

Polymetallic Cluster Catalysts

SUPERIOR PROPERTIES FOR SPECIFIC APPLICATIONS

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Highly dispersed metallic clusters composed of two or more metals within Group VIII, or combinations of one or more Group VIII metals with a Group IB metal, when supported on a carrier, form catalysts of considerable theoretical interest which also have practical industrial applications. The simpler bimetallic clusters have provided useful model systems for investigating basic concepts and have demonstrated that their catalytic behaviour can be very different for different types of reactions. The idea of polymetallic clusters could be applicable to a number of combinations of elements, so increasing the range of catalytically useful systems.

Historically, bimetallic catalysts have been of interest in the development of ideas related to an electronic factor in catalysis by metals (1, 2). The bimetallic catalysts employed in such investigations have typically been alloys in which the metal dispersion or surface area is very low, at least by comparison with the supported platinum reforming catalysts (3, 4) which have long been of great importance in the petroleum industry.

For a bimetallic catalyst to be of interest for industrial applications, it is necessary that the catalyst be prepared in a high surface area form and that it be resistant to loss of surface area during use. Deposition of the components of a bimetallic catalyst on a carrier provides an approach to this problem (5, 6). In considering the nature of such a supported bimetallic catalyst, one might ask the following question: Will the atoms of two different metals interact to form a "bimetallic cluster" or will the individual metal components exist as separate entities on the carrier? If two completely miscible metals are co-deposited on a carrier surface, one might expect on purely statistical grounds that the individual metal clusters formed would contain atoms of both metals; that is, it is unlikely that the metal components would be

completely isolated from each other in the form of monometallic clusters containing atoms of only one or the other of the two components. Various combinations of completely miscible metals provide interesting candidates for highly dispersed, supported bimetallic catalyst systems. Surprisingly, perhaps, experience has shown that systems of interest include metallic combinations which do not form alloys in the bulk (5). Consequently, the term "bimetallic clusters" rather than alloys is preferred when referring to highly dispersed supported bimetallic systems where there is evidence of significant interaction between the metallic components. Very highly dispersed bimetallic clusters are composed mainly of surface atoms, and one can obtain compositions not possible in bulk crystals.

The term "polymetallic clusters" is used when referring more generally to clusters containing atoms of two or more metals, and includes bimetallic clusters as a special case. Polymetallic clusters provide great flexibility in the design of metal catalysts. Virtually any property of a metal catalyst, including activity, selectivity, or surface stability, may be influenced by combining it with one or more other metals in the form of polymetallic

clusters. The metallic portion of polymetallic cluster catalysts may constitute a very small fraction of the total mass of metal plus carrier, as in the case of catalysts employed in the catalytic reforming of petroleum naphthas for production of high anti-knock quality motor gasolines (3). In such catalysts the metallic portion commonly comprises less than 1 per cent of the total catalyst mass. Correspondingly, the degree of coverage of the carrier surface by the metal clusters is typically lower than about 1 per cent in reforming catalysts.

