

SELECTIVITY, ACTIVITY AND METAL-SUPPORT INTERACTIONS
OF GROUP VIII BIMETALLIC CATALYSTS

Gary L. Haller

Department of Chemical Engineering
Yale University
New Haven, Connecticut 06520

Research Scope and Objectives

Our objective is to characterize by physical and chemical methods the nature of metal-metal and metal-oxide interactions and to determine the effect of these interaction on activity and selectivity. Two classes of bimetallic catalysts are under investigation: immiscible group VIII-group Ib and intra-group VIII bimetallics. Principal bimetallic catalyst systems to be investigated are Rh-Pt, Rh-Ir, Rh-Ag, and Rh-Cu, supported on TiO_2 , Al_2O_3 and SiO_2 . Extended X-ray absorption fine structure (EXAFS) and magic angle spinning nuclear magnetic resonance (MAS-NMR) are the primary physical tools and the catalytic activity for hydrogenolysis, alkane isomerization, and CO/H_2 reactions are the principal test reactions.

Description of Research Effort

All of the intra-group VIII systems so far investigated, i.e., Rh-Ir, Rh-Pt and Ir-Pt, behave in a similar fashion with regard to activity for structure sensitive reactions (hydrogenolysis) as a function of overall composition. The general activity pattern is a non-linear decrease in the hydrogenolysis activity as the more active component, e.g., Rh in Rh-Pt, is diluted by the less active component. Broadly speaking, the pattern is analogous to that observed in the group VIII-group Ib bimetallics and can be interpreted as the result of breaking up ensembles of the more active component by incorporation of the less active component. For example, Pt in Rh-Pt plays a role similar to Cu in Ni-Cu. The specific activity pattern depends strongly on the specific reaction, the degree of surface enrichment relative to the overall composition and the relative reactivity for the reaction under consideration.

The Rh-Pt/ SiO_2 is of particular interest because among the triad of group VIII elements considered, the relative hydrogenolysis activities, alkane isomerization activities, and preference for C_2 - versus iso-unit mode hydrogenolysis mechanism differ the most for Rh and Pt. The C_2 -unit mechanism involves bonding of the intermediate to an ensemble site through two adjacent carbon atoms; the iso-unit mode involves bonding of the intermediate to a single metal atom site through three carbon atoms to form a surface metallocycle. Rh, the more active component, prefers the

former mechanism while Pt favors the latter. The hydrogenolysis of n-butane can occur by either mechanism but the initial products are two molecules of ethane for the C₂-unit mechanism and methane and propane for the iso-unit mechanism. Thus there is a large change in the hydrogenolysis selectivity as the composition is varied; except for pure Rh and the Rh rich bimetallics, the selectivity over most of the composition range approaches that of pure Pt. The activity decrease by about a factor of 10⁴ as the Pt content of the bimetallic is increased for the hydrogenolysis of n-butane. However, the hydrogenolysis of 2,2-dimethylpropane, for which only the iso-unit mode mechanism is possible, decreases only about two orders of magnitude as the overall composition is varied from Rh to Pt.

The degree of metal-metal interaction of a given bimetallic system is a strong function of the preparation procedure. This has been most dramatically demonstrated for the system of Ru-Cu/SiO₂. For catalysts which have identical Ru:Cu ratio and total metal loading, the depression of ethane hydrogenolysis by Cu varies from a factor of 10-1000 depending on the salts used to impregnate the SiO₂ and the texture of the SiO₂; time and temperature of reduction have only a modest effect. The apparent effects of catalyst preparation on metal-metal interaction are, in part, a reflection of preparation variables on the dispersion of the metals.

The degree of metal-metal interaction is also strongly affected by the chemical nature of the support. In an earlier comparison of Rh-Ag/SiO₂ and Rh-Ag/TiO₂, it had been deduced that the metal-metal interaction was greater on the TiO₂ than on SiO₂ support based on chemisorption and ethane hydrogenolysis activity. This deduction has been qualitatively confirmed by recent EXAFS work on these catalysts. The apparent coordination numbers for Rh are 7-8 on both SiO₂ and TiO₂ and do not change much with reduction temperature. The Ag coordination number for Rh-Ag/SiO₂ and Rh-Ag/TiO₂ increase from 6 to 9 and 9 to 11, respectively, following low and high temperature reduction. The temperature dependence of the radial distribution magnitudes and the effects of ethane hydrogenolysis activity suggest that Ag is mostly surrounded by other Ag atoms on SiO₂ and by Rh atoms on TiO₂.

Future Research

During FY 84 we plan to complete two comparative catalytic investigation of intra-group VIII and group VIII-group 1b, i.e., Ir-Pt compared to Ir-Au and Rh-Pt compared to Rh-Ag. We will continue our EXAFS analysis with particular attention to direct metal-oxide interaction differences between TiO₂ and SiO₂ for both group VIII and group 1b metals and initiate magic angle spinning nuclear magnetic resonance investigation of the same systems.