



Modelling of a liquid-liquid-solid-gas system: Hydrogenation of dispersed liquid sodium to sodium hydride

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HIGHLIGHTS

- Production of NaH from Na is a liquid-liquid-gas-solid system.
- A new mathematical model was developed for the production of NaH.
- The DAE system was solved numerically.
- The model described very well the kinetic data from the slurry reactor.
- The model can be used for process design.

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ABSTRACT

Sodium hydride is a powerful reduction agent used in chemical industry. Industrial production of sodium hydride through hydrogenation of melt sodium dispersed in mineral oil is very demanding because of the complex multiphase system (liquid-liquid-gas-solid) and safety aspects. A new mathematical model was developed for the production of solid sodium hydride from dispersed liquid-phase sodium and molecular hydrogen. New rate equations were derived for the hydrogenation process of dispersed sodium droplets in a semi-batch reactor. The model comprises surface reactions as well as liquid-solid mass transfer effects of hydrogen. The properties of the differential-algebraic model were investigated by numerical simulations and the model was verified with experimental data of sodium hydrogenation in an isothermal, intensively agitated semi-batch reactor. The kinetic and mass transfer parameters included in the model were estimated successfully with non-linear regression analysis and the model gave a good reproduction of the experimental data. The molecular-level model can be used for the design and optimisation of sodium hydride production processes.

1. Introduction

Sodium hydride (NaH) is a strong reducing agent and the raw material of sodium borohydride (tetrahydroborate, NaBH_4), which has large applications in chemical and process industries, for instance, in the reduction processes involved in the production of pharmaceuticals and bleaching agents [1,2]. Sodium borohydride is kinetically stable in alkaline aqueous solutions [3], whereas sodium hydride reacts spontaneously and vigorously with water releasing hydrogen and heat [1,2]. Sodium hydride is used as such in for many reactions in organic synthesis, such as alkylation, acylation and Claisen condensation [1]. Sodium hydride is stable up to 300 °C, at which starts to decompose [1].

Early attempts to make sodium hydride directly via hydrogenation of melt sodium were not very successful, because the solid sodium

hydride formed remained dispersed with sodium and inhibited the hydrogenation process. Later on, attempts were made to spread melt sodium and surface-active components on a porous support, which resulted in an improved yield of sodium hydride, but did not lead to a true breakthrough. The method was developed at DuPont and was published by Hansley [4]. Dispersion of sodium in an inert liquid, in which hydrogen is soluble, was the decisive innovation for an efficient industrial production of sodium hydride. The American company Metal Hydrides Inc patented and started the production with the dispersion method in 1957 [5,6], evidently based on the early ideas of Muckenfuss [7]. Nowadays sodium hydride is produced industrially through hydrogenation of metallic sodium (Na(l)) in liquid state. Melt sodium is dispersed in a mineral oil and molecular hydrogen is bubbled through the liquid dispersion. Solid NaH is formed as the reaction product. The

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Nomenclature

A	surface area, m^2
a	merged parameter in Eq. (46)
a', b'	coefficients in the correlation for Sherwood number, Eq. (35) –
c	concentration, mol/m^3
c^*	concentration on the sodium surface, mol/m^2
c_0	total concentration of sites on the sodium surface, mol/m^2
D	diffusion coefficient, m^2/s
D'	denominator of Eq. (17), –
d	droplet diameter ($=2R$), m
E_a	activation energy, J/mol
F	test function in Eq. (50), –
ΔH	enthalpy, J/mol
K	adsorption equilibrium constant, m^3/mol
K'	merged parameter, Eq. (19), –
k	reaction rate constant
k'	merged rate constant, Eq. (18), $mol/(m^2s)/(mol/m^3)^{1/2}$
k''	merged rate constant, Eq. (51), s^{-1}
k_L	mass transfer coefficient, m/s
M	molar mass, kg/mol
N	diffusion flux, $mol/(m^2s)$
n	amount of substance, mol
n_p	number of droplets in the liquid phase
R	droplet radius, m
R_G	gas constant, $8.3143 J/(Kmol)$
r	rate, $mol/(m^2s)$
s	shape factor, –
T	temperature
t	time, s

