

Synthesis/Characterization and Novel Applications of Molecular Sieve Materials

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SURFACE CHEMISTRY OF HETEROBIMETALLIC Ge-M (M = Mo, W)
COMPLEXES IN ZEOLITE Y

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ABSTRACT

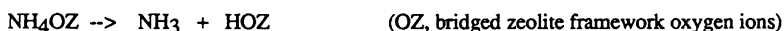
The intrazeolite chemistry of the two germylene complexes $\text{Cl}_2(\text{THF})\text{GeM}(\text{CO})_5$ (M = Mo, W) was studied with x-ray absorption spectroscopy (Ge, Mo, W edge EXAFS) and in-situ FTIR/TPD-MS techniques. The slightly decarbonylated GeMo complex interacts with the framework of NaY zeolite at room temperature and retains the Ge-Mo bond up to about 100⁰ C. In proton-loaded HY zeolite, framework interactions increase at elevated temperature, and the attached complex retains the Ge-Mo bond up to about 120⁰ C. The Ge-Mo bond is cleaved at higher temperatures. MoCl_x and Mo-Mo species are formed in NaY and HY zeolite, respectively, while GeCl_x fragments are anchored to the zeolite framework.

The complex $\text{Cl}_2(\text{THF})\text{GeW}(\text{CO})_5$ retains all five CO ligands up to about 100⁰ C in both NaY and the proton form. Detectable anchoring occurs at room temperature in NaY and at about 80⁰ C in the proton form. WCl_x species are formed upon cleavage of the Ge-W bond at higher temperatures.

INTRODUCTION

This article describes a study of the chemistry of Ge-metal complexes in zeolite cages. As part of our efforts to develop novel immobilization concepts for organometallic fragments in porous solids, we have introduced heterobinuclear compounds as candidates for linking catalytic functions to zeolite frameworks. The premise is that the complexes can be anchored to the support via an oxophilic element, whereas catalytic reactions may proceed at the second metal center. This anchoring concept is aimed at the stabilization of the metal species against agglomeration under reducing conditions.

The present work focuses on the use of zeolite Y with 1.2 nm large cages connected by 0.75 nm windows. Alkali metal cations coordinated to oxygen rings (with C_{3v} and C_{2v} symmetry in zeolite Y) can be exchanged with NH₄⁺ to obtain the acid form by degassing at elevated temperatures¹:



A preliminary report on our intrazeolite attachment of $\text{Cl}_2(\text{THF})\text{GeMo}(\text{CO})_5$ has been published². The present article describes the chemistry of this complex and its tungsten analog in different forms of zeolites Y. The study addresses the anchoring process and the stability of the complexes as a function of zeolite acidity, the nature of the transition metal, and temperature.

EXPERIMENTAL

Precursors $\text{Cl}_2(\text{THF})\text{GeMo}(\text{CO})_5$ [1] and $\text{Cl}_2(\text{THF})\text{GeW}(\text{CO})_5$ [2] were synthesized following a method for complex [2] using Schlenk techniques³. The complexes were characterized by IR, ¹H and ¹³C NMR, EXAFS, and mass spectrometry. Mass spectra were taken with a Finnigan mass spectrometer by heating the complexes from 50 to 200^o C at a rate of 20^o C/min.

The precursors [1] and [2] were absorbed into three different supports: NaY (commercial Linde LZ-Y52 [Na₅₇Al₅₇Si₁₃₅O₃₈₄]), partially proton-exchanged H2Y (2H⁺/sc, sc = supercage) derived from LZ-Y52 via ion exchange with 2 NH₄⁺/sc, and highly acidic H6Y (6 H⁺/sc) from

Linde LZ-Y62 $[(\text{NH}_4)_{45}\text{Na}_{10}\text{Al}_{55}\text{Si}_{137}\text{O}_{384}] \times 235 \text{H}_2\text{O}$. Heating the ammonium-exchanged zeolites under vacuum at $1^\circ \text{C}/\text{min}$ up to 450°C resulted in the desired acid form of the zeolites. The dehydrated zeolites were kept in sealed vials in a glove box prior to further treatments. The zeolites were loaded with an average of 0.8 molecules of $\text{Cl}_2(\text{THF})\text{GeM}(\text{CO})_5$ ($\text{M} = \text{Mo}, \text{W}$) per supercage (determined by AAS) by stirring a slurry of 0.500 g of zeolite with the required amounts of complex [1] or [2] in 50 ml pentane for 12 hours under dry nitrogen atmosphere. The solvent was removed by vacuum filtration on a frit.

