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Structure and Catalytic Function of Re-Oxo Species Grafted onto H-MFI Zeolite by Sublimation of Re_2O_7

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The formation of single-site heterogeneous catalysts remains a formidable challenge.[1] Sites with uniform structure and catalytic function seldom prevail in microporous inorganic solids prepared by aqueous exchange of high-valent cations because of the size and charge of aqueous metal-oxo oligomeric precursors and their diverse structures at conditions of pH and temperature consistent with the structural integrity of aluminosilicates. Anchoring of high-valent metal-oxo species leads to structures that are less reducible than the corresponding bulk oxides and to relatively unreactive oxidation catalysts.[2] Here, we report the exchange of isolated and uniform Re^{7+}-oxo cations of significant catalytic relevance for oxidation of alcohols via reactions of $Re_2O_7(g)$ with acidic protons in H-MFI. The structure and catalytic function of these species do not depend on Re content, a hallmark of single-site catalysts with isolated and uniform active sites.

Re_2O_7 and organometallic Re-oxo species form volatile species at conditions required for oxidation catalysis. As a result, they cannot be used for oxidation reactions at elevated temperatures despite their high reactivity in alkene epoxidation.[3] Re_2O_7, NH_4ReO_4, and MTO (methyltrioxorhenium) have been grafted onto several inorganic oxide supports in order to stabilize active sites and allow their use as catalysts.[3,4] The structures of ReO_x species during synthesis, thermal treatment, and catalysis, and even their presence at exchange sites in H-MFI, remain uncertain.

Raman spectra were used to probe the structure of Re-oxo species in H-MFI (Figure 1) after removing fluorescing compounds using a novel UV irradiation treatment (Supporting Information). Raman spectra for Re_2O_7/H-MFI (0.4 Re/Al_f) mixtures resembled those for crystalline Re_2O_7[6,7] before thermal treatment. Re_2O_7 bands disappeared during treatment in dry air at 823 K for samples with Re/Al_f ratios of 0.3−0.8; broad bands emerged concurrently at 1020, 980, and 347 cm^{-1}, similar to those for ReO_4^-(aq), but shifted to slightly higher frequencies, consistent with the formation of Si−$O_f$$ReO_3$−Al ($O_f$ is framework O) centers distorted from perfect tetrahedra. Changes in local Re−O coordination upon heating Re_2O_7/H-MFI were also evident in Re L_I edge X-ray absorption spectra (Figure 2A). The intensity of the pre-edge feature increased after treatment at 723 K in dry air because of an increase in the tetrahedral character of Re centers as in distorted tetrahedral NH_4ReO_4, compared with Re_2O_7, in which 50% of the Re exhibits distorted octahedral symmetry.

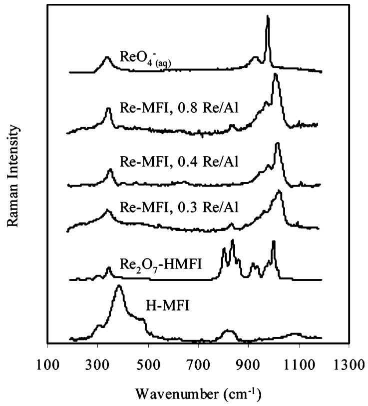

Figure 1. Raman spectra of Re-MFI (MFI background subtracted) and rhenium reference compounds.

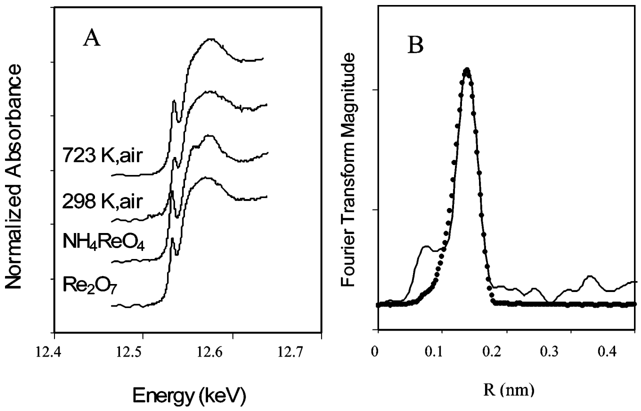

Figure 2. Re L_I X-ray absorption spectra of Re_2O_7, NH_4ReO_4, and Re_2O_7/H-MFI (Re/Al_f = 0.2) at 298 and 723 K (A). Re L_{III} radial structure function (B) of Re-MFI (Re/Al_f = 0.2) after treatment at 773 K in dry air (solid line). Simulation results shown as circles.

