

References

- 1 (a) A. Juris, V. Balzani, F. Barigletti, S. Campagna, P. Belzer and A. v. Zelewski, *Coord. Chem. Rev.*, 1988, **84**, 85; (b) K. Kalyanasundaram, "Photochemistry of Polypyridine and Porphyrine Complexes", Academic Press, London, 1992, and references cited therein
- 2 M. K. Nazeeruddin, A. Kay, J. Rodicio, R. Humphrey-Baker, E. Müller, P. Liska, N. Vlachopoulos, and M. Grätzel, *J. Am. Chem. Soc.*, 1993, **115**, 6382
- 3 B. O'Regan and M. Grätzel, *Nature (London)*, 1991, **335**, 737
- 4 R. Eichberger and F. Willig, *Chem. Phys.*, 1990, **141**, 159
- 5 G. Hodes, I. D. J. Howell and L. M. Peter, *J. Electrochem. Soc.*, 1992, **139**, 3136
- 6 A. Hagfeldt, U. Björkstén and S. Lindquist, *Sol. Energy Mater. Sol. Cells*, 1992, **27**, 293
- 7 D. Liu and P. V. Kamat, *J. Phys. Chem.*, 1993, **97**, 10769
- 8 A. Hagfeldt, S. Lindquist and M. Grätzel, *Sol. Energy Mater. Sol. Cells*, 1993, **32**, 245
- 9 B. O'Regan, J. Moser, M. Anderson and M. Grätzel, *J. Phys. Chem.*, 1990, **94**, 8720
- 10 N. Vlachopoulos, P. Liska, J. Augustynski and M. Grätzel, *J. Am. Chem. Soc.*, 1988, **110**, 1216
- 11 M. K. Nazeeruddin, P. Liska, J. Moser, N. Vlachopoulos and M. Grätzel, *Helv. Chim. Acta*, 1990, **73**, 1788
- 12 R. Knödler, J. Sopka, F. Harbach and H. W. Grünling, *Sol. Energy Mater. Sol. Cells*, 1993, **30**, 277
- 13 A. Hagfeldt, B. Didriksson, T. Palmquist, H. Lindström, S. Södergren, H. R. Tensmo and S. Lindquist, *Sol. Energy Mater. Sol. Cells*, 1994, **31**, 481
- 14 T. A. Helmer, C. A. Bignozzi and G. J. Meyer, *J. Phys. Chem.*, 1993, **97**, 11987
- 15 J. Desilvestro, M. Grätzel, L. Kavan, J. Moser and J. Augustynski, *J. Am. Chem. Soc.*, 1985, **107**, 2988
- 16 R. Amadelli, R. Arguzzi, C. A. Bignozzi and F. Scandola, *J. Am. Chem. Soc.*, 1990, **112**, 7099
- 17 G. Smestad, *Sol. Energy Mater. Sol. Cells*, 1994, **32**, 259
- 18 N. Papageorgiou and M. Grätzel, to be published

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, $(\text{NMe}_2\text{CH}_2\text{Ph})^+(\text{Ru}_6\text{C}[\text{CO}]_{10}\text{Me})^-$, which has a μ_6 -carbido ligand inside the octahedral Ru framework, was examined during ethene hydroformylation. The stability of this cluster is attributable 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 μ_6 -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 Ru_6 cluster framework, from dissociative to oxidative carbon monoxide hydrogenation, the latter having higher turnover frequencies and selectivities. Products changed from hydrocarbons and methane to methanol, dimethyl ether and formaldehyde, respectively. Electronic effects of the carbido carbon and cluster 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 μ_6 -ligands; and elements, such as carbon and nitrogen inside metal cluster frameworks behave as a new type of catalytic promoter, not interacting with reactant molecules, but affecting the catalytic properties without blocking the catalysis. 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.