Coordination Chemistry on Surfaces: A New Method To Graft Rhenium(VII) Oxide on Highly Dehydroxylated Oxides

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Metal oxide overlayers deposited on inorganic supports are an important category of heterogeneous catalysts.[1] The presence of reactive surface hydroxyl groups is thought to be a necessary condition for their formation.[2] The metathesis catalyst rhenium(VII) oxide on alumina or silica–alumina is traditionally prepared by wetness impregnation of the support material with acidic aqueous solutions of Re_2O_7 or $HReO_4$.[3] In that chemistry, perrhenic acid undergoes condensation with surface hydroxyl groups during calcination and drying at ca. 500 °C, leading to the formation of surface perrhenates, eq 1,[4]

$$-OH + HOReO_3 \rightarrow -OReO_3 + H_2O \qquad (1)$$

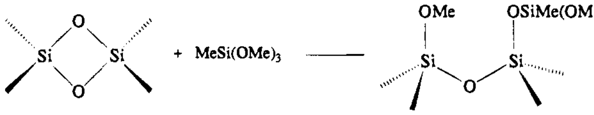
where –OH represents a surface hydroxyl group.

We sought a new method to introduce Re(VII) onto oxide surfaces without using hydroxyl groups and avoiding the formation of H_2O. Guided by molecular chemistry, we noted that the reaction of Re_2O_7 with hexamethyldisiloxane results in the cleavage of a siloxane (Si–O) bond, eq 2.[5]

$$O_3Re-O-ReO_3 + Me_3Si-O-SiMe_3 \rightarrow 2Me_3Si-O-ReO_3 \qquad (2)$$

We reasoned that Re_2O_7 should react similarly with silica even in the absence of hydroxyl groups, via the siloxane bridges which are always present on the silica surface.

Silica dehydroxylated at 1100 °C contains very few hydroxyl groups.[6] The high-temperature treatment causes condensation of vicinal hydroxyl groups, giving rise to highly strained and reactive siloxane bridges with a maximum density of 0.15/nm^2.[7] These siloxane bridges are thought to be part of four-membered rings, characterized by IR-active vibrational modes at 908 and 888 cm^{-1}. Grafting onto these sites has recently been reported for mixed alkyl(alkoxy)silanes, eq 3.[8]



(3)

Sublimation of dry Re_2O_7 under O_2 onto silica$_{1100}$[9] resulted in the disappearance of the yellow color of Re_2O_7. The sample was then calcined at 350 °C under 200 Torr of O_2 to remove physisorbed Re_2O_7. In situ transmission IR spectroscopy of a self-supporting silica wafer before and after sublimation of Re_2O_7 showed little change in the ν(OH) region, Figure 1a, ruling out the possible reaction of Re_2O_7 with residual silanol groups.[10] However, the IR bands at 908 and 888 cm^{-1}

