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## Reactions of a Cobalt-Tin Complex in Zeolite Y

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### INTRODUCTION

The development and understanding of catalysts combining organometallic molecular species with a solid support structure (hybrid catalysts) continues to be of great interest (1, 2). One anticipates that facile product separation, flexibility in the choice of reactant medium, and stability of heterogeneous systems could be combined with the high selectivity and activity of some organometallic catalysts. Furthermore, catalytic centers encapsulated in zeolites (3, 4) promise to provide shape selectivity, if so desired. However, complications encountered with zeolite-based and other hybrid systems can involve leaching of the catalyst into solution, or instability of the metal phase against agglomeration (5).

We have recently developed a novel concept for stabilizing low-valent transition metal moieties in large-pore zeolites, by using bimetallic complexes such as  $\text{Cl}_2(\text{THF})\text{GeMo}(\text{CO})_5^6$  or  $\text{Me}_3\text{SnMn}(\text{CO})_5^7$  where the oxophilic main-group element serves to attach the complex to the internal zeolite cage surface.

In this communication we discuss the surface chemistry and stability of  $\text{Me}_3\text{SnCo}(\text{CO})_4$  in different forms of zeolite Y. The potential catalytic activity of the  $\text{Co}(\text{CO})_4$  moiety is of particular interest. The reactivity of this complex and the stability of the Sn-Co bond under different conditions have been studied. Substitution of carbonyl ligands with phosphines leads to monosubstituted products (8). Heterolytic cleavage of the Sn-Co bond and recombination is possible in certain ionizing solvents such as

DMF (9) and acetone (10). The precursor is expected to react with the internal surface hydroxyl groups of the zeolites by loss of methane gas whereas the Sn-Co bond and the coordination sphere of Co should remain intact under certain conditions.

### EXPERIMENTAL

#### Sample Preparation

All manipulations were carried out under nitrogen atmosphere, and solvents were distilled from appropriate drying agents. Prior to each measurement, samples were kept in a nitrogen glove box. The precursor  $\text{Me}_3\text{SnCo}(\text{CO})_4$  (m.p. 73-74°C,  $^1\text{H-NMR}$ : 0.67 ppm in  $\text{CDCl}_3$ ,  $J^{119}\text{Sn-C} = 53.1 \text{ Hz}$ ,  $J^{117}\text{Sn-C} = 32.9 \text{ Hz}$ ) was synthesized from the reaction between  $\text{Co}_2(\text{CO})_8$  and  $\text{Me}_3\text{SnCl}$  in MeOH fol-

lowing a modified reported method (11).

The structural features of  $\text{Me}_3\text{SnCo}(\text{CO})_4$  were determined by EXAFS spectroscopy at both the Co-edge and Sn-edge. The precursor was immobilized into two types of zeolite Y containing different proton concentrations. NaY (commercial Linde LZ-Y52  $[\text{Na}_{57}\text{Al}_{57}\text{Si}_{135}\text{O}_{384}] \times 235 \text{ H}_2\text{O}$ ), and highly acidic H6Y ( $6 \text{ H}^+/\text{sc}$ ) from Linde LZ-Y62  $[(\text{NH}_4)_{45}\text{Na}_{10}\text{Al}_{55}\text{Si}_{137}\text{O}_{384}] \times 235 \text{ H}_2\text{O}$ , were used. Heating the ammonium-exchanged zeolite under oxygen flow at 100°C for 4 h and at 400°C for 10 h, then under vacuum at the same temperature for 5 h (at a rate of 1°C/min) resulted in the desired acid form. The dehydrated zeolites were kept in sealed vials in a glove box prior to further treatments. An amount of 0.500 g of each zeolite was loaded with one molecule/supercage of  $\text{Me}_3\text{SnCo}(\text{CO})_4$  in 50 ml hexane by stirring the slurry for 15 hours under dry nitrogen atmosphere. The slurry was filtered and washed several times with hexane. The intrazeolite samples were dried at  $10^{-4}$  Torr for 30 min. The solvent was decolorized almost completely after impregnation, thus loading is nearly quantitative.

EXAFS samples for thermal stability studies were prepared by heating 0.5 g-batches of loaded zeolites in a tube furnace between 90 and 300°C under  $10^{-5}$  torr vacuum. The temperature was ramped up at a heating rate of 1°C/min to the desired temperature and kept constant for 6 h. The treated samples were transferred under vacuum to the dry nitrogen box. The powdered samples were mixed with a molten, degassed 1:1 mixture of octadecane and eicosane at 30-35°C, and the encapsulated

samples were packaged in EXAFS sample holders, sealed with Kapton tape and kept under nitrogen until EXAFS measurements were performed.

