A Reversible Mo_2–O_2 Complex Chemically Fixed on an SiO_2 Surface

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The first reversible Mo_2–O_2 complex chemically fixed on a silica surface, which provides an example of a new class of oxygen carrier, and its oxidation activity are reported.

The syntheses and chemical properties of reversible dioxygen complexes of metals such as Co,[1] Fe,[2] Ru,[3] Pd,[4] Cu,[5] etc.,[1] have attracted much attention in relation to oxygen carriers in bio-organisms as well as fundamental aspects of catalytic oxidation. We report the first example of a reversible dioxygen complex of molybdenum chemically fixed on a silica surface and also the reactivities of the complexed dioxygen with NO, CO, and cyclohexene.
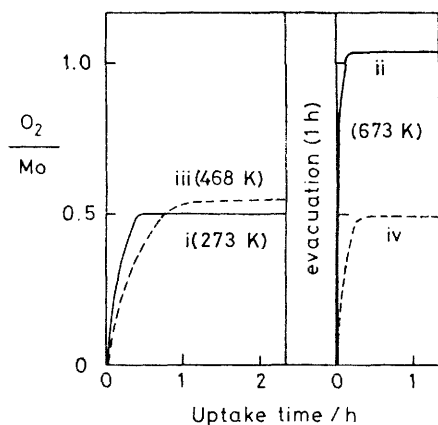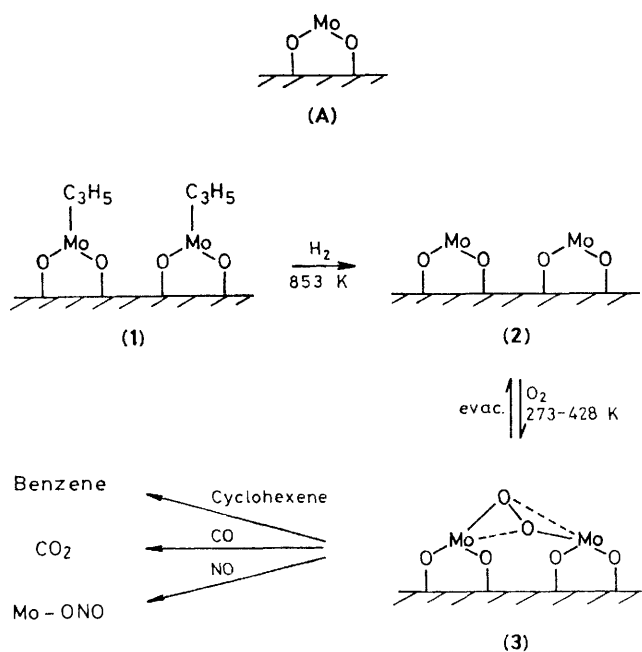
Figure 2. Langmuir plots for reversible O_2 uptake on the Mo_2 structure (2) according to the equation $(O_2/Mo_2)^{-1} = 1 + K_{eq}^{-1}$-$P(O_2)^{-1}$, where (O_2/Mo_2) represents the fraction of saturation at equilibrium.

Figure 1. O_2 uptake on the paired Mo^{II}_2 structure (2): step a, ——, i, O_2 (100 Torr) at 273 K followed by evacuation at 273 K for 1 h, then ii, O_2 (70 Torr) at 673 K; step b, — — —, iii, O_2 (70 Torr) at 468 K followed by evacuation at 468 K for 1 h, then iv, O_2 (70 Torr) at 673 K.

It has been demonstrated that the group 6A metals form mononuclear metal–oxygen or –dioxygen complexes irreversibly[6] and that SiO_2- or Al_2O_3-supported low-valent molybdenum ions, including the 'single' Mo^{II} species (A),[7] are instantaneously and irreversibly oxidized with dioxygen at 273 K.

