# Catalyst Development for the Hydrogen Release from Ammonia Borane – A Systematic Study on Bimetallic Metal Complexes – Cobalt Copper Methanolysis

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## Introduction

One of the most difficult environmental problems facing society today is the disruption of the climate caused by the depletion of fossil fuels. Since it can be produced from renewable resources, like water, and can reach carbon neutrality, hydrogen, as a clean energy carrier, can offer solutions for these issues. A number of technical bottlenecks, including those in manufacturing, transportation, and storage—the last of which continues to be a barrier to the widespread use of hydrogen for automotive applications—need to be immediately addressed in order to implement the hydrogen economy in a society. Methanolysis offers several advantages over hydrolysis in ammonia borane (AB) hydrogen releasing, and it represents a promising alternative to hydrolysis in ammonia borane hydrogen release reactions, offering numerous benefits in terms of product yield, reaction efficiency, and environmental impact.

## Technical Challenge

Hydrolysis can produce undesirable byproducts, such as boric acid and ammonia gas, which can be difficult to separate and purify. Hydrolysis also requires the use of large amounts of water, which can increase the risk of corrosion and safety hazards. These byproducts require further processing and recovery, increasing the complexity and cost of the reaction process. The ammonia gas produced from hydrolysis is a toxic gas that requires further processing and discharge. In addition, the boric acid produced from hydrolysis is corrosive and toxic, requiring further processing and disposal, which increases the risk and cost of the reaction process.

For hydrolysis:

$$NH_3BH_3 + 2H_2O \rightarrow NH_4^+ BO_2^- + 3H_2;$$

For methanolysis:

$$NH_3BH_3 + 4CH_3OH \rightarrow NH_4B(OCH_3)_4 + 3H_2.$$

## Objectives

This study aims to develop the synergy between single-atom and nanoparticle catalysts for the release of hydrogen from solid $H_2$ storage materials using CoCu (as a catalyst) in methanol and to optimize the reaction conditions to pave the way for the design of the continuous $H_2$ generation system using the above-synthesized catalysts (CoCu), including the recycling performance of the catalysts in the methanolysis.

## Results

As an alternative to hydrolysis, it has a similar performance. Methanolysis also has the advantage of performing better at higher temperatures, which can be useful in certain applications. It is possible that methanolysis may be a more efficient or cost-effective process than hydrolysis in some situations, particularly those involving high temperatures. The rate in different temperature has shown in **Figure 1a**.

The results can be explained by the term called activation energy.