X	conversion of sodium
x	dimensionless hydrogen concentration, –
y	dimensionless amount of sodium, –

Greek letters

α, β	dimensionless parameters, Eqs. (32) and (33), –
α', β'	exponent in the correlation (35) for Sherwood number –
δ	film thickness, m
ε	dissipated energy, W/kg
κ	dimensionless parameter, –
ν	stoichiometric coefficient, –
ν	kinematic viscosity, m^2/s
ρ	density, kg/m^3
τ	reaction time for complete conversion, s

Dimensionless numbers

Da	Damköhler number, –
Re	Reynolds number, –
Sc	Schmidt number, –
Sh	Sherwood number, –

Subscripts and superscripts

H	hydrogen
L	mass transfer or solubility in liquid phase
P	droplet
ref	reference
$*$	surface site
0	initial state

reaction can be successfully conducted at 250–300 °C at atmospheric or higher hydrogen pressures. Continuous operation is enabled by using stirred tank reactors coupled in series.

The reaction stoichiometry is given below,



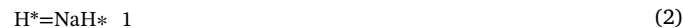
Even though the overall reaction is very well-known [1,2], the detailed surface reaction mechanism between liquid Na and dissolved H_2 has not been thoroughly investigated and analysed hitherto.

In the present work, a hypothesis for the surface reaction mechanism is presented and the corresponding rate equation will be derived. The rate expression is coupled to the mass balances of sodium and sodium hydride. The reaction is presumed to proceed in a semi-batch reactor, where the mineral oil and dispersed sodium co-exist in batch, but gaseous hydrogen is continuously bubbled through the liquid phase. The isothermal reactor is assumed to operate at atmospheric pressure. Experimental data from literature are used to validate the new model for the reaction kinetics and the mass transfer of hydrogen.

2. Reaction mechanism and rate equations

The reaction between $Na(l)$ and H_2 is of topochemical nature, proceeding on the outer surfaces of the dispersed Na droplets. H_2 is assumed to adsorb and dissociate on the $Na(l)$ surface, after which it reacts with a surface atom of Na forming NaH which is released from the surface. The process is thus very analogical with a catalytic Eley-Rideal mechanism, but in this case, the material of the reactive surface ($Na(l)$) is consumed during the reaction. Based on these hypotheses, the reaction mechanism can be written as follows,

Reaction step Stoichiometric number of the step



where H^* denotes adsorbed hydrogen on a sodium atom and NaH^* is the key intermediate, reduced hydrogen, i.e. adsorbed sodium hydride. De facto $*$ denotes a sodium atom on the surface, i.e. $* = Na^*$, but the notation $*$ is used for the sake of brevity.

The hydrogen adsorption step is assumed to be rapid, so that the quasi-equilibrium hypothesis can be applied, whereas the quasi-stationary state hypothesis is applied to the sodium hydride (NaH^*) on the surfaces of the dispersed sodium droplets. The quasi-equilibrium hypothesis implies for step (1)

$$K_H = \frac{c_H^*}{c_H c^*} \quad (4)$$

where K_H and c_H denote the adsorption equilibrium constant and the concentration of dissolved H_2 in the mineral oil. The concentration of adsorbed hydrogen is solved from Eq. (4),

$$c_H^* = (K_H c_H)^{1/2} c^* \quad (5)$$

The application of the quasi-stationary state hypothesis on NaH^* implies for the surface intermediate NaH^* that its generation rate is zero,

$$r_{NaH^*} = r_2 - r_3 = 0 \quad (6)$$

For the rate of the overall reaction (r) is valid:

$$r = r_2 = r_3 \quad (7)$$

The rates of the elementary steps (2) and (3) can be conveniently expressed as

$$r_2 = k_2 c_H^* - k_{-2} c_{NaH^*} \quad (8)$$

$$r_3 = k_3 c_{NaH^*} - k_{-3} c_{NaH} c^* \quad (9)$$

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