

# ANCHORING STRATEGIES FOR BIMETALLIC SPECIES IN ZEOLITES

**Progress Report**

**March 1993**

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**DEPARTMENT OF ENERGY**

**Basic Energy Sciences**

**Grant Number: DE-FG02-92ER14281**

**MASTER**

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## I. PROJECT SUMMARY

Our research program is aimed at the development of new immobilization concepts for organometallic fragments in the crystalline pore structure of zeolites and other microporous materials. We explore a new approach by introducing heterobinuclear organometallic compounds as candidates for linking catalytic functions to zeolite frameworks. With two different metals present, the complexes are being anchored to the support via one oxophilic metal, whereas ligand exchange and catalytic reactions may proceed at the second metal center. Furthermore, it is planned to prepare intrazeolite bimetallic clusters through controlled decomposition of zeolite-anchored heterobimetallic compounds.

The anchoring chemistry, thermal stability and reactivity of  $\text{Me}_3\text{SnMn}(\text{CO})_5$  in zeolite NaY and acid forms of zeolite Y was studied with X-ray absorption spectroscopy (Sn, Mn edge EXAFS) and in-situ FTIR/TPD-MS techniques. Subsequently, the tin - cobalt complex  $\text{Me}_3\text{SnCo}(\text{CO})_4$  has been a focus of detailed synthetic and spectroscopic studies. The reactivity of tricarbonyl(cyclopentadienyl)(trimethylstannyl)molybdenum in new mesoporous hosts has been explored. A recent development is the design of vanadium oxo species in different micro- and mesoporous hosts. These are of great interest for (i) the selective reduction of nitrogen oxides by ammonia, and (ii) selective oxidation of different hydrocarbons, such as xylenes, olefines and alkanes.

We utilize a comprehensive combination of analytical techniques that allow us to probe local structural changes at the molecular level. These techniques include EXAFS (Extended X-Ray Absorption Fine Structure) spectroscopy utilizing synchrotron radiation, in situ FT-IR coupled to thermodesorption/MS, UV-NIR, and CCD Raman. Diagnostic catalytic studies of hydrocarbon conversions will address issues such as the location of catalytically active sites, stability against migration, and shape selectivity introduced by the molecular sieve pore structure.

## II. RECENT PROGRESS

### Reactivity of Trimethyltin Manganesepentacarbonyl in Zeolite Cavities.

The anchoring chemistry, thermal stability and reactivity of  $\text{Me}_3\text{SnMn}(\text{CO})_5$  in zeolite NaY and acid forms of zeolite Y was studied with X-ray absorption spectroscopy (Sn, Mn edge EXAFS) and in-situ FTIR/TPD-MS techniques. In the NaY host, the precursor is physically adsorbed from hexane solution into the dehydrated zeolite cages at room temperature without further chemical reaction. Symmetry changes of the  $\text{Mn}(\text{CO})_5$  moiety indicate interaction with the  $\text{Na}^+$  ions of the zeolite framework. The intrazeolite complex in NaY is accessible to external reactants and undergoes carbonyl substitution with  $\text{PEt}_3$  at the manganese center. At  $120^\circ\text{C}$  under vacuum, the  $\text{Mn-CO}$  ( $N=3.9$ ,  $R=1.79 \text{ \AA}$ ) and  $\text{Mn-CO}$ -coordination ( $N=4.3$ ,  $R=2.96 \text{ \AA}$ ) derived from EXAFS data shows that most of the CO coordination sphere is still intact. The intrazeolite complex decomposes at about  $150^\circ\text{C}$  by loss of all CO ligands and, subsequently, cleavage of the Sn-Mn bond. Mn and Sn cluster species are formed at  $250^\circ\text{C}$ .

In contrast to NaY, the acidic HY host interacts with the  $\text{Me}_3\text{Sn}$  moiety of the bimetallic complex. The compound attaches to the zeolite framework at the oxygen rings of the supercage already at room temperature. The attachment of the molecule occurs through the Sn moiety by loss of  $\text{CH}_4$  gas while the Sn-Mn bond and the CO ligand sphere are still intact. Different degrees of substitution of the methyl groups by the acidic oxygen framework are observed. Both mono- and di-substituted species,  $(\text{Oz})\text{Me}_2\text{SnMn}(\text{CO})_5$  and  $(\text{Oz})_2\text{MeSnMn}(\text{CO})_5$ , are formed under retention of the Sn-Mn bond. At room temperature, the mono-substitution is favored while di-substitution is more pronounced at higher temperature, i.e.  $100^\circ\text{C}$ . At this temperature, the Mn-CO coordination data still indicate 5 CO ligands ( $\text{Mn-CO}$ ,  $R=1.84 \text{ \AA}$ ;  $\text{Mn-CO}$ ,  $R=2.97 \text{ \AA}$ ), and the Sn-Mn bond is still intact ( $N=0.9$ ,  $R=2.58$ ). After the Sn-Mn bond is cleaved at  $150^\circ\text{C}$ , Sn is still anchored to the zeolite framework through oxygen coordination while Mn cluster species are formed. At  $250^\circ\text{C}$ , both Sn and Mn are attached to the zeolite oxygen framework.

