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Generation of finely-divided nickel particles in a protective medium and their use as high-activity catalysts

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Summary

In this technique, a relatively unreactive substance is transformed into a catalytically-active one within a protective environment. In this illustrative case, nickel formate was dissolved in a solution of poly(ethylene oxide) (PEO) in ethylene glycol, and then thermally decomposed in-situ to form finely-divided nickel particles. The mixture was dried, thereby protecting the nickel by encapsulating it in the polymer matrix. The distribution and the dispersity of nickel particles were investigated by electron microscopy. Upon adding portions of the catalyst-containing polymer to a reaction medium, the protective polymer dissolves, which releases the nickel particles and permits them to catalyze the reaction. In this particular case, the Ni-PEO sample was evaluated for the hydrogenation of an olefin, and found to be a highly efficient catalyst.

Introduction

In order for a substance to be effective as a catalyst, it must generally be highly reactive. This can be a problem because the substance can then also react with and become partially deactivated by inadvertent or unavoidable exposure to the atmosphere (water vapor, carbon dioxide, oxygen, nitrogen, ozone, etc.).

In the approach developed here to mitigate this problem, finely divided particles of a catalytically-active substance are generated from a relatively inactive precursor within a polymer matrix. The example chosen to illustrate this method is the generation of catalytically-active nickel by in-situ thermal decomposition of nickel formate within a matrix of poly(ethylene oxide) (PEO).

In-situ reactions represent a novel method for introducing particles into a polymer matrix. Numerous papers have been published in this area, most notably on the precipitation of silica by catalyzed hydrolysis of an alkoxysilane or silicate. The resulting particles provide excellent reinforcement in the case of elastomeric polymers (1-3). Another application involves the thermolysis of a metal carbonyl in a polymer solution to form a colloidal dispersion (4). The method typically yields very fine particles, with narrow size distributions, which are well dispersed within the matrix.

The possibility of generating such finely-divided metal particles of high surface area in an inert atmosphere suggested the idea of making polymer-protected catalysts. The metal particles would have very small diameters and be unagglomerated. The high surface area of the particles and their having been generated in a protective environment could give them long-term reactivity.

Experimental Details

Choice of System

Nickel is one of the most commonly used metal catalysts, and is particularly widely used for hydrogenation and dehydrogenation (5). Most nickel catalysts are prepared by mixing a soluble nickel salt such as the sulfate, nitrate, or chloride with sodium, potassium, or ammonium hydroxide, carbonates, and bicarbonates. The nickel hydroxides, or basic nickel carbonates thus formed are precipitates, which are usually susequently reduced with hydrogen gas in the presence of a carrier such as diatomaceous earth (6). In some cases, polymer has been employed as a carrier for nickel hydroxide and then pyrolyzed with hydrogen to produce nickel particles on active carbon (7). In our experiments, fine nickel particles in a polymer matrix will be produced by thermal decomposition of a nickel compound, specifically nickel formate. The decomposition reaction is (8):

$$Ni(HCOO)_2 \xrightarrow{200^oC} Ni + CO\uparrow + H_2O\uparrow + H_2\uparrow + CO_2\uparrow$$

The distribution and the dispersity of the nickel particles thus generated will be investigated by electron microscopy, and their catalytic activity will be evaluated in the hydrogenation of an olefin.

In-Situ Precipitation of Nickel into the Polymer Matrix

0.75 g of nickel formate [$Ni(HCOO)_2$] (K & K Laboratory) and 2.5 g of PEO (Aldrich Chemical Company) having a number-average molecular weight of 900,000 g/mol were added to 75 ml of ethylene glycol with stirring. The mixture was heated to 200 °C and allowed to reflux for 8 hours. The ethylene glycol was then removed by distillation under reduced pressure, and the sample dried in a vacuum oven to constant weight. The dried sample was molded into a sheet by placing it in an aluminum mold, heating it to 100 °C under high pressure, and then cooling it to room temperature.

Electron Microscopy

A piece of the Ni-POE sheet was fractured under liquid nitrogen, and part of the fractured surface was coated with gold. It was examined with a Cambridge 600 Scanning Electron Microscope at a magnification of 5 K, and Energy dispersive X-ray analysis was used to identify the elements and their distribution at the surface.

Another small piece of sample was dissolved in hot water. A drop of the resulting suspension was placed on a polymer-coated grid and then dried. It was examined with a Hitachi H-600 Transmission Electron Microscope.

Measurement of Catalytic Activity

The specific reaction employed was the hydrogenation of n-octene-1 in ethanol solution. The reference material chosed was Harshaw 0104 P (a nickel catalyst on kieselguhr manufactured for olefin hydrogenations). For both catalysts, the conversion of octene-1 to octane was analyzed by gas-liquid chromatography (GLC).

Some of the Harshaw catalyst was added to a 4.93 % octene-1 ethanol solution. The solution (300 ml) was placed into a Parr autoclave and pressurized to 860 psi with hydrogen, then heated to 125 °C with stirring (at which point the pressure was 1140 psi). The reactor was allowed to cool and a sample of the mixture (H1) removed. The mixture was repressurized with hydrogen and stirred overnight at room temperature, with a final pressure of 830 psi, and a sample (H2) removed. About 0.1 g of 5 % Pd on carbon was then added, the mixture was pressurized to 900 psi and heated to 60 °C for a short time, allowed to cool slowly over an hour and a portion removed (sample H3).