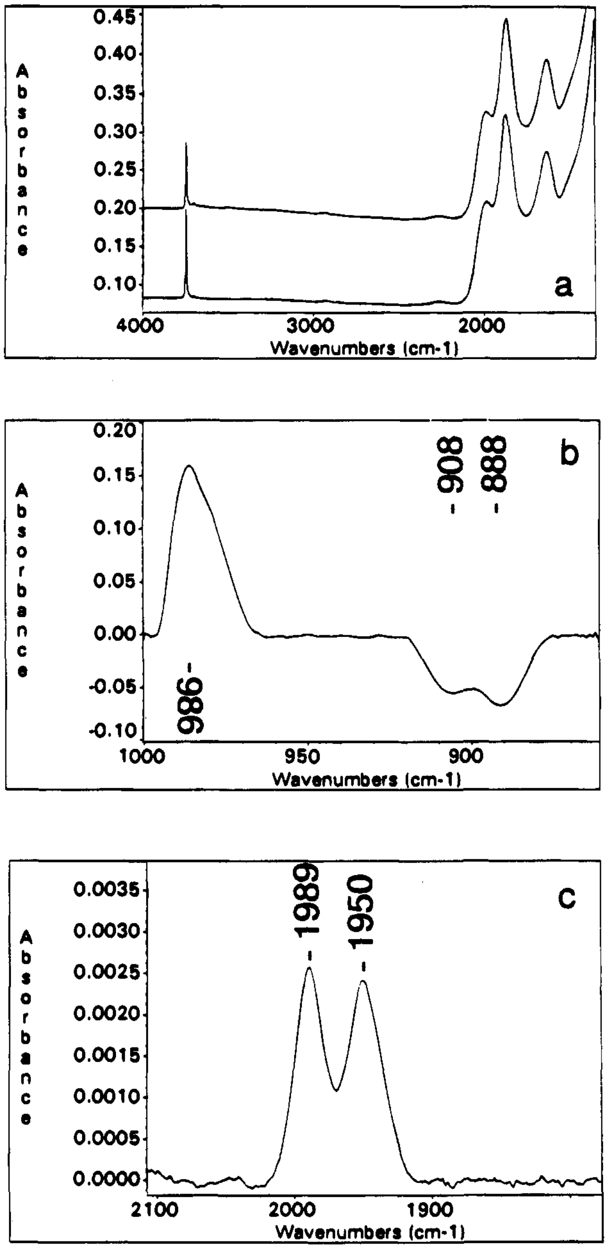


Figure 1. (a) IR spectra of a thin self-supporting silica pellet calcined for 4 h at 400 °C under 200 Torr of O_2 then dehydroxylated 16 h under dynamic vacuum (10^{-5} Torr) at 1100 °C. Lower: before reaction with Re_2O_7. Upper: after sublimation of Re_2O_7 onto the silica wafer. Excess Re_2O_7 was desorbed by calcination under 200 Torr of O_2 at 350 °C. (b) Difference spectrum showing the disappearance of silica defect bands associated with highly strained siloxane bridges (negative peaks), and the appearance of a ν(Re=O) fundamental (positive peak). (c) Difference spectrum showing the appearance of ν(Re=O) overtones.

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(6) Aerosil, specific area 200 m^2/g, was dehydroxylated in vacuum (10^{-4} Torr, 16 h) at 1100 °C. At this temperature, sintering is not important. The density of surface OH remaining after this treatment is approximately 0.4/nm^2. Curthoys, G.; Davydovm, V. Y.; Kiselev, A. V.; Kiselev, S. A.; Kuznetsav, B. V. *J. Colloid Interface Sci.* **1974**, *48*, 58–72.

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(8) Dubois, L. H.; Zegarski, B. R. *J. Phys. Chem.* **1993**, *97*, 1665–1670.

(9) Re_2O_7 was sublimed at 250 °C under vacuum (10^{-5} Torr) or 350 °C in the presence of 200 Torr of O_2. The latter procedure was preferred since heating Re_2O_7 under vacuum led to its partial reduction to ReO_3.

(10) We did not attempt to demonstrate that Re_2O_7 will not react under any conditions with surface hydroxyl groups. However, this possible reaction does not seem to be important under our grafting conditions. The density of residual hydroxyl groups on silica$_{1100}$ is approximately 0.4/nm^2 (ref 6) whereas the quantity of grafted rhenium is 1/nm^2. At the same time, the ν(OH) vibration decreases slightly in intensity and becomes broader. Thus the change in the hydroxyl group population is very small compared to the total reaction with rhenium.

