



Gas-phase S-alkylation of benzenethiol with aliphatic alcohols, ethers, esters, alkyl halides and olefins over halide cluster catalysts of Groups 5 and 6 transition metals

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ABSTRACT

Benzenethiol was reacted with methanol under a hydrogen stream over $[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_2(\text{H}_2\text{O})_4] \cdot 6\text{H}_2\text{O}$ supported on silica gel. Catalytic activity of the cluster commenced above 250 °C, yielding methyl phenyl sulfide. The selectivity was 98% at 400 °C. Molybdenum, tantalum and tungsten halide clusters with the same octahedral metal framework also catalyzed the reaction. Primary alcohols with shorter alkyl chains were effective reagents for the S-alkylation. Aliphatic ethers, dialkyl carbonates, orthoesters and alkyl halides were effective reagents for the S-alkylation. When 1-hexene was applied to the reaction, spontaneous and catalytic S-alkylation proceeded simultaneously above 200 °C, yielding *n*-hexyl phenyl sulfide. When alkyl acetates were subjected to this reaction, the niobium cluster afforded S-phenyl thioacetate, and the other clusters afforded alkyl phenyl sulfides selectively. A Brønsted acid site attributable to a hydroxo ligand, which is formed on the cluster complex by thermal activation, is proposed as the active site of the catalysts.

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1. Introduction

Various types of halide cluster complexes have been synthesized by combining 19 types of Group 3–7, lanthanide and actinide transition metals with four types of halogen atoms as ligand [1–4]. These halide clusters have several characteristic features: metal–metal bonds that are similar to those in bulk metals, multicenter and multielectron systems, intermediate oxidation states of the metal atoms between 1+ and 3+, a diversity of metal atoms and halogen ligands, and low vapor pressure and high melting point for the metal halogenated complexes. Taking these features into consideration, we have been studying the application of halide cluster complexes as catalysts and found various reactions, e.g., synthesis of 3-methylbenzofuran from phenol and acetone [5] and synthesis of indenes from benzaldehyde and ketones [6].

In parallel to halide cluster catalysis, we have been studying the catalysis by rhenium sulfide clusters such as $\text{Eu}_2[\text{Re}_6\text{S}_8]\text{S}_{6/2}$ and $\text{K}_4[\text{Re}_6\text{S}_8]\text{S}_{4/2}(\text{S}_2)_{2/2}$ with an octahedral metal framework [7,8]. Coordination of the sulfur atom to the cluster framework

is not too strong, and it is moderately easy to remove at elevated temperatures; treatment of $\text{Eu}_2[\text{Re}_6\text{S}_8]\text{S}_{6/2}$ in a hydrogen stream above 250 °C partially removed the sulfur ligand as hydrogen sulfide, resulting in the development of catalytic activity. Although sulfur compounds with a lone pair of electrons coordinate to metal atoms and act as strong catalyst poisons for the Group 8–10 transition metals, molybdenum and niobium sulfides are used as hydrodesulfurization catalysts to denote moderate adsorption strength of the sulfur compounds. A niobium halide cluster catalyzed cyclization of 1,2-benzenedimethanethiol to afford 1,3-dihydrobenzo[c]thiophene by eliminating hydrogen sulfide [9]. Accordingly, sulfur compounds interacted moderately with the halide cluster and did not act as a catalyst poison. This prompted us to use halide clusters of Groups 5 and 6 transition metals as a catalyst for sulfur-containing substrates.

Alkyl phenyl sulfides are useful synthetic intermediates for medicines, pesticides and agricultural chemicals, and are used as solvents. Many synthetic methods have been reported. In the case of S-alkylation of benzenethiol, several alkylating reagents have been reported: alcohols, ethers, alkyl carbonates, alkyl halides, olefins and, in rare cases, alkyl carboxylates. Although many examples of stoichiometric reactions and homogeneous catalyses have been reported, heterogeneous catalyses, which are advantageous for the

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