficiency in the silica overlayer was sometimes noted by RBS (33–36% Si:67–64% O). Catalytic activity due to platinum on the silica surface at concentrations below the detection limit of our analytical techniques ($\approx 10^8$ Pt atoms/cm²) was excluded by the lack of activity after impregnation and activation of SiO₂/Si films with readily detectable Pt concentrations of 10^8 – 10^{14} Pt/cm².^[13]

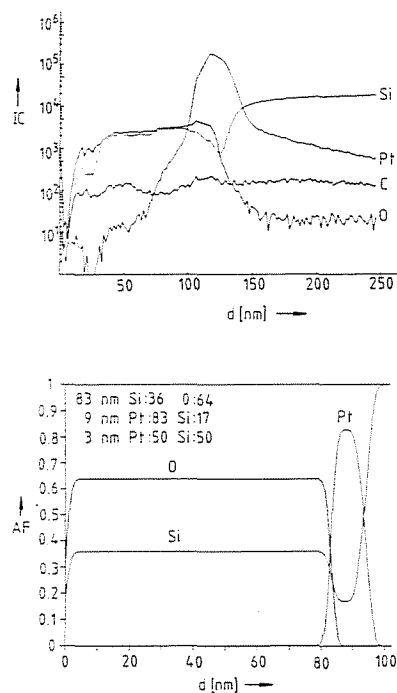


Fig. 2. Representative SIMS (left) and RBS (right) depth profiles of a used, active SiO₂/Pt/Si catalyst. Chemical composition of overlayers is given in atom-% in the upper left corner of the RBS profile. IC = ion counts, d = layer thickness, AF = atomic fraction.

Single crystal experiments have shown that prompt and extensive carbonation occurs on Pt during dehydrogenation of **1** while the reaction continues.^[3] To test for sensitivity of SIMS for carbon at the SiO₂-Pt interface, we used a Pt/Si film for the catalytic reaction and then deposited the silica overlayer. The SIMS profile of this film indicated extensive carbonation at the SiO₂-Pt interface showing that SIMS can detect low carbon concentrations in these overlayers. Other overlayer films show no detectable increase of the carbonation below the SiO₂ surface upon use. This also serves as evidence against catalysis at the interface

due to cracks or pores or diffusion of hydrocarbons through the silica layer.

Upon prolonged use of these films RBS and SIMS indicate sometimes that there is a slow diffusion of Pt into the silica overlayer (concentration 30 ppm Pt in SiO₂) which is currently under investigation. In this study each experiment was run on an unused film for time periods too short for significant Pt diffusion (confirmed by SIMS and RBS).

The effect of temperature on the rate (turnover frequency, N_f , molecules cm⁻² sec⁻¹) and selectivity of a 72 nm SiO₂/Pt/Si was remarkably similar to that on a Pt/Si catalyst (Fig. 3). Over the temperature range studied the 3/2 ratio was slightly lower on the SiO₂/Pt/Si. The activation energies for the overall reaction of cyclohexene are: Pt/Si = 2.09 ± 5 kJ/mol, SiO₂/Pt/Si = 16.3 ± 5 kJ/mol; for formation of benzene: Pt/Si = 82.8 ± 14 kJ/mol, SiO₂/Pt/Si = 92.5 ± 6 kJ/mol. The differences between the exposed Pt and the overlayer films are not believed to be significant.

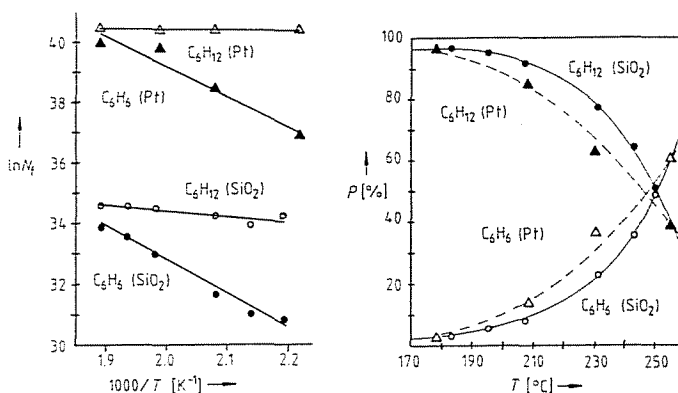


Fig. 3. Comparison of the Arrhenius plots (left) and the temperature dependence of the product composition (right) of cyclohexene conversion (low conversion conditions) on a 72 nm SiO₂/Pt/Si film with that on an exposed Pt/Si film.

Since isotopic product distributions have been useful as characteristic fingerprints for substrate catalyst interactions it was hoped to observe differences between the deuteration patterns obtained on the oxide and on the Pt surface upon substitution of dideuterium for dihydrogen as carrier gas. However, the isotopic distributions of the products benzene and cyclohexane are very similar and show only a slightly higher deuterium content on Pt/Si relative to the products obtained on SiO₂/Pt/Si.

The similarity of the catalysis on the oxide overlayer to that on the Pt film suggests that this dissociated hydrogen^[14] (whatever its nature on the surface) and not the exposed metal represents the active site for this catalytic reaction. The presence of active hydrogen on a surface may then be more important than the chemical nature of the surface. This conclusion is consistent with the wide variety of surfaces known to catalyze this reaction.^[1-6]

In summary, inert silicon dioxide thin films become catalytically active in the presence of a platinum underlayer. Additional studies in our laboratory have shown that this phenomenon is not limited to SiO₂ on Pt, but has been observed with many other over-underlayer combinations. The most promising potential features of such catalysts—induction of catalytic activity on new surfaces and the resistance to poisoning due to protection of the transition metal by the overlayer—have now to be investigated.

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