Metal-oxo cations with M^{7+} centers can exist as either monomers (Structure I, Scheme 1) or dimers (Structure II) at exchange sites. Dimers might resemble a distorted C_{2v} symmetry with two bridging O atoms and two terminal Re═O bonds at each Re center as depicted in Scheme 1; there are, however, no precedents for di-μ-O linkages in Re-oxo complexes. Re−O−Re stretches in dimers, expected at 456 and 185 cm^{-1} (from bands in molten ditetrahedral Re_2O_7(l)),[6] were not detected after thermal treatment of Re_2O_7/H-MFI mixtures. Bridging μ-O bands in metal-oxo clusters on Al_2O_3 are weak, however, because of nonuniform coordination;[2] thus, we cannot exclude the coexistence of Structures I and II from the absence of these bands. Extended X-ray absorption fine structure (Figure 2B) for Re-MFI (Re/Al_f = 0.2) also did not detect Re−O−Re bonds, expected in Re-oxo dimers. A fit of the spectra gave two Re−O shells with coordination of 3 and 1 at 0.17 and 0.18 nm, respectively, without the second shell expected for Re−O−Re structures.

The isolated and accessible nature of grafted ReO_x species was confirmed by Raman shifts detected upon exposing samples to weakly coordinating H_2O molecules. Bands shifted to lower frequencies for ReO_x on Al_2O_3 but not for NH_4ReO_4(s) crystals with inaccessible Re^{7+} centers.[8] The symmetric Re−O stretch in Re-MFI shifted to 975 cm^{-1} upon contact with H_2O(g) (3 kPa) at ambient temperature. The antisymmetric (941 cm^{-1}) and bending

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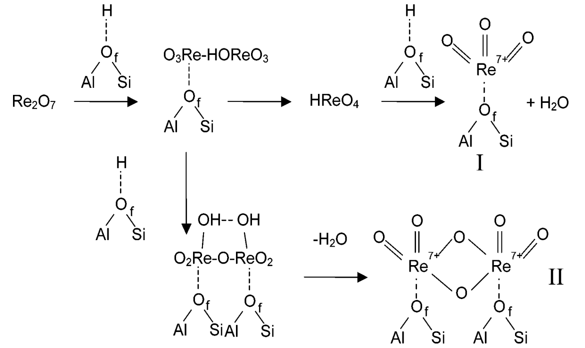
Scheme 1. Re_2O_7(g) Exchange Pathways



(334 cm^{-1}) modes also shifted to lower frequencies. In Re_2O_7/Al_2O_3, exposure to ambient air gave spectra identical to those of ReO_4^-(aq) (970, 919, and 332 cm^{-1}),[6] but Re-MFI gave bands that were higher in energy. These shifts indicate that all tetrahedral Re-oxo centers are accessible and distorted by coordination with H_2O.

The Re-oxo exchange stoichiometry was measured from the number of OH groups detected in the infrared spectra of samples before and after exchange with Re_2O_7(g) at several Re/Al_f ratios. Infrared bands for acidic Si−OH−Al and Si−OH silanols are present in H-MFI, but silanols are minority species. Differences in OH band intensities (3400−3700 cm^{-1}) between Re-MFI and H-MFI samples treated at 673 K reflect the number of OH groups replaced by Re during exchange. The intensity of OH bands decreased linearly with increasing Re/Al_f ratio: 0.25 and 0.5 OH/Al_f were replaced with 0.22 and 0.44 Re/Al_f, respectively. Thus 1.1 H^+ are replaced by each ReO_x cation at both Re contents, consistent with either monomer or dimer Re-oxo species (Scheme 1), but not with unexchanged or crystalline ReO_x.

