

GLUCOSE HYDROGENATION OVER NICKEL BORIDE CATALYST

Delicia E. Acosta*, Hugo A. Destéfánis, Elio E. Gonzo

Instituto de Investigaciones para la Industria Química, INIQUI, Universidad Nacional de Salta, CONICET, Buenos Aires 177-4400, Salta, ARGENTINA.

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Abstract

Glucose hydrogenation in aqueous medium has been studied over nickel boride catalyst. The boride was prepared using an "HOMOGENEOUS ROUTE" following a technique previously reported. The reaction rate was measured over a wide range of pressure, temperature and catalyst loading in a batch reactor system. It was found that nickel boride shows a good catalytic activity for carbonyl group hydrogenation. The reaction rate is first-order in glucose concentration and half-order in hydrogen pressure.

1. Introduction

The most technically important sugar alcohols industrially produced today are sorbitol, xylitol and mannitol. Their large industrial manufacture is almost exclusively carried out by means of the catalytic hydrogenation of the appropriate sugar. Sorbitol is thus manufactured from crystalline D-glucose (Dextrose) or from cheaper hydrolysates of starch containing up to 99.5 percent D-glucose.

Sorbitol is commercially used in a variety of chemical and physical processes due to its chemical properties. Its major use is in the synthesis of vitamin C. Other industrial applications are in food stuff, in the pharmaceutical and cosmetic industries.

Approximately 80 percent of the world's production of sugar alcohols is manufactured by batch processes using suspended catalysts. Raney nickel and activated-nickel catalysts are used exclusively as the catalyst for this process (Albert *et al.*, 1981). A general survey on sorbitol (Wright, 1974) indicates that glucose is normally hydrogenated in aqueous solution at temperatures of 120°-160°C and hydrogen pressure of 70-140 atm with supported nickel and Raney nickel catalysts. Brahma *et al.* (1964) and Wisniak and Simon (1979) studied the hydrogenation

of glucose to sorbitol in an aqueous medium, using Raney nickel as catalyst. They found that the reaction is first-order in glucose concentration and half-order in hydrogen pressure.

The use of metal borides as catalysts in many reduction processes has been widely reported in the literature (Ganem and Oshby, 1986). It is interesting to note that some contributions were made (Collins *et al.*, 1982) in order to compare Raney nickel and nickel boride as hydrogenation catalysts.

Nevertheless carbonyl group hydrogenation over nickel boride catalysts has not been reported yet.

In the present contribution the aqueous phase hydrogenation of glucose on nickel boride is presented and the results are compared with that obtained on Raney nickel.

2. Experimental

CATALYST PREPARATION: Nickel boride was prepared following a technique previously reported (Destéfánis *et al.*, 1992). The reducing solution, a diborane-THF complex generated "in-situ", was obtained by reacting NaBH₄ (Aldrich) with water in stoichiometric amount in tetrahydrofuran (THF) medium. This solution was used to reduce the metal salts, which were added to the system as Ni(CH₃CO₂)₂·4H₂O in methanol solution.

* Author to whom correspondence should be addressed.

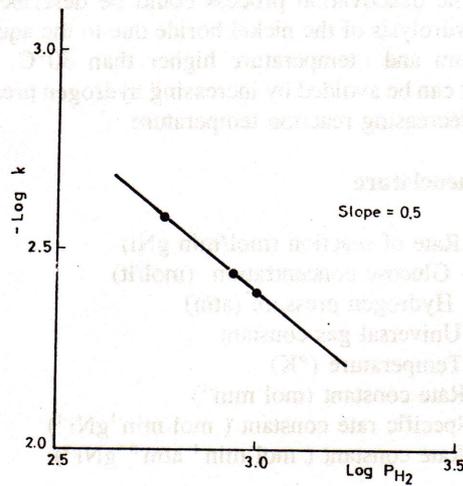


Fig. 3: Effect of Hydrogen Pressure on Reaction Rate
Conditions: T 60°C and catalyst loading 3 wt%.

Mass transfer resistances at the gas-liquid interphase and in the liquid phase can be assumed negligible based on the fact that the rate of reaction is independent of the agitation rate and varies linearly with the catalyst loading (kinetic regime).

Table I : Effect of the catalyst loading on specific rate constant*.

| %Ni | k 10 ³ mol min ⁻¹ | k* 10 ³ mol min ⁻¹ gNi ⁻¹ |
|-----|--|---|
| 1.5 | 1.12 | 4.15 |
| 3 | 2.26 | 4.18 |
| 7 | 5.14 | 4.16 |

* Temp. 60°C; P_{H₂} 50 atm.

The possible mechanism can involve only adsorption, desorption and/or surface reaction steps as the controlling stage.

