A Stable Supported Re Metathesis Catalyst derived from $[Re(CO)_3OH]_4$ on SiO_2

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An active, stable supported rhenium catalyst for alkene metathesis was formed by heating $[Re(CO)_3OH]_4$ on SiO_2 under a propene–helium atmosphere at 423 K.

Supported metals derived from organometallic compounds are a new class of catalyst, some having activities as much as 10^8 times as great as their conventionally prepared analogues.[1—3] Thermal activation of supported molecular species can produce metal catalysts with otherwise unattainable co-ordination environments and oxidation states; even Mo^0–Al_2O_3 has been isolated.[3] Here we report the first active and stable SiO_2-supported rhenium catalyst for alkene metathesis, prepared by the thermal activation of a surface complex derived from $[H_4Re_4(CO)_{12}]$.

$[H_4Re_4(CO)_{12}]$,[4] a co-ordinatively unsaturated Re^0 cluster, reacted with adsorbed water on the surface of SiO_2 (Cabosil) in reluxing n-octane to yield supported $[Re(CO)_3OH]_4$. This conclusion is drawn from the close agreement between the i.r. and electronic absorption spectra of the $[H_4Re_4(CO)_{12}]$-derived surface species and those of $[Re(CO)_3OH]_4$[5] and the surface complex prepared by bringing $[Re(CO)_3OH]_4$ directly from a refluxing n-octane solution onto SiO_2 (Figures 1 and 2). Formation of the hydroxo rhenium complex was not observed in the absence of water on the SiO_2. We infer that SiO_2 donated electrons to the unsaturated metal framework to fragment the hydrido cluster into mononuclear rhenium carbonyls, which react with surface water to form $[Re(CO)_3OH]_4$.[†]

The carbonyl complex could be extracted from the surface with tetrahydrofuran (THF) or alcohols, with yields >93%. We infer that a new synthetic route to this complex is opened up by the surface reactivity. Close agreement was observed between the spectra of the extract solutions and the spectra of $[Re(CO)_3OH]_4$ in solution (Figures 1 and 2). The ^1H n.m.r. spectrum of a $[^2H_4]$methanol extract (after subtraction of the solvent spectrum) exhibited a single resonance at δ 6.16, and a comparison with the value for $[Re(CO)_3OH]_4$ (δ 6.12) confirms the identification of $[Re(CO)_3OH]_4$ as the species extracted from the surface. Non-donor solvents did not remove the surface complex, and we infer that the predominant mode of surface attachment is hydrogen bonding involving the OH groups of the complex and those of the SiO_2 surface.

Catalytic reaction experiments were carried out with the $[H_4Re_4(CO)_{12}]$-derived surface complex in a flow reactor operating at atmospheric pressure with on-line gas chromatographic analysis of the products. The catalyst was active for the methathesis of propene, giving ethene and but-2-ene in equal proportions at 423 K. In a typical experiment, the catalyst [100 mg; 3.3 wt% Re] was subjected to alternating flows of He (0.25 $cm^3\ s^{-1}$) and propene (0.15 $cm^3\ s^{-1}$) + He (0.1 $cm^3\ s^{-1}$) at 423 K for approximately one week until the catalytic activity reached a steady state. No deactivation was observed during the balance of an experiment (5 days). The i.r. spectrum of the working catalyst was at first identical to that of the original catalyst; the spectrum after 12 days use was the same, except that the intensities of the peaks indicative of the Re complex were reduced relative to the SiO_2 peak at 1865 cm^{-1}.

[†] Re supported on oxides gives high yields of alcohols in the catalytic hydrogenation of CO.[6] The i.r. spectrum of the used catalyst (ν_{CO} 2030 and 1920 cm^{-1}) has recently been reported.[7] Our results identify the surface species as $[Re(CO)_3OH]_4$, one of several possible structures suggested before.[7]