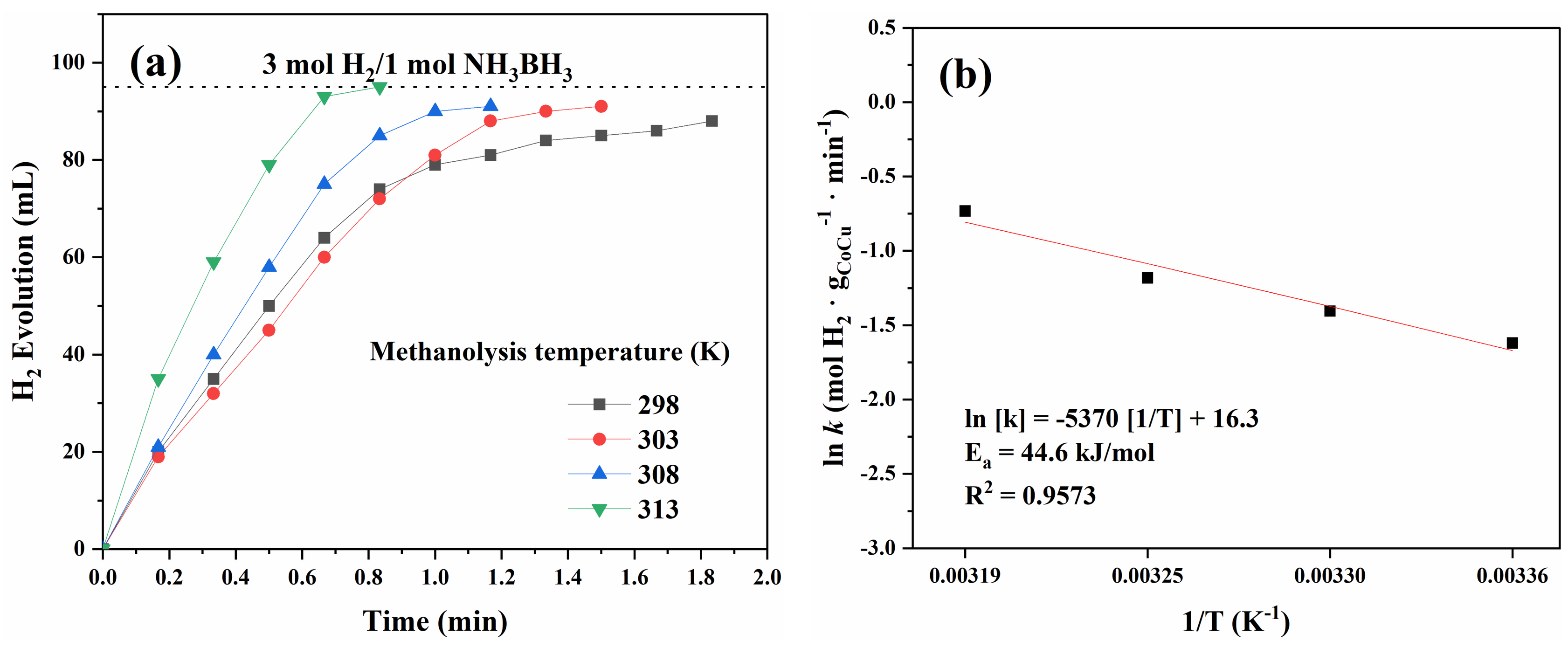


**Figure 1. a)** The performance in 298K(24.85° C), 303K(29.85° C), 308K(34.85° C) and 313K(39.85° C); **b)** activation energy was calculated to be 44.6 kJ/mol.

We also conducted ICP-OES tests to measure the metal content in the catalyst. ICP-OES (Inductively Coupled Plasma-Optical Emission Spectroscopy) is a technique commonly used for the quantitative analysis of trace elements in various samples, including catalysts. By using this technique, we were able to determine the precise concentrations of metals present in the catalyst, which is important for understanding its properties and performance. The results of the ICP-OES analysis can provide valuable information for further optimizing the catalyst and improving its efficiency.

The total metal content of 3wt% CoCu (1:1) -CNT800 is determined in two ICP-OES results. The total metal content in the first batch was found to be 22.0 wt% of Co and 28.7 wt% of Cu. As shown in the table below:

| Actual ICP-OES results | Total Co wt% | Total Cu wt% |
|---|---|---|
| 3wt% CoCu (1:1) -CNT800 | 22.0 | 28.7 |

**Table 1** The metal content of Co and Cu by ICP-OES test.

It is noticed that the catalyst performs better at higher temperatures in methanolysis compared to hydrolysis.

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It can be explained in terms of activation energy($E_A$). As shown in **Figure 1b**, the activation energy for the catalyst is 44.6 kJ/mol, which is relatively high compared to other catalysts. Activation energy is the energy required to start a chemical reaction, and a higher activation energy indicates that more initial energy is needed to initiate the reaction. In the case of the catalyst, the high activation energy may mean that it requires more energy input to start the reaction, but once the reaction is initiated, it may proceed more efficiently. Understanding the activation energy of the catalyst can be useful for optimizing its performance and designing more effective catalytic systems.