All samples studied with EXAFS were heated at 50, 80, 100, 120, and 250°C under vacuum for 10 h (with a heating rate of $1^\circ \text{C}/\text{min}$). EXAFS measurements were carried out at NSLS (Brookhaven National Laboratories) at beamline X-11A with a stored energy of 2.5 GeV and ring currents between 90-180 mA. The data were collected at the Ge K-edge (11103 eV) and the Mo K-edge (20000 eV) of the $\text{Cl}_2(\text{THF})\text{GeMo}(\text{CO})_5$ samples, and at the Ge edge and W L₃-edge (10207 eV) of the $\text{Cl}_2(\text{THF})\text{GeW}(\text{CO})_5$ samples. The experiments were performed at about -170°C in transmission using a double crystal Si(400) monochromator. The EXAFS data were analyzed using standard procedures⁴. References and samples were processed similarly to avoid artefacts.

RESULTS AND DISCUSSION

(1) $\text{Cl}_2(\text{THF})\text{GeMo}(\text{CO})_5$ in NaY

EXAFS results of Mo-absorption edge data

The Fourier-transformed (FT) EXAFS data of $\text{Cl}_2(\text{THF})\text{GeMo}(\text{CO})_5$ in NaY at room temperature (Figure 1a) show imaginary parts similar to that of the precursor [1] with the exception of a reduced Mo-Ge contribution. Data analysis shows the presence of 3-4 carbons at a distance of 2.05 Å. A bond distance of 3.16 Å is found for Mo-CO, and 2.48 Å for 0.6 Ge atoms. Upon heating the sample to 50, 80, 100, 120 and 250°C , carbonyl intensities decrease drastically (starting at 80°C), while the Mo-Ge bond survives to about 100°C . The overall change is most obvious at 120°C (Figure 1b). Three coordination shells are found; the first and third shell still represent the CO ligands at much reduced intensity (Mo-C_{0.6}, Mo-CO_{1.0}), and a dominant shell appears at about 2 Å, which differs from the Ge-Mo contribution at room temperature. This shell is due to unidentified Mo-chloride species (Mo-Cl_{1.2} at 2.46 Å). At 250°C , the CO ligands have vanished and exclusive chloride coordination remains at the Mo center.

Ge-absorption edge

When the precursor [1] is introduced into NaY at room temperature, the FT spectrum at the Ge-edge (Figure 1d) broadens compared to the non-supported precursor. 1.1 chlorine atoms are found at a distance of 2.22 Å in addition to 2.3 oxygen atoms at 1.99 Å. The reduced chloride coordination suggests that the precursor [1] begins to attach to the zeolite framework already at room temperature.

Very similar data were obtained when the temperature was raised to 80°C . At 100°C the Ge-Mo contribution is reduced remarkably and at 250°C it disappears. At 120°C (Figure 1e) a good fit with the Ge-Cl reference shows that the chloride coordination (1.2 Cl at 2.20 Å) is almost unchanged to the room temperature sample. At 250°C (Figure 1f) chloride is still present and 2.6 oxygen atoms are located at 1.97 Å. A small peak at ca. 2.5 Å (uncorrected) assigned to framework Si/Al is now more visible than at room temperature.

Thus it appears that the attachment of the precursor complex [1] to the NaY zeolite framework via the Ge moiety starts already at room temperature by substitution for one chloride ion. The second chloride remains attached to the Ge atom even at 250°C . The Ge-Mo bond is

