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Reaction of Bis(dialkyl dithiophosphato)nickel(II) with High-Surface-Area Solids: A Novel Method To Anchor Metal Complexes within Zeolite Cages

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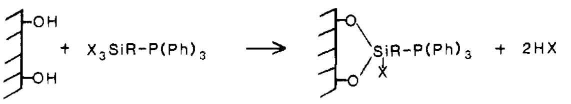
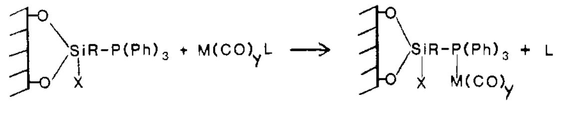
Since about 1970, the prognosis of unique catalytic properties, unusual stability, or corrosion inhibition under process conditions has generated interest in normally soluble transition-metal complexes anchored to solid-phase supports such as cross-linked polymers or inorganic oxides.[2,3] Preparative methods include the incorporation of ligand groups such as phosphine[3,4] or amine[5] onto surfaces of, typically, silica by the reaction of a functionalized silane with surface silanol groups:



(1)

This reaction is followed by exchange of a labile ligand of the molecular complex with the pendent surface functionality:



(2)

Alternatively, direct reaction of metal-carbon bonds with surface silanol groups may be utilized[2b,6-9] as an anchoring method. On zeolite supports, the preparation of anchored complexes has been limited to direct ion exchange of cationic molecules[10-12] or has required in situ complexation of low-valent metallic species by ligands such as carbon monoxide or ethylene.[13-16] We have focused our interests on zeolite-supported complexes, especially the planar bis complexes of the d^8 transition metals with dithiophosphates because of their coordinatively unsaturated structures. We hoped to demonstrate unusual activation of coordinated adducts in the zeolite environment. The free complexes are inert toward ligand labilization under the conditions of interest and have been well characterized in solution and as solids.[17-19]

We report here the novel preparation of a substitution-inert neutral nickel dithiophosphate complex bonded to a zeolite supercage by a reaction of the ligand. The tethering reaction is influenced by surface basicity as well as steric factors and maintains the integrity of the ligand structure immediately adjacent to the metal atom.

Experimental Section

Preparation of Solid Substrates. Na^+-X zeolite was prepared according to ref 32 from an aged gel (18 h, 26 °C) by crystallization for 8 h at 100 °C. The isolated solid was boiled in aqueous sodium hydroxide (pH 10) for 15 min followed by repetitive washing with hot water to remove soluble silicate impurities. Purity was judged to be essentially 100% by X-ray powder diffraction in comparison with a standard. Unit cell size was found to be 24.88 Å, BET surface area 633 $m^2\ g^{-1}$ (16.2 $Å^2/N_2$ molecule is assumed), and unit cell formula $0.99Na_2O{\cdot}3.01SiO_2{\cdot}Al_2O_3$.

Na^+-Y and Na^+-A zeolites were purchased from Linde Division, Union Carbide Corp., and purified by boiling in hot water to remove soluble silicate impurities.

$Na^+NH_4^+$-Y was prepared by repetitive batchwise exchanges of Na^+-Y with 2 M NH_4NO_3(aq) (pH 3.5, 83 °C) to various sodium levels. Several of these samples were deaminated by heat treatment in a fluidized bed under N_2.

H-Zeolon 100 was purchased from Norton Co. and exchanged with 6 N H_2SO_4 at 80 °C.

HiSil 233 was purchased from PPG Industries, Pittsburgh, PA.

Acidic silica-alumina gel was prepared according to ref 29, dried, pulverized, and washed repeatedly with 1% NH_4OH followed by water.

Preparation of Ni(R-DTP)$_2$, Where R = C_2H_5, *n*-C_3H_7, *i*-C_3H_7, or *t*-BuPhO. The alkyl-substituted compounds were prepared according to ref 17 and references therein from the potassium salt of dithiophosphoric acid and recrystallized from CCl_4. The *t*-butylphenoxy complex was prepared from a melt of *t*-butylphenol with P_2S_5 at 120 °C to form a clear yellow liquid; the cooled solid acid was recrystallized from chloroform. Several batches of excess $Ni(NO_3)_2$(aq) were then shaken with a chloroform solution of the acid, and the complex was recovered by evaporation of the organic layer followed by recrystallization from dry ether. The nickel compounds were characterized by their infrared and electronic spectra and elemental analyses.

