Preparation And Catalytic Properties of Supported Nanoscale Metal Particles

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Heterogeneous catalysts composed of metal particles supported on transition metal oxides (e.g. Al_2O_3, SiO_2) are utilized for many important applications such as the reforming of petroleum,[1] the purification of automotive exhaust,[2] and methanol synthesis.[3] Depending upon the method of catalyst preparation, the size of the metal particles present in these catalysts may range from 1 to 100 nm in diameter.[4] The rate and selectivity of most reactions are highly sensitive to the size and local composition of the metal particles that catalyze them.[5] In order to develop these structure-activity relationships, it is critical that methodologies be developed for the controlled preparation of nanoscale metal particles.

The cluster compound, $Ir_4(CO)_{12}$, was selectively formed inside the microcrystalline lattice of zeolite NaY by carbonylation of absorbed $Ir(CO)_2acac$.[6] The same cluster compound was also deposited on the external surface of zeolite NaY from a cyclohexane solution. Activation of these two materials (H_2, 773 K) produced zeolite NaY-supported Ir catalysts termed "Ir in NaY" and "Ir on NaY", respectively. The two catalysts have been extensively characterized by EXAFS, XANES, IR, STEM, and temperature programmed reaction of CO. "Ir in NaY" was found to contain Ir particles ca. 0.8 nm in diameter and composed of ca. 4-6 atoms, whereas "Ir on NaY" was found to contain Ir particles ca. 2 nm in diameter and composed of ca. 150 atoms (Figure 1a).

The two Ir/NaY catalysts displayed very different activities and selectivities in the hydrogenolysis of butane. The catalyst containing Ir particles larger than 1 nm, "Ir on NaY", was 85% selective towards ethane, whereas the catalyst containing Ir particles smaller than 1 nm, "Ir in NaY", was 50% selective towards ethane. The former catalyst was ca. 30 times more active than the latter catalyst (Figure 1b). The low activity of "Ir in NaY" for butane hydrogenolysis is similar to the decrease in activity reported for these particles in the hydrogenation of toluene[7] and benzene.[8] The catalytic differences exhibited by these two systems are ascribed to particle size limitations and not to differences in the electronic character of the supported metal particles.
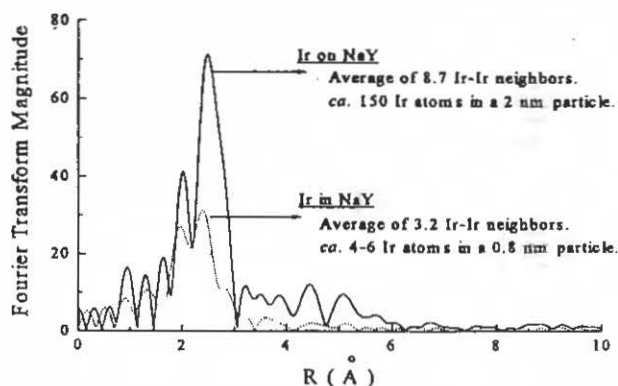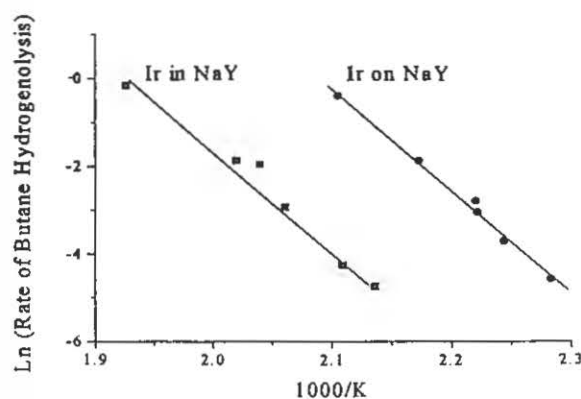

Figure 1a

Figure 1b

Figure 1. (a) Fourier transform magnitude of the EXAFS function for "Ir in NaY" (dashed line) and "Ir on NaY" (solid line). (b) Arrhenius plots for the hydrogenolysis of butane by "Ir in NaY" (squares) and "Ir on NaY" (circles).

Zeolite NaY-supported nanoscale Ir/Sn particles have been prepared by the activation (H_2, 773 K) of absorbed organometallic precursors. The use of $Ir(CO)_2acac$ and $SnMe_3OH$ as dual source catalyst precursors resulted in the formation of supported metal particles that were ca. 1 nm in diameter, as established by electron microscopy. Energy dispersive X-ray analysis (EDX) confirmed that the metal particles were bimetallic. The use of $(COD)_2Ir-SnMe_3$ as a single source catalyst precursor resulted in the formation of a material that was visibly speckled with metal particles ca. 0.5 mm in diameter. Examination of this material by electron microscopy and EDX also revealed the presence of bimetallic particles ca. 1 - 10 nm in size. The infrared spectra and temperature programmed reaction of adsorbed CO (Figure 2) indicate that the Ir centers in the Ir/Sn/NaY system are more electron rich than the Ir present in Ir/NaY.

