Clusters as Models for Surface Catalysis: a Model for Sulfide Effects on Pt–Re Catalysts

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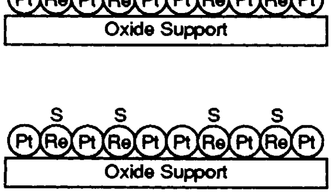
By reaction with propene sulfide, one or two sulfur atoms are added to the tetrahedral cluster cation $[Pt_3\{Re(CO)_3\}(\mu\text{-dppm})_3]^+$ **1** (dppm = $Ph_2PCH_2PPh_2$), to give $[Pt_3\{Re(CO)_3\}S_n(\mu\text{-dppm})_3]^+$ (n = 1, **2**; n = 2, **3**); the reactions provide an interesting model for sulfidation of heterogeneous Pt–Re catalysts.

Supported bimetallic catalysts, of which Pt–Re on alumina is a prime example, are important in selective reforming of petroleum. In industrial practice, the supported Pt–Re catalyst is sulfided before use.[1] It is thought that the Re atoms at the surface are converted to ReS units and the rhenium centres are then deactivated. The ReS units then act as an inert diluent and serve to reduce the size of local ensembles of platinum atoms, as illustrated in Scheme 1. In turn, this reduces hydrogenolysis of alkanes, since this reaction requires several adjacent, active platinum atoms. Hence, the catalysts are more selective for the desirable dehydrocyclization and isomerization reactions which increase the octane rating of the petroleum. The theory is based mostly on catalytic properties, but there is also some direct evidence for selective sulfidation of rhenium.[2] Here we report the first cluster model for the sulfidation of the Pt–Re catalysts.

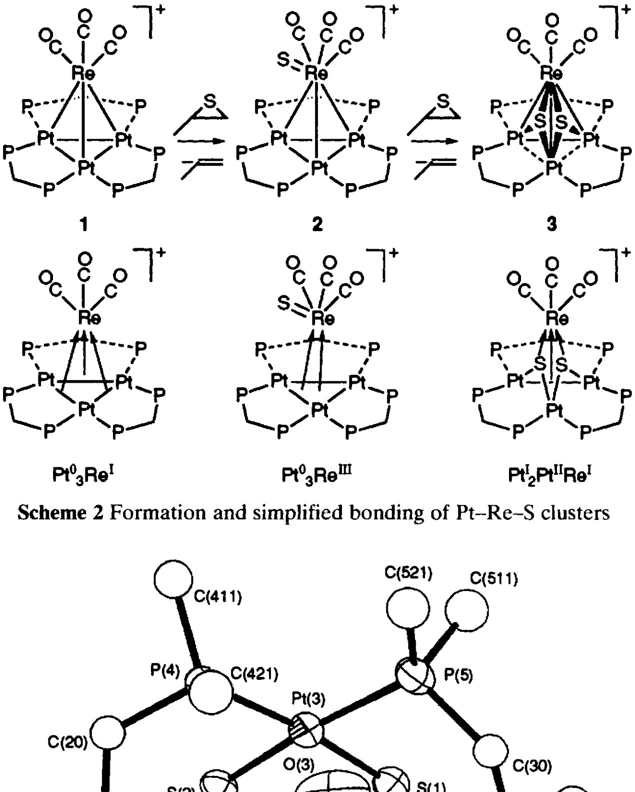
The cluster cation $[Pt_3\{Re(CO)_3\}(\mu\text{-dppm})_3]^+$ **1** is coordinatively unsaturated and, in principle, can add ligands to Re or at the Pt_3 or Pt_2Re faces of the tetrahedral cluster.[3,4] Reaction of the cluster with one or two equiv. of propene sulfide gave propene and the new clusters $[Pt_3\{Re(CO)_3\}S_n(\mu\text{-dppm})_3]^+$ **2** and **3** with n = 1 and 2, respectively (Scheme 2, complexes isolated as $[PF_6]^-$ salts). These reactions occur under very mild conditions; thus the reaction to give **2** occurs at −90 °C in CH_2Cl_2 solution, and they represent the first examples of sulfur atom addition to Pt–Re clusters.

Complex **3** is indefinitely stable in air at room temperature and is unreactive towards further sulfur atom addition. It has been characterized both spectroscopically and by an X-ray structure determination (Fig. 1).† The addition of the two sulfur atoms to **1** leads to an increase in the cluster electron count from 54 to 62 electrons in **3** and there is a large increase in metal–metal distances. The distances Pt(3)···Re = 3.625(2), Pt(3)···Pt(1) = 3.720(2), Pt(3)···Pt(2) = 3.213(2) Å are too long for significant bonding, and so Pt(3) appears to have square planar PtP_2S_2 coordination only. The other metal–metal distances Pt(1)–Pt(2) = 3.038(2), Pt(1)–Re = 2.946(2), Pt(2)–Re = 3.002(2) Å are also long, especially when compared to the average Pt–Pt and Pt–Re distances of 2.60 and 2.67 Å respectively in **1**,[3] indicating weak metal–metal bonding within the Pt(1)Pt(2)Re triangle.[3] According to the simple bonding model shown in Scheme 2, the formal metal oxidation states in **3** may be considered to be $Re^IPt^I_2Pt^{II}$.

