

EPR STUDIES OF RHODIUM AND RUTHENIUM COMPLEXES IN Y ZEOLITES

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Ruthenium and rhodium exchanged zeolites are becoming increasingly important as catalysts for a variety of chemical reactions, such as the Fischer-Tropsch reaction, [1] the water-gas shift reaction, [2] the reduction of NO_x to N_2 , [3] and the dimerization of polyenes. [4] Transition metal complexes in zeolites are of interest as possible catalytic intermediates in these reactions. [5] It may also be possible to relate these complexes to intermediate species in homogeneous catalysis. [6]

Zeolites are aluminosilicate framework molecules, consisting of AlO_4^- and SiO_4 tetrahedra linked together through common oxygen atoms. These zeolites have a three-dimensional network of channels or linked cavities in which molecules may be adsorbed. [7-9] Zeolite Y, a synthetic analogue of faujasite, is often used in catalysis because of its large pore size compared to other zeolites.

Transition metal ions or cationic complexes may be exchanged into zeolites. The stability of these complexes in the zeolite may be considerably altered with respect to their stability in solution. [10] The cations can be located at defined sites within the framework. [11] The geometries of the complexes are often governed by the zeolite morphology. [12]

EPR spectroscopy has been used to study transition metal complexes in zeolites, particularly those of the first transition series. [10,13] More recently, complexes of ruthenium and rhodium have been studied with EPR.

Rhodium zeolites are prepared by the ion exchange of $[\text{Rh}(\text{NH}_3)_5\text{Cl}]^{2+}$ onto NaY zeolite. Samples are activated at high temperatures. This treatment completely decomposes the chloro-ammine complex. After treatment, paramagnetic species are formed which have been observed with EPR spectroscopy. Naccache and co-workers assign the paramagnetic species to rhodium(II) ions located at site I, coordinated octahedrally to six oxide framework ions. [14] Atanasova and co-workers propose the formation of paramagnetic ion pairs of rhodium. [15] A new paramagnetic species is formed upon adsorption of CO on the activated rhodium zeolite. This species is thought to be a mononuclear, monocarbonyl rhodium(II) complex. [14,16] Paramagnetic adducts with O_2 are also formed. Naccache and co-workers propose formation of a μ -peroxo binuclear rhodium(II) species, formed from the oxidation of rhodium(I) ions by O_2 . [14] This complex is thought to have C_{3v} symmetry. It is also postulated that the formation of the CO- and O_2 - adducts involve different rhodium sites. When the O_2 - adduct is exposed to water, a new paramagnetic species is observed. Naccache and co-workers propose a double trigonal bipyramidal structure for this complex, linked through the μ -peroxo bridge. [14] A paramagnetic species is also formed when NO is adsorbed onto the activated rhodium zeolite. Atanasova and co-workers propose a complex containing two NO molecules coordinated to a single rhodium(II) ion. [17]

Ruthenium zeolites are prepared by ion exchange of $[\text{Ru}(\text{NH}_3)_6]^{3+}$ onto NaY zeolite. The high temperature activation treatment completely decomposes the ammine complex. No EPR signal is observed following the dehydration treatment. Upon adsorption of CO, two different paramagnetic species are observed, depending on the pressure of CO used. Gustafson and co-workers propose formation of a monocarbonyl complex of ruthenium(III) at low pressures.[18] When excess CO is present, di- or tri- carbonyl species are formed. Adsorption of O₂ on the activated zeolite is thought to produce RuO₂ in the zeolite. Adsorption of O₂ on the monocarbonyl adduct produces a new paramagnetic species with the unpaired electron localized mainly on the oxygen. Gustafson and co-workers propose formation of a monocarbonyl ruthenium(IV) superoxide species.[18]

$[\text{Ru}(\text{III})(\text{bpy})_3]^{3+}$ is known to promote the photochemical dissociation of water.[19] Quayle and Lunsford have prepared a $[\text{Ru}(\text{III})(\text{bpy})_3]^{3+}$ complex within the cages of Y zeolite.[20] The complex, too large to be ion exchanged into the zeolite, is formed in the super cage from reaction of 2,2'-bipyridine with $[\text{Ru}(\text{NH}_3)_6]^{3+}$ with subsequent oxidation by Cl₂. This species has been characterized by EPR spectroscopy.

EPR studies in conjunction with other physical techniques are being used to probe the sites at which substrates react with transition metals to form weakly bonded complexes which may be analogous to intermediates in many catalytic systems.

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