Some of the Ni-PEO material also then placed in the Parr reactor together with 100 ml of ethanol and 10 ml of octene-1, representing 8.12 %. The autoclave was pressurized with hydrogen to 600 psi, then warmed to 100 °C and stirred under hydrogen at 680 psi. After several minutes a sample (P1) was removed under pressure, and after another half hour at 100 °C another sample (P2) was removed. The hydrogenation was continued for 15 hours at 100 °C and 620 psi, and sample P3 was removed. The pressure was raised to 940 psi and temperature to 125 °C, and the mixture was stirred for a half hour. It was then heated to 150 °C for 5 minutes, cooled slowly to 125 °C, and then cooled rapidly to room temperature, yielding sample P4.

All samples were filtered and analyzed by GLC to obtain values of the % conversion of the octene-1.

Results and Discussion

The amount of nickel in the dried PEO sample was found to be 7.6 %. The scanning electron micrograph taken of it is shown in Figure 1. The nickel particles are clearly in evidence, seem to be well dispersed, and appear to have diameters the order of 0.4 μ. The bonding between the particles and the polymer matrix is seen to be relatively poor, but this should not be a disadvantage in the present (non-mechanical) application.

The corresponding energy dispersive X-ray analysis spectrum is presented in Figure 2. As expected, the only elements found to be present are nickel (in the particles), and gold (in the coatings).

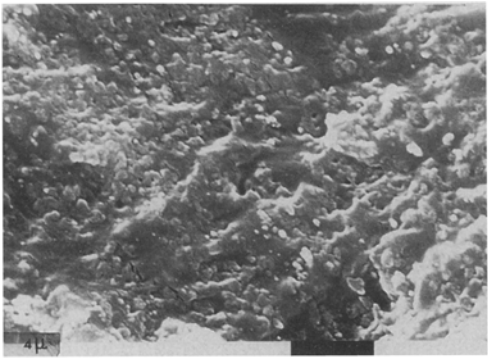

Fig. 1. Scanning electron micrograph of a PEO-Ni sample (7.6 % Ni) at a magnification of 5,000 x. The length of the bar corresponds to 4 μ.

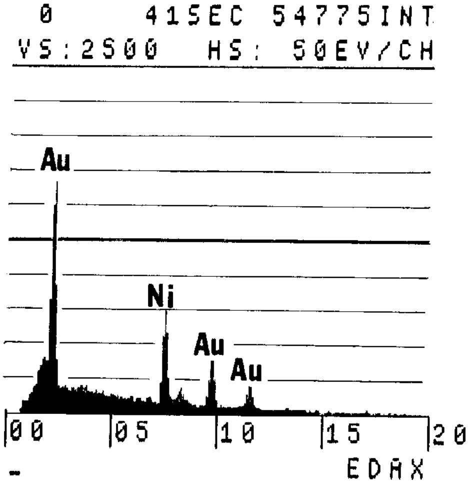

Fig. 2. EDXA spectrum of the same sample area shown in Figure 1.

The Ni distribution map of the same area, at the same resolution as in Figure 1, is shown in Figure 3. The particles are seen to be well dispersed, in agreement with the results shown in Figure 1.

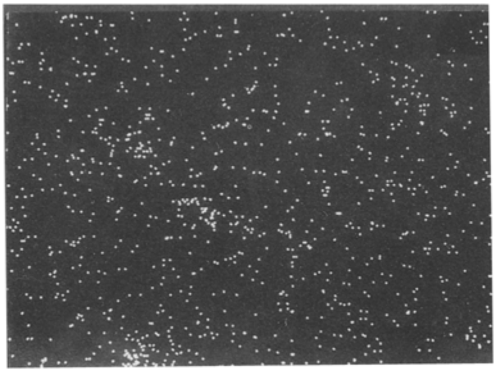

Fig. 3. The EDXA nickel distribution map of the same sample area shown in Figure 1.

In the transmission electron micrograph shown in Figure 4, the white

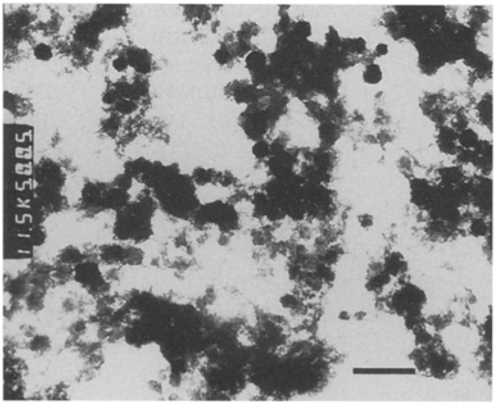

Fig. 4. Transmission electron micrograph of the Ni particles deposited from the water suspension. The length of the bar corresponds to 1 μ.

areas are uncoated parts of the grid, the grey areas the polymer, and the black areas the nickel. The sample was prepared by drying a suspension of the particles, which apparently caused their agglomeration. The average nickel particle size is seen to be approximately 0.4 μ, which is in agreement with the estimate made from Figure 1.

The results of the catalytic activity measurements are given in Table 1.

Table 1. Conversions of Octene-1 to Octane During Hydrogenation

	Harshaw			Ni-PEO			
Step	H1	H2	H3	P1	P2	P3	P4
Conversion (%)	23	62	100	18	15	75	99

The conversion at each step is listed for both the Harshaw product and the Ni-PEO sample. The results show that PEO-protected nickel catalyst is comparable to the commercial Harshaw product. It could have several advantages, including convenience and greatly increased shelf life.

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