Complex **2** was more difficult to characterize.‡ It reacted easily with propene sulfide to give **3**, and was oxidized slowly in air with loss of the sulfide ligand to give the known compound $[Pt_3\{Re(CO)_3\}(\mu_3\text{-}O)_2(\mu\text{-dppm})_3]^+$.[3] The ^{31}P NMR spectrum of **2** at 20 °C gave a singlet due to the dppm phosphorus atoms, but this split into six broad resonances at −90 °C; the coalescence temperature was *ca.* −60 °C, indicating a low activation energy for fluxionality. These data are consistent with structure **2**, with a terminal Re=S group in a low symmetry conformation, but not with the alternative structure $[Pt_3\{Re(CO)_3\}(\mu_3\text{-}S)(\mu\text{-dppm})_3]^+$, since the μ_3-S group would prevent rotation of the $Re(CO)_3S$ group needed to give the observed fluxionality. Terminal Re=S groups are well known, *e.g.* in the complex $[(S_4)_2ReS]^-$.[5] The Re 4f(7/2) XPS binding energies (Table 1) follow the sequence **2** > **3** > **1**, indicating initial oxidation at Re as the terminal Re=S group is formed, but primarily oxidation at platinum when the μ_3-S groups are formed. Similarly, for silica-supported Pt–Re catalysts, sulfidation was found to cause an increase in the



Scheme 1 Schematic illustration of Pt–Re catalysts before and after sulfidation



Scheme 2 Formation and simplified bonding of Pt–Re–S clusters

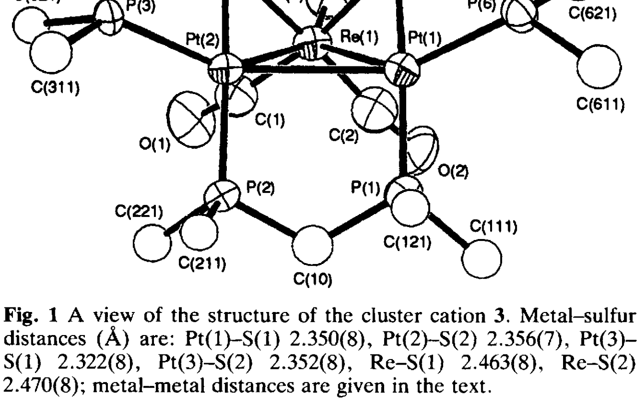


Fig. 1 A view of the structure of the cluster cation **3**. Metal–sulfur distances (Å) are: Pt(1)–S(1) 2.350(8), Pt(2)–S(2) 2.356(7), Pt(3)–S(1) 2.322(8), Pt(3)–S(2) 2.352(8), Re–S(1) 2.463(8), Re–S(2) 2.470(8); metal–metal distances are given in the text.

Table 1 Comparison of XPS binding energies (eV) in Pt–Re catalysts and model clusters

	Re 4f(7/2)	Pt 4f(7/2)
Pt-Re-SiO_2[a]	40.7	72.0
Pt-Re-S-SiO_2[a]	40.8[b]	72.1
1	41.6	72.6
2	42.0	72.8
3[c]	41.7	73.0

[a] From ref. 2. [b] This is the value for non-sulfided Re; about 20% of the peak was shifted to higher binding energy and this component is thought to be due to the Re═S groups. [c] Separate binding energies for the non-equivalent platinum centres were not resolved.

rhenium binding energy instead of platinum (Table 1), and so it was concluded that sulfidation occurred at rhenium and that terminal Re–S entities were formed.[2] The formal metal oxidation states in **2** may be considered to be $Re^{III}Pt^{0}_3$ (Scheme 2) and, although it is an extreme formulation, it does serve to rationalize the XPS binding energy trend shown in Table 1.

If the cluster–surface analogy holds, then it can be predicted on the basis of the above discussion that sulfidation of supported Pr–Re catalysts will occur initially at rhenium but that the sulfide is likely to be most stable as a surface μ_3-S ligand with $Pt_2Re(\mu_3\text{-}S)$ groups. In this way a surface sulfide is likely to deactivate towards catalysis not only the surface rhenium atoms but also the immediately adjacent surface platinum atoms, and so rationalize the sulfur effect on the Pt–Re catalysts at low sulfur coverage.[6] Thus, this model system supports and adds new detail to the current interpretation of the role of sulfidation of supported Pt–Re catalysts.

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Footnotes

† *Selected data* for **3**: IR (Nujol): ν(CO)/cm^{-1} 1979s, 1885s, 1863s. NMR data: ^{1}H δ 3.53 [2H, CH_2], 4.00 [2H, CH_2], 4.85 [1H, CH_2], 6.54 [1H, CH_2]; ^{31}P δ 14.8 [s, $^1J_{PtP}$ = 3850, $^2J_{PtP}$ 40, $^2J_{PaPa}$ 57 Hz, P^a], 2.6 [m, $^1J_{PtP}$ 3038, $^2J_{PtP}$ = 632, $^3J_{PbPb}$ 167 Hz, P^b], 15.6 [s, $^1J_{PtP}$ 2987 Hz, P^c].

Crystal data for **3**[PF_6]·acetone: monoclinic, $P2_1/n$, a = 17.321(4), b = 23.890(6), c = 19.932(3) Å, β = 94.36(1), V = 8224(3) Å^3, Z = 4, λ(Mo-Kα) = 0.71073 Å, μ = 0.65 mm^{-1}, D_c = 1.838, T = 290 K. A total of 12032 intensities of which 5137 with $F_0 > 4\sigma F_0$ were considered observed, were collected in the range $3.5 < 2\theta < 45°$ on a Siemens P4 four circle diffractometer. The data processing solution and refinement were carried out using SHELXTL-PC programs,[7] refinement proceeded to R = 0.064, R_w = 0.059. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

‡ *Selected data* for **2**: IR: ν(CO)/cm^{-1} 1979s, 1874s, 1850sh. NMR: 20 °C, ^{31}P δ −4.0 [s, $^1J_{PtP}$ 2700, $^2J_{PtP}$ 600, $^3J_{PP}$ 170 Hz, dppm]; −90 °C, ^{31}P δ −16, −11, −7.7, −5, 6.3, 8.5 [m, dppm]. Coalescence temperature −60 °C.

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