An analysis of the gas phase during the adsorption showed the presence of 0.93 mol of CO, 0.04 mol of CO_2, and 0.03 mol of H_2 per $Fe_2(CO)_9$ adsorbed. The basic character of the hydroxyl groups on alumina[15,16] and on alkali-metal cation-exchanged zeolites[17] has been shown. Reaction 1, similar to

$$3Fe_2(CO)_9 + 2OH^- \rightarrow 2HFe_3(CO)_{11}^- + 3CO + 2CO_2 \tag{1}$$

the formation of $HFe_3(CO)_{11}^-$ from $Fe_3(CO)_{12}$ in basic solution,[6] was concluded for the grafting of $Fe_2(CO)_9$ on the zeolite lattice. The appearance of IR bands at 1405 and 1350 cm^{-1} during the adsorption indicates that most of CO_2 remains adsorbed on zeolite as a hydrogen carbonate anion (eq 2). The

$$CO_2 + OH^- \rightarrow HCO_3^- \tag{2}$$

small amount of H_2 produced has been concluded to result from the water-gas shift reaction (WGSR), since the $HFe_3(CO)_{11}^-$/Na–Y system has been confirmed in a separate experiment to be active for the WGSR.[18]

The hydroxyl groups in reaction 1 are presumably generated through reaction 3, which has been generally proposed in water

$$O^{2-}(\text{lattice oxygen}) + H_2O \rightleftarrows 2OH^- \tag{3}$$

adsorption on an oxide surface. Although there is no report for such high reactivity of zeolite oxygen as that suggested in reaction 1, the experimental findings mentioned above strongly suggest reaction 1 to be reasonable. The framework oxygen atoms in zeolite have indeed been found to participate in the reversible exchange with the oxygen of water,[19] adsorbed oxygen,[20] and carbon dioxide,[21] though the reactions have been observed at 473 K or above. Furthermore, it is widely accepted that the hydrothermal treatment of zeolite causes easy transformation of the zeolite structure.[22] These facts suggest the relatively high reactivity of zeolite oxygen and support reaction 1.

In attempt to detect a precursor in the course of the grafting, ESR spectra of $g_I = 2.0545$, $g_{II} = 2.0395$, and $g_{III} = 2.0013$ were observed upon evacuation of the $Fe_2(CO)_9$/Na–Y system at room temperature. With progress of the reaction between $Fe_2(CO)_9$ and Na–Y, the spectrum at $g_{II} = 2.0395$ first developed and then the species with $g_{III} = 2.0013$ appeared. Further reaction of the samples resulted in a decrease in intensity of the spectrum at $g_{III} = 2.0013$ and the appearance of a third small spectrum at $g_I = 2.0545$. All of these spectra substantially disappeared when the sample was warmed to 333 K. The species with g_I, g_{II}, and g_{III} were assigned to $Fe_3(CO)_{11}^-$, $Fe_2(CO)_8^-$, and $Fe_3(CO)_{12}^-$, respectively, from the comparison with ESR spectra of iron carbonyl radicals in THF solution[23] or in CH_2Cl_2 solution.[24] These anions indicate the presence of electron-donating sites in the Na–Y zeolite and might be precursors for the $HFe_3(CO)_{11}^-$ species.

When $Fe_3(CO)_{12}$ was adsorbed on the hydrated Na–Y, the IR, UV, and volumetric studies indicated the formation of $HFe_3(CO)_{11}^-$ interacting via the bridging carbonyl with an acidic center (eq 4). The adsorption of $Fe_3(CO)_{12}$ was much

$$Fe_3(CO)_{12} + OH^- \rightarrow HFe_3(CO)_{11}^- + CO_2 \tag{4}$$

slower than that of $Fe_2(CO)_9$. This is due to the molecular size of $Fe_3(CO)_{12}$ (ca. 1.05 nm × 0.75 nm)[25] being close to the diameter of the zeolite window (approximately 1.0 nm).[26] This observation indicates that the hydride anion was generated inside the zeolite supercages. The $HFe_3(CO)_{11}^-$ species grafted on the hydrated zeolite was stable at 433 K under a dynamic vacuum and up to 473 K in the presence of CO.

When $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ was introduced on Na–Y zeolites dehydrated at 773 K, the carbonyl was adsorbed as it was and no hydride anion was observed. The adsorbed $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ was unstable under a static vacuum at temperatures higher than 373 K. Ballivet-Tkatchenko and Coudurier[2] have reported that $Fe_3(CO)_{12}$ or $Fe(CO)_4$ bonded to the zeolite was obtained as a stable species in a dehydrated H–Y zeolite matrix upon the admission of $Fe_3(CO)_{12}$, $Fe_2(CO)_9$, or $Fe(CO)_5$. It was further reported that treating $Fe_3(CO)_{12}$/zeolite under a CO atmosphere restored the IR spectra of the $Fe(CO)_5$- or $Fe_2(CO)_9$/zeolite system. The same research group has also presented that when the $Fe_3(CO)_{12}$/H–Y zeolite system was heated to 333 K, $H_2Fe_3(CO)_{11}$ was formed within the supercage and interacted with the zeolite through hydrogen bonding.[27] The difference among the behaviors of the iron carbonyls in hydrated and dehydrated Na–Y and dehydrated H–Y indicates the importance of the degrees of hydration of the zeolites and the acid–base properties of the zeolites used.

