SHORT COMMUNICATION

Hydrogenation of Heptaldehyde to Heptyl Alcohol with Nickel Catalysts[1]

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Hydrogenation of heptaldehyde to heptyl alcohol was studied with W2 Raney nickel catalyst, prepared in the laboratory, commercial Raney nickel catalyst and Rufert nickel catalyst by varying temperature, catalyst concentration, hydrogen pressure and reaction time. The products were analyzed by gas-liquid chromatography on SE-30 column. The optimum conditions found for quantitative conversion (99.6%) of heptaldehyde to heptyl alcohol were: temperature, 100°C, W2 Raney nickel catalyst concentration, 2% based on heptaldehyde (w/w), hydrogen pressure, 145 psig and reaction time, 1 h.

KEY WORDS: Heptaldehyde, heptyl alcohol, hydrogenation, Raney nickel.

Heptyl alcohol finds use as a base material for a variety of perfumery chemicals. The hydrogenation of heptaldehyde to heptyl alcohol was studied by reduction with sodium and ethanol, catalytic hydrogenation and metal hydrides (1–8). Triethylamine accelerates the hydrogenation of some aldehydes and ketones with large quantities of Raney nickel catalyst (7). Hydrogenation of carbonyl compounds with Raney nickel catalyst in aqueous sulfuric acid also has been reported (9,10). Aldehydes and ketones were hydrogenated to alcohols with Ni-Al alloy in aqueous alkaline solution (11). A number of patents are available on hydrogenation of aldehydes and ketones to alcohols (12–17). The present communication pertains to standardization of conditions for hydrogenation of heptaldehyde to heptyl alcohol with different nickel catalysts such as W2 Raney nickel, prepared in the laboratory, and commercial Raney nickel and Rufert nickel catalysts.

EXPERIMENTAL PROCEDURES

Materials. Heptaldehyde [99% pure by gas-liquid chromatography (GLC)] was obtained from M/s. Alchem Laboratories, Bombay, India. Commercial Raney nickel catalyst was purchased from Kallin Industries, Bombay, India. Rufert nickel catalyst (nickel content, 16%) was obtained from Hindustan Lever Ltd., Bombay, India. W_2 Raney nickel catalyst (18) was prepared in the laboratory by dissolving sodium hydroxide (190 g) in water (750 mL) in a beaker and cooling the solution to 10°C in an ice bath. Nickel-aluminium alloy (150 g) was added in small portions over 2 h with stirring, while maintaining the temperature of the contents below 25°C. The reaction mixture was then heated gradually on a water bath for 8 h and allowed to settle, and the supernatant liquid was decanted. The nickel was transferred to a stoppered graduated cylinder with distilled water, and the supernatant liquid was again decanted. Sodium hydroxide solution (10%, 250 mL) was added, and the contents were shaken thoroughly to disperse the catalyst. The alkali solution was decanted, and the catalyst was washed repeatedly with distilled water until the washings were neutral to litmus. The catalyst was washed with rectified spirit (95%) and subsequently with absolute alcohol. It was finally stored in a tightly stoppered glass bottle under absolute alcohol. The catalyst thus prepared contains about 0.6 g nickel per mL of settled material.

Methods. GLC was carried out with a Tracor 540 Gas Chromatograph (Tracor Instruments, Austin, Inc., TX) equipped with a flame-ionization detector, a data processor and a glass column (1.8 m × 6.5 mm) packed with 5% SE 30. The column temperature was programmed from 60 to 230°C at the rate of 10°C per min. Injection port and detector block were maintained at 250 and 300°C, respectively. The flow rate of carrier gas, nitrogen, was 20 mL/min. Integration was achieved through a PC/XT connected through the Nelson Analytical 900 series Interface with the PC Integrator Software of Nelson Analytical (Cupertino, CA).

Heptyl alcohol. The typical reduction procedure was as follows. A stainless-steel autoclave (0.5 L) was charged with heptaldehyde (100 g) and W2 Raney nickel (2 g). The contents were stirred (480 rpm) and gradually heated to 100°C over 30 min while maintaining the hydrogen pressure at 145 psig. Hydrogenation was carried out at this temperature and pressure for 1 h. Samples were withdrawn intermittently, filtered and analyzed by GLC. The results obtained in different experiments are given in Tables 1, 2 and 3. The preparation was scaled up twenty times for a 2-kg batch of heptaldehyde with W2 Raney nickel catalyst prepared in the laboratory.

