

There has been much interest in bimetallic heterogeneous catalysts since the 1940's [1]. The addition of a second less or non-active metal to a monometallic catalyst has often been found to increase activity, promote favorable selectivity and/or enhance durability. A conventional industrial preparation of these catalysts was by bulk mixing of the metal salts or oxides with the supported material, leading to ill-defined surface species. In addition, the metal salts often contained counterions or ligands with elements known to inhibit specific catalytic reactions [2].

Organometallic compounds, commonly metal carbonyls, have recently gained attention as precursors in heterogeneous catalysis [3,4]. They provide better control over the purity and dispersion of supported metal particles by comparison with conventional methods. The use of heteronuclear clusters has added an additional aspect to this expanding field. With these discrete clusters, one has for the first time the potential of controlling surface metal particle stoichiometry. This may allow one to discern the role of components in a bimetallic catalyst, and perhaps effectively create catalysts with the optimal mixed-metal composition and/or structure. Applications have been limited due, in part, to a lack of suitable compounds [5].

The compounds $(\eta^5\text{-C}_5\text{H}_5)_x\text{M}_x\text{Ir}_{4-x}(\text{CO})_{12-x}$ ($\text{M} = \text{Mo}, \text{W}; x = 1, 2$) have previously been prepared by Foose [3]. The crystal structures of the tungsten-containing clusters show a tetrahedral core of metal atoms. The molybdenum-containing clusters are assumed to be isostructural [6]. These compounds have been supported on alumina (Al_2O_3), with studies of $\text{W-Ir}/\text{Al}_2\text{O}_3$ initially being carried out by Hardwick [3,7]. The properties of the mixed-metal cluster derived catalysts were compared with those derived from stoichiometric mixtures of $\text{Ir}_4(\text{CO})_{12}$ and $(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_6$.

The samples were slowly heated to 500°C in flowing hydrogen. This activation procedure removed surface carbon in the form of methane. The methane evolution profiles for the mixed-metal samples were different from those of the stoichiometric mixtures. The stoichiometric mixtures appeared to be reacting as separate components on the surface, by comparison with the profiles of $\text{Mo}_2/\text{Al}_2\text{O}_3$ and $\text{Ir}_4/\text{Al}_2\text{O}_3$.

Further characterization of the activated samples included selective chemisorption measurements, reactive thermal desorption of adsorbed carbon monoxide and iridium-based n-butane hydrogenolysis. Both mixed-metal cluster-derived samples exhibited unique properties, not obtainable with the stoichiometric mixtures ($[\text{Ir}_4 + \text{Mo}_2]/\text{Al}_2\text{O}_3$). These properties can be attributed to various mixed-metal interactions.

Direct observation of proposed mixed-metal interactions was carried out by x-ray absorption spectroscopy of the molybdenum K-edge [8]. The x-ray absorption near edge structure (XANES) provided information related to the chemical nature (oxidation state and coordination

sphere) of the absorbing atom. The extended x-ray absorption fine structure (EXAFS) was used to determine the identity, radial distances and coordination number of atoms surrounding the absorbing atom. Results indicate that the mixed-metal cluster precursors did provide molybdenum-metal interactions not obtainable through stoichiometric mixtures. The initial tetrahedral metal core apparently did not remain intact on the alumina surface.

References

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