

Catalytic Sites in the Hydrogenolysis of Cyclopropane on Platinum

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Summary The hydrogenolysis of cyclopropane on Pt/SiO₂ occurs on the actual platinum surface of the catalyst and not on any carbonaceous deposit.

It has long been known that slowly reacting species containing carbon and hydrogen ('a carbonaceous deposit') accumulate on the surfaces of metallic catalysts during reactions between hydrogen and hydrocarbons.¹ In recent years, several groups have suggested that various catalytic reactions between hydrogen and hydrocarbons occur not at the actual surface of the metal but rather on some carbonaceous deposit or that there is a catalytically important interaction between the deposit and sites on the metal.² In conventional flow or batch reactors, a carbonaceous deposit might form in the first moments on stream and the catalytic reaction under study might then proceed on the deposit. One could not decide whether the metallic sites or the sites on the carbonaceous deposit were responsible for the catalytic reaction. For the hydrogenolysis of cyclopropane, this problem has been obviated by use of a pulse reactor in which C₃H₆/Pt_s per pulse (where the subscript s designated a surface atom) was small, 3.5–5. The results indicate that the reaction occurs on the actual platinum surface of Pt/SiO₂ and the interactions with a carbonaceous deposit are catalytically unimportant at least initially.

In this work, a 0.963 cm³ pulse of cyclopropane + hydrogen (1:15) was injected into hydrogen or helium carrier flowing at 40 cm³ min⁻¹ over ca. 0.22 g of catalyst maintained at 0 °C. The product (only propane was detected) and unchanged cyclopropane were collected in a silica gel trap at -78 °C following the catalyst. Warming released a pulse of propane + cyclopropane which was analysed by gas chromatography. Recovery of total hydrocarbon was usually at least 99%. A sequence of 11 pulses was passed. The interval between pulses was 12 min. After completion of this sequence, the carbon content was measured to an accuracy of ±0.01 in C/Pt_s.³ In all experiments, C/Pt_s was 0.10 ± 0.03.

The preparation and physical characteristics of the catalyst (40-SiO₂-PtCl-S) are described elsewhere.³ The catalyst was prepared by impregnating Davison Grade 62 wide-pore silica gel (120–140 mesh) with aqueous H₂PtCl₆ to give 1.17 wt. % Pt. Two different pretreatments of the catalyst were investigated. Both involved preliminary exposure to flowing oxygen at 300 °C for 30 min and then flowing hydrogen at 300 °C for 1 hr. This was followed either by flowing helium for 1 h at 450 °C or by flowing hydrogen for 1 h at 450 °C. The catalyst was cooled in the gas last employed. The two pretreatments are designated cool-He and cool-H₂ respectively. The percentage exposed (dispersion) of the platinum was 40% after both pretreatments.

The Figure shows conversion *vs.* pulse number for the four combinations: cool-H₂-carrier-H₂, cool-H₂-carrier-He, cool-He-carrier-H₂, and cool-He-carrier-He.

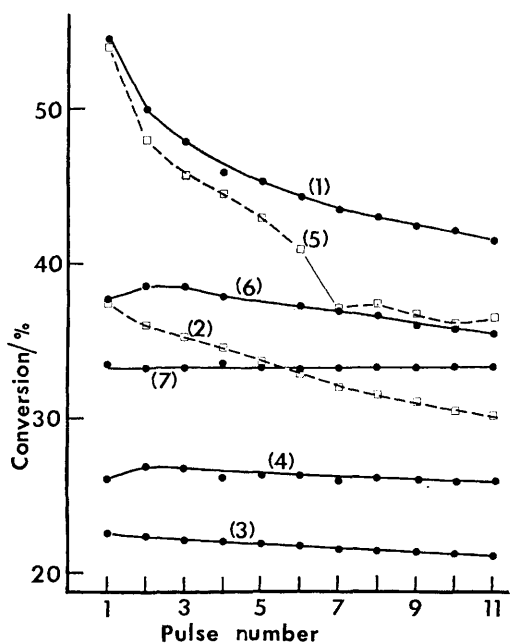


FIGURE. Conversion *vs.* pulse number as a function of pretreatment and carrier gas. (1) Cool-He-carrier-He; (2) cool-He-carrier-H₂; (3) cool-H₂-carrier-H₂; (4) cool-H₂-carrier-He; 5% has been added to all conversions; (5) as curve (1) but exposed to H₂ for 5 min between pulses 6 and 7. 0.0205 g of catalyst was used rather than 0.022 g as in curve (1); (6) as curve (1) but exposed to H₂ at 0 °C for 1 h just before the start of the run; (7) as curve (3) but MnO/Celite inserted just before the catalyst.

If hydrogenolysis were to occur only on a carbonaceous deposit, reaction would proceed by preliminary formation of a carbonaceous deposit and only then would formation of propane begin. As noted, a carbonaceous deposit does form, but in the first pulse $[C_3H_8]/Pt_s$ does not exceed 0.01. However, as the Figure shows, activity decreases with pulse number. Therefore, either (i) the catalytic sites for hydrogenolysis are initially surface atoms of platinum, or (ii) there

is a very rapid reaction of cyclopropane with platinum during the first 1 or 2% of the period of exposure to cyclopropane in pulse 1 which leads to a very small coverage by some carbonaceous material; all catalytic activity is confined to this material, and carbonaceous material deposited subsequently is catalytically inactive. Alternative (ii) appears improbable. Further, the turnover frequency (in molecules of propane formed per second per surface atom of platinum) is 0.16 in hydrogenolysis on the same catalyst in a flow reactor at 0 °C⁴ and we estimate that it is 0.1–0.3 s⁻¹ in cool-H₂-carrier-H₂. Although comparison between the two kinds of reactors can only be very rough, this comparison does suggest that hydrogenolysis occurs predominantly, if not entirely, at the actual surface of platinum even after times on stream of over 1 h.

The deactivation exhibited by cool-He-carrier-He (curve 1 of the Figure) results from some form of chemisorption of hydrogen as is shown by curve 5 in which the catalyst was exposed to a flow of hydrogen for 5 min between pulses 6 and 7. The activity dropped substantially. Exposure to hydrogen for 1 h at 0 °C before pulse 1 led to curve 6 being well below curve 1 and exposure to hydrogen at 25 °C led to a curve lying about 20% above curve 3. Cool-H₂ results in less active catalysts than does cool-He but it gives catalysts for which the rate of deactivation is small (curves 3 and 4).

In fact, deactivation in curves 3 and 4 appears to result from traces of oxygen in the carrier gases. The content in oxygen at the catalyst was less than 0.05 p.p.m., the limit of detectability by our technique.³ However, this level of oxygen coupled with the very small amount of Pt_s employed (*ca.* 0.6 μmol) could give O/Pt_s = 0.05 during a run. The data of curve 7 resulted from inserting a bed of 0.09 g of MnO/Celite⁵ just ahead of the catalyst. This material was shown to be catalytically inactive for hydrogenolysis. The deactivation was eliminated. The larger extent of conversion results from the widening of the pulse during passage through the MnO/Celite. The MnO/Celite removed oxygen which probably entered the carrier gas at Swagelok joints with Teflon ferrules which occurred frequently in the apparatus which used Nupro bellows valves and no greased stopcocks.

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⁵ C. R. McIlwrick and C. S. G. Phillips, *J. Phys. E.*, 1973, 6, 1208. Content in oxygen is reduced to one part in 10^{6.5}.