Both Ir/Sn catalysts displayed a significant decrease in hydrogenolysis activity in comparison to an analogously prepared Ir-only catalyst. In the presence of H_2, both Ir/Sn catalysts are highly efficient for the dehydrogenation of propane, producing propene at thermodynamic limits and with a selectivity of greater than 95%. The catalytic behavior of the Ir/Sn system may be understood by considering the geometric and electronic modifications of Ir by Sn.
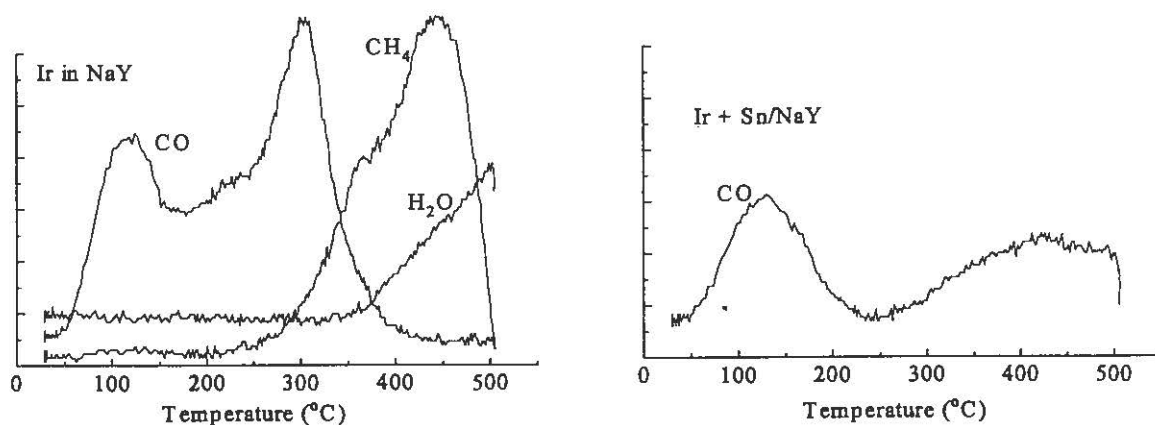

Figure 2. Temperature programmed reaction (in H_2) of CO adsorbed on
(**a**) "Ir in NaY" and (**b**) Ir + Sn/NaY.

A series of carbon-supported Pt, Pt/Ru, and Ru nanoparticles were prepared by treatment of the organometallic precursors $Pt(C_8H_{12})_2$, $Pt_2Ru_4(CO)_{18}$, $PtRu_5C(CO)_{16}$, and $Ru_5C(CO)_{15}$ dispersed on amorphous carbon (Vulcan XC-72) in H_2 at 723 K. Scanning transmission electron microscopy (STEM) and extended X-ray adsorption spectroscopy (EXAFS) revealed that these materials contained highly dispersed metal particles with average particle sizes falling between 1 and 2 nm. Energy dispersive X-ray analysis (EDX) indicated the bimetallic particles had elemental compositions similar to the respective bimetallic molecular precursors.[9]

The carbon-supported materials were all active catalysts for the decomposition of methanol to CO and H_2, but the catalyst derived from $Pt_2Ru_4(CO)_{18}$ displayed comparatively enhanced activity as well as stability (Figure 3a). Isotope effects determined by use of deuterated methanol indicated that both O-H and C-H activation were important in determining

the overall rate of reaction (Figure 3b). The behavior of these materials as thermal catalysts is expected to relate to their behavior as electrooxidation catalysts (anodes) in Direct Methanol Oxidation Fuel Cells (DMFCs).[10] It is hoped that extensive examination of the two Pt/Ru catalysts will provide the insight required to develop DMFC anodes of enhanced catalytic activity and stability.
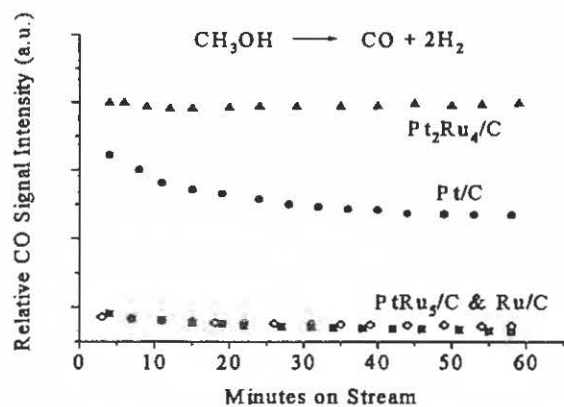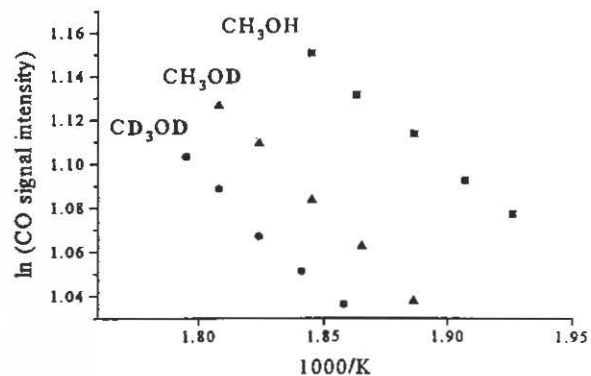

Figure 3a

Figure 3b

Figure 3. (a) Relative activity and stability of carbon-supported Pt/Ru catalysts for the decomposition of methanol to CO and H_2. (b) Arrhenius plots for the decomposition of deuterated methanol by Pt_2Ru_4/C.

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