Our results suggest that the possible hydrogenation mechanism could be one that involves the surface reaction between unadsorbed sugar and chemisorbed hydrogen. In that way, under present conditions, the rate of reaction *r* can be expressed as follow:

$$r = k' C_G P_{H_2}^{1/2} \quad (2)$$

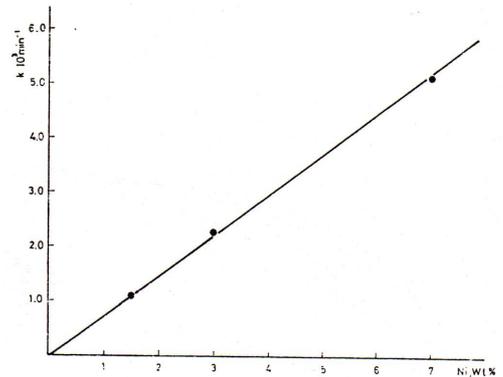
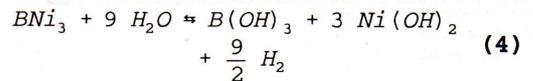


Fig. 4: Effect of Catalyst Loading on Reaction Rate
Conditions: T 60°C and pressure 50 atm.

The rate constant under the conditions above mentioned could be expressed as:

$$k' = 0,255 e^{-\frac{3998}{RT}} \quad (3)$$

Fig. 5 shows experimental plots of glucose conversion versus time at a hydrogen pressure of 50 atm and different temperatures. The slope changes after glucose conversion reaches 60 %. That change is more drastic when temperature is higher than 80°C. This behaviour suggests that a catalyst deactivation process could be occurring. Since metal borides are readily oxidizable in the reaction medium used, it is possible that the following hydrolysis reaction takes place:



Reaction (4) shows that the hydrolysis process depends on hydrogen partial pressure and reaction temperature. When the hydrogenation processes was carried out at 94°C (see Fig.5) the initial slope of the curve X-time was lower than 80°C. It confirms that the deactivation process is more drastic at higher temperature although the hydrogen pressure was constant in both cases. When the process finished the liquid phase was colorless. After reducing hydrogen pressure a green color appear in the liquid phase (characteristic of the Ni²⁺ ions).

The glucose hydrogenation with Raney nickel needs higher hydrogen pressures and temperatures (see Table II) to reach similar conversions than with nickel boride, using the same catalyst loading

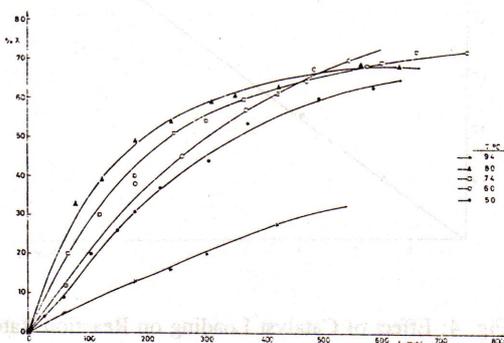


Fig.5: Glucose Conversion at Different Temperatures
Conditions: Pressure 50 atm and Catalyst Loading 3 wt %

Table II : Glucose Hydrogenation over nickel boride and Raney nickel catalysts.

| T° (°K) | P _{H₂} (atm) | k 10 ³ (min ⁻¹) |
|---------|----------------------------------|--|
| 363 | ---a | 10 ^b (Wright,1974) |
| 358 | 55 | 4.01 ^b (Wisniak,1979) |
| 333 | 50 | 2.26 ^c (Our Work) |
| 353 | 50 | 3.09 ^c (Our Work) |

(a) Pressure value is not reported

(b) Raney nickel

(c) Nickel boride

(Wisniak and Simon, 1979; Wright, 1974).

4. Conclusions

Glucose hydrogenation in the liquid phase on nickel boride it is possible to carry out to good extent under less restrictive conditions than on Raney nickel.

Nickel boride can be assumed as capable catalyst to reduce carbonyl groups in addition to double bonds reduction.

The reaction rate follows a kinetic expression which is first-order in glucose concentration and

half-order in hydrogen pressure.

The deactivation process could be described by the hydrolysis of the nickel boride due to the aqueous medium and temperature higher than 80°C. This effect can be avoided by increasing hydrogen pressure and decreasing reaction temperature.

Nomenclature

r = Rate of reaction (mol/min gNi)

C_G = Glucose concentration (mol/l)

P_{H_2} = Hydrogen pressure (atm)

R = Universal gas constant

T = Temperature (°K)

k = Rate constant (mol min⁻¹)

k^* = Specific rate constant (mol min⁻¹gNi⁻¹)

k' = Rate constant (mol min⁻¹ atm^{-0.5}gNi⁻¹)

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