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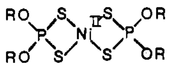
Anchoring Reactions. Zeolite samples were dried in vacuo at 200 °C overnight. The solid nickel complexes were dissolved in a few milliliters of solvent (dry CCl_4 or toluene) and deaerated with nitrogen. The zeolite was suspended in pure solvent in an all-glass apparatus and the slurry deaerated for 15 min prior to dropwise addition of the solution of Ni(R-DTP)$_2$ with stirring. After complete addition, the mixture was heated to reflux under N_2 for 6–20 h. Colored solids were isolated, washed with hot solvent, and dried in vacuo.[33]

Results and Discussion

We have observed the reaction of disubstituted nickel(II) dithiophosphates, **1**, with various zeolites and other high-surface-area supports.



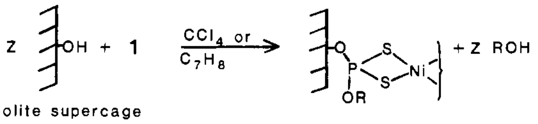
1

R = Et, *n*-Pr, *i*-Pr, *t*-BuPhO

In refluxing toluene or carbon tetrachloride solution, the square-planar, neutral complexes **1** are adsorbed irreversibly onto suspended Na^+–X zeolite powder to yield isolable pigmented solids. When R = *i*-Pr, analysis of the lavender product indicates a Ni:P:S ratio of 1:2:4.[34] This stoichiometry is consistent with retention of the basic sulfur–phosphorus ligand framework after reaction with the zeolite.

A similar anchoring reaction was observed over non-calcined $Na^+NH_4^+$–Y zeolites, but irreversible entrainment of the nickel complex did not occur when HiSil 233 silica gel was pretreated similarly to and used in place of the Na^+–X zeolite. In the latter case, the lightly colored solid that was isolated could be washed clean of complex with hot solvent. No spectroscopic or X-ray fluorescence evidence for the presence of the complex on the washed solid was found.

Since it is known that **1** can undergo scrambling reactions in hot alcoholic solution to yield mixed alkyl dithiophosphate complexes,[20] a reasonable postulate to explain our observations would be the analogous reaction (3). However, gas chromatographic analysis of the resulting filtrate from one reaction of **1** where R = *i*-Pr in toluene solvent established the release of only a small amount of isopropyl alcohol (equivalent to 0.2 mol/mol of Ni adsorbed). This quantity is too small to account for the extent of reaction observed. Furthermore, the only hydroxyl groups present in group 1A zeolites such as Na^+–X are those resulting from cationic deficiency caused by partial hydrolysis, introduced by slight amounts of siliceous impurities, or those terminating the lattice.[35] Thus, reaction 3 fails to account for the different reactivity of **1** with silica compared to that with Na^+–X.



(3)

2

z = 1 – 4

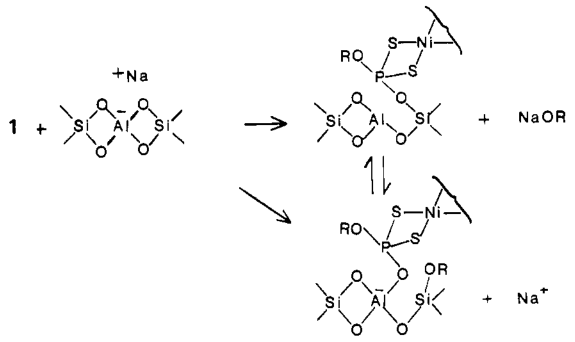
Table I. Reaction of Na^+-X with Ni(*i*-PrDTP)$_2$ at Various Ratios

amt of Na^+-X, g	amt of Ni(*i*-PrDTP)$_2$, g	wt % Ni theor	wt % Ni found	Ni:S:P
10.0	1.4	1.60	1.59	1:4.0:2.1
10.0	1.0	1.20	1.19	1:4.1:2.0
10.0[a]	0.5	0.60	0.63	1:4.3:1.6
5.0	1.0[b]	2.40	1.59	1:4.1:2.1
1.0	0.8	0.98	0.97	1:4.1:2.0

[a] Excess zeolite. [b] Excess complex.

