Intrazeolite Attachment of a Ge–Mo Heterobimetallic Complex

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HY zeolite encapsulated Cl_2(thf)GeMo(CO)$_5$ (thf = tetrahydrofuran), studied by EXAFS, *in situ* Fourier transform spectroscopy, and temperature programmed desorption (TPD) MS, attaches to the zeolite pore system through the Ge-moiety with retention of the Ge–Mo bond, whereas a large fraction of the intrazeolite –Mo(CO)$_5$ moieties remain unaffected by the anchoring reaction.

The structural and chemical features of zeolites, *i.e.*, crystalline, open pore structures with well-defined co-ordination sites, ion exchange capability, and controlled acidity, make them promising candidates for selective hybrid systems. However, the instability of many zeolite catalyst systems

Figure 1. Ge-edge EXAFS data. k^2-weighted Fourier transformations (FT) of A, Cl_2(thf)GeMo(CO)$_5$ precursor; B, Cl_2(thf)GeMo(CO)$_5$ loaded into acid zeolite HY at room temperature; and C, heated at 520 K. The FTs are uncorrected for phase shifts, thus bond distances appear to be reduced by 0.3—0.5 Å.
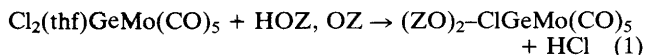
under reaction conditions has been a limiting factor for applications. Different approaches to zeolite-based hybrid catalysts include physisorption of neutral metal carbonyls[1] (weak binding at metal cations[2] does not always prevent diffusion and agglomeration), cation-derived species such as Rh-carbonyls,[3] assembly of diffusionally blocked large complexes such as Co- and Fe-phthalocyanines,[4] and the use of zeolite hydroxy groups for attaching, *e.g.*, Rh(allyl)$_3$[5] or organoiron complexes.[6]

We have explored a new approach, introducing heterobinuclear organometallic compounds as candidates for linking catalytic functions to zeolite frameworks. With two different metals present, the complexes can be anchored to the support *via* one oxophilic metal, whereas catalytic reactions may proceed at the second metal centre.

Zeolite HY, derived from Linde LZ-Y62 [(NH$_4$)$_{45}$-Na$_{10}$Al$_{55}$Si$_{137}$O$_{384}$] by degassing at 700 K for 10 h (1 K min^{-1}), was used as a support. A slurry of 0.500 g of the zeolite in 50 ml of pentane was loaded, stirring under nitrogen for 12 h with 1 molecule of Cl_2(thf)GeMo(CO)$_5$ (**1**) (thf = tetrahydrofuran) per supercage, prepared from Na$_2$[Mo$_2$(CO)$_{10}$] and GeCl$_4$ in THF at 120 K.[7] The solvent was removed by filtration on a frit. EXAFS data at the Ge K-edge (11 103 eV) and the Mo K-edge (20 000 eV) of sealed samples at 100 K were obtained at NSLS (Brookhaven National Laboratories) at beamline X-11A. The EXAFS data were analysed using structural parameters taken from appropriate reference compounds.

The EXAFS data of the precursor Cl_2(thf)GeMo(CO)$_5$ (**1**) (no crystal structure has been published) show, at the Ge edge, the expected co-ordination to thf (Ge–O$_{1.1}$ at 2.06 Å), to Cl (Ge–Cl$_{2.0}$ at 2.15 Å), and the Ge–Mo bond at 2.64 Å (Figure 1A). The corresponding Mo-edge data reveal Mo–CO at 2.05, Mo–CO at 3.18, and Mo–Ge co-ordination at 2.68 Å.

If (**1**) is diffused into the acid zeolite host at 295 K [HY/(**1**)], no substantial changes in the FTIR spectrum of the precursor are observed, indicating the presence of intact –Mo(CO)$_5$ moieties in the zeolite. We note that the strong CO-stretch of (**1**) in a NaY host shifts to lower frequency, probably due to Na$^+$–OC– interactions similar to those of nickel carbonyl complexes in NaY.[2] The Ge-edge EXAFS data of HY/(**1**) (Figure 1B) show reduced co-ordination to Cl (Ge–Cl$_{1.3}$ at 2.20 Å) and increased co-ordination to oxygen at a longer distance (Ge–O$_{1.8}$ at 2.13 Å) which indicates that the complex (**1**) has attached to the zeolite framework oxygen atoms, according to equation (1).

$$Cl_2(thf)GeMo(CO)_5 + HOZ, OZ \rightarrow (ZO)_2\text{-}ClGeMo(CO)_5 + HCl \quad (1)$$

