Synthesis and Characterisation of an Alumina–supported $RuOs_3$ Cluster Catalyst

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The alumina-supported anion cluster $Al^+[H_3RuOs_3(CO)_{12}]^-$ was formed by heating $[H_2RuOs_3(CO)_{13}]$ adsorbed on γ-Al_2O_3 to 373—473 K under an H_2 + CO atmosphere; the material is catalytically active for ethylene hydrogenation at 340 K and for but-1-ene isomerization at 330 K.

Supported metals with molecular structures are a new class of catalyst; the uniformity of their metal centres provides opportunities for determining fundamental structure–catalytic property relationships and possibly even for highly selective catalysis.[1–3] Most supported metal clusters, however, are unstable, forming structurally complex and non-uniform metal aggregates. Here we describe the synthesis, characterisation by i.r. spectroscopy, and catalytic activity of Al_2O_3-supported anion clusters, $Al^+[H_3RuOs_3(CO)_{12}]^-$, which are stable at 473 K under H_2 + CO.

The cluster $[H_2RuOs_3(CO)_{13}]$ was prepared by the literature method[4] [i.r. (hexane): ν(CO), 2081vs, 2066vs, 2056vs, 2028m, 2023m, 2017s, 2007w, and 1867w(br.) cm^{-1}]. This cluster was adsorbed from dry hexane solution onto Degussa γ-Al_2O_3-C (100 m^2/g), previously dried at 473 K under vacuum (10^{-6} Torr, 2 h). Total metal loadings as great as 0.89 wt% were obtained. The following results suggest that an anionic cluster carbonyl was formed on the surface. (i) The i.r. spectrum of the initially adsorbed cluster [Figure 1(a)] shows a shift of the carbonyl bands to lower wavenumbers relative to the bands of the unsupported cluster; (ii) the i.r. spectrum of the related anion cluster $[HRu_4(CO)_{13}]^-$ in tetrahydrofuran shows ν(CO) at 2020s, 2000s, 1970m(sh.), and 1850w(br.) cm^{-1};[5] and (iii) no CO, H_2, or CO_2 evolution was detected during the adsorption.

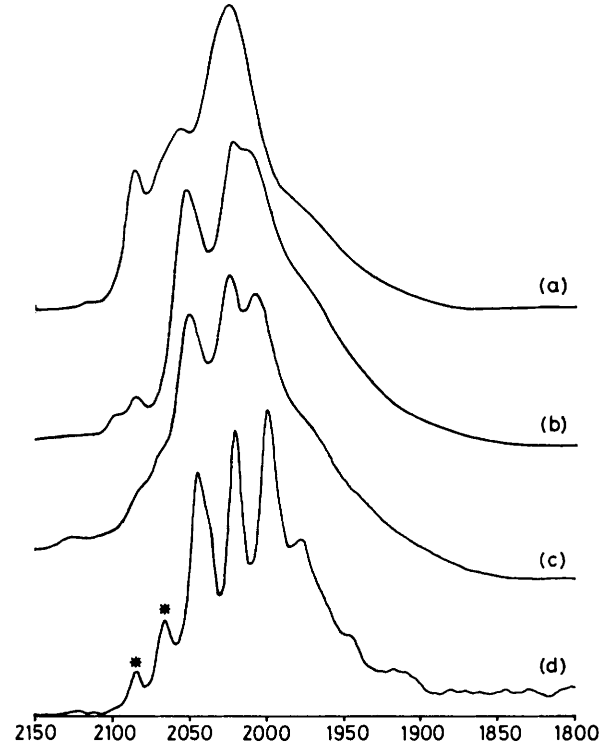

Figure 1. I.r. spectra in ν_{CO} region of $[H_2RuOs_3(CO)_{13}]$ adsorbed from hexane solution, at room temperature, onto γ-Al_2O_3, previously dried at 473 K under vacuum: (a) the initially adsorbed material; (b) after heating at 473 K under H_2 + CO (1 : 1) at atmospheric pressure; (c) sample exposed to air after heating at 473 K under H_2 + CO; and (d) material extracted into a solution of Ph_4AsCl in CH_2Cl_2 after a H_2 + CO treatment at 473 K. The peaks marked with (*) at 2085 and 2065 cm^{-1} are attributed to a small amount of $[H_4RuOs_3(CO)_{12}]$.

