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Notes

Preparation and Catalytic Properties of Finely Divided Nickel Obtained by Reduction of Nickel Halide in Tetrahydrofuran or Ethanol

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The reaction of a reducing agent with a transition-metal salt provides a good method for obtaining hydrogenation catalysts. The reducing agent may be a metal with an oxidation potential lower than of the transition metal,[1-7] a hydride such as $LiAlH_4$,[8] $NaBH_4$,[9-11] and $SiHR_3$,[12,13] or the associations NaH-*t*-BuOH[14] or NaH-*t*-AmOH.[15]

The purpose of this work is to study the reduction, in organic media, of nickel halide with low-oxidation-potential metals. This procedure allows one to obtain a finely divided pure metal, exhibiting, in general, catalytic activity greater than commercial Raney nickel.

Results and Discussion

The catalyst is prepared under an inert atmosphere (N_2 or Ar) by treating a vigorously stirred suspension (or solution) of anhydrous nickel halide with the reducing metal. The speed of reaction depends principally upon the thermal conditions, solvent used, and division state of the reducing metal.

When the reaction is complete, the fine black precipitate is washed first with water then with ethanol. From that time on, it is ready for use. Without washing, reduced nickel has a weak catalytic activity. This fact probably arises from the inhibitor effect of halide ions.

For preparation of catalyst, three reducing metals were used successfully: sodium magnesium, and zinc. Only two nickel salts were examined: bromide and chloride. As regards the solvent, we have employed tetrahydrofuran and ethanol.

The change in either halide or reducing metal does not induce an important difference in the development of the reaction as well as in the catalytic activity of nickel. But, a change of solvent is of great importance. (Consequently, our study is divided in two parts according to the solvent used.)

Table I. Hydrogenation of Typical Substrates over Raney Nickel and Reduced Nickel[a]

	Raney nickel		reduced nickel	
substrate	v_i[b]	t_{50}[c]	v_i[b]	t_{50}[c]
1-hexene	40	8	59	6
1-hexyne	15.5	37	29	22
3-hexyne	38	9[d]-19[e]	54.5	6[d]-12[e]
cyclohexene	18	20[f]	9.6	40

[a] Hydrogenation of 29 mmol of substrate over 3.4 mmol of catalyst in ethanol at 20 °C (1 atm). [b] Average rate from 0 to 20% reaction, in cubic centimeters of H_2 per minute. [c] Time in minutes for uptake of 0.5 molar equiv. [d] 3-Hexyne → 3-hexene. [e] 3-Hexyne → hexane. [f] Measurement agrees identically with that of BROWN.[10]

Reduction in THF. First we investigated the reduction in THF. When the mixture was heated under reflux, the reaction was relatively fast (from 2 to 5 h according to the reducing metal used). When we worked at room temperature[16] or at low temperature[17] it went more slowly (10 h). In any case we have verified that the reaction was quantitative. At the end point of the reaction, all the nickel is in a zero state of oxidation; one part attracted by the magnetic stirring bar is at the bottom of reactor, the other part is made up of a fine precipitate with a very slow sedimentation speed. When the reduction is allowed to proceed under boiling, almost all the nickel is gathered around the magnetic bar. On the other hand at low temperature almost all of the metal is in the form of a very fine and nonferromagnetic precipitate.[18] It would appear that the lower the temperature, the smaller the size of nickel particles. The catalytic activity of metal prepared at low temperature has not yet been studied because the precipitate was too fine to be washed by decanting.

Quantitative tests of hydrogenation were carried out to compare the catalytic activity of Raney nickel with that of nickel prepared by reduction of bromide with magnesium in boiling THF.[7] The substrates used were as follows: aliphatic alkene (1-hexene), monosustitued alkyne (1-hexyne), disubstitued alkyne (3-hexyne), cyclic alkene (cyclohexene).

As shown in Table I, for aliphatic compounds the reduced nickel activity is higher than for that Raney nickel. Thus, for 1-hexyne hydrogenation, the initial rate is approximately twice as great, but it is twice as weak for cyclohexene hydrogenation.

Raney nickel is not selective in the semihydrogenation of monoalkyl acetylenes,[19] but for a disubstituted alkyne the rate of uptake drops sharply after absorption of the first molar equivalent. Prepared in THF, the reduced

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(16) In this case, sodium can be used. With magnesium or zinc, it is necessary to grind the metal finely.

(17) The reduction is possible only with sodium (with temperatures down to a minimum of -40 °C).

(18) We are presently verifying that it is superparamagnetic.

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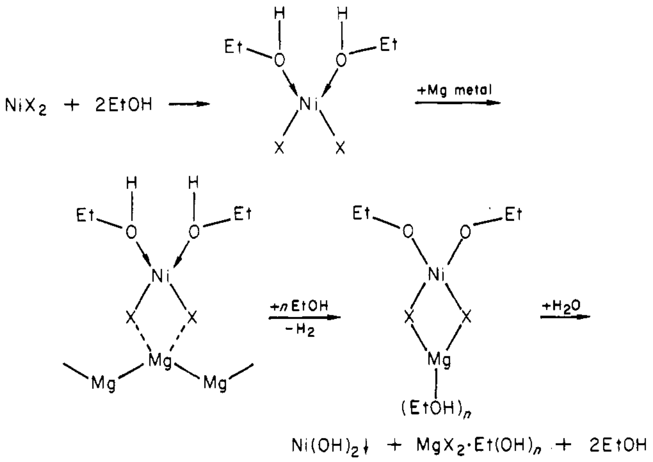
Scheme I



nickel has similar behavior; however, the decrease in the rate of reaction after absorption of 1 equiv is less important. In addition to their great activity, one of the strong advantages of our catalysts is their preparation in the total absence of hydrogen. Their utilization is then possible for deuteriation of unsaturated molecules. Thus we have been able realize the deuteriation of organogermanium alkynes such as $Et_3GeCH_2C{\equiv}CH$.[20]