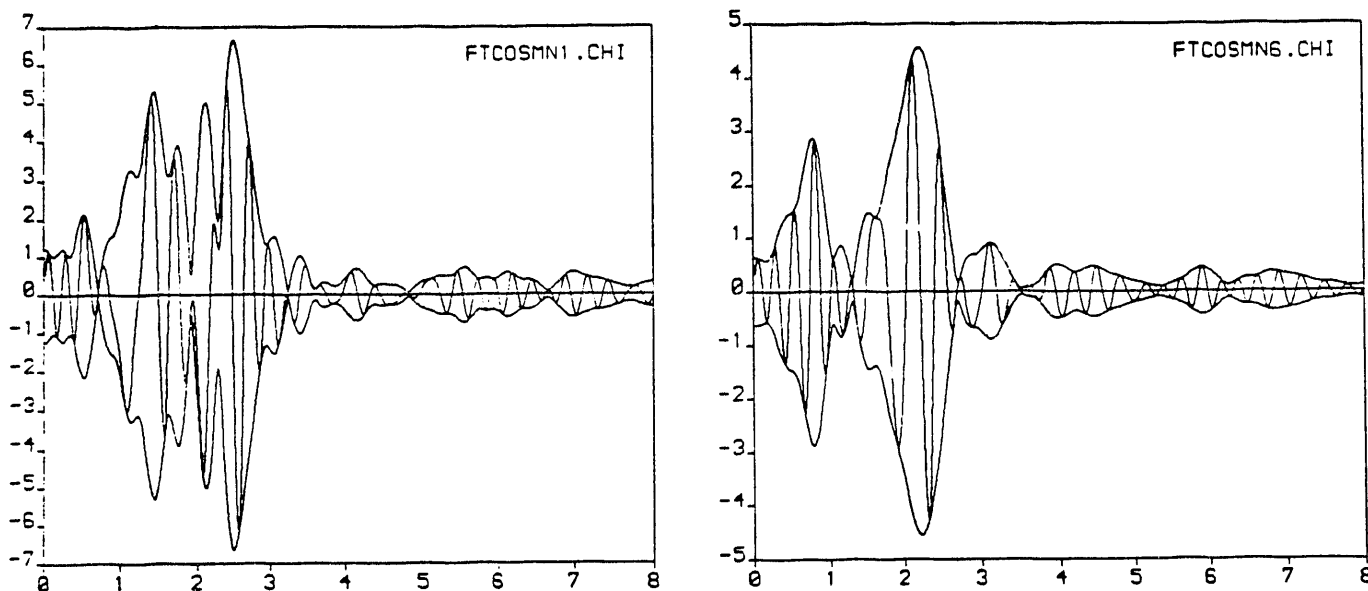
### Intrazeolite Chemistry of (Trimethylstannyl)tetracarbonylcobalt

We have extended our research on heterobimetallic complexes as follows. The tin-cobalt complex  $\text{Me}_3\text{SnCo}(\text{CO})_4$  has been a focus of detailed synthetic and spectroscopic studies. This precursor was adsorbed from solution into the sodium and proton forms of zeolite Y. In situ infrared spectroscopy coupled with temperature-programmed desorption was used to explore the attachment reaction (if present), the byproducts of the surface reaction such as methane or carbon monoxide, and the thermal stability of the intrazeolite complex. Furthermore, the intrazeolite complex was also reacted with small trialkyl phosphines such as trimethyl phosphine. Molecular access into the pore system of the zeolite was demonstrated by the complete conversion to a substituted product. Nitrogen sorption experiments show that the volume displaced by the organometallics (usually one molecule per supercage) is small compared to the total pore volume.