We believe our observations are better represented by the interaction of **1** with *basic* AlO_4^- sites unique to the alkali-zeolite system,[36] perhaps through a phosphonium-like intermediate.[37]

Reaction 4 represents the novel formation of a neutral metal complex covalently bonded to the zeolite substrate through the ligand via basic surface sites.[21] The small quantity of free alcohol observed could have arisen from a minor competitive reaction by route (3) or from hydrolysis of structures such as **3** in the presence of traces of water.



(4)

3

Reaction of **1** with more acidic substrates such as $NH_4^+H^+$–Y, H^+–mordenite, or acidic SiO_2–Al_2O_3 gels resulted in various degrees of decomposition of the nickel complex, presumably to charged species which could then ion exchange.[22] The reactions over silica–alumina gels and H^+–mordenite resulted in green solids with virtually no phosphorus or sulfur contents. Reactions with substrates of intermediate acidities, however, resulted in poorly characterized brown solids. For example, reaction of Ni(*i*-PrDTP)$_2$ with zeolite Y that had been previously exhaustively NH_4^+(aq) exchanged and heat-treated in a fluid bed under nitrogen at 350 °C[24] resulted in a brown solid exhibiting a Ni:S:P ratio of about 1:3:2. In a similar reaction, adsorption of 2.06 mmol of nickel resulted in the formation of 1.8 mmol of H_2S. These results are consistent with the approximate loss of one sulfur per zeolite-entrained nickel via a reduction reaction of the ligand.

That the reaction site between Na^+–X and **1** is primarily within the zeolite supercage may be inferred from several observations. An upper limit of 1.59% (volatile free basis) nickel was adsorbed by Na^+–X when the zeolite:nickel ratio was varied in a series of experiments (Table I). With the assumption of 8 supercages/unit cell[25] at a SiO_2:Al_2O_3 ratio of 3.0, this quantity corresponds to 0.5 nickel atom/supercage, a reasonable loading based on model building. In addition,

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(33) The pigments were analyzed by the Analytical Department of the Minerals and Chemicals Division, Engelhard Corp. Ni, P, S analyses were performed by X-ray fluorescence of pelletized samples compared to standards on a Phillips or Siemens SRS-200 instrument. Referee analyses were conducted by Galbraith Laboratories, Knoxville, TN. P was also determined by dc plasma emission spectroscopy after appropriate sample decomposition. FT IR spectra were measured by Professor J. San Fillipo at Rutgers University on an IBM 97 instrument equipped with a Harrick diffuse-reflectance accessory. Electronic spectra were measured on a Varian DMS-90 spectrophotometer equipped with a diffuse-reflectance attachment. IR and UV–vis spectra were plotted according to the Kubelka–Monk function.[30,31]

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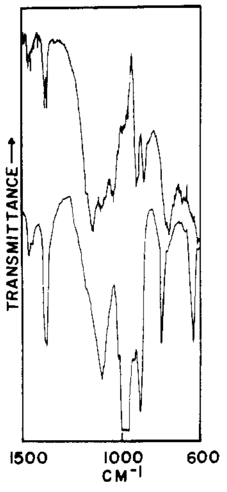

Figure 1. FT IR diffuse-reflectance ratio spectra. The upper curve is Ni(*i*-PrDTP)$_2$–Na$^+$–X/Na$^+$–X; the lower curve is Ni(*i*-PrDTP)$_2$–HiSil 233/HiSil 233.

X-ray powder diffraction patterns of dehumidified Ni(*i*PrDTP)$_2$–Na$^+$–X pigment indicated large losses of intensity in the low-angle diffraction maxima, which are influenced by intracage perturbations,[15] and a unit cell size increase by nearly 0.05 Å relative to that for the zeolite treated only with solvent and dried similarly. The X-ray parameters returned to normal when the anchored complex was allowed to react with 1 N NaOH(aq) at 90 °C, which resulted in stripping of most of the nickel. BET surface area was also reversibly reduced in the pigment although it can be argued that pore blockage by external surface-anchored molecules could similarly reduce nitrogen adsorption. Reaction of excess Ni(*i*-PrDPT)$_2$ with Na$^+$–A zeolite resulted only in trace adsorption of the nickel species by the solid (≤0.02% Ni). Na$^+$–A cages are too small to admit the complex[25] but exhibit an external surface similar to that of Na$^+$–X. An estimate of maximum external surface anchoring can be made from the analysis of the reaction product between a large excess of Ni(*t*-BuPhODTP)$_2$ and Na$^+$–X. A pale yellow solid was isolated which contained only 0.34% Ni.