We tentatively assign the 2023 and 1980(sh.) cm^{-1} peaks in Figure 1(a) to $[HRuOs_3(CO)_{13}]^-$. The remaining peaks are assigned to a small amount of the starting cluster, since these diminished in intensity with time. The surface reaction is therefore suggested to be that shown in equation (1). Similar reactions have been proposed to explain the adsorption of $[H_4Ru_4(CO)_{12}]$ and $[HFeCo_3(CO)_{12}]$ on γ-Al_2O_3.[6]

$$Al\text{–}OH + H_2RuOs_3(CO)_{13} \xrightarrow{-H_2O} Al^+[HRuOs_3(CO)_{13}]^- \quad (1)$$

When $[H_2RuOs_3(CO)_{13}]$ physisorbed on γ-Al_2O_3 was heated under an equimolar H_2 + CO mixture at atmospheric pressure and 373—473 K, an i.r. spectrum indicating a new surface species was obtained [Figure 1(b)]. Exposure of the sample to air altered the spectrum slightly [Figure 1(c)], but the changes were reversed by evacuating the sample or reheating it under H_2 + CO; the i.r. spectrum of the surface species is apparently sensitive to moisture. The organometallic species on the support could be extracted into a solution of tetraphenylarsonium chloride in dichloromethane. The i.r. spectrum of the extracted complex is shown in Figure 1(d).

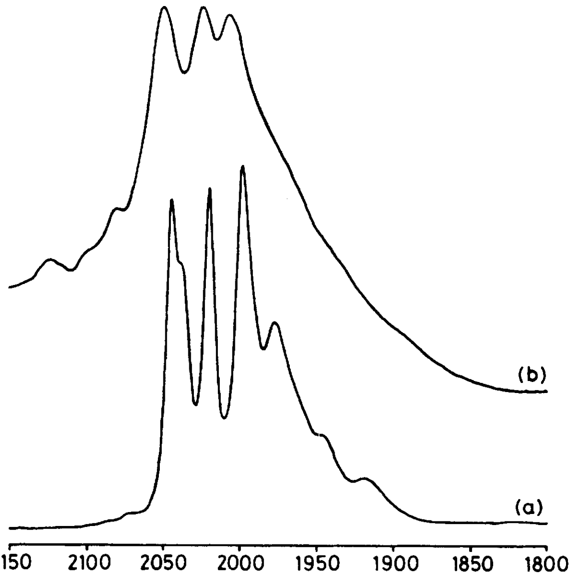

Figure 2. I.r. spectra in ν_{CO} region of $(Ph_4As)[H_3RuOs_3(CO)_{12}]$: (a) in CH_2Cl_2 solution and (b) adsorbed onto γ-Al_2O_3 from ethanol solution.

We infer that the new surface species was the anion cluster $[H_3RuOs_3(CO)_{12}]^-$. To test the inference, we have independently prepared and isolated the tetraphenylarsonium salt of $[H_3RuOs_3(CO)_{12}]^-$, as follows (the method of preparation followed that for the related complexes $[H_3Ru_4(CO)_{12}]^-$ and $[H_3Os_4(CO)_{12}]^-$[7]): $[H_2RuOs_3(CO)_{13}]$ was refluxed in octane under H_2 to give $[H_4RuOs_3(CO)_{12}]$, which was treated with 1 equiv. of KOH in absolute ethanol at 328 K. Ph_4AsCl hydrate in ethanol was then added to precipitate $(Ph_4As)[H_3RuOs_3(CO)_{12}]$ in 52% yield {i.r. (CH_2Cl_2): ν_{CO}, 2044s, 2040(sh.), 2020s, 1999s, 1976m, 1946w, and 1918w cm^{-1}; ^1H n.m.r. $[(CD_3)_2CO]$ at 298 K: δ 7.97 (m, 20H, Ph) and -18.7 (br., 3H, H^-)}. The close similarity in the i.r. and n.m.r. spectra of $(Ph_4As)[H_3Ru_4(CO)_{12}]$ and $(NMe_4)[H_3Os_4(CO)_{12}]$ suggests that they are structurally related.[8]