The study of the complex in NaY zeolite was complemented with comprehensive EXAFS (Extended X-ray Absorption Fine Structure) characterization of the reaction products at different temperatures and after reaction with phosphines. Preliminary EXAFS data analysis in conjunction with the other results allows us to conclude the following (Figure 1): The bimetallic complex remains intact when adsorbed into the dry sodium form ( $\text{Co-CO}$ : 4.1 ligands at  $1.79 \text{ \AA}$ ;  $\text{Co-CO}$ , 3.6 at  $2.93 \text{ \AA}$ ). The tin-coordination sphere is consistent with three methyl groups remaining ( $\text{Sn-C}_{2.8}$  at  $2.10 \text{ \AA}$ ), and the Sn-Co bond can also be detected. Infrared data indicate association of at least one CO ligand with the sodium ions, thus distorting the complex symmetry. On heating in vacuum, the complex is

stable up to about 90°C, starts to release CO above 120°C, and fragments at about 160°C under evolution of methane. Beyond this temperature, EXAFS data show formation of extremely small cobalt/tin clusters (average Co-Co coordination at 300°C: 1.4 (at 2.46 Å), average tin coordination: Sn-Sn<sub>0.7</sub> at 2.95, with only one small outer shell in the cluster (Co-Co<sub>1.3</sub> at 3.45 Å; Sn-Sn<sub>2.2</sub> at 3.71 Å). There is some indication that both metals 'see' each other, which would imply formation of nanometer size alloys in the zeolite cages (Co-Sn<sub>1.8</sub> at 2.73 Å; Sn-Co<sub>2.8</sub> at 2.68 Å). This interesting possibility will be further explored.

The reactivity of the SnCo complex in proton-containing zeolite Y is very different from that of NaY. Initial EXAFS analysis shows that the cobalt carbonyl coordination remains intact on introduction of the complex into the acidic zeolite. Slight CO evolution begins already at about 60°C, and IR studies indicate that the complex fragments completely above 120°C. Consumption of the zeolite hydroxyl groups up to 300°C is observed. This could be associated with progressive oxidation of the Co<sub>n</sub>(CO)<sub>x</sub> fragments, resulting in zeolite-attached Co(II) ions. This interpretation is confirmed by the EXAFS data, where no indication for metal clusters but attachment of cobalt to the zeolite framework is observed.



**Figure 1.** Fourier transformed cobalt EXAFS spectra of Me<sub>3</sub>SnCo(CO)<sub>4</sub> in NaY zeolite. (A) (left) at room temperature. (B) (right) after heating to 300°C. The conversion of the carbonyl/tin coordination at RT to Co-Co and Co-Sn coordination at high temperature can be derived from analysis of these data.

### Organometallics in Mesoporous Channel Hosts: Reactivity of Tricarbonyl(cyclopentadienyl)(trimethylstannyl)molybdenum.

We have extended the concept of bimetallic complexes in zeolite Y to accommodate larger species in the new mesoporous MCM-41 host discovered by workers at Mobil.<sup>1</sup> We have succeeded in the synthesis of several of the MCM materials with typical pore openings of 35 Å. Nitrogen sorption measurements confirm the enormous sorption capacity of these materials (pore volume ca. 0.70 cc/g). The bimetallic complex Me<sub>3</sub>SnMo(CO)<sub>3</sub>Cp

was adsorbed into MCM host from hexane solution. The in situ infrared spectra show a weakly distorted CO coordination environment at room temperature, consistent with the absence of Na-ions in the channels of the host. This complex exhibits a striking thermal stability in MCM: the CO ligands are only removed on heating above 250°C. The stability of the Sn-Mo bond in this system, ligand substitution chemistry, and the nature of the decomposition products is presently under investigation.

#### **Metal oxide species in zeolites and MCM hosts.**

A recent development in our research program is the design of vanadium oxo species in different micro- and mesoporous hosts. These are of great interest for (i) the selective reduction of nitrogen oxides by ammonia, and (ii) selective oxidation of different hydrocarbons, such as xylenes, olefines and alkanes. There are many open questions as to the nature of the active species on the surface of the heterogeneous catalysts.

Our synthetic approach entails adsorption of different vanadyl alkoxides such as vanadyltri(isopropoxide), and other precursors into the sodium or proton forms of zeolite Y and other hosts. Subsequent calcination leads to decomposition of the precursor and oxide cluster formation. By encapsulating the vanadium species in the zeolite with its well-defined surface structure, we expect to be able to create vanadium oxo species ranging from simple vanadyl to  $VO_x$  clusters with bridging oxo- or hydroxy ligands, to clusters representing segments of the bulk  $V_2O_5$  structure. EXAFS spectra of several samples have been obtained during our recent beamtime at Brookhaven. Evaluation of these data in conjunction with complementary in situ IR, Raman, UV, ESR, and sorption results will provide a comprehensive picture of the structure and reactivity of these species in microporous hosts.