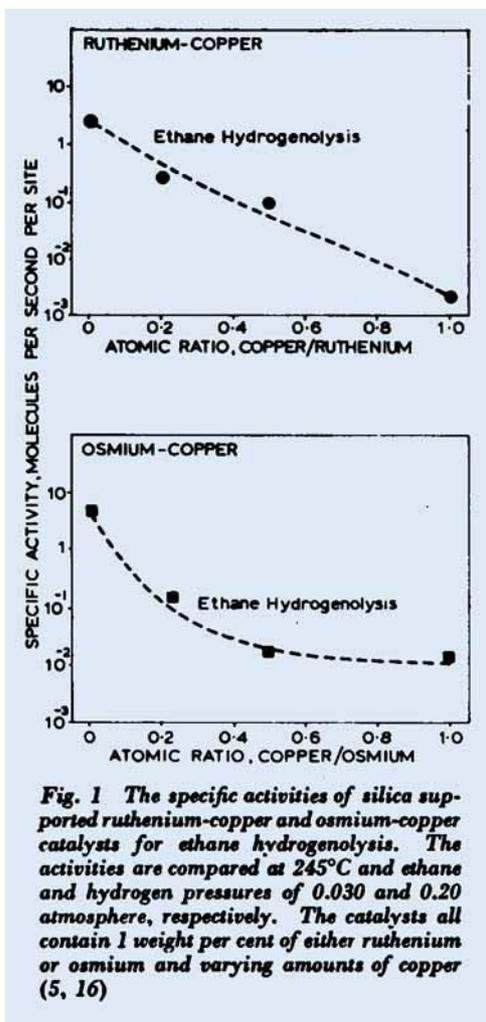
Examples of types of polymetallic clusters of interest include combinations of two or more metals within Group VIII and combinations of one or more Group VIII metals with a Group IB metal. Bimetallic combinations of a Group VIII metal and a Group IB metal provide useful model systems for investigating the basic concept (5). Reactions such as the hydrogenolysis of ethane to methane and the dehydrogenation of cyclohexane to benzene have been very valuable in probing into the nature of these model bimetallic catalysts. The studies have demonstrated a strong element of catalytic specificity, the Group VIII-Group IB clusters behaving very differently for different types of hydrocarbon reactions. With such information, one is in a position to exert considerable control over the catalytic behaviour of metallic systems.

Experimental Evidence for Bimetallic Clusters

Direct experimental verification of the existence of highly dispersed bimetallic clusters is complicated by limitations in the ability of physical methods to obtain structural information on highly dispersed systems. For example, conventional X-ray diffraction procedures are unsatisfactory for the investigation of metal crystallites or clusters in the size range of 10 to 20 Å. Recently, a method based on the analysis of the fine structure in X-ray absorption spectra on the high energy side of an X-ray absorption edge has shown

promise for structural investigations on highly dispersed materials (7). The application of this method, known as EXAFS, to bimetallic clusters is currently being explored (8), but no results are yet available. In the absence of information by physical methods, however, chemisorption or a catalytic reaction can serve as a sensitive probe to obtain evidence of interaction between the atoms of the two metallic components in a bimetallic catalyst.

Bimetallic clusters of a Group VIII and a Group IB metal are good model systems for chemisorption and catalytic studies, since the individual components have very different properties. Thus, the Group VIII metals exhibit strong hydrogen chemisorption whereas the Group IB metals do not (9, 10, 11). Similarly, the Group VIII metals exhibit catalytic activities for the hydrogenolysis of alkanes which are many orders of magnitude higher than those of the Group IB metals (12). Incorporation of a Group IB metal with a Group VIII metal in an alloy or bimetallic cluster leads to a marked decrease in the extent of strong hydrogen chemisorption and in the catalytic activity for hydrogenolysis of ethane to methane (5, 11, 12, 13). Interestingly, these effects are observed even for Group VIII-Group IB metal combinations which exhibit very limited miscibility in the bulk (5). Examples of such systems are ruthenium-copper and osmium-copper. Specific catalytic activities of silica supported ruthenium-copper and osmium-copper clusters for the hydrogenolysis of ethane to methane are given in Figure 1. The catalysts of Figure 1 contain 1 weight per cent of either ruthenium or osmium and varying amounts of copper, the atomic ratio of copper to the Group VIII metal ranging from 0 to 1. The specific activity for ethane hydrogenolysis declines markedly as the copper content increases. For clusters containing one atom of copper per atom of ruthenium or osmium, the hydrogenolysis activity is three orders of magnitude lower than that of the supported Group VIII



metal alone. These data clearly demonstrate an interaction between copper and the Group VIII metal, and thus provide evidence for the existence of bimetallic clusters. If copper and the Group VIII metal existed as separate entities on the carrier, one would not expect the hydrogenolysis activity of the bimetallic catalyst to be significantly different from that of the supported Group VIII metal alone. The interaction between copper and either ruthenium or osmium may be considered analogous to that in chemisorption, manifesting itself as a surface rather than a solution effect. If one visualises chemisorption of copper atoms on ruthenium or osmium entities consisting entirely of surface

atoms, a model of a highly dispersed bimetallic cluster emerges. From this point of view, it is readily seen how bimetallic clusters may exist with compositions far outside the range of those possible in bulk solid solutions.