The i.r. spectra of $(Ph_4As)[H_3RuOs_3(CO)_{12}]$ in CH_2Cl_2 solution and physisorbed onto γ-Al_2O_3 from ethanol solution are shown in Figure 2. These spectra correspond almost exactly with those shown in Figures 1(c) and (d) and therefore confirm the identification of $[H_3RuOs_3(CO)_{12}]^-$ as the surface species obtained from $[H_2RuOs_3(CO)_{13}]$ adsorbed on γ-Al_2O_3. Further, the results of Figure 1(d) show that it is possible to extract the *intact* cluster from the γ-Al_2O_3 support after treatment at 473 K under H_2 + CO; this result demonstrates a remarkable stability of surface-bound $[H_3RuOs_3(CO)_{12}]^-$ under these conditions.

The surface cluster $Al^+[H_3RuOs_3(CO)_{12}]^-$ was relatively stable when heated at temperatures up to 373 K under vacuum. At higher temperatures, however, cluster decomposition occurred to give oxidized osmium[9] and ruthenium[6,10] carbonyl species. The much greater thermal stability of $Al^+[H_3RuOs_3(CO)_{12}]^-$ in the presence of H_2 + CO is inferred to be an indication that these reactants maintain the ligand environment of the cluster and thereby prevent the oxidative reaction with surface hydroxy-groups.[9] At 573 K cluster decomposition occurred in the presence of H_2 + CO.

Preliminary catalytic reaction experiments were carried out with $Al^+[H_3RuOs_3(CO)_{12}]^-$ in a flow reactor operating at atmospheric pressure with on-line g.c. analysis of products. The material was catalytically active for ethylene hydrogenation at 340 K [$H_2/C_2H_4 = 2$; rate *ca.* 2×10^{-4} (molecules of C_2H_6)/(cluster s)] and but-1-ene isomerization at 330 K [rate *ca.* 4×10^{-3} (molecules of butene isomerized)/(cluster s)]. *In situ* i.r. experiments indicated that $Al^+[H_3RuOs_3(CO)_{12}]^-$ was stable under the reaction conditions and was the only detectable metal carbonyl species.

In summary, the results demonstrate the remarkable stability of $[H_3RuOs_3(CO)_{12}]^-$ on γ-Al_2O_3 and its potential use for the investigation of metal-cluster catalysis over a wide range of conditions. The stability at 473 K under H_2 + CO may offer an opportunity to assess the CO hydrogenation activity of an intact bimetallic cluster.

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References

1 J. Evans, *Chem. Soc. Rev.*, 1981, 159.
2 D. C. Bailey and S. H. Langer, *Chem. Rev.*, 1981, **81**, 109.
3 B. C. Gates and J. Lieto, CHEMTECH, 1980, **10**, 195, 248.
4 E. W. Burkhardt and G. L. Geoffroy, *J. Organomet. Chem.*, 1980, **198**, 179.
5 C. C. Nagel and S. G. Shore, *J. Chem. Soc., Chem. Commun.*, 1980, 530.
6 V. L. Kuznetsov, A. T. Bell, and Y. I. Yermakov, *J. Catal.*, 1980, **65**, 374.
7 S. A. R. Knox, J. W. Koepke, M. A. Andrews, and H. D. Kaesz, *J. Am. Chem. Soc.*, 1975, **97**, 3942, 3947; B. F. G. Johnson, J. Lewis, P. R. Raithby, G. M. Sheldrick, K. Wong, and M. McPartlin, *J. Chem. Soc., Dalton Trans.*, 1978, 673.
8 P. F. Jackson, B. F. G. Johnson, J. Lewis, M. McPartlin, and W. J. H. Nelson, *J. Chem. Soc., Chem. Commun.*, 1978, 920; B. F. G. Johnson, J. Lewis, P. R. Raithby, and C. Zuccaro, *Acta Crystallogr., Sect. B*, 1978, **34**, 3765.
9 R. Psaro, R. Ugo, G. M. Zanderighi, B. Besson, A. K. Smith, and J. M. Basset, *J. Organomet. Chem.*, 1981, **213**, 215; M. Deeba and B. C. Gates, *J. Catal.*, 1981, **67**, 303; H. Knözinger and Y. Zhao, *ibid.*, 1981, **71**, 337.
10 A. Zecchina, E. Guglielminotti, A. Bossi, and M. Camia, *J. Catal.*, 1982, **74**, 225, 240, 252.