Preparation and Catalytic Activities of Supported Nickel Clusters on a Silica Surface

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Summary Active supported nickel clusters were prepared by pyrolysis of di- and tri-nickel cyclopentadienyl carbonyl cluster compounds dispersed on silica gel and Vycor glass; they exhibited specific H_2 and CO adsorption and catalytic activity for olefin hydrogenation and the 'oxo' reaction.

SUPPORTED nickel clusters chemically bound to a silica surface have been prepared by evacuation at 80—120 °C of deposited nickel cyclopentadienyl cluster compounds such as $[Cp_2Ni]$, $[Cp_2Ni_2(CO)_2]$, and $[Cp_3Ni_3(CO)_2]$ (Cp = η^5-C_5H_5). Each nickel complex was highly dispersed (0·1—0·5 Ni wt %) on silica gel (Aerosil, surface area 200—380 m^2 g^{-1}) or Vycor glass (no. 7930, surface area 240 m^2 g^{-1}, 3 × 15 mm rod) from a solution in tetrahydrofuran by evaporation. Upon raising the temperature to 120 °C, the nickel cluster compounds readily reacted with surface SiOH to produce a stoicheiometric amount of cyclopentadiene and CO, confirmed quantitatively by mass spectrometry and gas chromatography. The i.r. spectra of $[Ni_3Cp_3(CO)_2]$ (silica disc) showed peaks at 1750 cm^{-1} (three-centred CO), and 800 and 650 cm^{-1} (Cp). Upon evacuation at 120 °C, these absorptions decreased and disappeared completely after 0·5 h, and the broad peaks of surface SiOH at *ca.* 3750 and 3650 cm^{-1} decreased considerably. When CO (100 Torr) was admitted at 25 °C on to the resultant silica disc after evacuation, the characteristic three-centred CO absorption reappeared only in the 1740 cm^{-1} region. Moreover, a strong e.s.r. signal ($g_\perp$ $2·02_6$ and $g_\parallel$ $2·13_4$) was observed, over the range −150 to 25 °C, upon introducing CO (5–100 Torr) on to the supported nickel cluster prepared from $[Ni_3Cp_3(CO)_2]$ with silica gel and Vycor glass. This signal

resembles that of the parent cluster compound[1] (Figure). These results suggest that the supported nickel atoms retain a three-centred disposition similar to that in the parent complex. From volumetric measurements for H_2 and CO adsorption on the supported nickel clusters prepared from di- and tri-nickel cyclopentadienyl complexes with silica gel, it was found that the adsorption took place homogeneously with final adsorption stoicheiometries, $H_{ads}/Ni_{total} = 1{\cdot}98$ and 1·1 and $CO_{ads}/Ni_{total} = 2{\cdot}0$ and 0·67 for Ni_2 and Ni_3 complexes respectively, on silica.

Acetylene readily trimerized to benzene at room temperature (75% yield in 2 h) over the dispersed Ni from $[NiCp_2]$ on silica gel (0·5 Ni wt %). However, the acetylene oligomerization did not proceed at 25—120 °C over supported nickel atoms from $[Ni_2Cp_2(CO)_2]$ and $[Ni_3Cp_3(CO)_2]$ on silica gel. Instead almost 1 mol of acetylene per mol of Ni_2 and Ni_3 units were adsorbed, and the pale grey samples rapidly became red or violet, which may imply the formation of acetylene cluster complexes analogous to $[Ni_2Cp_2(RC{\equiv}CR)]$. In contrast, H_2–D_2 exchange and hydrogenation of ethylene and benzene occured readily at room temperature over the supported di- and tri-nickel aggregates. When a 1:1:1 mixture of H_2, CO, and C_2H_4 (1 atm) was admitted on to supported nickel cluster catalysts which had been prepared by pyrolysis of $[Ni_2Cp_2(CO)_2]$ and $[Ni_3Cp_3(CO)_2]$ (0·1 g) deposited on silica gel (5 g) propionaldehyde was obtained in low yield at 50—100 °C. Upon raising the temperature to 120 °C, a considerable amount of $[Ni(CO)_4]$ was formed, and the 'oxo' reaction activity decreased in several runs. The 'oxo' reaction did not proceed over the mono-atomically dispersed Ni catalyst obtained from $[NiCp]_2$ on silica gel even in the presence of $[Ni(CO)_4]$ under similar conditions.

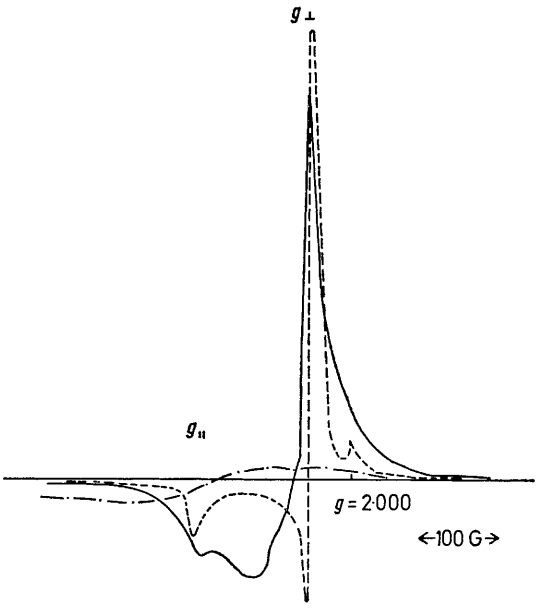

FIGURE. E.s.r. spectra of: ———— $[Ni_3Cp_3(CO)_2]$ on silica gel (0·3 Ni wt % dispersion), $g_\perp$ $2{\cdot}02_6$, $g_\parallel$ $2{\cdot}12_6$; — — — — — after evacuation at 10^{-4} Torr, and 120 °C for 10 min; – – – – – – by admitting CO (100 Torr) on to the resultant sample at 25 °C for 5 min; $g_\perp$ $2{\cdot}02_6$, $g_\parallel$ $2{\cdot}13_4$.

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