In order to show that methanolysis is a much better process than hydrolysis, we have investigated the problem from an economic point of view. The current economic problem associated with the commercialization of ammonia borane is the cost of recycling. Since the byproduct of AB after hydrolysis is ammonium borate, and the byproduct is ammonium methoxyborate, more steps are required for the former process to recover back to the original AB materials. We have modeled the process using Superpro Designer and attempted to understand the recovery cost, as shown in **Figure 2** for the recovery process of ammonium borate and **Figure 3** for the recovery process of ammonium methoxyborate.

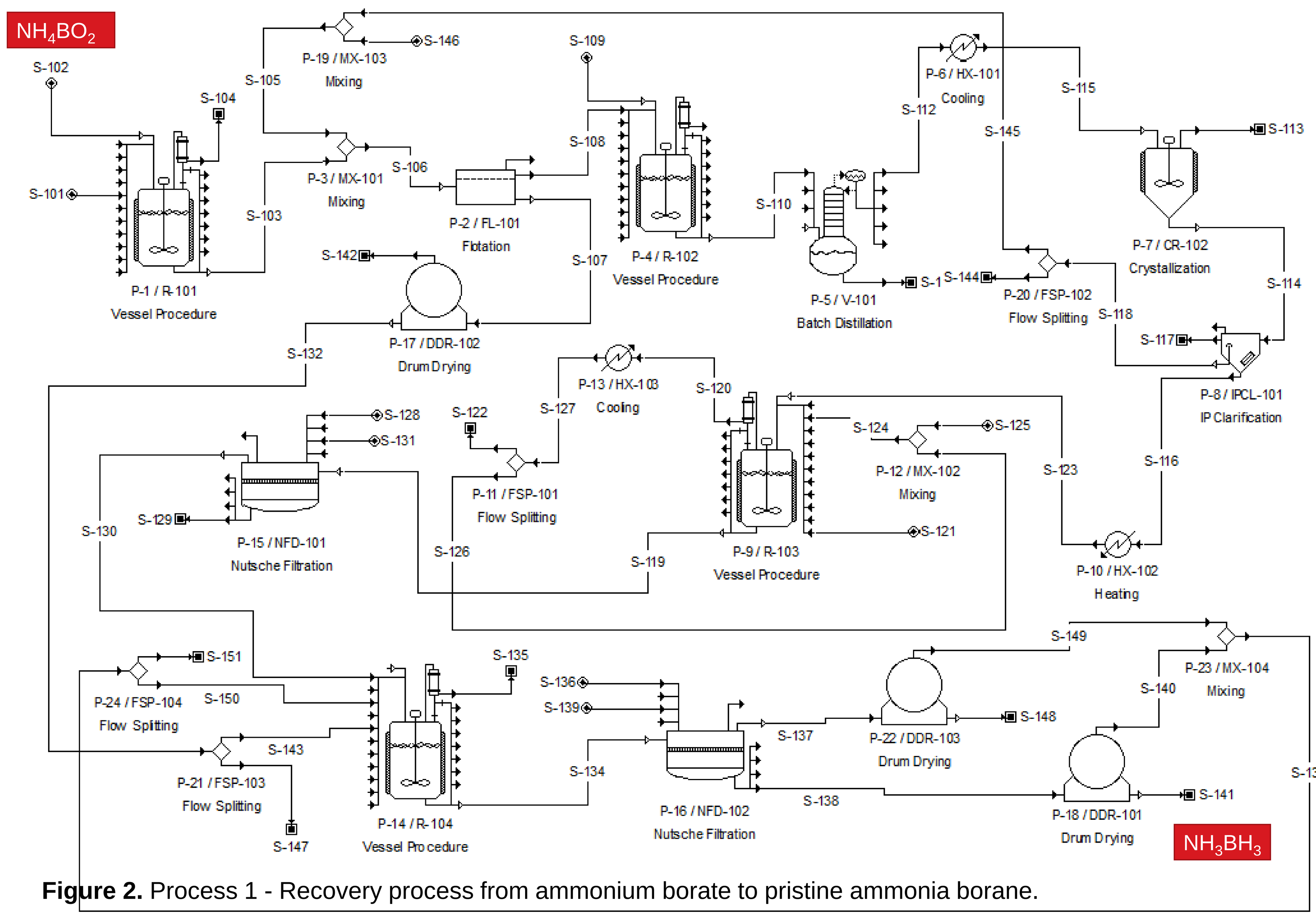


**Figure 2.** Process 1 - Recovery process from ammonium borate to pristine ammonia borane.

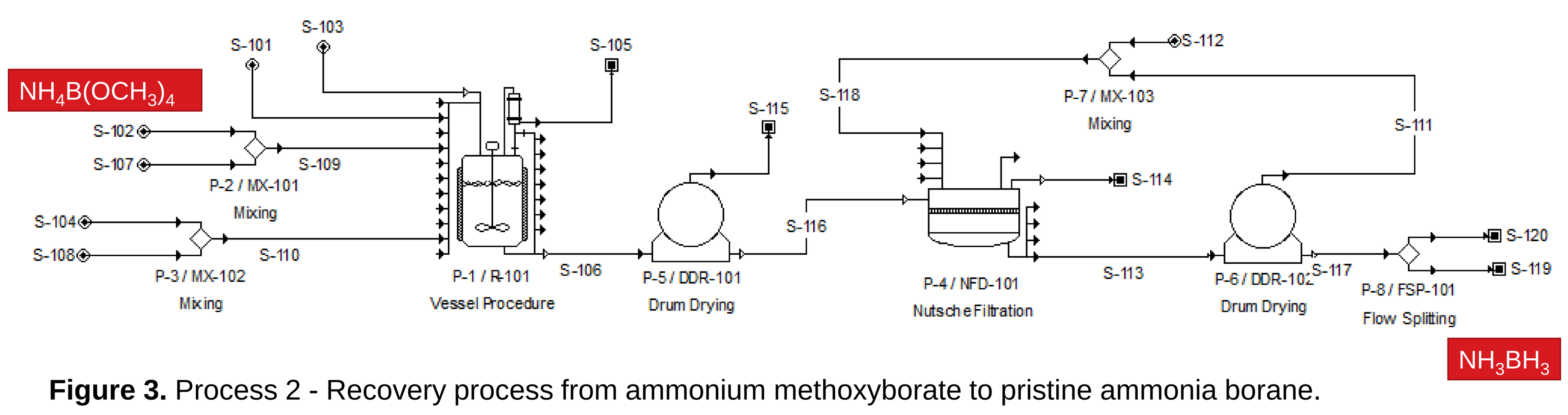


**Figure 3.** Process 2 - Recovery process from ammonium methoxyborate to pristine ammonia borane.

The preliminary economic parameters are shown in **Table 2**. For a process plant to be operated for 7,920 hr/year.

| | Process 1 | Process 2 |
|---|---|---|
| Investment (US$) | 3,954,397 | 1,996,680 |
| Annual Operating Cost (US$/yr) | 2,935,664 | 3407449 |
| Total annual Revenues (US$/yr) | 470,690 | 11,438,134 |
| Unit Production Cost (US$/ kg of main product) | 29,741.48 | 4,825.90 |
| Unit Production Revenue (US$/ kg of main product) | 4,480 | 16,199.6 |
| Payback time | N/A | 0.4 years |
| NPV (US$ at 7.00%) | -21,977,154 | 32,053,765 |

**Table 2** Economic comparison between Processes 1 & 2.

## Conclusion

In summary, methanolysis exhibits similar performance to hydrolysis, and in some cases, such as at higher temperatures, it performs better. Additionally, methanolysis produces fewer harmful byproducts, such as ammonia, compared to hydrolysis, making it easier to recycle and more environmentally and economically friendly. Therefore, using methanolysis for hydrogen production is a good choice, as it offers advantages over traditional hydrolysis methods. Further research and development may be needed to optimize the process and improve the efficiency of methanolysis for hydrogen production.