#### Characterization

FTIR data of thin zeolite dispersions on Si wafers in a steel cell were taken with a Mattson Polaris spectrometer at  $4\text{ cm}^{-1}$  resolution. The samples were evacuated with a molecular sieve/turbomolecular pump combination until the total pressure (including  $\text{H}_2$ ) was  $<10^{-6}$  Torr prior to any treatment. Up to 5 mass fragments could be monitored as a function of time/temperature in the TPD-MS experiment. Zeolite samples were heated at  $2^\circ\text{C}/\text{min}$  while FTIR and mass spectra were monitored.

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 100-200 mA. Data were collected at the Co K-edge (7709 eV) and the Sn K-edge (29200 eV). The experiments were performed at about 100 K in transmission using double crystal Si(311) and Si(111) monochromators. The EXAFS data were analyzed using standard procedures, as described in previous articles (6).

## RESULTS AND DISCUSSION

If the carbonyl stretching region of the molecular precursor  $\text{Me}_3\text{SnCo}(\text{CO})_4$  (in fluorolube: 2084, 2021,  $1988\text{ cm}^{-1}$ ) is compared with that of the complex in NaY zeolite, drastic changes are observed. (Figure 1C,B). The number of bands increases from the three bands of the precursor (consistent with a  $\text{C}_{3v}$  symmetry of a trigonal bipyramidal structure) to at least six, and the major intensity shifts to lower energy. This effect is now well-known for carbonyl complexes in zeolites (e.g., ref. 5), and is indicative of association of the carbonyl ligand(s) with the Lewis-acidic sodium cations, i.e.,  $\text{Co-CO-Na}^+$ ,

and associated symmetry changes. Because one type of complex can have no more than four bands when distorted, there must be at least two types of species present. The bands at 2074, 2001, 1946, and  $1883\text{ cm}^{-1}$  simultaneously diminish in intensity on heating (see below), thus they are assigned to one less strongly bound species, while the more stable set of bands, including a high energy vibration at  $2104\text{ cm}^{-1}$ , survives up to over  $170^\circ\text{C}$ . In the H6Y host, a moderate shift to higher energies is observed in the CO stretching region (major peaks: 2108, 2016, and  $1950\text{ cm}^{-1}$ ). This shift is indicative of a possible substitution of one or more methyl ligands by the zeolite oxygen framework, similar to the reaction observed with  $\text{Me}_3\text{SnMn}(\text{CO})_5$  (7). The presence of other potential products, such as  $\text{Co}(\text{CO})_4^-$  ( $1886\text{ cm}^{-1}$  in THF) or  $\text{HCo}(\text{CO})_4$  (2116, 2053 and  $2030\text{ cm}^{-1}$  in hexane) (12) is considered of minor importance in either of the supports. A small peak coinciding with the former species is observed in NaY, but its intensity diminishes together with that of three others. The volatile hydrido-complex is not expected to remain in the H6Y host under high vacuum at elevated temperature. Furthermore, EXAFS data indicate the presence of Sn-Co bonds in both cases.

In situ FTIR-TPD experiments with the precursor in NaY show a slow decrease of the above-mentioned group of four bands when heating up to about  $150^\circ\text{C}$  (Figure 2). Drastic changes occur between 150 and  $210^\circ\text{C}$  where most

of the CO intensity is lost, peaks are broadened, and a shift to lower energy is observed. A small broad band at ca.  $1730\text{ cm}^{-1}$  indicates the presence of bridged carbonyl ligands. These observations are explained with the cleavage of the Sn-Co bond and formation of metal carbonyl clusters in the zeolite cages.

Preliminary EXAFS data analysis of the complex in NaY in conjunction with the other results allows us to conclude the following: The bimetallic complex remains intact when adsorbed into the dry sodium form (Co-CO: 4.1 ligands at  $1.79\text{ \AA}$ ; Co-CO,  $4.2$  at  $2.9\text{ \AA}$ ). The tin coordination sphere is consistent with three methyl groups remaining (Sn-C<sub>2.8</sub> at  $2.10\text{ \AA}$ ), and the Sn-Co bond can also be detected. On heating in vacuum, the complex is stable up to about  $90^\circ\text{C}$ , starts to release CO above  $120^\circ\text{C}$ , and fragments at about  $160^\circ\text{C}$  under evolution of methane (see Figure 3 for mass-spectrometric data). Beyond this temperature, EXAFS data show formation of extremely small cobalt/tin clusters (average Co-