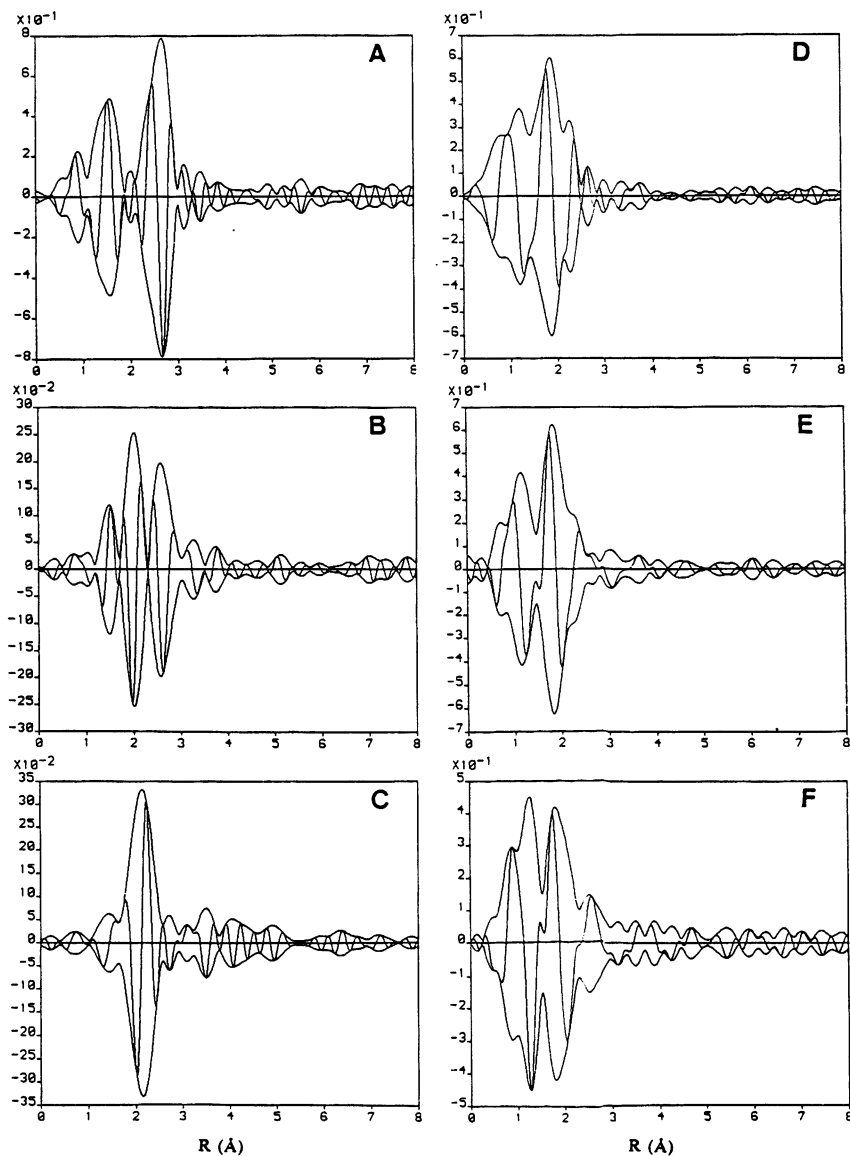


Figure 1. Fourier transformed EXAFS data of $\text{Cl}_2(\text{THF})\text{GeMo}(\text{CO})_5$ in NaY (all k^2 -weighted): A-C, Mo-edge spectra; A, at room temperature ($\Delta k = 3.3-13 \text{ \AA}^{-1}$); B, at 120° C ($\Delta k = 3.3-12 \text{ \AA}^{-1}$); and C, 250° C . D-F, Ge-edge spectra; D, at room temperature ($\Delta k = 2.7-13 \text{ \AA}^{-1}$); E, 120° C ; and F, 250° C .

fairly stable up to ca. 100° C, while complex decomposition and formation of molybdenum chloride occurs at higher temperatures.

In-situ FTIR-TPD-MS Results

The IR spectrum of the carbonyl region of [1] in KBr shows three bands at 2082, 1947(br) and 1908(sh) cm^{-1} . After introduction of [1] into NaY, the spectrum shows four major CO bands at 2085, 2043, 1951(br), 1904(sh) and a minor band at 1642 cm^{-1} (In situ experiments with zeolite dispersions on Si wafer in a vacuum chamber; no water is present in the zeolite as there are no OH stretch vibrations around 3500 cm^{-1}). The split of the higher frequency band indicates a lower symmetry of the molybdenum carbonyl moiety in NaY, due to an interaction between carbonyls and sodium in the zeolite which is also observed for intrazeolite $\text{Ni}(\text{CO})_4$ ⁵ and iron carbonyls⁶.

After heating to 60° C, two additional bands appear at 1904 and 1852 cm^{-1} while the band at 1642 cm^{-1} has almost vanished. The lower frequency bands are assigned to molybdenum fragments with less than 5 carbonyls. This is consistent with the reduced CO coordination number as found in the EXAFS analysis.

Simultaneous detection of species desorbed from the zeolite samples was carried out by mass spectrometry. A TPD-MS spectrum is shown in Figure 8. Carbonyl fragments (mass 28) appear in the mass spectrum at ca. 50° C and reach a maximum at 67° C. These observations are in agreement with the IR results discussed above. No HCl or any metal carbonyl fragments were detected in the TPD-MS profile.

(2) $\text{Cl}_2(\text{THF})\text{GeMo}(\text{CO})_5$ in H6Y

Mo-absorption edge

The FT EXAFS spectrum of the precursor [1] in H6Y zeolite at room temperature is comparable to the one in NaY but shows a slightly more resolved Mo-Ge shell. This is due to less intense carbonyl peaks which were found to correspond to an average of 3.5 CO ligands instead of 4 in NaY. The spectrum of the sample at 120° C is comparable to that of NaY at 250° C. No Mo-Ge interaction and no carbonyl remain at this temperature. In addition to three chlorine atoms at 2.53 Å, a Mo-Mo interaction with a bond distance of 1.93 Å is indicated. This short Mo-Mo bond distance, close to that of Mo-Mo quadruple bonds, (2.09 Å for $\text{Mo}_2(\text{ac})_4$) is retained in the sample at 250° C. Based on mass balance, three Cl per Mo are not possible; a non-resolved convolution with Mo-oxygen coordination may be present.