RESULTS AND DISCUSSION

The hydrogenation of heptaldehyde to heptyl alcohol was studied at different temperatures and at a pressure of 145 psig, and the results are presented in Table 1. When

TABLE 1

Effect of Temperature on Conversion of Heptaldehyde to Heptyl Alcohol with Freshly Prepared W2 Raney Nickel Catalyst (2% by weight based on heptaldehyde) at 145 psig

Temp. (°C)	Reaction time (h)	Heptyl alcohol (GLC, %)[a]
60	3	98.0
80	2	98.8
100	1	99.6
120	0.7	95.9

[a]GLC, gas-liquid chromatography.

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freshly prepared, W2 Raney nickel catalyst (2% based on heptaldehyde, w/w) was used; as the reaction temperature increased from 60 to 100°C, the conversion increased from 98.0 to 99.6% with a decrease in the reaction time from 3 to 1 h. On further increase of temperature from 100 to 120°C, a conversion of 95.9% was observed in 0.7 h. The higher temperature appears to have resulted in the formation of some side products, as shown by GLC. Hence, the optimum temperature chosen was 100°C. The effect of variation of catalyst concentration and pressure on hydrogenation was studied at the optimum temperature, and the results are shown in Table 2. Catalyst concentration of 1–3% (based on heptaldehyde, w/w) was taken for study at 145 psig. A reaction time of 5 h was needed for a conversion of 98.6% at a catalyst concentration of 1%, while 1.0 and 0.7 h were required for 99.6 and 98.4% conversion, respectively, at catalyst concentration of 2 and 3%. Hence, from the data in Table 2, it could be inferred that the use of 2% by weight of Raney nickel catalyst was optimum for quantitative conversion of heptaldehyde to heptyl alcohol. At a lower pressure of 70 psig, the time needed for a conversion of 98.3% was 2 h; while at 215 psig, the time required for a conversion of 96.2% was 0.75 h, a lower yield showing formation of some side products. It was thus concluded that the optimum pressure required for maximum conversion of heptaldehyde to heptyl alcohol was 145 psig at a catalyst concentration of 2%.

Comparative data for different catalysts, *viz.*, catalyst prepared in the laboratory and catalysts purchased from the market, are given in Table 3. It was observed that the time taken for the conversion of heptaldehyde to heptyl alcohol with the freshly prepared W2 Raney nickel catalyst is less, when compared to the commercially available Raney nickel and Rufert nickel catalysts. It was also observed that formation of side products is negligible in the process of conversion of heptaldehyde to heptyl alcohol with freshly prepared W2 Raney nickel catalyst, as the conversion is higher (99.6%) when compared to the conversions obtained with commercial Raney nickel and Rufert nickel catalysts (98.4 and 96.7%).

TABLE 2

Effect of Catalyst Concentration and Hydrogen Pressure on Conversion of Heptaldehyde to Heptyl Alcohol at 100°C Using Freshly Prepared W2 Raney Nickel Catalyst

Catalyst concentration (wt%)	Hydrogen pressure (psig)	Reaction time (h)	Heptyl alcohol (GLC, %)[a]
1	145	5	98.6
2	145	1	99.6
3	145	0.7	98.4
2	70	2	98.3
2	215	0.75	96.2

[a] GLC, gas-liquid chromatography.

TABLE 3

Effect of Different Nickel Catalysts on Conversion of Heptaldehyde to Heptyl Alcohol at 100°C and 145 psig Hydrogen Pressure

Catalyst	Amount of catalyst used (wt%)	Time (h)	Heptyl alcohol (GLC, %)
Freshly prepared W2 Raney nickel	2	1	99.6
Commercial Raney nickel	2	2	98.4
Rufert nickel[a]	12.5	3	96.7

[a] 12.5 g of Rufert nickel contains 2.0 g of nickel. GLC, gas-liquid chromatography.

The conditions standardized on 100-g scale with freshly prepared W2 Raney nickel catalyst were used for hydrogenation on 2-kg scale. The yield of heptyl alcohol (>99% pure) on distillation was *ca.* 85%. The procedure reported for hydrogenation of heptaldehyde to heptyl alcohol is mild and requires low hydrogen pressure, catalyst concentration and temperature.

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