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Supported Cluster Calculations

Oxidation of Supported Rhodium Clusters by Support Hydroxy Groups**

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Metal clusters or particles on porous-oxide and zeolite supports are important industrial catalysts, with the role of the support often going beyond that of a mere platform for the stable dispersion of the metal.[1–3] The metal–support interaction involves support ligands, inferred to be surface oxygen or OH groups. How the bonding, reactivity, and catalytic properties of the metal depend on these ligands is essentially unresolved. Furthermore, supported metal catalysts often facilitate “spillover”, whereby an adsorbate, typically H_2, reacts with the metal to give species that migrate onto the support. Molecular hydrogen dissociates on metals, and some of the H_2 ultimately forms OH groups on the support. Spillover has been demonstrated,[4] but its chemistry is ill defined; it must involve redox processes, since H_2 is converted into a hydride bound to the metal and the protons in OH groups.

To help clarify metal–support interactions and spillover effects, we modeled computationally the interaction of the bridging OH groups of zeolites with a supported cluster, Rh_6, and compared the theoretical results with the experimental results. The model system was selected because of its close correspondence[5] to the EXAFS-derived structure parameters for zeolite-supported Rh_6 clusters.[6] Our calculations show that the interaction of the hexanuclear cluster with OH groups from the support leads to the oxidation of Rh atoms that are in close contact with the support; the energy released per OH group is estimated to be about 120 kJ mol^{-1}. The results demonstrate the redox character of hydrogen spillover, which includes changes in the oxidation state of the supported metal.

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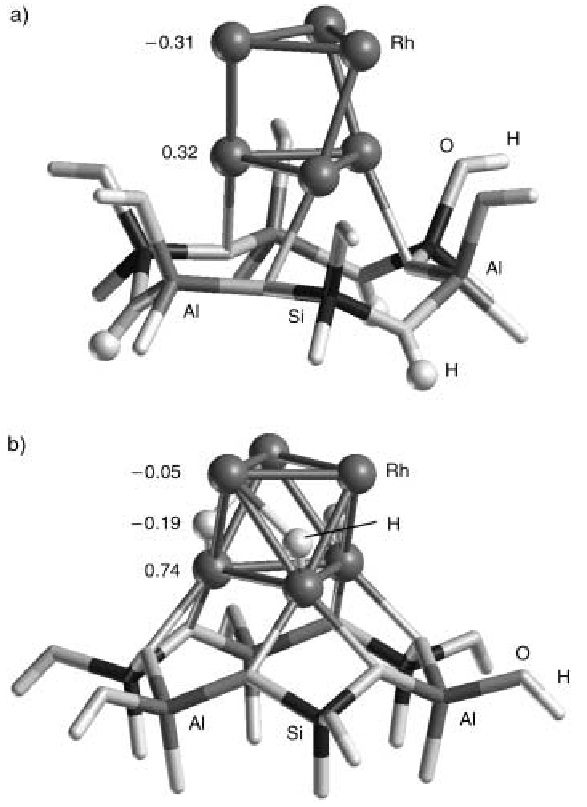

Figure 1. Calculated structures of Rh_6 clusters supported on a zeolite fragment (Zeo): a) nonreactive adsorption, Rh_6/Zeo(3H); b) reactive adsorption, Rh_6(3H)/Zeo. Also shown are Mulliken charges (in e) of the atoms in the supported cluster.

Table 1: Interatomic distances [pm] in zeolite-supported Rh_6 clusters.

Model	Separations				
	Rh–Rh	$\langle R\rangle$[a]	ΔR[b]	Rh–H	$Rh–O_z$
experiment[c]	267–269	-	-	-	210–217
Rh_6/Zeo(3H)	251–307	265	56	-	237
Rh_6(3H)/Zeo	260–267	262	7	176	218, 220

[a] Average value of the Rh–Rh bond lengths in the cluster. [b] Difference between the smallest and largest nearest-neighbor Rh–Rh separation in the cluster. [c] Experimental value for zeolite-supported rhodium clusters, reference [6]. O_z = zeolite oxygen atom.

The structural model represents an Rh_6 cluster adsorbed at a six-ring model cluster of the faujasite structure with C_3 symmetry that contains three Al and three Si T atoms (Figure 1); the representation of the zeolite is as in our previous work.[7] The electronic-structure calculations were carried out with a density-functional method.[8–13] To evaluate the reaction energy for reverse hydrogen spillover from the OH groups of the zeolite to the supported Rh_6 cluster, we considered two systems: a) Rh_6/Zeo(3H), in which the cluster is adsorbed on the model zeolite fragment with three bridging OH groups (Figure 1 a) corresponds to "nonreactive" adsorption of the Rh_6 cluster on the zeolite, and b) Rh_6(3H)/Zeo, formed by reverse spillover from a), in which the hydrogen atoms are bound to the Rh_6 (Figure 1 b).