The corresponding Mo-edge data of HY/(**1**) show a moderate reduction of the average Mo-carbonyl co-ordination number from 5 to 3, indicating that even the highly acidic environment of the HY host attacks only a minor fraction of the precursor (**1**). A distinct Ge–Mo interaction at 2.70 Å (Ge- and Mo-edges, co-ordination numbers *ca.* 1) shows that the binuclear complex is maintained intact in the zeolite cage
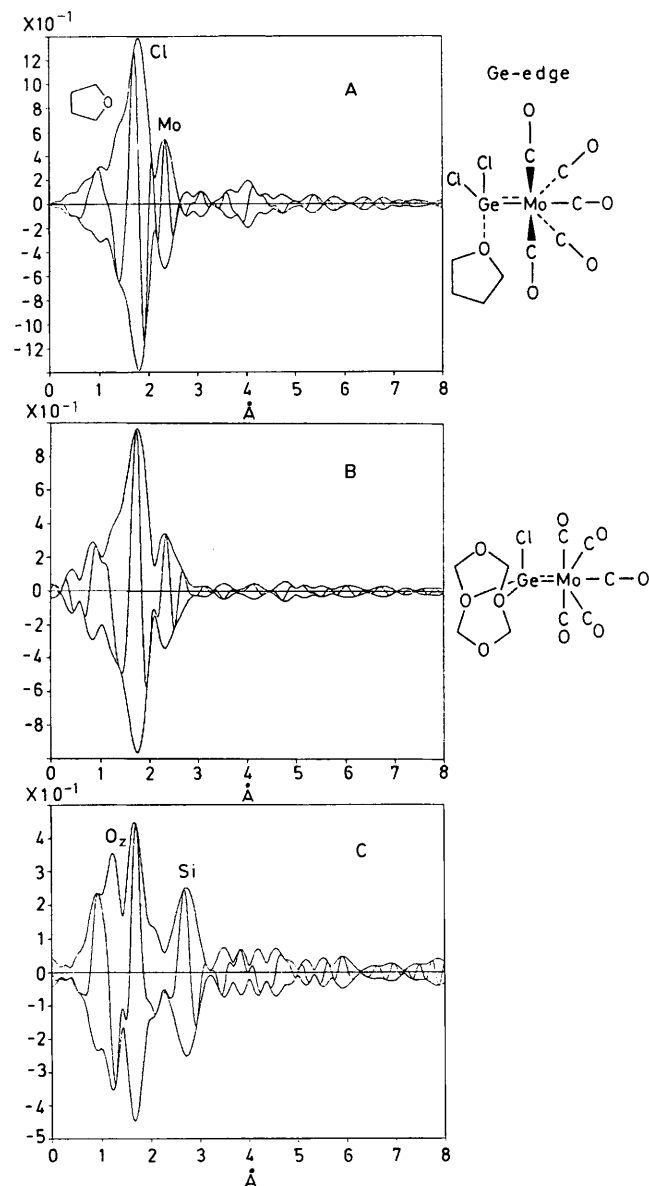
system. A small additional fraction of $Mo–Mo_{0.7}$ at 2.15 Å is observed. Apparently, the acidic environment transforms some of the precursor molecules into multiply bonded Mo–Mo species, in analogy to the formation of Mo_2 compounds from $Mo(CO)_6$ under acidic conditions.[8] In contrast, no Mo–Mo species are detected in partially acidic zeolite Y or NaY hosts, and the average Mo–CO co-ordination number remains higher.

Experiments exploring the thermal stability of the intra-zeolite Ge–Mo complex demonstrate drastic changes in the EXAFS data after heating at 520 K. At the Ge-edge, the most striking changes are cleavage of the Ge–Mo co-ordination, and an enhanced outer-shell contribution associated with backscattering from the zeolite framework metals (Figure 1C). The fit for the nearest Ge-co-ordination results in $Ge–O_{2.0}$ at 1.98 Å and $Ge–Cl_{1.1}$ at 2.17 Å, while the zeolite framework co-ordination appears at a distance of 3.23 Å, typical for metals co-ordinated to zeolite 6-ring and 4-ring ion-exchange sites. The Mo-edge data of the heated samples show several convoluted shells indicating Mo–Mo species (e.g., $Mo–Mo_{0.7}$ at 2.20 Å) and Mo co-ordination to cation-exchange sites ($Mo–O_{1.1}$ at 1.78 Å). Temperature programmed desorption (TPD) MS data reveal exclusive evolution of CO up to ca. 360 K and a small amount of HCl at

higher temperatures. These observations show that the Mo and Ge metal fragments must be retained in the zeolite host.

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