**Reaction engineering approach to the preparation of sodium hydride and sodium borohydride**

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**Highlights**

* Sodium hydride and sodium borohydride are industrially important reducing agents
* Mathematical models for two complex multiphase processes were developed: synthesis of sodium hydride and sodium borohydride
* Experimental data obtained in laboratory scale were used in the modelling
* The advanced multiphase model is useful in process simulation and optimization

1. **Introduction**

Sodium hydride and sodium borohydride are strong reducing agents with widespread industrial applications. The synthesis of sodium hydride (NaH) and sodium borohydride (NaBH4) are very demanding multiphase and multistep processes. Sodium hydride is produced industrially by letting melt sodium to react with gaseous hydrogen. In spite of many attempts to develop new processes for the industrial production of sodium borohydride, the procedure discovered by Schlesinger and Brown in 1940’s and 1950’s is still the dominant one. The process is based on the use of sodium hydride and trimethyl borate (B(OCH3)3) as raw materials. The reaction steps are carried out in dispersions of inert mineral oil at elevated temperatures. A typical reaction temperature for the preparation of NaH is 230-260oC, while temperatures 250-270oC are typical for the synthesis of NaBH4. In spite that these processes are very classical, a vast majority of the published literature is of qualitative character only. Nowadays the understanding of complex multiphase processes has advanced very much and the modelling and computational tools enable a reaction engineering approach to these industrially important and technically demanding systems. Mathematical modelling of the reactions 4Na(l) + 2H2 (g) → 4NaH(s) and 4NaH(s) + B(OCH3)3(l) → NaBH4 (s) + 3NaOCH3 (s) is considered in the present work.

**2. Methods**

Both reactions are carried out in semibatch reactors. The processes were modelled based on plausible surface reaction mechanisms. The hypothesis for the formation of NaH was that it proceeds through a surface reaction between adsorbed hydrogen atoms on the droplets of finely dispersed Na in mineral oil. Solid NaH particles are formed and they react in the next step in a surface reaction with dissolved B(OCH3)3 in the oil phase forming NaBH4 and Na(OCH3). A partially hydrogenated intermediate (X1) is detected in the NaBH4 formation step. Based on these mechanistic hypotheses, rate equations were derived and they were coupled to the mass balances of the components, taking into account the interfacial mass transfer effects.

The rate equation for the formation of NaH is, including two adjustable parameters (*k*’ and *K*’) only: *r*=*k*’*c*H 1/2 /(1+*K*’ *c*H 1/2)

For the formation of NaBH4, the rate equation is (B=B(OCH3)3) and X1=reaction intermediate)

*r*=*k’*’*c*X1/(1+ KBcB + KX1cX1)

The mass balances for the multiphase systems were described by taking into account the transfer of hydrogen from the gas phase to the mineral oil and from the mineral oil to the Na droplets. In the synthesis of NaBH4, the mass transfer of B(OCH3)3 from mineral oil to the surfaces of the NaH particles was included. The correlations for Sherwood numbers were used to obtain expressions for the interfacial mass transfer coefficients. The behaviours of the Na droplets and the dispersed NaH particles were described with the generalized shrinking particle model developed by our group. The experimental data collected previously by us was used in the modelling.

**3. Results and discussion**

Examples of the modelling results of the NaH and NaBH4 formation processes are provided in Figure 1. As revealed by the figure, the model describes well the behaviour of the system at a wide range of rotation speeds of the disperser. The yields of the main product (P=NaBH4) and the reaction intermediate (X1) are very well predicted by the complex multiphase model.



**Figure 1.** Effect of the stirring rate on the sodium conversion (X) to NaH and sensitivity analysis of the yields of NaBH4 and X1 (ϕ) Continuous lines represent model predictions.

**4. Conclusions**

New multiphase models were developed for the industrial synthesis of NaH and NaBH4. The model parameters were determined from experimental data obtained from laboratory-scale semibatch reactors. The models can be used for process design and optimization.