

Active site structures in supported catalysts prepared by grafting

Susannah L. Scott, Bradley F. Chmelka, Baron Peters

Sam Fleischman, Ryan C. Nelson, Brian C. Vicente, Anthony W. Moses, Naseem Ramsahye, Juergen Eckert

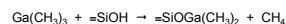
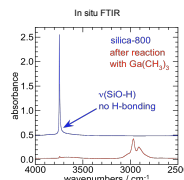
Department of Chemical Engineering, University of California, Santa Barbara



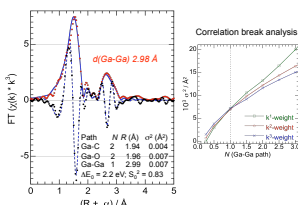
Evidence for an intrinsically non-random distribution of the hydroxyl groups on highly dehydroxylated silica

On silicas treated thermally at 800 °C, the surface hydroxyl density is only ca. 0.4 OH/nm². The IR spectrum shows a narrow, symmetrical peak for the O-H stretching vibration, indicating that the residual hydroxyls are non-interacting (not hydrogen-bonded). The conventional explanation is that these hydroxyls are widely separated ("isolated"), since they are not readily removed by mutual condensation. The implication for catalysis is that the reactions of organic or organometallic molecules with these hydroxyl sites occurs to give non-interacting grafted sites, accomplishing an site isolation often desired in catalysis to stabilize coordinatively-unsaturated or otherwise highly reactive intermediates.

The room temperature reaction of Ga(CH₃)₃ with a silica pretreated at 800 °C liberates methane. The quantity of methane formed indicates that grafting occurs predominantly at the surface hydroxyl sites, which the IR spectrum shows to be completely consumed.

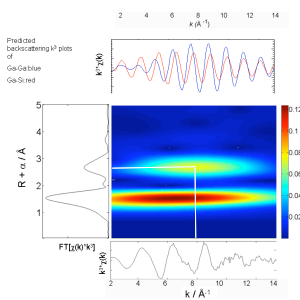


Ga K-edge EXAFS of grafted Ga(CH₃)₃



The Ga K-edge EXAFS contains a strong feature at ca. 2.7 Å in *R*-space. Its imaginary phase is consistent with a Ga-Ga path, not a support interaction (i.e., Ga-Si backscattering). Correlation break analysis reveals *N* = 1.0, implying that all Ga absorbers experience this path. Thus the grafted dimethylgallium sites are *not* isolated; they are instead paired.

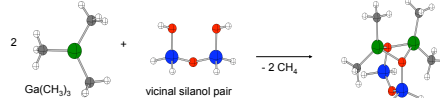
Further analysis of the EXAFS was performed using the Continuous Cauchy Wavelet Transform (CCWT),¹ in order to visualize the contribution of this long-range scattering path simultaneously in *k*- and *R*-space. Since the backscattering amplitudes of Ga and Si differ in the position of their *k*-space maxima, these atoms give rise to cross-peaks in the 2D contour plot at different *k*-values. The center of the feature corresponding to *R* ≈ 2.7 Å occurs at *k* = 8.0 Å⁻¹, consistent with a Ga backscatterer.



M. Muñoz, P. Argoul, F. Farges, *Am. Mineral.* 2003, 88, 694.

Structure of the digallium site

A DFT investigation of digallium structures shows that 3-coordinate dimethylgallium fragments attached to vicinal silanols (hydroxyl groups on Si atoms separated by a single oxygen bridge) form a disilanolate-bridged structure, with two 4-coordinate Ga atoms separated by 2.98 Å.



The presence of vicinal silanol pairs on silica even after 800 °C pretreatment is consistent with their energetically unfavorable condensation reaction to give highly-strained 4-membered Si₂O₂ rings. Consistent with the IR spectrum, and despite their proximity, vicinal silanols cannot engage in mutual hydrogen-bonding, due to the long O-O distance caused by the large Si-O-Si angle. Our results suggest that vicinal pairs are the dominant hydroxyl type on this silica.

Seeking evidence for additional support interactions in heterogeneous perhenate catalysts

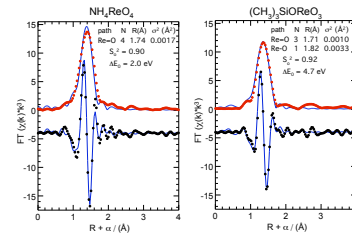
Vibrational spectra suggest that perhenate is attached on all oxides via a single hydroxyl site:



However, the ability of these sites to initiate olefin metathesis depends strongly on the nature of the oxide support. Silica confers no activity, silica-alumina gives a catalyst active at low Re loadings, and alumina gives an active catalyst only at high Re loadings. We hypothesize that additional perhenate-support interactions alter the reactivity of the grafted sites. The nature of these interactions was probed using EXAFS.

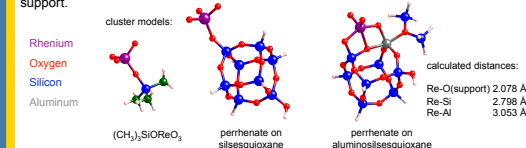
Re L₃-edge EXAFS of model compounds

Polycrystalline NH₄ReO₄ and (CH₃)₃SiOReO₃ were investigated as models. Attenuation of the *R*-space feature due to Re-O scattering paths in the first coordination sphere for trimethylsilyl perhenate relative to ammonium perhenate is caused by lowering of the symmetry from *T_d* to *C_{2v}*, and the consequent destructive interference between inequivalent paths. Fitted bond lengths agree with crystal structure data. Neither compound shows appreciable EXAFS intensity for paths beyond the first coordination sphere.



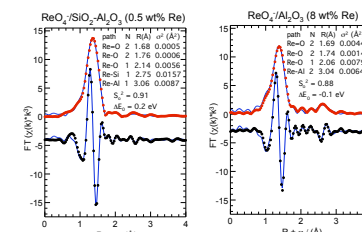
DFT models for supported perhenates

Computational analysis of perhenate attached to a silsesquioxane monosilanol cube as a model for the silica surface predicts that local *C_{3v}* symmetry should be preserved in perhenate grafted on silica. Re remains far from the support due to the large Re-O-Si angle. However, when a Lewis acidic Al site is introduced at an adjacent cube corner, the grafted perhenate interacts with the Al via one of its oxo ligands, bring Re closer to the surface. There is a new Re interaction with an oxygen atom of the support.



Re L₃-edge EXAFS of supported perhenates

The EXAFS of perhenate supported on silica-alumina and alumina (post-calcination) show evidence of the predicted symmetry-lowering. There are two short and two longer Re=O multiple bonds in the curvet model. A fifth Re-O path has a distance (ca. 2.1 Å) which suggests interaction with a support oxygen. On alumina, a prominent feature at 3.0 Å is consistent with a Re-Al path (*N* = 2). On silica-alumina, the Re-Si and Re-Al paths have different distances, leading to destructive interference and therefore less intensity at ca. 2.7 Å. However, agreement between the fitted bond lengths and the DFT model distances is very good.



Acknowledgements

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