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# Hydrogen production from the methanolysis of ammonia borane by Pd-Co/Al<sub>2</sub>O<sub>3</sub> coated monolithic catalyst

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## ABSTRACT

The aim of this study is to enable high hydrogen production yield from catalytic methanolysis of ammonia borane (AB) in the presence of a cordierite type ceramic monolithic. The monolithic channel surfaces were coated with Al<sub>2</sub>O<sub>3</sub> by wash-coating method and then this layer was impregnated with 1 wt%Pd-2 wt%Co bimetallic catalyst. SEM-EDX and multi-point BET analysis were used in order to characterize the catalyst. The experimental studies were conducted in a continuous flow type reactor, which was used for the first time in this study. The reactions were carried on low temperature (40 °C), and with various AB feed concentrations and flow rates. It was found that the highest hydrogen production yield (88.5%) was obtained from AB flow rate of 3.3 mL/min, and AB feed concentration of 0.1 wt%. It was concluded that Pd-Co/Al<sub>2</sub>O<sub>3</sub> coated monolithic, which is a stable, active and low-cost catalyst, was a very promising catalyst for on-board hydrogen production from the methanolysis of ammonia borane.

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## Introduction

Storage of hydrogen in chemical materials is the current state-of-the art. Solid-state hydrogen storage materials would appear to be a very promising solution for portable and mobile applications. Hydrogen is put in storage in complex hydrides like LiAlH<sub>4</sub>, NaBH<sub>4</sub>, CaH<sub>2</sub>, LiH etc. Among these complex hydrides, ammonia borane (NH<sub>3</sub>BH<sub>3</sub>, AB) [1,2] is a stable amine compound containing 19.6% hydrogen as a mass in its structure. The high energy density and its non-toxicity coupled with the mild decomposition temperature makes ammonia borane an attractive hydrogen source for fuel cell

applications. All of the hydrogen in the structure can be released by thermolysis [3–5], catalytic hydrolysis [3,4] or methanolysis [4,6]. Three equivalent moles of hydrogen can be evolved from 1 mol equivalent of AB at moderate temperature through methanolysis or hydrolysis. Though, the releasing of ammonia gas, which can be poisonous for Proton Exchange Membrane (PEM) fuel cells can be rendered during the hydrolysis of AB in concentrated solutions. Nevertheless, ammonium metaborate, a by-product of the hydrolysis that is not facile to recycle, which can bring out huge problems for practical applications. Ramachandran [6] discovered that these challenges can be excluded by means of preferring

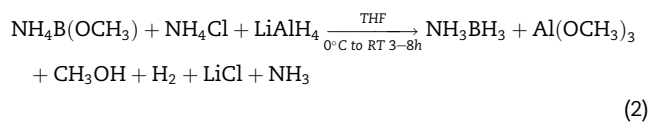
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methanol as a solvent instead of water, which resulted in producing ammonium tetramethoxyborate and hydrogen gas (Eq. (1)). Differently from AB hydrolysis, the methanolysis by-product of ammonium tetramethoxyborate can be recycled into ammonia-borane prepared by a reaction between  $\text{LiAlH}_4$  and  $\text{NH}_4\text{Cl}$  at the room temperature (Eq. (2)).



The catalytic methanolysis of ammonia borane is one of the novel studies which has attracted considerable attention because of the aforementioned reasons in recent years. Although a lot of substances have been recognized as highly effective for the methanolysis reaction of AB such as Raney-Ni [6] and  $\text{MCl}_x$  (M: Ru [6,7], Pd [6], Co [6,8], Ni [6], x: 2 or 3), non-noble metal catalysts have been studied; such as copper (Cu) [9], nickel (Ni) [4,6,10], and cobalt (Co) [8] and either mono or bimetallic incorporation with a noble-metal catalyst due to their cost-efficient production. In case of practical application of an apparatus, the addition of  $\text{MCl}_x$  directly causes problems, for instance decreasing controllability of reactions. For that reason, supported catalysts like zeolite [11], PVP-40 [7,10],  $\text{TiO}_2$  [12], activated carbon [9], montmorillonite [13] and  $\text{Pd-Al}_2\text{O}_3$  [14] have been used.

In order to provide some advantages over traditional batch processes, continuous flow procedures have recently come to light as a widespread approach for conducting chemical reactions. In this regard, a ceramic monolith coated  $\text{Pd-Co/Al}_2\text{O}_3$  catalyst was developed for the methanolysis of AB. This catalyst was tested in the continuous flow reactor, which was different from the previous studies in order to stimulate its hydrogen generation performance for the fuel cells. The current study shows that monolithic  $\text{Pd-Co/Al}_2\text{O}_3$  catalyst can be conceived as a highly stable, very active, and reusable catalyst to produce hydrogen gas in the methanolysis of AB.

