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Fast Catalysis of a Hydrogen Exchange Reaction at Low Temperatures by Gold

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Summary Evaporated gold films exhibit extremely high catalytic activity at 195 K for the hydrogen exchange reaction between $\mathrm{MeSiH_3}$ and $\mathrm{MeSiD_3}$; only protium and deuterium bonded to silicon participate in the exchange and the activity is diminished at higher temperatures owing to poisoning of the surface by products of methylsilane chemisorption.

Gold is normally regarded as a metal of very low catalytic activity. In formic acid decomposition temperatures of 373—523 K are required to obtain favourable rates of reaction.[1] Evaporated gold films catalyse the hydrogenolysis of the carbon–nitrogen bond at 473 K and above,[2] and this range of temperature is required for the activation of molecular hydrogen.[3] Catalysis of hydrocarbon hydrogenation by gold has only recently been reported;[4] ethylene and pent-1-ene hydrogenation were observed at about 373 K, buta-1,3-diene hydrogenation at 400 K, and but-2-yne hydrogenation at 490 K. Thus, gold normally exhibits weak activity at elevated temperatures.

We now report that gold is an extremely active catalyst for the exchange of hydrogen atoms bonded to silicon. Hydrogen–deuterium exchange occurs at an immeasurably fast rate when $\mathrm{MeSiH_3}$–$\mathrm{MeSiD_3}$ mixtures are contacted with gold in the range 195—245 K. This is also the first report of the metal-catalysed exchange of protium and deuterium bonded to silicon.

Reactions were carried out in a Pyrex reaction vessel connected to a stainless steel ultra-high vacuum apparatus fitted with a quadrupole mass spectrometer. The whole apparatus was baked at 523 K before use. Before gold films were prepared, the catalytic activity of the apparatus for the $\mathrm{H_2}$–$\mathrm{D_2}$ exchange reaction and for the $\mathrm{MeSiH_3}$–$\mathrm{MeSiD_3}$ exchange reaction were measured under the conditions later to be used for the gold-catalysed reaction. A slow rate of exchange was observed in each of these blank experiments. Gold (Johnson Matthey 99·99 + % Au, 80 p.p.m. Ag, 10 p.p.m. Cu, 3 p.p.m. Fe) wire supported on a thick tungsten loop was evaporated onto the surface of the reaction vessel. During evaporation the vessel temperature was 195 or 273 K and the pressure in the vessel was typically 5×10^{-9} torr. Film weights were about 5 mg. Activity for $\mathrm{H_2}$–$\mathrm{D_2}$ exchange was then re-determined. The rates before and after film deposition were always identical, thus demonstrating that the films were not contaminated with tungsten from the supporting loop. Films prepared and tested in this way were used to investigate (a) the chemisorption of methylsilane and (b) isotope exchange in $\mathrm{MeSiH_3}$–$\mathrm{MeSiD_3}$ mixtures.

On first admitting $\mathrm{MeSiD_3}$ to a clean gold film at 273 K, 1·2 deuterium molecules were formed in the gas phase per molecule of $\mathrm{MeSiD_3}$ adsorbed, together with a trace of methane which was mostly MeD. Subsequent admission of $\mathrm{MeSiD_3}$ resulted in this substance being detected in the gas phase. No products having deuterium bonded to carbon or protium bonded to silicon were observed, *i.e.* the rate of self exchange was zero. The yield of deuterium demonstrates that one product of the chemisorption was probably the $\alpha\alpha$-diadsorbed species $\mathrm{Me}\underset{**}{\mathrm{Si}}\mathrm{D}$.

When about 0·5 torr of a 1 : 1 mixture of $\mathrm{MeSiH_3}$ and $\mathrm{MeSiD_3}$ was admitted to the vessel mutual exchange occurred giving the four isotopically distinguishable methylsilanes having protium and/or deuterium bonded to silicon. Mutual exchange has been examined at 195, 245, 273, and 293 K. Isotope equilibration was achieved within a few seconds at 195 and 245 K, the rates being too fast for reliable measurement. Repetition of the reaction many times at 195 K resulted in no apparent loss of activity.

At 245 K the rate became measurable in the fifth of a series of experiments. The first reactions at 273 and 293 K gave measurable rates. This indicates that the surface is poisoned by the products of the dissociation of methylsilane, and that this poisoning occurs more rapidly the higher the temperature.

The observation of mutual exchange demonstrates that the dissociative chemisorption of methylsilane provides adsorbed protium and deuterium atoms, and that chemisorbed fragments from methylsilane are reactive. Mutual exchange may proceed as in equations (1) and (2) although

$$\underset{**}{\text{MeSiH}} + 2\underset{*}{\text{X}} \longrightarrow \text{MeSiHX}_2 + 4* \qquad (1)$$

$$\underset{**}{\text{MeSiD}} + 2\underset{*}{\text{X}} \longrightarrow \text{MeSiDX}_2 + 4* \qquad (2) \quad [\text{X}=\text{H or D}]$$

participation of the α-adsorbed species $\text{Me}\underset{*}{\text{Si}}\text{X}_2$ is also likely.

The reactivity of the silyl group in company with the inert character of the methyl group is striking. Possibly the initial interaction of methylsilane with gold is one of associative chemisorption in which a co-ordinate Au–Si bond is formed utilising the empty *d*-orbitals of silicon; the methylsilane thus activated may then lose one or more hydrogen atoms to provide a more stable chemisorbed species.

In the present work this mutual exchange reaction has also been catalysed by films of tungsten, molybdenum, rhodium and nickel. The specific activity of gold is at least comparable with that of these metals. Thus a reaction has been found in which the nominally full *d*-band of gold does not hinder this element from exhibiting a degree of catalytic activity more usually associated with elements having unfilled *d*-bands.

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