### **III. Plans for the Next Budget Period**

#### (a) Bimetallic complexes in zeolites.

We will extend the detailed study of the reactivity of tin-cobalt complexes in zeolite Y. Our initial EXAFS measurements of the temperature stability in the acid and sodium forms will be analyzed, and conclusions regarding the influence of proton/complex stoichiometry on stability will be drawn. Initial catalytic studies at temperatures below the stability limit (hydrogenation of bulky cycloalkenes vs. linear alkenes, and bulky aromatics vs. benzene) will elucidate the influence of host acidity and temperature on reactivity, determine if hydrogenation is selective for olefinic or aromatic bonds, and evaluate the potential for shape-selective conversions. Catalytic activity associated with complexes attached to the external zeolite surface can be identified with selective poisoning experiments, and from the size-selectivity exhibited by the systems.

Hybrid catalysts with partially acid-exchanged zeolites will be studied in comparison, and other examples of main group/transition metal complexes will be explored as promising candidates for surface anchoring reactions.

Our recent EXAFS results on the tin-cobalt complexes in NaY zeolite strongly suggest that subnanometer tin-cobalt alloy clusters can be formed above about 250°C. We will explore the utility of this approach for the rational design of migration-stabilized alloy clusters in more detail. Issues such as sintering at higher temperature, possible phase separation, distribution throughout the zeolite crystal, and catalytic reactivity of these novel systems will be addressed. We also consider extending this very promising approach to other bimetallic systems of this type.

#### (b) Bimetallic complexes in mesoporous (MCM) hosts.

Full characterization of our first system explored so far,  $Me_3SnMo(CO)_3Cp$  in 35 Å MCM-41, will include a study of the attachment chemistry of the tin moiety, thermal

stability of the Sn-Co bond, reactivity with potential ligands such as phosphines or olefines, and catalytic activity for hydrogenation. The acidity of the mesoporous hosts is less than that of zeolites, thus possible acid-catalyzed side reactions of olefines (e.g., isomerization) are expected to be less pronounced than in highly acidic zeolites. The wide channel diameter of these hosts will diminish possible size selectivity, but will offer the advantage of admitting both large complexes as catalyst precursors as well as large substrate molecules. The intra-channel surface of the hosts is expected to be much better defined than that of most amorphous oxide supports (well-defined pore size, rather homogeneous environment of the acid sites). We anticipate that this will endow these hybrid catalysts with correlations between structure and reactivity that can be much better understood than with conventional supports.

(c) Metal oxide species in zeolites and MCM hosts.

In the near future we expect to perform additional EXAFS experiments at Brookhaven in order to obtain more comprehensive characterization of the different vanadium-containing species in zeolite Y and in mesoporous hosts. From those structural data, it will be possible to derive a relationship between the nature of the molecular vanadium precursor, acidity and structure of the host, thermal treatment, and the resulting vanadium-oxo species. Solid-state NMR experiments on some of these systems are being planned in collaboration with Professor N. Delgass in Chemical Engineering. We expect that the NMR data will be complementary to the EXAFS structural results. Catalytic measurements on some of the best-defined systems with distinct structural features will also be initiated. Reactions on model substrates (which could help distinguish external vs. intrazeolite reactivity) during the next project period will initially include the oxidation of xylenes and of olefines.

(d) Intrazeolite Bimetallic Complexes as Precursors for Highly Dispersed Metal Alloy Catalysts

We will explore the preparation of intrazeolite bimetallic clusters formed by controlled thermal and/or chemical decomposition of zeolite-anchored bimetallic compounds. Comparable systems such as Mo/Pt, Mo/Sn, Ge/Co and IrSn<sup>2</sup>, derived from organometallic precursors on amorphous supports, have been reported. The bimetallic clusters will be prepared by thermal decomposition of the zeolite-anchored species in vacuo or, for comparison, they will be formed in O<sub>2</sub>/H<sub>2</sub> treatment schemes. In addition to the potential high selectivity related to the zeolite pore structure, we expect the following benefits from this approach:

1. Since the precursor compounds are anchored to the zeolite surface, there should be a higher barrier towards migration and agglomeration than in other preparation schemes.
2. The precursor contains the two metals in intimate contact and in homogeneous, atomic dispersion, which should facilitate the formation of well-defined intrazeolite bimetallic clusters.

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1 Beck, J. S., U. S. Patent 5,057,296, Oct. 15, 1991.

2 Lazar, K.; Bussiere, P.; Guenin, M.; Frety, R. Appl. Catal. 1988, 38, 19

**List of Publications for Current Period.**

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**J. Phys. Chem.**, 1992, 96, 6713-6724

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Methyl Irondicarbonyl.

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**Proc. 9th Intern. Zeolite Conference**, Elsevier, in press

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Christian Huber and Thomas Bein,

**J. C. S., Chem. Commun.**, submitted

*Budget reviewed.  
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