## Experimental

### Materials

Ammonia borane (97%) was supplied from Aldrich.  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  ( $\geq 98\%$ ) was purchased from Sigma Aldrich. Methanol (99%),  $\text{PdCl}_2$  (99.9%) and HF (48%) were purchased from Merck. Dispersed alumina ((Disperal 40, Sasol) containing of 80%  $\text{Al}_2\text{O}_3$ , 20 ppm  $\text{Na}_2\text{O}$ , 100 ppm  $\text{Fe}_2\text{O}_3$ , 120 ppm  $\text{SiO}_2$ ); a cordierite type of monolithic ceramic (60% porosity, height = 7.37 cm, diameter = 2 cm, 0.1 mm  $\times$  0.1 mm square channel - (Kale Ceramic-Canakkale)) was used.

### The preparation of catalyst

#### Cordierite monolith support

Commercial monolith of cordierite support was washed three times with boiling water to remove the traces of

contamination. After dried in the oven at 150 °C for 3 h, a treatment process, which is defined as etching, was carried out to provide a greatly enhanced surface roughness. The etching process was performed with HF solution (8 wt%) in ultrasonic bath, followed by drying in the oven at 150 °C and 450 °C, respectively. At the end of the etching treatment, the weight loss of the original monolith support was found as 5%–10%, which was identified as COR.

#### $\text{Al}_2\text{O}_3$ coating onto monolith walls

The treated monolith support was coated with  $\text{Al}_2\text{O}_3$  using wash-coat sol-gel method. The entire cycle was repeated three times until the total increase in weight percentage which was around 8%. This was identified as  $\text{Al}_2\text{O}_3\text{-COR}$ .

#### Incorporation of Pd-Co to the $\text{Al}_2\text{O}_3\text{-COR}$

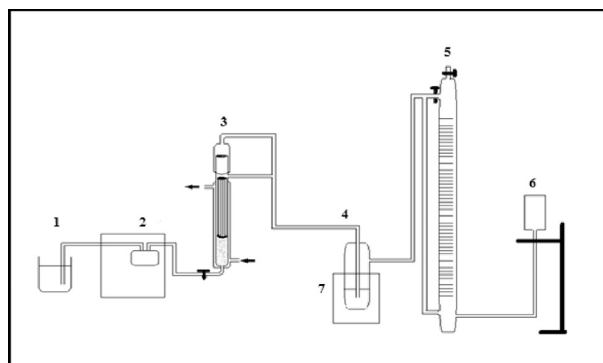
Impregnation method was applied for the incorporation of Pd and Co metals onto  $\text{Al}_2\text{O}_3\text{-COR}$  supports.  $\text{Al}_2\text{O}_3\text{-COR}$  sample was immersed into 2 wt% of  $\text{CoCl}_2$  solution and subsequently immersed into 1 wt% of  $\text{PdCl}_2$  solution for 30 min and then was calcined at 500 °C for 2 h. It was identified as  $\text{Pd-Co/Al}_2\text{O}_3\text{-COR}$  or 1%Pd- 2%Co/ $\text{Al}_2\text{O}_3\text{-COR}$ . Prior to the reaction test, the catalyst was reduced in  $\text{H}_2$  flow at 500 °C for 1 h.

#### Characterization of the catalyst

The analysis of Scanning Electron Microscopy (SEM-EDX) was performed on QUANTA 400F Field Emission operating at 20 kV, 10 000–20 000 magnification.  $\text{N}_2$  adsorption desorption analysis were obtained on Quantachrome Nova 2200e model Brauner-Emmett-Teller (BET). The relative pressure is between in the range of  $P/P_0 = 0.05\text{--}0.9$ . The surface area and the average pore diameter of the catalyst used in the catalytic methanolysis of AB was obtained with multi-point BET method.

#### Catalytic methanolysis of AB

The reaction tests were performed in a continuous system. Fig. 1 illustrates the schematic diagram of the monolithic flow reactor used in the experiments. Jacketed pyrex glass



**Fig. 1 – Continuous reactor system experimental setup, (1) AB-methanol solution, (2) peristaltic pump, (3) monolithic reactor, (4) wash bottle, (5) gas burette system (6) drip hopper (7) cold water tank.**

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