For systems whose components exhibit limited miscibility in the bulk, it is interesting to consider what happens as the degree of dispersion of the system is varied (14). In the case of ruthenium-copper, for example, one might expect a large aggregate to consist of a core of ruthenium covered by a layer of copper, corresponding to the "cherry" model of Sachtler for bimetallic systems with a large miscibility gap (15). Because of the almost complete immiscibility of ruthenium and copper in the bulk, it is useful to make the simplifying assumption that the copper in a ruthenium-copper aggregate is confined strictly to the surface. In considering an aggregate consisting of a monolayer of copper on a core of ruthenium, we note that the atomic ratio of copper to ruthenium in the aggregate will increase with decreasing aggregate size. As the degree of metal dispersion becomes very high the atomic ratio of copper to ruthenium in such an aggregate eventually attains a value of the order of unity. The bimetallic entity generated in this manner is a highly dispersed ruthenium-copper cluster. According to this view of the ruthenium-copper system, the atomic ratio of copper to ruthenium required to achieve a given extent of inhibition of hydrogenolysis activity will be much higher for highly dispersed ruthenium-copper clusters than for large aggregates. This is indeed found to be the case, as shown in Figure 2. The metal dispersion, expressed as the percentage of metal atoms present in the surface, is of the order of 1 per cent for the large ruthenium-copper aggregates and of the order of 50 per cent for the clusters. In the case of the clusters a thousand-fold decrease in hydrogenolysis activity is obtained for a copper to ruthenium atomic ratio equal to one. With the large aggregates, however, the same

Fig. 2 Influence of the state of dispersion of ruthenium-copper catalysts on the relationship between ethane hydrogenolysis activity and catalyst composition. The large ruthenium-copper aggregates have a metal dispersion of the order of 1 per cent while the highly dispersed ruthenium-copper clusters have a metal dispersion of the order of 50 per cent (14)

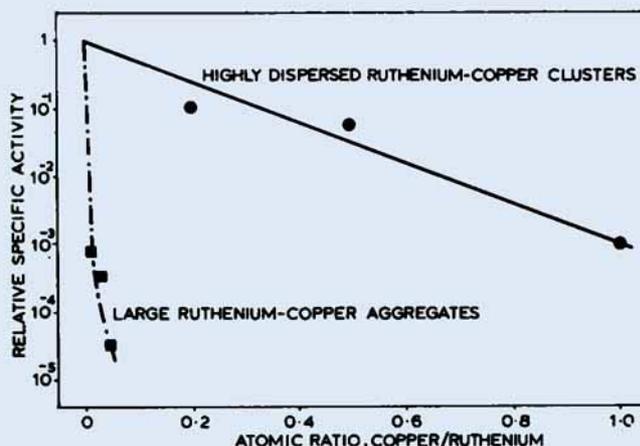
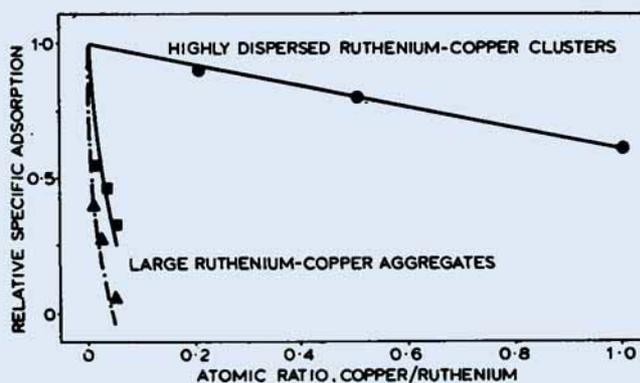