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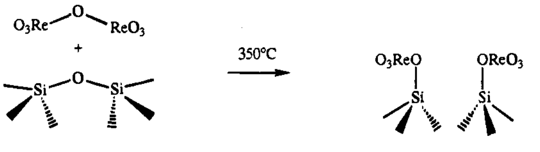
disappeared, demonstrating that Re_2O_7 reacted with the strained siloxane bridges. Simultaneously, a new band appeared at 986 cm^{-1}, Figure 1b. This band is attributed to the ν_{as}(Re=O) mode of a pseudotetrahedral perrhenate species, by comparison to the IR spectrum of impregnated Re_2O_7/SiO_2, with ν_{as}(Re=O) at 985 cm^{-1}.[11a] The higher frequency ν_s(Re=O) mode is not observed because of the intense absorbance of silica near 1000 cm^{-1}. However, the overtones of both modes appear as weak bands at 1989 and 1950 cm^{-1}, Figure 1c.[11b]

The surface reaction is proposed to be cleavage of one Re–O bond and one Si–O bond, to give two perrhenates on adjacent silicon atoms, eq 4. Coordination of intact (molecular) Re_2O_7 onto the siloxane bridge is likely the first step in the reaction. Adduct formation between Re_2O_7 and oxygen-containing bases such as H_2O, THF, and dioxane is known and is proposed to induce the cleavage of a Re–O bond.[12]



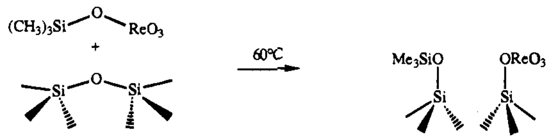
(4)

By elemental analysis, the calcined material contained up to 7 wt % Re chemisorbed on the silica surface, corresponding to ca. 1 Re/nm^2. This amount of grafted Re requires that, in addition to the reaction with highly strained siloxane bridges, less strained or unstrained siloxane bridges are also cleaved. The reaction with less strained siloxane bridges probably occurs during the subsequent calcination at 350 °C, which is necessary to desorb excess Re_2O_7.

The number of Re=O bonds in the chemisorbed perrhenate was determined by titration with excess *tert*-butyl isocyanate, eq 5. The amount of CO_2 evolved corresponds to (3.0 ± 0.1) mol/mol Re,[13] consistent with the perrhenate structure proposed in eq 3. In addition, elemental analysis after desorption of unreacted *tert*-butyl isocyanate gave (2.9 ± 0.1) N/Re, as expected for the formation of a tris(imido)rhenium species on the silica surface,[14] and analogous with the formation of molecular imidorhenium complexes.[15]

$$\equiv SiOReO_3 + 3\,{}^tBuNCO \rightarrow \equiv SiORe(=N^tBu)_3 + 3CO_2 \quad (5)$$

In order to investigate the cleavage of siloxane bonds at lower temperatures, we attempted the analogous grafting reaction with $Me_3SiOReO_3$, eq 6. Sublimation of $Me_3SiOReO_3$ onto silica$_{1100}$ followed by desorption at 60 °C resulted in the grafting of a maximum of ca. 1 wt % Re, with the appearance of IR bands at 2966, 2909, 1468, 1430, and 878 cm^{-1} due to vibrations of the $(CH_3)_3Si$ group. The ^{13}C CP-MAS solid-state NMR spectrum contains a single peak at −3.1 ppm, assigned to methyl groups coordinated to Si. The quantity of grafted Re corresponds to (0.14 ± 0.01) Re/nm^2, in good agreement with the previous estimate of the concentration of highly strained four-membered rings (0.15/nm^2, see above) on the surface of silica$_{1100}$.[7] Therefore we conclude that $Me_3SiOReO_3$ reacts only with these highly strained siloxane bonds. The lower desorption temperature of $Me_3SiOReO_3$ (60 °C vs 350 °C for Re_2O_7) is proposed to account for the apparent lower reactivity of $Me_3SiOReO_3$ toward siloxane bonds.