In compounds with the P–O–C linkage, characteristic IR bands are found in the regions 1065–905 and 875–730 cm^{-1} assignable to (P)–O–C stretching modes and to P–O–(C) stretching modes, respectively.[17,26] Generally speaking, these bands would be expected to shift to lower frequencies upon substitution of a silicon (or aluminum) atom from the zeolite framework for carbon. Comparison of the room-temperature FT IR diffuse-reflectance ratio spectrum of Ni(*i*-PrDTP)$_2$ supported on silica gel vs. silica gel with that of the complex on Na$^+$–X vs. the Na$^+$–X support phase reveals striking differences in regions assignable to P–S and P–O stretching modes[19] (Figure 1). The Na$^+$–X-supported complex shows additional structure, most notably two bands at 1038 and 886 cm^{-1}. Also, the relative intensity of the very strong band at 960 cm^{-1} for Ni(*i*-PrDTP)$_2$ on SiO$_2$ gel (possibly C–C stretch) is reduced in the zeolite phase. The 886-cm^{-1} band is reasonably assigned to a P–O–T (T = Al, Si of zeolite framework) stretching vibration, lower in energy than the corresponding antisymmetric P–O–C modes,[17] and probably diagnostic of the anchoring linkage.

Diffuse-reflectance electronic difference spectra of the supported complex (vs. those of the respective supports) showed blue shifts of the two ligand field bands on Na$^+$–X or Na$^+$-NH$_4^+$–X ($\bar{\nu}_1$ = 15.4 × 10^3 cm^{-1}, $\bar{\nu}_2$ = 19.4 × 10^3 cm^{-1}) compared to HiSil 233 supported species or to the complex in fluid CCl$_4$ solution ($\bar{\nu}_1$ = 14.5 × 10^3 cm^{-1}, $\bar{\nu}_2$ = 19.1 × 10^3 cm^{-1}). Porta has shown a correlation between the $\bar{\nu}_1$ spectral frequency of the NiS$_4$ square-planar chromophore and the Ni–S bond distance.[27] Specifically, as more electron donation from sulfur to nickel occurs, the bond order increases and the $\bar{\nu}_1$ band shifts to higher frequency. From Porta's correlation,[27] one may estimate the Ni–S bond distance in the Na$^+$–X-encapsulated species to be ca. 2.215 Å as compared to 2.233 Å for the HiSil 233 supported or free complex.

The nickel complex is potentially deactivated toward adduct formation in the zeolite system as a consequence of enhanced electron donation by sulfur into the nonbonding p orbital of nickel. Experimentally, it can be shown that adducts with primary amines do not readily form for the zeolite-encapsulated species but are observed with the HiSil 233 supported complex and are known to occur with unsupported compounds or in solution.[17,18] Our original goal of activating such adducts toward further reactions consequently was not achieved.

To gauge thermal stability, differential thermal analysis of the Ni(*i*-PrDTP)$_2$ complex in Na$^+$–X was performed under flowing N$_2$ and compared to an analysis of the pure zeolite substrate. A sharp exothermic peak centered at 290 °C superimposed onto the broad endothermic water loss peak for the Na$^+$–X substrate was observed. The silica gel support system yielded a much broader decomposition curve between 150 and 320 °C for the complex; apparently the zeolite-supported complex exhibits a higher threshold decomposition temperature, which may reflect a hindrance of the alkene elimination reaction thought to operate during the thermal decomposition of metal dithiophosphates.[28] Despite its apparent thermal stability, the Ni(DTP)$_2$–Na$^+$–X pigment exhibits the characteristic pungent odor of the ligand system after several weeks of storage at room temperature indicative of some, if minor, decomposition.

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cis- and *trans*-[(en)$_2$Co(NO$_2$)(C$_2$O$_4$)], Cobalt(III) Complexes Containing a Monodentate Oxalato Ligand

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Anations of *cis*- and *trans*-[(en)$_2$Co(H$_2$O)(NO$_2$)]$^{2+}$ with nitrite and thiocyanate are stereoretentive,[1] and the cis isomer aquates slowly in acid solutions at elevated temperatures.[2] These reports prompted us to use anation of the aqua–nitrito-*N* complexes with dinegative, potentially bidentate ligands to compel their monodentate ligation. Although oxalato is well-known both as a monodentate[3-5] and as a bridging[5a,6] species, it occurs more commonly as a bidentate ligand.[5] We report here the stereoretentive preparation and characterization

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