In Rh_6/Zeo(3H), the zeolite fragment is formally neutral; the negative charge of the six-ring, which arises from the presence of three Al atoms, is compensated by the three protons of the bridging OH groups (Figure 1 a). Accordingly, the Rh_6 moiety is also formally neutral. The optimized geometry of the supported Rh_6 unit is a triangular prism twisted by 34° (compared to 60° of an octahedron); the shortest Rh–O bonds are 237 pm (Table 1), that is, ~20 pm longer than the experimental values determined by EXAFS spectroscopy,[6] 210–217 pm. The difference is far greater than the errors of current DF methods for such systems[14]

In Rh_6(3H)/Zeo, the three H atoms bridge metal atoms of the supported Rh_6 cluster. (Bridge-bonding of H atoms in the gas-phase Rh_6 was found to give the most stable conformation.[5]) In this structure, the zeolite fragment can be considered to bear a formal charge of −3 e, whereas the supported Rh_6(3H) cluster bears a formal charge of +3 e. The Rh atoms of this cluster form a triangular prism twisted by 58°, that is, close to an octahedron (Figure 1 b). A comparison of the Rh_6(3H)/Zeo model cluster with the EXAFS data, which were interpreted as being indicative of octahedral clusters,[6] suggests[5] that the structural parameters of the theoretical model are in satisfactory agreement with the experimental results characterizing the zeolite-supported Rh_6,[6] namely, 1) the average calculated Rh–Rh bond of 262 pm is close to the experimental values, 267–269 pm (allowing for a typical experimental error of 1 %); 2) the difference between the smallest and largest calculated Rh–Rh bond length is only 7 pm, consistent with the high quality of the EXAFS data[6] and the estimated experimental accuracy of 10 pm;[15] and 3) the optimized distances between of the "lower-layer" rhodium atoms and the zeolite oxygen centers, $Rh_z–O_z$, 218 and 220 pm, agree well with the EXAFS values, 210–217 pm.

On the basis of these comparisons, we conclude that the zeolite-supported Rh_6 clusters prepared experimentally were not actually Rh_6, but instead were clusters decorated by H atoms. These clusters, which form by the migration of protons of the zeolite OH groups onto the cluster by reverse hydrogen spillover, are consistent with the calculated relative energies of the two model structures. The structure Rh_6(3H)/Zeo (Figure 1 b) with three H atoms on the cluster is more stable (by 370 kJ mol^{-1}) than Rh_6/Zeo(3H) (Figure 1 a).[16]

In addition to the structural and energetic aspects of the interaction of the Rh_6 cluster with the support, our results characterize significant chemical changes in the supported cluster. These changes were diagnosed by an analysis of the charge distribution in the model systems, which combined a Mulliken population analysis with core level binding energy shifts ΔE(Rh 3d).[17] Nonreactive adsorption of the Rh_6 cluster on a Zeo(3H) fragment is not accompanied by transfer of electron density between the metal cluster and the support; $q(Rh_6) = 0.03$ e. However, the support polarizes the electron density of the Rh_6 cluster, and two different types of Rh center result. The first type are the metal atoms, Rh_z, close to the zeolite support; they have a slightly cationic character,[18] with a positive charge of 0.32 e per atom and ΔE(Rh 3d) = −0.1 eV. The second type are the metal atoms, Rh_t, in the "top" layer of the cluster, which are negatively charged, −0.31 e per atom; correspondingly, their ΔE(Rh 3d) value is more negative, −0.6 eV. The redistribution of electron density in metal clusters is expected to be important for the reactivity and catalytic activity of such species on supports.

The charge distribution in the other model cluster, $Rh_6(3H)$/Zeo, clearly shows oxidation of the lower layer of the rhodium atoms, probably to Rh^I; the charge of these Rh_z centers is 0.74 e, and $\Delta E(\mathrm{Rh\,3d}) = 2.1$ eV. The charges of the Rh_t atoms are close to zero, $q(\mathrm{Rh_t}) = -0.05$ e, but their core levels are also strongly stabilized compared to those of the neutral gas-phase Rh_6 cluster, $\Delta E(\mathrm{Rh\,3d}) = 1.7$ eV. This high positive value of $\Delta E(\mathrm{Rh\,3d})$ of the Rh_t atoms is ascribed to the large overall positive charge of the moiety $Rh_6(3H)$, +1.50 e. This value compares to the formal charge +3 e. The difference in the $\Delta E(\mathrm{Rh\,3d})$ values characterizing Rh_t and Rh_z atoms is essentially the same for nonreactive and reactive adsorption; the core levels of the Rh_t atoms are 0.4–0.5 eV less stable than those of Rh_z. Reactive adsorption of the metal cluster decreases the electron density in both layers of rhodium atoms with respect to nonreactive adsorption, as shown by the charges in Figure 1.