(6)

This new grafting mechanism can be generalized to other highly dehydroxylated oxide surfaces such as those of alumina$_{1000}$ and zirconia$_{750}$.[14,16] Oxide-supported Re(VII) can therefore be prepared in the absence of hydroxyl groups, protons, or water. This method may also be applicable to the *in situ* preparation of other supported metal oxides[17] (and perhaps metal chlorides or even alkyl catalysts) especially where the presence of water or surface hydroxyl groups would interfere with the subsequent catalytic activity. For example, it is known that in the field of olefin metathesis the presence of water or hydroxyl groups promotes double-bond isomerization, which renders the metathesis reaction unselective. It is also possible that this new molecular approach of grafting one oxide onto another oxide surface might be related to the so-called dry dispersion of metal oxides, which was observed recently.[17]

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(11) (a) Vuurman, M. A.; Wachs, I. E.; Stufkens, D. J.; Oskam, A. *J. Mol. Catal.* **1992**, *76*, 263–285. (b) On silica, the material prepared by conventional impregnation contains a single perrhenate species characterized by two Raman fundamentals, ν_{as}(Re=O) and ν_s(Re=O) at 975 and 1015 cm^{-1}.[2] The spectrum of the overtone region was not reported. On the basis of symmetry considerations, four overtone bands are expected. The doubly degenerate antisymmetric mode should give rise to two closely spaced overtones at ca. 1950 cm^{-1}. The symmetric overtone is expected at 2030 cm^{-1} but is weak. The combination overtone is expected at 975 + 1015 = 1990 cm^{-1}. Thus we assign the observed bands at 1950 and 1989 cm^{-1} to the antisymmetric and combination overtones, respectively.

(12) Kiprof, P.; Herrmann, W. A.; Fühn, F. E.; Scherer, W.; Kleine, M.; Elison, M.; Rypdal, K.; Volden, H. V.; Gundersen, S.; Haaland, A. *Bull. Soc. Chim. Fr.* **1992**, *129*, 655–662.

(13) A 100 mg sample of silica, containing 15.8 μmol of Re (by elemental analysis), was treated with excess *tert*-butyl isocyanate. The gas phase was trapped and analyzed for CO_2 by GC on a capillary column terminated by a methanation oven. The yield of 47.4 μmol of CO_2 was corrected by the amount of CO_2 produced in a blank experiment containing no Re, 0.4 μmol of CO_2.

(14) Scott, S. L.; Basset, J. M. Manuscript in preparation.

(15) The conversion of rhenium–oxo ligands into rhenium–imido ligands is a facile process with aryl isocyanate reagents: Horton, D.; Schrock, R. R. *Polyhedron* **1988**, *7*, 1841–1853. Herrmann, W. A.; Weichselbaumer, G.; Paciello, R. A.; Fischer, R. A.; Herdtweck, E.; Okuda, J.; Marz, D. W. *Organometallics* **1990**, *9*, 489–496. Roesky, H. W.; Hesse, D.; Bohra, R.; Noltemeyer, M. *Chem. Ber.* **1991**, *124*, 1913–1915. Only one case has been reported using *tert*-butyl isocyanate: Schoop, T.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H. G. *Organometallics* **1993**, *12*, 571–574.

(16) The reaction of Re_2O_7 with alumina$_{1000}$ gave three ν(Re=O) fundamentals at 1016, 990, and 975 cm^{-1}, with overtones at 2004, 1978, and 1950 cm^{-1}. (The weak ν(Re=O) mode expected at ca. 1006 cm^{-1} was not observed.) On zirconia$_{750}$, four fundamentals at 1001, 978, 957, and 937 cm^{-1} were observed. These results suggest that, on alumina and zirconia, surface perrhenates exist in two slightly different environments. A similar conclusion was reached in a Raman study of supported perrhenates prepared by conventional impregnation.[2]

(17) In the "dry" dispersion of metal oxides on oxides, MoO_3 and Al_2O_3 were mixed mechanically in the open air (Leyrer, J.; Mey, D.; Knözinger H, *J. Catal.* **1990**, *124*, 349–356). The extent of dryness is necessarily much less than in our reactions.