plex by Kondow, Inokuchi, and Wakayama (*7*).

Not only the exchange reactions, but also the hydrogenation and the isomerization reactions are being studied over these electron donor–acceptor complexes of phthalocyanines.

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The Role of Coordination Compounds in Poisoning of Heterogeneous Group VIII Reduced Metal Catalysts

Poisoning of metallic catalysts is a well documented but poorly understood phenomenon. It is generally considered to be a preferential adsorption effect dependent upon the formation of abnormally strong bonds between a catalyst and certain types of adsorbed species (*1*). While it is recognized that these bonds are of definite chemical type, neither the exact nature of the poison–metal interaction nor the chemical constitution of the adsorbed moiety has been defined. Empirical data indicate that formation of catalyst–poison bonds is limited to definite electronic structural features, namely, vacant *d* orbitals in the catalyst (*2*) and nonbonding electron pairs in the poison (*3*). These and similar observations coupled with the rapidly expanding knowledge of transition metal coordination chemistry have led to suggestions that there should be a strong correspondence between heterogeneous catalysis and the organometallic chemistry of the transition metals (*4*). However, direct evidence for the formation of specific coordination compounds on the surface of solid metal catalysts has not, as yet, been obtained. In this communication, we wish to report spectroscopic evidence that a specific type of coordination compound is formed on the surface of a silica-supported nickel catalyst when this catalyst is poisoned by H_2S while being used in the hydrogenation of an olefin.

Sulfur compounds are very effective poisons for reduced nickel and other Group VIII hydrogenation catalysts. However, toxicity is limited to compounds in which the sulfur possesses nonbonding electron pairs. These are believed to be involved in forming the strong chemisorptive bond with the catalyst, and, indeed, magnetic susceptibility data indicate, in the case of methyl sulfide poisoning, that the unshared electrons of the sulfur fill vacant *d* orbitals of the metal that otherwise would be available for catalysis (*5*). In view of the nickel sulfide–hydrogen equilibrium (*6*), the outstanding toxicity of sulfur, particularly at high temperatures and high partial pressure of hydrogen, cannot be explained on the basis of site-blocking or electronic changes associated with nickel sulfide formation alone. Moreover, the reported high ratio of sulfur to metal, i.e., 3.7 S/Pt for a poisoned platinum-on-alumina catalyst (*7*Q, is inconsistent with metal sulfide formation and requires a more involved answer; perhaps formation of a stable complex in which the olefin as well as the poison and metal play a role.

Recently, unusually stable square-planar bis(dithioketone) complexes of Group VIII transition metals have been reported and characterized (*8*, *9*). These are remarkably stable at the high temperatures common to most hydrogenation processes and are not readily reduced by hydrogen. Complexes of this type can be prepared by reaction of suitably substituted acetylenically unsaturated hydrocarbons with metal sulfides under moderate conditions (*8*). Infrared spectra (*10*) clearly demonstrate the reversible formation of hydrogen-poor residues on the surface of metal catalysts in the presence of olefins, suggesting that during the hydrogenation of olefins a finite concentration of acetylenically unsaturated species may be present at or near the catalyst surface. If these findings are correct, then, when a sulfur-containing poison enters the hydrogenation system, all of the ingredients required for the formation of bis(dithioketone) complexes will be available at the surface. The complexes, once formed, will be stable under reaction conditions and, being incapable of olefin or hydrogen chemisorption, will poison the reaction. The experimental data reported below give evidence in support of this hypothesis.

An authentic sample of nickel bis(dithio-2,3-butanedione) (I) was prepared and purified according to the procedure described by Schrauzer (*9*). Its visible spectrum in methylene chloride solution was identical to that reported and consisted of three principle bands at 7700, 5700, and 4260 Å. Since porous glass was to be used as a support for the metal catalyst, a platelet of Corning 7930 porous glass (previously calcined and evacuated at 550°C) was impregnated with (I) from methylene chloride solution. After solvent removal by evacuation, the spectrum of the adsorbed complex was measured in a vacuum cell using techniques described elsewhere (*11*). It was found that the absorption band at 7700 Å was substantially reduced in intensity while the other bands remained largely unaltered. Subsequent extraction of the platelet with methylene chloride led to the removal of excess, loosely held, complex from the surface. While the extract showed all three characteristic bands, the 7700-Å band in the strongly adsorbed material remaining on the platelet was completely absent. These observations indicate that in its interaction with porous glass, (I) is either decomposed or its electronic structure is perturbed. Since the other bands (5700 and 4260 Å) are unaffected by interaction with the silica surface, we conclude that electronic perturbation rather than destruction of the complex has occurred. The 7700-Å band is known to be very responsive to environmental factors such as donor properties of surrounding molecules and the oxidation state of the complex itself (*9*). For example, neither the mono- or di-anion of (I) exhibit a band at 7700 Å.

