by building metal microframeworks on support pose into fragments, or aggregate together into larger clusters, and while the states of such cat-
tionally supported catalysts. In conventional surfaces have a different chemistry to conven-
tional catalysts before and after the reaction, addition little is known about catalysts cluster catalysis the supported clusters decom-
date. Additionally little is known about catalysts whose activity originates from promoters inside a metal framework, or their effects.

Rhodium clusters (“CO-Breathing Ruthenium Clusters Breathing Carbon Monoxide”) has been discovered by researchers in Japan to discover what happens to the carbido carbon, and perhaps to metal-sup-
port, when supported on basic oxides, that the metal species


Support clusters were observed for the supported clus-
ters. Electronic effects of the carbido carbon and clus-
ter is attrib-
utable to binding between the framework and the carbido carbon, and perhaps to metal-sup-
port interactions.

The reactions were followed by extended X-ray absorption fine structure. It was observed, when supported on basic oxides, that the metal core framework of the surface-attached ruthenium species shrank on loss of CO ligands; while expansions in the framework were induced by CO uptake. When CO was released again, either by evacuation or decreasing the CO pressure, the expanded cluster shrank. This process can be called “CO breathing”.

Also on supports, a switchover in the reaction path was observed during carbon monoxide hydrogenation as carbido carbon was inserted into the Ru₆ cluster framework, from dissociative to oxidative carbon monoxide hydrogenation, the latter having higher turnover frequen-
cies and selectivities. Products changed from hydrocarbons and methane to methanol, dimethyl ether and formaldehyde, respectively. Electronic effects of the carbido carbon and clus-
ter metal framework were also found, and inverse isotope effects for hydrogen, dependent on support, were observed for the supported clusters.

Two other supported rhodium and ruthenium clusters show structural chemical control by μ₇-ligands; and elements, such as carbon and nitro-
gen inside metal cluster frameworks behave as a new type of catalytic promoter, not interact-
ing with reactant molecules, but affecting the catalytic properties without blocking the cata-
lysis. These promoters also act like a central spring making the cluster flexible at the surface. This feature could be used with a wide range of main and transition metal elements.

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Ruthenium Clusters Breathing Carbon Monoxide

It has been noticed that catalysts constructed by building metal microframeworks on support surfaces have a different chemistry to conventionally supported catalysts. In conventional cluster catalysis the supported clusters decompose into fragments, or aggregate together into larger clusters, and while the states of such catalysts are known before and after the reaction, not much is known about them during catalysis. Additionally little is known about catalysts whose activity originates from promoters inside a metal framework, or their effects.

Therefore work has been undertaken by researchers in Japan to discover what happens in metal microframeworks during catalytic reactions involving supported ruthenium and rhodium clusters (“CO-Breathing Ruthenium and Rhodium Clusters”, Y. Izumi and Y. Iwasawa, Chemtech, 1994, 24, (7), 20–27). The ruthenium cluster, (NMe₂,CH₂,Ph)(Ru₄C]CO)₇(Me), which has a μ₇-carbido ligand inside the octahedra Ru₆ framework, was examined during ethene hydro-
formylation. The stability of this cluster is attrib-
utable to binding between the framework and the carbido carbon, and perhaps to metal-support interactions.

The reactions were followed by extended X-ray absorption fine structure. It was observed, when supported on basic oxides, that the metal core framework of the surface-attached ruthenium species shrank on loss of CO ligands; while expansions in the framework were induced by CO uptake. When CO was released again, either by evacuation or decreasing the CO pressure, the expanded cluster shrank. This process can be called “CO breathing”. The μ₇-carbido carbon inside the cluster acted, in effect, like a central spring, making the cluster framework expand and shrink.

Also on supports, a switchover in the reaction path was observed during carbon monoxide hydrogenation as carbido carbon was inserted into the Ru₆ cluster framework, from dissociative to oxidative carbon monoxide hydrogenation, the latter having higher turnover frequen-
cies and selectivities. Products changed from hydrocarbons and methane to methanol, dimethyl ether and formaldehyde, respectively. Electronic effects of the carbido carbon and clus-
ter metal framework were also found, and inverse isotope effects for hydrogen, dependent on support, were observed for the supported clusters.