Registry No. $Fe(CO)_5$, 13463-40-6; $Fe_2(CO)_9$, 15321-51-4; $Fe_3(CO)_{12}$, 17685-52-8; $HFe_3(CO)_{11}^-$, 55188-22-2.

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Sulfide Bronzes: Preparation and Characterization of (RE)Pd_3S_4 (RE = Rare Earth)

Sir:

The platinum-group bronzes, $M_xPt_3O_4$ and $M_xPd_3O_4$ where M = Li, Na, Ni, Cd, etc. and $0 < x \leq 1$, are a widely studied class of materials of considerable technological interest. The platinum bronzes have been used as chlor-alkali anodes[1] and as H_2–O_2 fuel-cell electrocatalysts.[2] Moreover, $Na_xPt_3O_4$ is the active component of Adam's catalyst, a mixture of Pt, α-PtO_2, and $Na_xPt_3O_4$ used for the reduction of organic compounds.[3]

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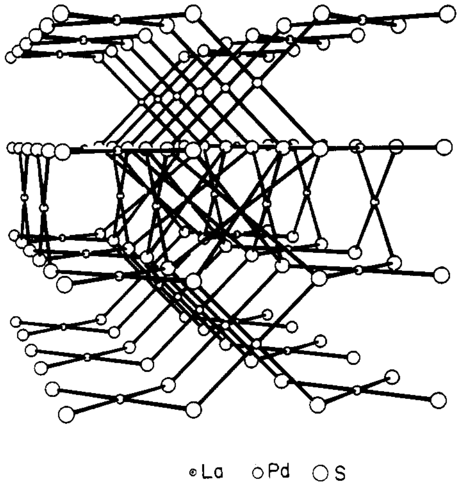

Figure 1. Sketch of the $LaPd_3S_4$ structure.

We report here the first chalcogenide analogues of the platinum-group bronzes. Interest in the sulfides, as for the oxides, arises in large measure from the surface properties of such materials. The use of the simple binary platinum-metal sulfides for the preparation of industrially important haloaromatic amines[4] and in hydrodesulfurization processes has been demonstrated.[5,6]

The compound $LaPd_3S_4$ was prepared from a stoichiometric combination of the elements heated at 1125 K in a sealed evacuated silica tube lined with carbon. The charge was heated for 3 weeks with intermediate grindings every 4 days. Thus far, no single crystals of the sulfide have been obtained, but the structure has been established from X-ray powder data and the refinement of neutron powder data.[7] The compound forms with the ideal $NaPt_3O_4$ structural type as illustrated in Figure 1.[7] Important bond lengths are La–S = 2.918 (1) Å, Pd–S = 2.383 (1) Å, and Pd–Pd = 3.370 (1) Å.

The results of a general survey indicate that similar materials are formed for most of the rare-earth elements. The small crystal radius of Sc^{III}[8] appears to preclude the formation of $ScPd_3S_4$. The corresponding Pt analogues do not form under the same experimental conditions as for the Pd compounds. The materials prepared thus far appear to be stoichiometric, based on the rare earth concentration $LaPd_3S_4$ vs. $Na_xPt_3O_4$, $0 \leq x \leq 1$.

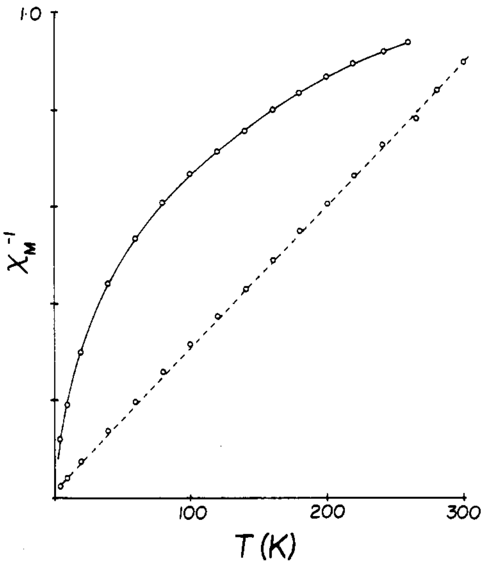

Figure 2. Normalized reciprocal molar susceptibility vs. temperature for (---) $TbPd_3S_4$ ($\chi_m^{-1}(300) = 27$ emu/mol) and (—) $SmPd_3S_4$ ($\chi_m^{-1}(260) = 752$ emu/mol).

As illustrated in Figure 2 by the Tb and Sm analogues, the magnetic properties are characterized by paramagnetic behavior. The Tb compound exhibits a Curie–Weiss temperature dependence, and the uncorrected magnetic moment of 9.4 μ_B is consistent with Tb^{III}.[9] Similarly, the data for the Sm analogue are in agreement with the Van Vleck theory of closely spaced multiplets for Sm^{III}.[9]

From the current results a simple valence description is: RE^{III}, Pd^{II}, S^{-II}. The compounds are thus formulated as $[((RE)Pd_3S_4) + e^-]$. This model is supported by the observation of metallic conductivity for a pressed powder of $LaPd_3S_4$. Insofar as we know, this is the first example of a metallic Pd bronze.

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Registry No. $LaPd_3S_4$, 87206-69-7; $TbPd_3S_4$, 87206-71-1; $SmPd_3S_4$, 87206-70-0.

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