

An EPR Study of a Palladium Catalyst using a PBN (*N*-Benzylidene-*tert*-butylamine *N*-Oxide) Spin Trap: Direct Demonstration of Hydrogen Spillover

A. F. Carley,^a H. A. Edwards,^a B. Mile,^{*a} M. W. Roberts,^a C. C. Rowlands,^a S. D. Jackson^b and F. E. Hancock^b

^a School of Chemistry and Applied Chemistry, UWCC, PO Box 912, Cardiff, UK CF1 3TB

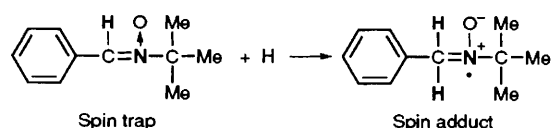
^b ICI Katalco, R, T & E Group, PO Box 1, Billingham, UK TS23 1LB

EPR spectroscopy, in conjunction with spin trapping, is shown to provide a convenient, simple technique for detecting the dissociation of hydrogen on a supported palladium catalyst and leads to a direct demonstration of the occurrence of spillover on to the alumina support.

There is a consensus that adsorbed free atoms and radicals are important participants in many complex heterogeneous catalytic reactions, such as the hydrogenation of alkenes and alkynes, and the synthesis of methanol from carbon dioxide and hydrogen.^{1,2} Electron paramagnetic resonance (EPR) spectroscopy is the natural technique for detecting such paramagnetic moieties on catalytic metal particles and their supports. We show here how EPR, in conjunction with spin trapping methods, can be readily and conveniently used to detect the established dissociation of hydrogen on a supported palladium catalyst at ambient temperatures, and also provides direct evidence for hydrogen spillover on to the support. This is still a matter of some controversy largely because of the indirect nature of much of the experimental information.³⁻⁵ The technique is an extension of a somewhat neglected method first used by Howe *et al.* for examining hydrogen dissociation on ZnO.⁶ X-Ray photoelectron spectroscopic studies of the doped catalyst during similar hydrogen treatment provide unambiguous evidence for the facile reduction of Pd²⁺ to Pd⁰ from the observed shifts (2.1 eV) in the binding energies of the Pd 3d electrons.⁷

We have studied the dissociation of hydrogen on palladium at 25 °C in a direct fashion by using the spin trap *N*-benzylidene-*tert*-butylamine *N*-oxide (PBN) to garner efficiently (*k ca.* 10⁸ dm³ mol⁻¹ s⁻¹) any loosely bound chemisorbed hydrogen atoms that may be formed on the palladium surface to give a stable spin adduct (SA) which is paramagnetic and accumulates to concentration levels detectable by EPR (Scheme 1).

A crushed commercial catalyst (0.04% Pd on commercial alumina), pre-treated at 400 °C for two hours under vacuum, was exposed to one atmosphere of hydrogen at 25 °C for ten minutes and then exposed to solutions of PBN (0.01 mol dm³) in deoxygenated CH₂Cl₂. The isotropic EPR spectrum of the solution after contact with the catalyst is shown in Fig. 1(a); there are hyperfine interactions (hfi) of *a*_N = 1.53 mT with one nitrogen nucleus and *a*_H = 0.82 mT with two equivalent hydrogen nuclei. This spectrum can be assigned unequivocally to the hydrogen atom spin adduct by comparison with well established spectra and hfi for the monohydrogen atom adduct of PBN.^{6,8} No EPR transitions were detected when the undoped support was similarly treated. No EPR transitions were detected in the following blank experiments: (i) treatment of the catalyst with the spin trap solution in the absence of hydrogen; (ii) treatment of the γ -alumina support containing no added palladium with hydrogen and the spin trap solution in the same sequence as that for the catalyst itself. These experiments show that the molecular hydrogen is the source of the hydrogen atoms adding to the spin trap and that the alumina support itself is incapable of producing loosely



Scheme 1 The highlighted nuclei are those leading to hyperfine interactions

bound hydrogen atoms under the mild conditions of our experiments.

The experiments were repeated using deuterium (>99.8% purity) instead of hydrogen. The resulting EPR spectrum [Fig. 1(b)] is composite and shows in addition to the expected transitions from the monodeuterio spin adduct, those from the dihydrogen adduct (indicated in the spectrum by H). The dihydrogen spectrum of the monodeuterio adduct shows hyperfine interactions with one nitrogen nucleus, *a*_N = 1.53 mT, one hydrogen, *a*_H = 0.82 mT and one deuterium, *a*_D = 0.12 mT. The ratio *a*_H:*a*_D 6.83 is compatible with a gyromagnetic ratio of 6.54. The presence of the dihydrogen adduct from the catalyst treated with pure deuterium is surprising, especially since it constitutes 23% of the paramag-

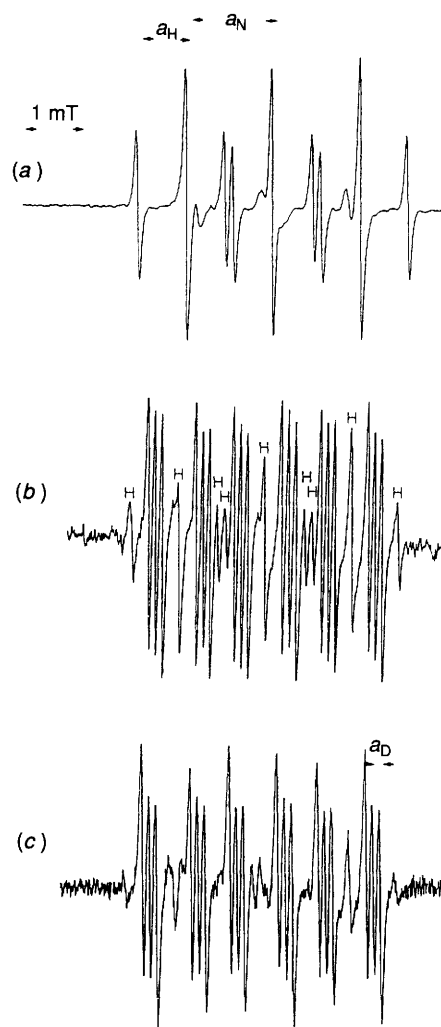


Fig. 1 EPR spectra of PBN spin adduct formed on a Pd/ γ -Al₂O₃ catalyst after exposure at 1 bar and 25 °C for 10 min to (a) H₂, (b) D₂ (>99.8%) (transitions marked H indicate those from the dihydrogen spin adduct) and (c) D₂ after treatment of the catalyst with D₂O