Fig. 3 Influence of the state of dispersion of ruthenium-copper catalysts on the relationship between hydrogen chemisorption capacity and catalyst composition. The catalysts are the same as in Fig. 2. The square and triangular points represent total hydrogen chemisorption and strongly chemisorbed hydrogen, respectively, on the large ruthenium-copper aggregates (14)



inhibiting effect is observed for a fifty-fold lower ratio of copper to ruthenium. Similar effects are observed in hydrogen chemisorption studies, in which a given degree of inhibition of hydrogen chemisorption requires a much higher atomic ratio of copper to ruthenium in the highly dispersed clusters than in the large aggregates (see Figure 3).

Selectivity Effects

Recent research on alloys and bimetallic clusters has revealed that selectivity effects may be very important in such systems. Catalytic studies on Group VIII-Group IB alloys and bimetallic clusters provide a striking example of specificity with regard to the type of reaction. In particular, it has been found that the addition of a Group IB metal to a Group VIII metal leads to marked

inhibition of the hydrogenolysis activity of the latter, while the dehydrogenation activity is affected relatively little (5, 11, 12, 13). This is illustrated in Figure 4 by data on the conversion of cyclohexane on supported ruthenium-copper and osmium-copper cluster catalysts (5). On pure ruthenium and osmium, cyclohexane undergoes appreciable hydrogenolysis to lower carbon number alkanes in addition to dehydrogenation to benzene. The major product of the hydrogenolysis reaction is methane, even at very low conversions. As copper is added to ruthenium or osmium to form bimetallic clusters, the hydrogenolysis activity decreases relative to the dehydrogenation activity, resulting in improved selectivity to benzene. Selectivity is defined here as the ratio of dehydrogenation activity (D) to hydrogen-

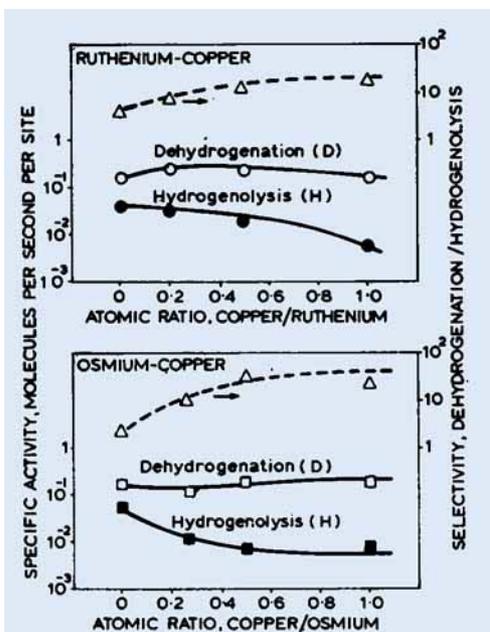


Fig. 4 The specific activities of silica supported ruthenium-copper and osmium-copper catalysts for the dehydrogenation and hydrogenolysis of cyclohexane. Activities are compared at 316°C and cyclohexane and hydrogen partial pressures of 0.17 and 0.83 atmospheres, respectively. The catalysts are the same as in Fig. 1. Selectivity, defined as the ratio of dehydrogenation activity (D) to hydrogenolysis activity (H), is also shown as a function of catalyst composition (5, 16)

olysis activity (H), and is represented by the dashed curves in Figure 4. The different effects of copper on the hydrogenolysis and dehydrogenation activities of the Group VIII metals may be rationalised on the basis of differences in the nature of the rate determining step for the two reactions, as has been discussed by the author elsewhere (11, 16).

Data which have recently become available on other hydrocarbon reactions on Group VIII-Group IB bimetallic catalysts suggest that reactions at carbon-hydrogen bonds in general behave differently from reactions at carbon-carbon bonds. Thus, the exchange reactions of cyclopentane (17) and methylcyclopentane (18) with deuterium on nickel-copper alloys are affected less than the accompanying hydrogenolysis reactions.