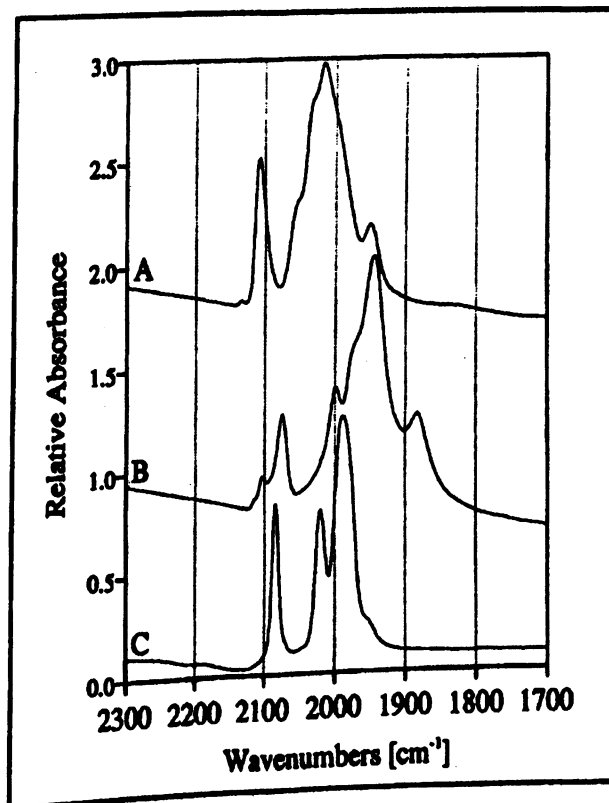


Figure 1. Infrared spectra of the carbonyl stretching region of  $\text{Me}_3\text{SnCo}(\text{CO})_4$  in different environments. (A) In H6Y host. (B) In NaY host. (C) In Fluorolube mull.

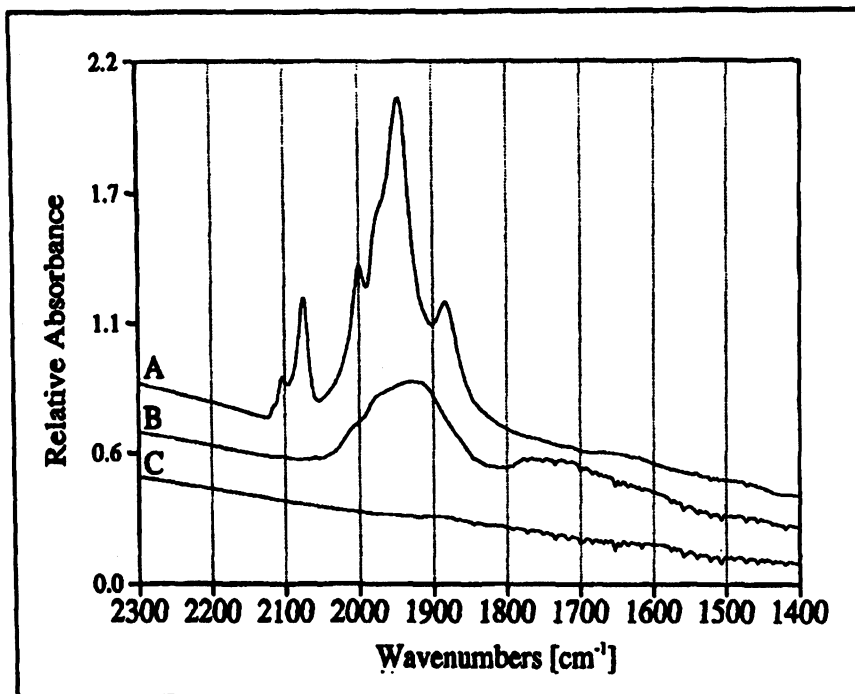


Figure 2. In situ FTIR spectra of  $\text{Me}_3\text{SnCo}(\text{CO})_4$  in NaY host under vacuum. (A) At room temperature. (B) At 160°C. (C) At 300°C.

Co coordination at 300°C: 1.4 (at 2.46 Å), average tin coordination: Sn-Sn<sub>0.7</sub> at 2.95 Å, 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).

The reactivity of the SnCo complex in proton-containing zeolite Y is very different from that of NaY. Figure 4 shows the thermal decomposition of the carbonyl moiety. In contrast to the NaY system, there is barely any change of the carbonyl pattern except a concomitant decrease in intensity. A small broad band remains at ca. 2000  $\text{cm}^{-1}$ , which shifts to lower energy until all CO ligands are lost at 300°C. These data show that the zeolite-attached species is decomposed at lower temperature than in the NaY host (loss of CO begins at 60°C, significant loss of methane at 120°C, see Figure 3, bottom). Initial EXAFS analysis shows that the cobalt carbonyl coordination remains intact on introduction of the complex into the acidic zeolite at room temperature, and on heating to

90°C. Spectra of the hydroxyl region (not shown) indicate continuous consumption of protons up to 300°C when all protons are removed. Together with EXAFS evidence, this shows that cobalt species react with the acidic zeolite via oxidative decarbonylation to form Co(II) ions attached to the zeolite framework. The EXAFS data show no indication for

formation of metal clusters at high temperatures in H6Y.

