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COMMUNICATION

ON THE NATURE OF ACTIVATION OF ANCHORED RHODIUM CATALYSTS BY BOROHYDRIDE

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Abstract—The nature of the active polymer anchored rhodium catalysts used for hydrogenation has been deduced to be a mono- or dihydridorhodium(III) species.

Rhodium complexes anchored on polymers containing ligands like phosphine[1] and anthranilic acid derivatives[2] have been employed as hydrogenation catalysts. The systems containing polymers with anthranilic acid derivatives were synthesized from $RhCl_3$ and were subsequently treated with $NaBH_4$.[2] In this process,[2] it is considered that Rh(III) is reduced to Rh(I) as evidenced from the colour change observed as well as from XPS results. The purpose of this communication is to examine the nature of activation caused in the catalyst as a result of borohydride treatment.†

Normally, rhodium (III) chloride complexes containing nitrogen ligands on treatment with borohydride yield either mono- or dihydrido species by nucleophilic displacement of chloride or undergoes reduction to Rh(I) or Rh(O).[4] It is also known that a dihydrorhodium(III) complex can be obtained by oxidative addition of molecular hydrogen to Rh(I) species.[5] It is therefore deduced that treatment of Rh(III) complexes with borohydride (which can also act as a source for hydrogen[6]) can result in a di- or monohydridorhodium(III) complex depending upon the nature of the ligands. However, hydrido species could not be formed from Rh(III) complexes by treatment with other reducing agents like sodium amalgam, hypophosphorus acid or molecular hydrogen.[4] It is likely, therefore, that the active hydrogenating polymer-anchored catalysts can contain Rh(III) hydrido species. The reports available in the literature[2] have unfortunately identified this species as Rh(I) on the basis of a low value ($\sim$308 eV) of the binding energy of the Rh $3d_{5/2}$ emission. Furlani *et al.*[7] have analysed the XPS data of a number of rhodium compounds and have shown that: (i) the binding energy as well as the FWHM of Rh $3d$ line is strongly dependent on the nature and the number of co-ordinating species, and (ii) the rhodium species on the polymer surfaces are predominantly in the higher oxidation state. The lower binding energy values for Rh $3d_{5/2}$ ($\sim$308 eV) observed for these species could arise from: (i) the initial-state chemical shifts resulting from the nature of the ligands, and (ii) the final-state relaxation shifts whose contribution could be significant especially in view of the extended nature of the polymer backbone used.

Borane generated during borohydride treatment[6] could also bind to the polymer (the presence of highly charged boron species is also reported in polymer-bound nickel catalysts[8]) and can activate the olefin. This could also account, at least partially, for the hydrogenation activity observed.

The hypotheses proposed in this letter, however, await further support from IR data of the active catalyst for ν_{B-H} (2300–2500 cm^{-1}), ν_{Rh-H} (1700–2200 cm^{-1}) and $\nu_{Rh-H-Rh(bridged)}$ (1150 cm^{-1}).[9]

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†Even though metallic rhodium is effective for the hydrogenation of olefins,[3] its role on polymer-anchored systems without elution is doubtful. In addition, the existence of Rh(0) was never identified by XPS.[2]

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