Industrial Applications

Research on the polymetallic cluster concept at the Exxon Corporate Research Laboratories has recently led to a new catalyst for the reforming of petroleum naphthas for motor gasoline production (19). While the composition of the catalyst, designated KX 130, has not yet been disclosed, data on its performance have been published (20). The catalyst is several fold more active than conventional platinum catalysts, as shown in Figure 5. Furthermore, the activity maintenance of KX 130 catalyst is far superior to that of a conventional platinum catalyst, as also shown in Figure 5. The superior activity maintenance of KX 130 relative to a platinum/alumina catalyst is related to a lower rate of deposition of carbonaceous residues on KX 130 catalyst. As is well known, the catalytic reforming process is conducted at elevated hydrogen pressures to suppress the formation of carbonaceous residues which deactivate the catalyst. A catalyst with better activity maintenance can be run for a longer period of

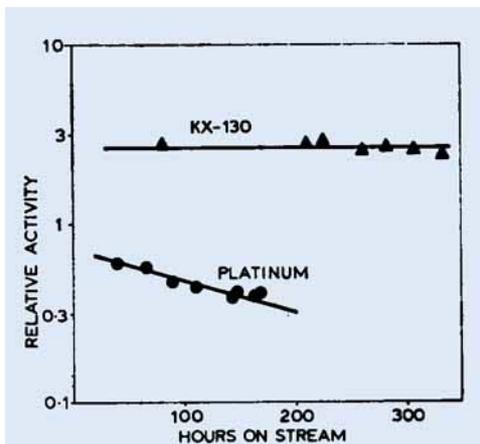


Fig. 5 Comparison of activities of KX-130 and platinum-alumina catalysts for the reforming of a highly paraffinic naphtha to produce 102.5 research octane number reformate. Reaction temperature and pressure were 500°C and 11 atmospheres respectively. KX-130 is a catalyst developed at Exxon Research and Engineering Co. as part of a research programme on polymetallic cluster catalysts (19, 20)

time before regeneration is required. Regeneration of a reforming catalyst involves the combustion of carbonaceous residues from the catalyst surface using a gas of low oxygen content with close attention to control of temperature and other operating conditions. An alternative way to take advantage of a catalyst with superior activity maintenance is to operate at lower pressure. For a given length of operation (cycle length) between regenerations, KX 130 catalyst can be used at lower pressures than a platinum/alumina catalyst. The advantage of operating at low pressure is associated with a higher yield of liquid reformat for inclusion in gasoline. The choice of the best way to take advantage of the improved activity maintenance depends on the particular situation.

Another catalyst which exhibits improved reforming performance relative to that obtained with platinum/alumina catalysts is the platinum-rhenium/alumina catalyst first announced by Chevron (21). The catalyst generally contains rhenium in an amount comparable to the amount of platinum present. Again, a major advantage of this catalyst over platinum/alumina is the improved activity maintenance, which makes it possible to obtain longer reforming cycles or to operate at lower pressures to take advantage of higher reformat yields. From a fundamental point of view, a question of interest with regard to the platinum-rhenium catalyst is the physical and chemical state of the rhenium in the catalyst. Whether or not a highly dispersed alloy or cluster of platinum and rhenium exists on the alumina surface is of interest to catalytic scientists working with this system. Some workers have presented evidence that the rhenium is present as a highly dispersed oxide on the alumina surface at typical reforming conditions (22), while others have claimed that rhenium can be reduced to the metallic state (23). The data supporting reduction to the metallic state have been obtained on catalysts containing much higher rhenium concentrations than exist in the commercial catalyst; it may

well be that rhenium concentration has an important bearing on its reducibility (24).

Conclusion

The concept of highly dispersed poly-metallic clusters introduces some intriguing features to the science of highly dispersed metals and would appear to have considerable generality. It should be applicable to a variety of combinations of metallic elements, thus extending the range of systems of interest in metal catalysis. Work in this area provides an example of how technological advances in catalysis can be realised within a framework of fundamental research.

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