## CONCLUSIONS

The combination of EXAFS data and in-situ FTIR coupled with TPD-MS measurements discussed above provides insights into the structure and chemistry of  $\text{Me}_3\text{SnCo}(\text{CO})_4$  encapsulated in zeolite cages. The thermal stability of the Sn-Co and the Co-CO bonds of the precursor in the zeolite hosts exceeds the melting point of the free complex. Further studies on the reactivity and catalytic activity of these and related hybrid systems are in progress.

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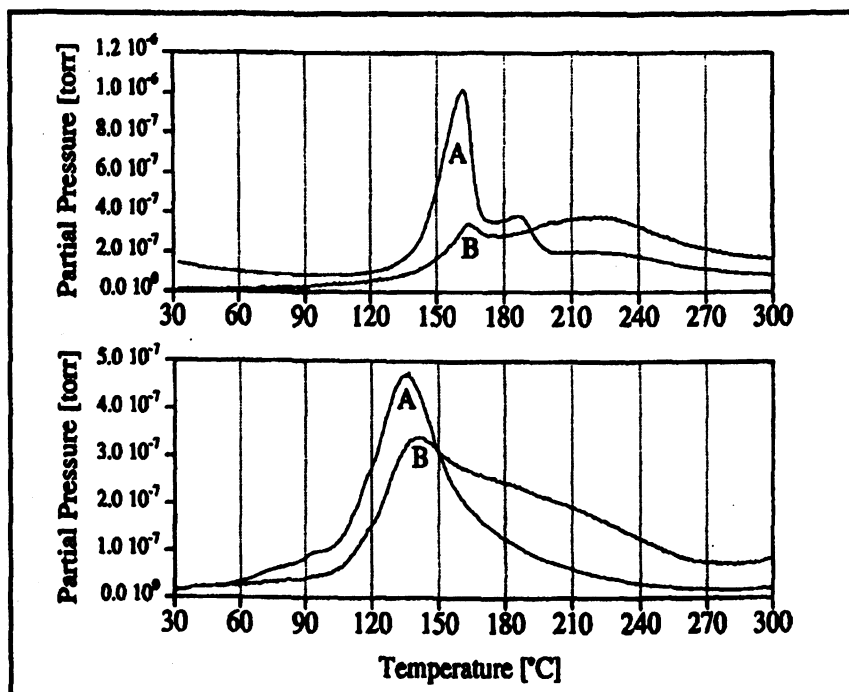


Figure 3. TPDMS data of  $\text{Me}_3\text{SnCo}(\text{CO})_4$  in NaY host (top) and in H6Y host (bottom). (A) CO ( $m/e = 28$ ). (B)  $\text{CH}_4$  ( $m/e = 16$ ). The methane signal is 10x enlarged.

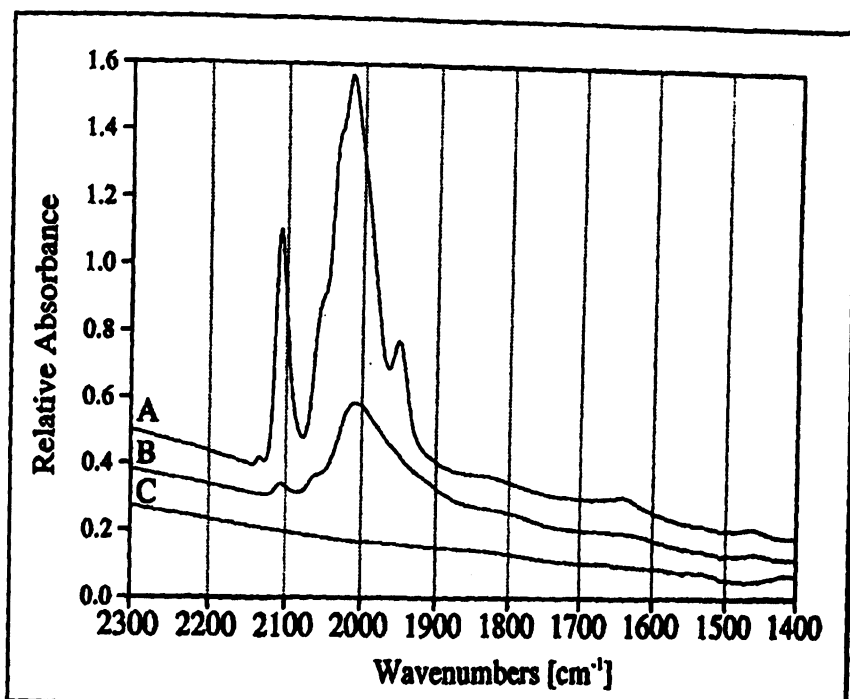


Figure 4. In situ FTIR spectra of  $\text{Me}_3\text{SnCo}(\text{CO})_4$  in H6Y host under vacuum. (A) At room temperature. (B) At 150°C. (C) At 300°C.

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