Ge-absorption edge

The FT spectrum of the H6Y sample at room temperature is similar to that of the intact precursor, with the exception of a smaller Ge-Mo shell and partial replacement of chloride by oxygen. The fit results show the presence of 1.4 oxygen atoms at Ge-O = 2.00 Å, 2.3 chloride at Ge-Cl = 2.15 Å and 0.7 molybdenum atoms at Ge-Mo = 2.52 Å. Upon heating, the chloride coordination number decreases steadily, accompanied by an increase in oxygen coordination. Finally, at 250° C, the fit results show only one chloride left in addition to two oxygen atoms. Simultaneously, a Si/Al contribution emerges that indicates attachment of Ge-Cl species to the zeolite framework, in a yet unidentified bonding mode. The Ge-Mo bond vanishes between 100 and 120° C.

Together with the results from the Mo-edge analysis it can be concluded that the precursor [1] attaches increasingly to the zeolite framework with rising temperature, until decomposition begins between 100 and 120° C. After the Ge-Mo bond is broken, multiply bonded Mo-Mo

species are formed in the acid environment. Similar reactions of Mo species in solution are known⁷.

(3) $\text{Cl}_2(\text{THF})\text{GeW}(\text{CO})_5$ in H6Y:

W absorption edge

The W-edge EXAFS spectra for $\text{Cl}_2(\text{THF})\text{GeW}(\text{CO})_5$ [2] in H6Y at room temperature, 120° C, 150° C and 250° C were analyzed. In contrast to the molybdenum samples, the overall features of the tungsten precursor complex in H6Y are retained up to about 120° C. A slight decrease of the CO coordination is reflected in the resulting average coordination number of 4, and the Ge-W bond is kept mostly intact ($N = 0.8$, $R = 2.54 \text{ \AA}$). At 150° C, the Ge-W bond is destroyed and chloride reacts with the W fragments. Higher temperatures increase the coordination of W to zeolite oxygen.

Ge-absorption edge

At room temperature, the Ge-coordination shell resembles that of the precursor (2.1 chloride and 1.3 oxygen atoms at Ge). No outer coordination shell is observed, as in the case of the NaY host. Together with the information of the tungsten edge data, it can be concluded that the precursor is unchanged at this temperature in zeolite H6Y. No attachment to the zeolite matrix has taken place.

At higher temperature a slow increase of the oxygen coordination and a concomitant decrease of chloride is determined from the EXAFS data. An outer shell due to zeolite coordination becomes visible at about 2.6 Å (uncorrected for phase shift). This process starts at 80° C and ends with an average coordination of 3.6 oxygens (disordered) at 2.03 Å and 1.2 chloride at 2.17 Å, at 250° C.

TPD-MS data of the evolving gases from an in situ IR experiment indicate a maximum release of CO at 130° C. A small amount of HCl which increased at higher temperature was detected at the same temperature. This corresponds to the decrease of chloride ligands derived from the EXAFS data between 150 and 250° C.

CONCLUSION

The $\text{Cl}_2(\text{THF})\text{GeMo}(\text{CO})_5$ precursor is found to be slightly less stable in zeolite environments than the tungsten homologue. Moderate decarbonylation occurs already at room temperature in NaY and H6Y. In NaY, complete loss of CO and transformation into molybdenum chloride species occurs between 120 and 250° C. In H6Y, this process is already observed around 100° C. The stability range of the completely anchored bimetallic complexes spans room temperature to about 120° C in NaY, while it is reduced to about 100° C in H6Y. The newly formed MoCl_x species remain present in NaY up to 250° C, while they transform predominantly into Mo-Mo species in H6Y.

In contrast to the molybdenum analog, no decarbonylation is detected for $\text{Cl}_2(\text{THF})\text{GeW}(\text{CO})_5$ in zeolite NaY and H6Y up to about 100° C. In NaY, the pentacarbonyl fragment then starts to transform into tungsten chloride compounds which are stable at 250° C. Attachment to the framework occurs already at room temperature. Most importantly, we conclude that the range where the complex is intact and attached to the framework ranges from 25 to at least 100° C in NaY. In H6Y, anchoring to the framework becomes only relevant at about 80° C. No metal-metal bonds are formed in the tungsten species in both hosts.

These results show that carefully chosen bimetallic complexes can be anchored into the cage systems of zeolites under retention of the Ge-metal bonds. The anchoring can prevent

potential agglomeration under catalytic reaction conditions. The chemical reactivity of these anchored species is currently under investigation, and preliminary studies indicate activity for ligand substitution at the transition metal center.

ACKNOWLEDGEMENTS

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