A nickel-on-silica hydrogenation catalyst was prepared by impregnation of a transparent platelet of porous glass [previously freed of acidic oxides by leaching with dilute nitric acid as recommended by Little (*12*)] with aqueous nickel nitrate, followed by calcination and reduction. The catalyst sample, containing 2% metal by weight, was placed into the optical cell–catalytic reactor previously described by Leftin and Hermana (*13*), where it was calcined in 760 torr of oxygen at 550°C for 24 hr, evacuated at this temperature, then reduced in hydrogen at 350°C for 48 hr. The background spectrum of the catalyst was then recorded (Fig. 1, Curve a) and a mixture of hydrogen and *cis*-2-butene was introduced into the cell at 105°C. Progress of the butene hydrogenation was followed by removing samples of the gas phase for VPC analysis. During the course of the reaction, the spectrum of the catalyst showed no change (Fig. 1, Curve b). When the reaction had proceeded to about 50% completion, a small dose of H_2S was added. After about

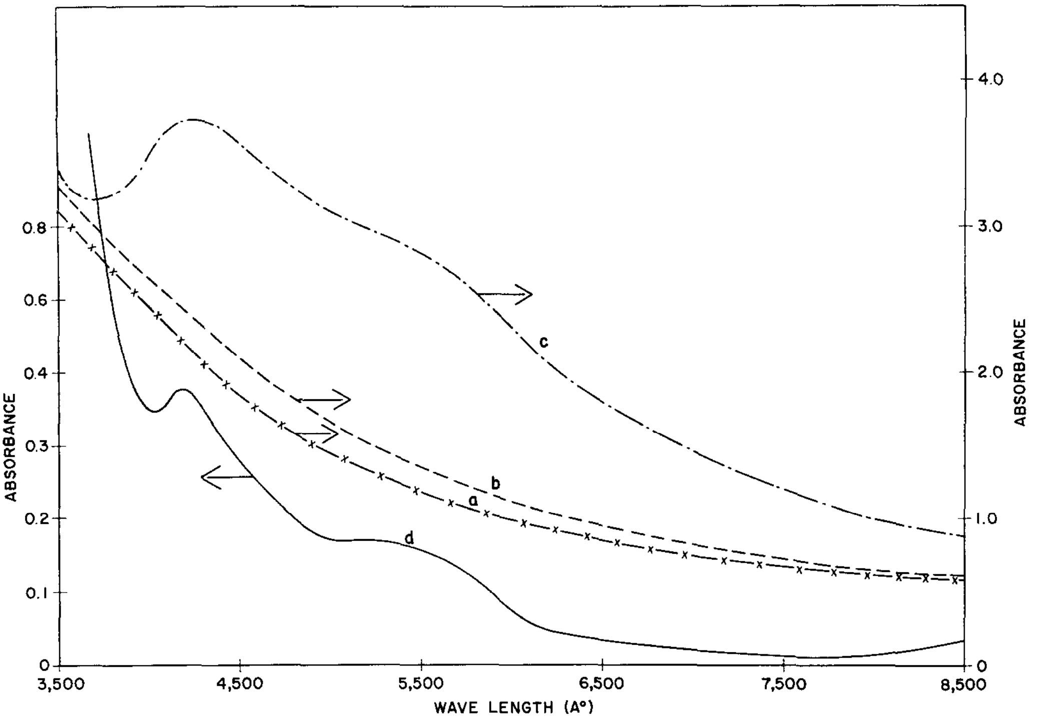

Fig. 1.

15 min, analysis of the gas phase indicated that the hydrogenation reaction had been effectively poisoned. Concomitant with this poisoning, the catalyst spectrum showed the development of an intense band at 4260 Å and a weak band in the 5700-Å region (Fig. 1, Curve c) the qualitative features being substantially those observed for (I) adsorbed on porous glass. *These results are believed to constitute the first direct evidence for the intermediacy of a specific type of coordination complex in sulfur poisoning of a nickel catalyst.*

An attempt was made to isolate the complex involved in catalyst poisoning for further characterization. A 15-g sample (30–60 mesh) of a 10% nickel-silica catalyst, treated as above, was used for the hydrogenation of *cis*-2-butene at 110°C. After about 50% reaction (indicated by pressure drop), a dose of H_2S was introduced. The system was then maintained at reaction temperature for a period of 2 hr, the gas phase removed and replaced with dried nitrogen. The catalyst was then transferred to a continuous extractor where it was extracted for 24 hr with methylene chloride. The extract solution had a pink-lavender color and its visible spectrum (Fig. 1, Curve d) exhibited two clearly defined absorption bands at 4260 and 5700 Å. Qualitative analysis confirmed the presence of nickel in the extract solution. However, further characterization was precluded by the extremely small quantity of substance available. The spectrum of the material removed from the nickel catalyst again indicates the formation of a specific coordination compound of the surface of the catalyst under conditions of sulfur poisoning of an olefin hydrogenation reaction.

While the exact structure of the complex formed during the poisoning experiments with nickel has not been fully established, the spectral data strongly resemble those reported for complexes of the square-planar dithioketone type, particularly the mono-anion of (I). It is to be expected that similar complexes will be found with other Group VIII metal catalysts and with other poisoning agents. These data, then, clearly are evidence for the inherent correspondence between heterogeneous catalysis and homogeneous transition metal catalysis and coordination chemistry. However, we shall not indulge in detailed speculation until we have completed investigations of other systems.

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