$Si{-}O_fReO_3{-}Al$ monomers can form via reaction of Re_2O_7(g) with $Si{-}O_fH{-}Al$ groups to form $Si{-}O_fRe_2O_6(OH){-}Al$, which then decomposes into $Si{-}O_fReO_3{-}Al$ and volatile perrhenic acid (Scheme 1).[9] $HReO_4$(g) can react with neighboring $Si{-}O_fH{-}Al$ groups to form another $Si{-}O_fReO_3{-}Al$ and H_2O(g). Re-MFI with Re/Al_f ratios above 0.5 could not be synthesized reproducibly (only about 60% of the OH groups reacted even for Re/Al_f ratios of unity), apparently because two monomers at next nearest neighbor Al sites sublime in the presence of trace amounts of H_2O ubiquitous in H-MFI samples. Reduction in H_2 formed 2.8 ± 0.1 H_2O per Re and consumed 3.4 ± 0.1 H_2 per Re for 0.1−0.44 Re/Al_f. The heptavalent nature of the Re centers, the proposed exchange pathways, and the prevalence of grafted $Si{-}O_fReO_3{-}Al$ monomers are consistent with the dynamics and stoichiometry of their reduction in H_2.[10]

Rates and selectivities for ethanol oxidation were measured on Re-MFI samples with Re/Al_f ratios of 0.1 and 0.4. $C_2H_5OH{-}O_2$ reactions formed ethyl acetate ($CH_3CH_2OCOCH_3$) and acetal ($(CH_3CH_2O)_2CHCH_3$) via secondary reactions of primary acetaldehyde (CH_3CHO) products.[11] Re-MFI contains both redox sites (ReO_x) and Brønsted acid sites (Si−OH−Al). Oxidative dehydrogenation turnover rates at 373 K were 2.2×10^{-3} and 2.3×10^{-3} mol C_2H_5OH (mol Re)$^{-1}$ s^{-1} on Re-MFI materials with 0.1 and 0.4 Re/Al_f ratios, respectively; no catalyst deactivation or ReO_x sublimation was detected during reaction (for ∼12 h). These findings indicate that the reactivity of Re-oxo species is independent of Re loading, consistent with the similar structure and stoichiometry shown by Raman and infrared spectra and by their reduction in H_2.

Re-MFI showed significant reactivity for acetaldehyde and acetal synthesis with <1% CO_2 selectivity at much lower temperatures (373 K) than on previously reported Re-based catalysts (>573 K).[12] At low Re/Al_f ratios (0.1), $(C_2H_5)_2O$ selectivities were relatively high (∼66%) because of abundant acidic OH groups, but $(C_2H_5)_2O$ selectivity decreased as grafted ReO_x replaced OH groups (26.3% for 0.4 Re/Al_f) that catalyze condensation reactions required for acetal synthesis.

This study shows that thermal treatment of Re_2O_7/H−MFI mixtures leads to the selective grafting of isolated and stable Re-oxo species via Re_2O_7(g) reactions with OH groups to form $Si{-}O_fReO_3{-}Al$ with similar structure irrespective of Re content ($Re/Al_f = 0.1{-}0.4$). These catalysts showed very high reactivity for C_2H_5OH oxidation, a reaction relevant to the conversion of biomass to fuels and chemicals, with turnover rates independent of Re content for samples with 0.1−0.4 Re/Al_f ratio. Grafting onto exchange sites prevented the ubiquitous sublimation of ReO_x species, which previously rendered Re-based materials unsuitable as oxidation catalysts. These materials and the synthetic protocols used here may also lead to novel catalysts for metathesis and epoxidation reactions, as well as to precursors and catalysts for reactions that benefit from spatial constraints within zeolites.

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Supporting Information Available: Experimental methods and extended C_2H_5OH reaction data. This material is available free of charge via the Internet at http://pubs.acs.org.

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