We have found that the 'paired' Mo^{II}–Mo^{II} structure (2) chemically fixed on an SiO_2 surface reversibly binds dioxygen in the temperature range 273—428 K. The paired Mo_2 structure (2) ($Mo/SiO_2 = 0.68$ wt%) was prepared from the surface complex (1) which was synthesized by the reaction between $Mo_2(\eta^3$-$C_3H_5)_4$[8] and surface OH groups of SiO_2 [obtained from colloidal silica-30 (Nissan Kagaku Inc.), 3.5 OH/nm^2, 120 m^2/g] at 273 K in a flow of high-purity argon (99.9995%) or in vacuo.[9] The occurrence of a direct interaction between the adjacent Mo ions, in the hexavalent state, was shown by photoluminescence studies.[9] The dioxygen uptake at 273 K reached equilibrium within 25 min as shown in Figure 1, while the co-ordinated dioxygen was com-
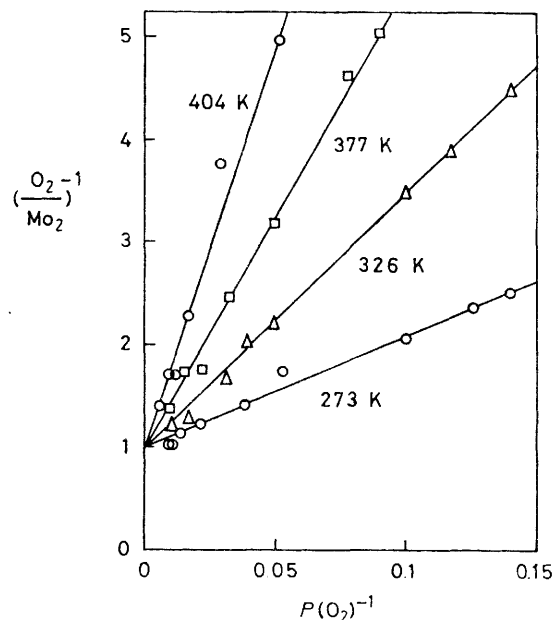
pletely desorbed within 15 min in vacuo. Irreversible uptake started at about 455 K to form the paired oxomolybdenum(IV) species, with stoicheiometric uptake at 673 K to give the Mo^{VI} species, as shown in Figure 1.

Figure 2 shows typical Langmuir plots for reversible dioxygen uptake at 273, 326, 377, and 404 K. The linear relations and the mass adsorbed at saturation which was independent of temperature indicate that one molecule of dioxygen co-ordinates to one Mo^{II}-pair. The reversible dioxygen complex was diamagnetic, as shown by e.s.r. studies. Thus the surface complex (3) may be represented formally as Mo^{3+}–$O_2{}^{2-}$–Mo^{3+}.

ΔH^0 and ΔS^0 for the process were calculated to be -14 kJ mol^{-1} and -71 J K^{-1} mol^{-1}, respectively, using the Van't Hoff isotherm. Comparison of the equilibrium constant ($K_{eq} = 0.069$ Torr^{-1}, or $P_{1/2} = 14$ Torr, at 293 K), ΔH^0, and ΔS^0 for the Mo_2–O_2 complex formation with those for other oxygen carriers demonstrates that the fixed Mo_2 species binds dioxygen more easily than Co–myoglobin,[10] Co–'picket fence' porphyrins,[11] and Co–protoporphyrins,[1,11]† but more weakly than human myoglobin,[12] Fe–'picket fence' porphyrins,[2a,b] and Co–Schiff base complexes.[1]† The surface Mo^{II}–pair (2) functioned as an oxygen carrier under mild conditions over a wide range of temperatures.

The fact that an i.r. absorption at 1415 cm^{-1}, which may be assigned to an ONO group[13] co-ordinated to molybdenum, appeared when NO was admitted on to the Mo_2–O_2 complex (3) at 293—373 K, indicates the presence of reactive dioxygen. The dioxygen of the complex (3) also reacted with cyclohexene to form benzene at 423 K. Under similar conditions the terminal oxygen (Mo=O) of the usual Mo^{VI} catalysts showed no reactivity. Carbon monoxide was oxidized to CO_2 over the complex (3) which also catalysed the oxidation of CO in the presence of O_2 [turnover frequency (CO_2 molecules formed

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† Most of the Co-complexes in homogeneous systems have been investigated at much lower temperatures for reversible dioxygen binding.

$Mo_2^{-1}\,s^{-1}) = 1.2 \times 10^{-5}\,s^{-1}$ at 423 K and 29.7 Torr of CO]; the rate of CO_2 formation at 423 K was comparable to the rate at 678 K for the Mo^{VI} catalysts. Thus the reversibly bound dioxygen is activated by electron transfer from the adjacent Mo^{II} ions.

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