An additional argument for the oxidation of the supported Rh_6 cluster as a result of an interaction with surface OH groups relies on a comparison of the Rh−O distances. Both experimentally measured (210–217 pm) and calculated[20] (218, 220 pm) Rh_z−O_z distances for the zeolite-supported hexarhodium cluster are close to the corresponding experimental and calculated values of the cationic dicarbonyl complex $Rh^I(CO)_2$ supported on a zeolite, 216 pm and 219–220 pm, respectively.[21] This observation suggests that the nature of the metal centers in the two types of supported species is similar, namely, the Rh centers bound to zeolite oxygen atoms in the supported hexarhodium cluster are oxidized with an effective charge similar to that of the Rh^I center in the supported dicarbonyl species, 0.53 e (Mulliken charge).[21]

Thus, our computational modeling suggests that transition-metal particles are oxidized by surface OH groups. This inference invites comparison with relevant experimental results. When metal clusters are prepared, for example, by the aggregation of smaller metal-containing species, or the decarbonylation of supported metal carbonyl clusters,[6,22] OH groups are necessary for successful syntheses, at least for those that give nearly uniform clusters. Hence, reference studies of samples without surface OH groups seemingly cannot be performed. However, when the supported particles are produced by vapor deposition, the experiments can be performed with a controlled density of surface OH groups. Because this technique is not appropriate for the preparation of metal clusters in zeolite cavities, we use experimental results obtained for rhodium particles supported on alumina films.[2] Freund and co-workers[2] have shown by infrared spectroscopy and X-ray photoelectron spectroscopy (XPS; O1s, Al2p) that the deposition of rhodium particles on hydroxylated alumina involved a consumption of surface OH groups. Simultaneously, the XPS of the Rh 3d level shows a concomitant positive binding energy shift by 0.3 eV, that is, a stabilization of the corresponding core level. This result can be rationalized by a direct interaction of the metal particles with surface OH groups, including oxidation of some of the metal atoms to Rh^I. This argument is in line with trends of our computational models.

The quantitative difference between our calculated $\Delta E(\mathrm{Rh\,3d})$ values, ≈2.0 eV, and experimental XPS results, 0.3 eV, is not entirely surprising. First, in our calculations, we used only a rather approximate estimate of core-level energy shifts.[17] More importantly, the small $\Delta E(\mathrm{Rh\,3d})$ value could be a consequence of the different sizes of the metal particles. In the experiment, relatively large particles, consisting of about 100 Rh atoms per island,[2] were used, in contrast to our six-atom clusters; therefore, only a small fraction of the Rh atoms in the particles interacted with the support and were oxidized. Furthermore, such large metal particles exhibit screening effects. It is evident that the cluster oxidation and effects of such a charge redistribution would be most pronounced for the smallest metal clusters, becoming negligible for increasingly larger clusters, which, in the limit (i.e. the largest clusters), have properties approaching those of bulk metals.[23]

Thus, we suggest that the redox processes of spillover shown by our results may be quite general for supported metal species, but the changes in the metal centers may be too small to detect, except when the clusters are small. A related inference is that bare metal clusters may not even exist on hydroxylated surfaces, because of reverse spillover. This suggestion is consistent with EXAFS data for small, nearly uniform supported clusters of Rh and of Ir, for which the metal–metal separations are larger than those of the free clusters.[7c,22a] Another consequence is related to the interpretation of hydrogen chemisorption data, which are often used to determine dispersions of supported metal clusters. The stoichiometry of adsorption of hydrogen on platinum, for example, was shown to a good approximation to be 1:1, even for clusters as small as those containing several tens of atoms.[24] But successful measurements of the amount of hydrogen chemisorbed require that the metal surface be cleaned before the adsorption. When supported metal clusters are sufficiently small, this cleaning may not be possible without reverse spillover replenishing the metal with hydrogen.[25] It remains to be determined how these effects depend quantitatively on the metal, support, and metal cluster size.

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[17] The value of ΔE(Rh 3d) is estimated from calculated Kohn–Sham orbital energies as the corresponding energy-difference shift with respect to an Rh_6 cluster in the gas phase. A positive value of ΔE(Rh 3d) corresponds to a stabilization of Rh 3d levels.

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