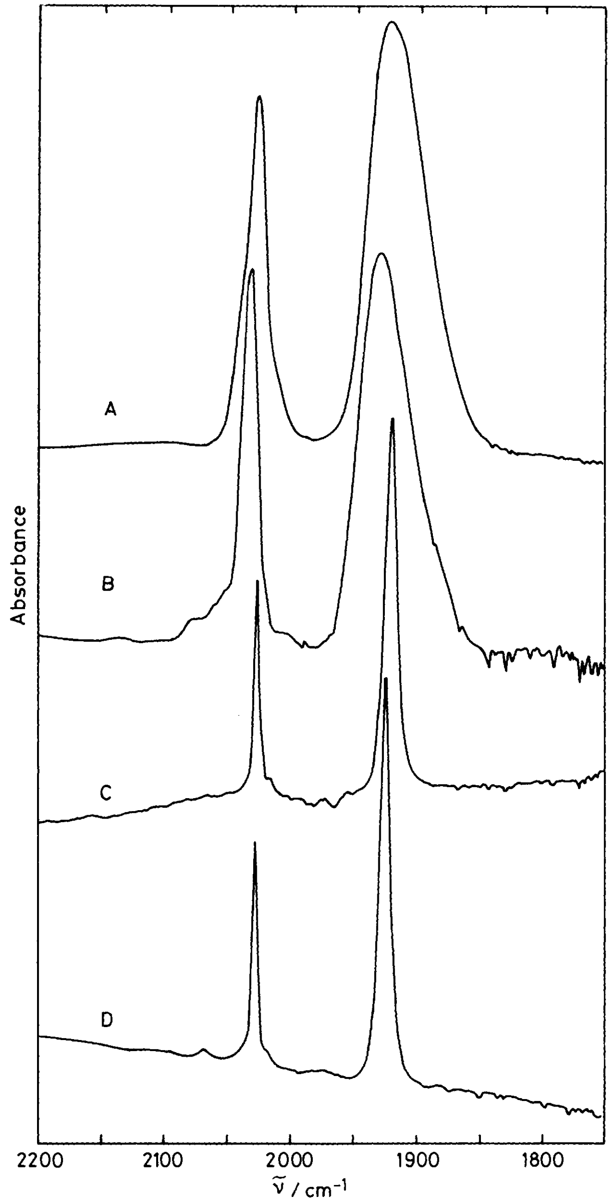

Figure 1. I.r. spectra in the ν_{CO} region of complex derived from $[H_4Re_4(CO)_{12}]$ (A) and $[Re(CO)_3OH]_4$ (B) supported on SiO_2; (C) THF extract of the $[H_4Re_4(CO)_{12}]$-derived complex; (D) $[Re(CO)_3OH]_4$ in THF.

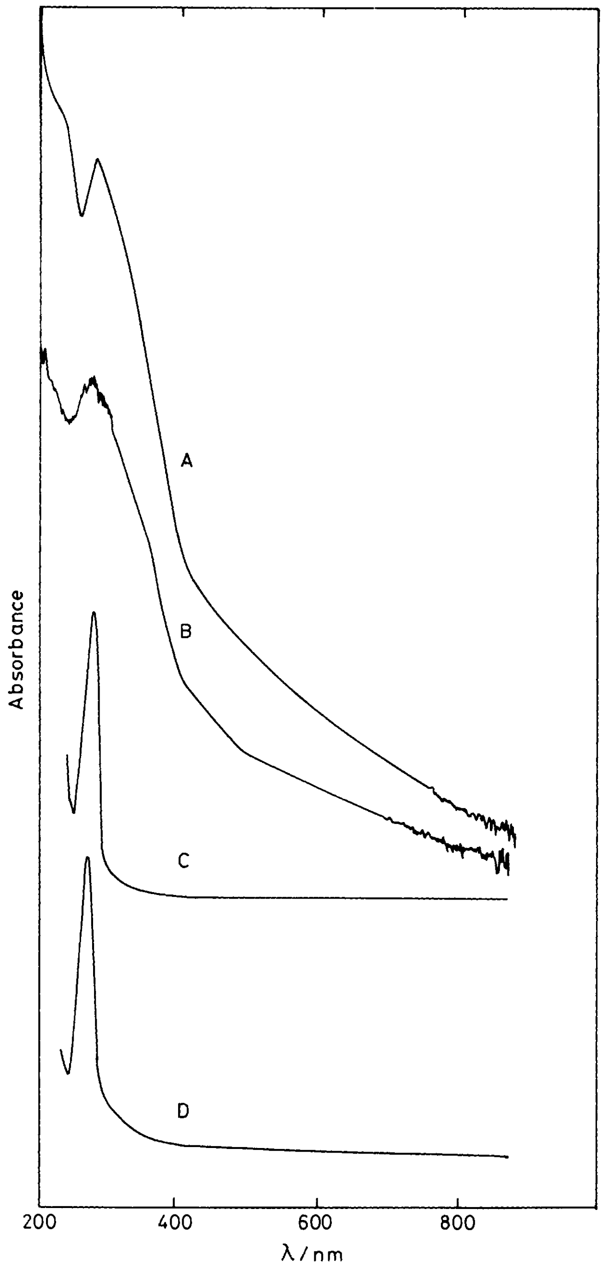

Figure 2. Electronic absorption spectra of complex derived from $[H_4Re_4(CO)_{12}]$ (A) and $[Re(CO)_3OH]_4$ (B) supported on SiO_2; (C) THF extract of the $[H_4Re_4(CO)_{12}]$-derived complex; (D) $[Re(CO)_3OH]_4$ in THF.

The metathesis reaction was first order in propene with an apparent activation energy of 48.4 kJ/mol; these values and the rate of reaction [4.0 × 10^{-6} mol (g of Re)$^{-1}$ s^{-1}] observed at steady state at 423 K and with 60 kPa of propene + 40 kPa of He are approximately equal to those observed with a conventional catalyst represented as Re_2O_7/Al_2O_3.[8,9]

The steady-state catalytic activity demonstrated by the SiO_2-supported $[H_4Re_4(CO)_{12}]$-derived catalyst is a new result. SiO_2-supported rhenium catalysts prepared in ways reported heretofore are unstable, rapidly losing activity for alkene metathesis at temperatures up to 453 K; it has been presumed that SiO_2 does not stabilize the necessary intermediate oxidation state of rhenium.[9,10] The similarities in the metathesis kinetics observed with the new catalyst and the Al_2O_3-supported catalyst suggest that the same Re species were the catalytically active sites in each; the i.r. spectra indicate that these species were only a small fraction of the supported Re on SiO_2, and the literature indicates that <1% of the Re on Al_2O_3 is catalytically active.[9,10] We infer that the reservoir of stable $[Re(CO)_3OH]_4$ precursor on the surface equilibrates with the active, oxidized Re species, providing the key to catalyst stability.

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