Comparison of catalysts consisting of site-isolated mononuclear rhenium complexes, trirhenium clusters, and larger rhenium clusters for n-butane conversion: effects of Re oxidation state and cluster size

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Introduction
Catalysts containing metal clusters of only a few atoms supported on porous materials offer new properties that in prospect can be controlled both by the structure of the metal-containing species and the oxidation state of the metal, which may depend strongly on the dispersion. Thus, we investigated catalysts consisting of the most highly dispersed supported metals, attempting to prepare them with well-defined structures and to separate the effects of cluster size and metal oxidation state on catalytic properties. Because traditional methods of catalyst preparation yield samples that are structurally non-uniform and therefore difficult to characterize incisively, we prepared catalysts from a molecular precursor, \( \text{H}_3\text{Re}_6(\text{CO})_{12} \), incorporating an oxophilic metal, which has a strong tendency to be present as cationic species. The specific goals were to prepare stable, site-isolated metal species with controlled numbers of metal atoms in the catalytically active species. Samples were characterized by EXAFS spectroscopy to determine cluster sizes, XANES to provide evidence of Re oxidation states, and IR spectroscopy to determine the presence of species bonded to the Re. The influence of the catalyst structure and metal oxidation state were determined with a hydrocarbon conversion reaction that is regarded as classically structure-sensitive and provides selectivity information, namely, the conversion of \( n \)-butane with \( H_2 \).

Materials and Methods
\( \text{H}_3\text{Re}_6(\text{CO})_{12} \), synthesized as before, [1] was adsorbed on \( \gamma \)-Al\(_2\)O\(_3\) (Degussa) calcined at 500°C. Samples were treated at 500°C in \( H_2 \) to produce bare Re\(_2\) clusters. [2] A sample was further treated in \( O_2 \) at 150°C to produce isolated Re atoms by cluster fragmentation. Part of this sample was reduced in \( H_2 \) to produce rhenium clusters larger than Re\(_2\). In the catalytic reaction experiments, samples in flowing helium were heated to 260°C, then the flow of \( n \)-butane + \( H_2 \) was started. The effluent gas was analyzed by on-line GC. Used catalyst samples were characterized by IR, EXAFS, and XANES spectroscopies.

Results and Discussion
EXAFS spectra characterizing the sample treated in \( H_2 \) and then \( O_2 \) were characterized by two short Re–O contributions (1.74 and 1.98 Å) but no Re–Re contribution, consistent with the presence of Re in site-isolated mononuclear species bonded to the support. EXAFS spectra characterizing the sample treated only in \( H_2 \) exhibit a Re–Re contribution with a coordination number (CN) of ca. 2, indicating Re\(_2\) clusters, on average, [2] which IR spectra show were decarbonylated. The sample treated in \( H_2 \) after the \( O_2 \) treatment was characterized by a Re–Re contribution with a CN of 4.9 at a distance of 2.71 Å, indicative of clusters containing, on average, approximately 9 Re atoms each. The sample containing Re\(_2\) clusters was characterized after catalysis—no significant aggregation occurred.

The Re L\(_3\) edge shift was essentially the same for both samples incorporating rhenium clusters (4.5 eV), indicating that the rhenium was cationic, independent of the average cluster size. The sample containing mononuclear Re was also characterized by a positive edge shift (6.9 eV), but the rhenium was in a higher oxidation state than that in the clusters.

Catalytic data (Figure 1A) show that the sample containing mononuclear Re and that containing Re\(_2\) had similar activities–after the initial induction period–but these catalysts were significantly less active than the catalyst containing the larger clusters. These results indicate that the activity was more sensitive to cluster size than to Re oxidation state.

Selectivity for methane and propane formation (Figure 1B) was, within error, the same for the samples containing Re\(_2\) clusters and larger clusters, and markedly different from that characterizing the sample containing mononuclear Re. We infer that the species containing neighboring Re centers, almost independent of cluster size, catalyze C–C bond breaking faster than the more highly oxidized mononuclear Re.

Significance
Use of the molecular precursor \( \text{H}_3\text{Re}_6(\text{CO})_{12} \) allowed the synthesis of catalysts with extremely small and well-defined supported metal sites, enabling their incisive characterization. In catalytic \( n \)-butane conversion, the activity of the sample is determined primarily by the cluster size and not the metal oxidation state, whereas the selectivity is determined primarily by the metal oxidation state and not the cluster size.

References

Figure 1. Catalyst performance data; A, activity and, B, selectivity for the major products for the conversion of \( n \)-butane in \( H_2 \) at 260°C in a once-through flow reactor; the catalysts contained mononuclear Re (black), Re\(_2\) clusters (gray), and rhenium clusters with an average nuclearity of 9 Re atoms (white).