

ACTIVATION OF REDUCING AGENTS. SODIUM HYDRIDE CONTAINING COMPLEX REDUCING AGENTS. VII¹
NiC, A NEW HETEROGENEOUS Ni HYDROGENATION CATALYST

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A wide variety of heterogeneous hydrogenation catalysts may be prepared by reaction of transition metal salts with reducing systems such as LiAlH_4 ², NaBH_4 ³, zinc dust⁴, alkali metal/ NH_3 liq.⁵ or Na/HMPA⁶. In previous publication⁷ we have described the preparation of new versatile reducing systems : Complex Reducing Agents (abbreviated CRA). Chemical reductions performed with these reagents led us to postulate the intervention of transition metal hydrides⁸. As M-H bonds formation is one of the postulated step in catalytic hydrogenations⁹ we investigated CRA as sources of hydrogenation catalysts. We wish to report here that NiCRA provides a source of new, non pyrophoric, very active and highly specific nickel catalysts for alkene and alkyne heterogeneous hydrogenations.

Preparation of the new nickel catalyst (designated NiC)

To a stirred suspension of NaH ¹⁰ (60 mM), washed with dry THF, and $\text{Ni}(\text{OAc})_2$ ¹¹ (10 mM) in 25 ml THF was added dropwise, at 45°C and under a nitrogen atmosphere, a solution of t.AmOH (20 mM) in 5 ml THF. A deep black colour rapidly developed. After 2 hours stirring at 45°C, t.AmOH (32 mM) was added to neutralize the remaining NaH, and the mixture was allowed to return to room temperature. A non pyrophoric black suspension resulted which could be stored for several months under inert atmosphere without appreciable loss of activity. For use, catalyst was withdrawn from the homogenized suspension by a syringe through a serum cap. Nickel concentrations were determined by atomic absorption¹².

Hydrogenation conditions

Hydrogenations were conducted at room temperature with a conventional atmospheric pressure hydrogenation apparatus equipped with magnetic stirring. Unless otherwise noted, the experiments were carried out on 10 mM substrate in 15 ml ethanol as solvent. For direct comparison with reported data on nickel catalysts¹³ experiments were performed with catalyst/substrate ratio equal to 1/20. With such a catalyst loading, the rate of absorption of hydrogen depends, as usual¹⁴, upon the stirring speed. For practical convenience, speeds of 2500 rpm (monitored by a stroboscope) were used. In these conditions, the hydrogen uptake was limited to 70 ml/mm by the gas/liquid mass transport¹⁴. Finally some experiments, not reported here showed that NiC is still efficient with catalyst/substrate ratio equal to 1/100.

Hydrogenation of alkenes

Hydrogen uptake often shows a noticeable decrease in rate toward the end. (Generally attributed to isomerisation of about 5 to 8 % of alkenes to less reactive isomers). Thus t 100 % has only a practical significance while t 50 %, t 90 % as well as the initial rate of H₂ uptake are more representative of the very activity of the catalyst. These data are provided in Table I for the hydrogenation with NiC in EtOH.

Table I : Hydrogenation of representative alkenes

Substrate	Initial rate ^(a)	t 50 %	t 90 %	t 100 %
1-octene	34	3,5 mn	7 mn	30 mn
1-hexene	35	3,5 mn	6 mn	25 mn
cis 2-hexene	12	11 mn	33 mn	60 mn
trans 2-hexene	12	11 mn	32 mn	60 mn
2-methyl 1-hexene	9,5	13 mn	37 mn	90 mn
2-methyl 2-hexene	0,5	> 8 hrs	-	-
styrene	44	3 mn	5 mn	10 mn
cyclohexene	10	13 mn	40 mn	70 mn
cyclooctene	3	70 mn	3,5 hrs	5,5 hrs
1-octene ^(b)	65	7 mn	20 mn	2,5 hrs

(a) ml/mn

(b) In this case 40 mM of 1-octene was used in 50 ml EtOH with a Ni/octene ratio = 1/30

These data favorably compare with those described in the literature for the most active nickel catalysts. The last experiment of Table I has been performed to effect direct comparison with the results described by C.A. Brown with P₁ and P₂ Nickel¹³. It appears that NiC is as active as P₁ or P₂, both described as more active than Raney Nickel.

Hydrogenation of alkynes

Typical alkynes were studied. Results are reported in Table II. In order to determine the maximum percentage of partially hydrogenated compounds, the course of the reaction was followed by sampling.

Table II : Hydrogenation of representative alkynes

Substrate	semi hydrogenated compound ^(a) (max %, time)	Δ (b)	t 100 % (mn)
$C_6H_5-C\equiv CH$	styrene (90 %, 11,5 mn)	0,5	70
$C_6H_{13}-C\equiv CH$	1-octene (78 %, 12 mn)	0,4	30
$C_3H_7-C\equiv C-CH_3$	cis 2-hexene (96 %, 6,5 mn)	3,7	60
$C_2H_5-C\equiv C-C_2H_5$	cis 3-hexene (98 %, 5,5 mn)	4,6	60

(a) Determined by g.l.c. analysis (50 m squalene capillary column) with internal standards.

(b) Δ represents the ratio of hydrogen uptake rates before and after the ethylenic maximum yield is obtained.

Very little saturated compound was formed until all the alkyne had been consumed even though the subsequent reaction to give the saturated hydrocarbon was ultimately faster than the initial reaction to give the corresponding alkene ($\Delta < 1$). This selectivity would be attributed to the rapid displacement of adsorbed alkenes by alkynes.

Hydrogenation of dienes

The selectivity of NiC in the partial hydrogenations of dienes was particularly interesting to investigate. Experiments performed in this aim are reported in the Table III.

Table III : Hydrogenation of dienes

Substrate	maximum % of semi hydrogenated compound (a) (time)	Δ (b)	t 100 %
4-vinyl cyclohexene	98 % (7,5 mn)	10	3 hrs
1,3-cyclooctadiene	98 % (10,5 mn)	60	> 10 hrs
2,5-norbornadiene	85 % (7,5 mn)	1	10 mn

(a) Determined by g.l.c. analysis (50 m squalene capillary column) with internal standards

(b) See footnote (b) in Table II

High selectivity (98 %) was obtained for the hydrogenation of 1,3-cyclooctadiene and 4-vinylcyclohexene. Partial hydrogenation of 2,5-norbornadiene was realized with 85 % selectivity. However it is noteworthy that even such a symmetric diene was partially hydrogenated with a very reasonable selectivity. For these reaction too, NiC favorably compares with previously described nickel catalysts¹³.

In conclusion it appears that NiCRA are good sources for very efficient and highly selective heterogeneous hydrogenation catalysts. In view that CRA may be prepared from numerous transition metallic salts¹ a wide variety of new catalysts may be obtained by the same way. Investigations in this field will be reported in the near future.

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