Morphologic and structural studies have been made to compare the two catalysts. They have shown that the mean size of reduced nickel particles is three times smaller than that for Raney nickel. Significant differences in particle arrangement and aggregate textures have also pointed out.[21]

Reduction in Ethanol. Second we investigated halide reduction in ethanol.[22] At room temperature, for whatever halide is used, the reaction proceeds in two steps. In the first place, hydrogen is released during attack of magnesium. Volumetric measurements of the gas released show that as many moles of hydrogen are formed as initial moles of nickel halide. At this step, aqueous hydrolysis of the solution directly yields a nickel hydroxide precipitate [$Ni(OH)_2$].

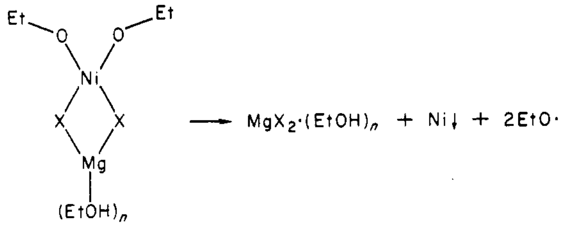
If the experiment is pursued further, black metallic nickel slowly appears; however, the metal yield can reach 100% only if the initial concentration of reactants becomes very low (halide/solvent mole ratio less than 10^{-2}).

On the other hand, if we heat the reaction mixture under reflux when the gas evolution ceases, nickel is produced quickly, and ethanal formation can be detected (yield 70% in comparison with nickel). If we carry out the reaction directly in the heat the reaction becomes too rapid to be able to distinguish the two reaction steps.

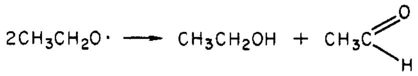
The hydrogen evolved can only originate from alcohol. Now the number of moles of hydrogen is equal to the number of moles of nickel halide. (With an excess of magnesium the released volume remains the same for the same quantity of halide.) Moreover, aqueous hydrolysis does not produce magnesium hydroxide but rather nickel hydroxide precipitate. So we can only consider the nickel attack by ethanol to give $Ni(OEt)_2{\cdot}MgX_2$. We suggest the mechansim shown in Scheme I.

Metal transition alcoholates are not usual compounds and, to our knowledge, only Klein has reported the synthesis of cobalt[23] and iron[24] alcoholates. If the experiment proceeds further, or if we heat the mixture under reflux, this complex undergoes a decomposition. On the assumption of a radical decomposition, ethanal formation can be explained as in Scheme II. In this way the ethoxy react upon one another in agreement with[25] Scheme III. The catalytic activity of nickel prepared by reduction in ethanol is less than of that prepared by reduction in THF. As noted above, neither Raney nickel nor the nickel produced in THF was selective for monosubstituted alkyne semihydrogenation. On the other hand, with nickel reduced in ethanol the rate of hydrogen take up beyond 1 equiv was almost nil. At this stage 98–99% of *cis*-hex-3-ene and only 1–2% of hexane were produced.

Scheme II



Scheme III



Experimental Section

Apparatus. Hydrogenations were conducted at room temperature with a conventional atmospheric pressure hydrogenator. The solvent was anhydrous ethanol (30 cm^3), and vigorous agitation was provided by a magnetic stirrer (about 1000 rpm).

Reagents. Reagents are pure commercial products except for magnesium percent impurities as follows: (Si, 0.03; Fe, 0.02; Cu, 0.002; Mn, 0.012; Zn, 0.003; Al, 0.008) which was supplied from Ste Italiana Per il Magnesio, Bolzano. Organic substrates were always distilled before use. Nickel bromide dihydrate and nickel chloride hexahydrate were dehydrated by warming with an infrared lamp inside an insulated enclosure. The warming time and warming intensity required for obtaining absolutely anhydrous product were determined in all cases by thermogravimetric measurements.

Catalyst Preparation. Nickel halide (24 mmol) and reducing metal (24 mmol) were introduced into the reactor. After air was flushed out with nitrogen or argon, the solvent (from 50 to 250 cm^3) was poured in and the reaction mixture was stirred and warmed. When the reaction was complete, the stirring was stopped. The catalyst was then washed three times with deoxygenated water (with the object of eliminiating halide ions) and twice with absolute ethanol. For a short period of time, the catalyst was kept in ethanol. With a syringe the required amount of catalyst was withdrawn (under vigorous stirring) for the hydrogenation reaction; after each one, the nickel was titrated by classical methods.

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Registry No. 1-Hexene, 592-41-6; 1-hexyne, 693-02-7; 3-hexyne, 928-49-4; cyclohexene, 110-83-8; nickel bromide, 13462-88-9; nickel chloride, 7718-54-9.

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