Catalytic Dehydrogenation of Ethylbenzene in Helium and Reductive Dealkylation in Hydrogen on Nb, Mo, Ta, W, and Re Halide Clusters

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Halide clusters of [(Nb6Cl12)(H2O)4]·4H2O and (H3O)[(M6Cl8)Cl6]·6H2O (M = Mo, W), which have an octahedral metal framework, and Re3Cl9, which has a triangular metal framework, developed catalytic activity for the dehydrogenation of ethylbenzene selectively to yield styrene when the halide clusters were treated in a stream of helium at 450°C. In the case of the Mo cluster, this catalytic activity appeared at 300°C. The activity increased with increasing temperature. Above 400°C, the catalytic activity decreased with time, and the selectivity for benzene increased noticeably. The reduction in the activity was caused by the formation of coke attributable to ethylene produced as a by-product. When the Nb and Ta clusters of the same structure were treated in a stream of hydrogen in the same way, no catalytic reaction proceeded. However, the Mo and W clusters in a stream of hydrogen catalyzed reductive dealkylation of ethylbenzene selectively yielding toluene and benzene. In the case of the Mo cluster, the catalytic activity appeared at 400°C, and increased with increasing temperature. The activity did not decrease with time even at high temperatures. The Re cluster, which was reduced to the metal by the treatment in hydrogen, catalyzed ring-opening degradation to yield gaseous hydrocarbons.

KEY WORDS: Catalysis by halide cluster; molybdenum halide; niobium chloride; dehydrogenation of ethylbenzene; reductive dealkylation.

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INTRODUCTION

The first report on the synthesis of a halide cluster, \( \text{MoCl}_2 \), was published in 1859 [1] (Fig. 1), though its definite structure was established long afterwards in 1967 by X-ray analyses [2]. Numerous clusters have been synthesized by combining 17 kinds of group 3–7 metal atoms and four kinds of \( \pi \)-donor halogen ligands [3]. The majority of these clusters have highly symmetric and aesthetically pleasing \([\text{M}_6\text{X}_8]\) or \([\text{M}_6\text{X}_{12}]\) unit [4]. These clusters are characterized by the middle oxidation states of the metal atoms that are bonded to each other. Polynuclear coordination could induce reactivity into a ligand that differs significantly from that produced by mononuclear coordination [5]. Thermal stability is the largest advantage of the halide clusters over carbonyl clusters as catalysts. That is to say, the former are usually synthesized by comproportionation above 650°C whereas the latter decompose at temperatures as low as 200°C. Since the synthesis of halide clusters was first reported over 140 years ago, it has lain dormant to catalysis, like “Sleeping Beauty.” The thermal stability of these clusters may even have hindered attempts to use them as catalysts. In recent years, we have reported a series of reactions catalyzed by the Sleeping Beauty: isomerization of olefins [6], dehydrohalogenation of halogenated alkanes [7], dehydration of alcohols [8], and decomposition of phenyl acetate to afford ketene and phenol [9]. Although these reactions proceed over conventional solid acid catalysts, closer inspection revealed some conspicuous features, particularly in terms of selectivity. In order to understand the scope and limitations of the Sleeping Beauty

![Fig. 1. Structure of molybdenum chloride MoCl\(_2\) ([Mo\(_6\)Cl\(_{12}\)]Cl\(_{2}\)).](image)