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# Hydrogen generation from alkaline NaBH<sub>4</sub> solution using Co–Ni–Mo–P/γ-Al<sub>2</sub>O<sub>3</sub> catalysts

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## ABSTRACT

Co–Ni–Mo–P catalysts were synthesized on the γ-Al<sub>2</sub>O<sub>3</sub> by electroless deposition. The as-prepared Co–Ni–Mo–P/γ-Al<sub>2</sub>O<sub>3</sub> catalysts were characterized by inductively coupled plasma atomic emission spectrometer (ICP-AES), field emission scanning electron microscope (SEM), energy dispersive X-ray spectrometer (EDS), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and nitrogen adsorption-desorption isotherm. The hydrogen generation activity of Co–Ni–Mo–P/γ-Al<sub>2</sub>O<sub>3</sub> catalysts was tested through hydrolysis of sodium borohydride alkaline solution. The concentrations of Na<sub>2</sub>MoO<sub>4</sub>, NaOH and NaBH<sub>4</sub>, electroless deposition time as well as solution temperature were found to have considerable influences on the hydrogen generation rate of hydrolysis of alkaline NaBH<sub>4</sub> solution. The results show that the obtained Co–Ni–Mo–P/γ-Al<sub>2</sub>O<sub>3</sub> catalysts exhibit excellent catalytic activity. The hydrogen generation rate increases apparently from 10.125 L min<sup>−1</sup> g<sup>−1</sup><sub>catalyst</sub> to 13.842 L min<sup>−1</sup> g<sup>−1</sup><sub>catalyst</sub> with the concentration of Na<sub>2</sub>MoO<sub>4</sub> increasing from 0.5 g L<sup>−1</sup> to 0.8 g L<sup>−1</sup> at 45 °C. The catalysts also exhibit favorable cycling performance and lower activation energy (52.43 kJ mol<sup>−1</sup>) in comparison with that of other reported catalysts.

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## Introduction

The depletion of fossil fuels and environmental pollution have stimulated much interest in the establishment of a clean and sustainable energy system [1,2]. Hydrogen is considered to be one of the most attractive energy carriers due to its high energy density, ideal usage efficiency and zero emission [3]. However, the widespread commercialization and use of hydrogen fuel cell vehicles are hindered by the issues of hydrogen generation and storage. Chemical hydrides as hydrogen sources for fuel cell vehicles have got much

attention. These hydrides can store hydrogen at much milder ambient compared with other technologies, including liquefaction, gas compression and so on [4]. Among the chemical hydrides, sodium borohydride is viewed as a potential candidate for pure hydrogen generation and storage due to its non-flammable and non-toxic nature, excellent stability in alkaline solution at room temperature and high hydrogen storage capability of 10.8 wt.% [5–7]. The hydrolysis reaction of alkaline NaBH<sub>4</sub> solution is given by Equation (1).



Schlesinger et al. [8] first investigated hydrogen generation

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from borohydride hydrolysis in 1953. They found metal borides prepared by reducing metal salts with sodium borohydride were favorable to accelerate the hydrolysis of alkaline  $\text{NaBH}_4$  solution. Since then, various metal catalysts have been prepared and used to accelerate the  $\text{NaBH}_4$  hydrolysis. Precious metals such as Pt [9,10], Ru [11,12] and Pd [13] show excellent catalytic activity, however their high cost and limited supply restrain their large-scale application [14]. To address this issue, strenuous efforts have been devoted to developing non-noble catalysts. Co–Ni–P [15–17], Ni–Co–B [18], Co–P–B [19], Ni–B [20], Co [21] and some similar catalysts have been widely investigated and their good catalytic performance toward  $\text{NaBH}_4$  hydrolysis has been observed. In order to further improve the catalytic activity of non-noble catalysts, transition metals such as Mo, W, Cr, Cu or Fe were added to the non-noble catalysts [22–26]. These transition metals usually act as an atom barrier to avoid agglomeration of the catalyst [22]. Ke DD et al. [27] prepared the Co–Mo–B nanoparticles by the co-deposition chemical reduction method. The Co–Mo–B nanoparticles show super catalytic activity in hydrogen generation by hydrolysis of alkaline  $\text{NaBH}_4$  solution. The effect of Mo in the Co–Mo–B catalyst and some influential parameters such as various reactant concentrations have also been investigated in their report. However, the cycling ability of Co–Mo–B catalysts is not studied. Wang WL et al. [28] reported that quaternary alloy Co–Ru–Mo–B catalyst powders exhibit high hydrogen generation rate in hydrolysis of  $\text{NaBH}_4$  alkaline solution. However, considering the limited source and high cost of precious metal elements, quaternary non-noble catalysts are more promising.

Supported non-precious-metal catalysts are ideal for use in  $\text{NaBH}_4$ -based hydrogen storage systems because of their robustness, low cost and ease of handling [29]. Various solid supports including carbon [10,18], zeolite [12] and metal oxides [11,16] have been employed to immobilize the metal catalysts to protect them against dissolution and aggregation. In recent years, there has been considerable research in the use of  $\text{Al}_2\text{O}_3$  as a carrier for immobilizing the metal catalyst [30–32]. Huang YH et al. [11] synthesized Ru nanoparticles supported on the  $\gamma\text{-Al}_2\text{O}_3$  for hydrogen generation from  $\text{NaBH}_4$  solution. The as-prepared catalysts show very good catalytic activity and high stability. In the work, we attempted to prepare supported non-precious-metal catalysts made of Co, Ni, Mo and P on the  $\gamma\text{-Al}_2\text{O}_3$  by electroless deposition. Though the addition of  $\text{Na}_2\text{MoO}_4$  in the bath could inhibit the electroless reaction, leading to the difficulty in preparing the Co–Ni–Mo–P/ $\gamma\text{-Al}_2\text{O}_3$  catalysts, we regulated the composition and parameters of the electroless bath and successfully synthesized the catalysts by electroless deposition in the end. Experiment results show that the Co–Ni–Mo–P/ $\gamma\text{-Al}_2\text{O}_3$  catalysts exhibit high catalytic activity towards the hydrolysis reaction of  $\text{NaBH}_4$ . The influences of preparation conditions and hydrolysis reaction conditions on the catalytic activity of Co–Ni–Mo–P/ $\gamma\text{-Al}_2\text{O}_3$  were studied systematically. Furthermore, the cycling capability and the kinetic parameters of Co–Ni–Mo–P/ $\gamma\text{-Al}_2\text{O}_3$  were also investigated by the hydrogen generation from alkaline  $\text{NaBH}_4$  solution.

## Experimental

### Preparation of Co–Ni–Mo–P/ $\gamma\text{-Al}_2\text{O}_3$ catalysts

The  $\gamma\text{-Al}_2\text{O}_3$  pellets with the diameter in the range of 2.5–3.5 mm were used as the carriers. They were first washed in anhydrous ethanol to get rid of the purities and greasy dirt on their surface. Then the pellets were sensitized in  $10\text{ g L}^{-1}$   $\text{SnCl}_2$  solution and subsequently activated in  $0.5\text{ g L}^{-1}$   $\text{PdCl}_2$  solution before electroless deposition. The use of ultrasonic agitation can be favor of the removal of dirt and the formation of active Pd on the support surface. The electroless deposition of Co–Ni–Mo–P alloys were performed in an alkaline solution, containing  $25\text{ g L}^{-1}$  metal salts (cobalt sulfate heptahydrate, nickel sulfate hexahydrate and sodium molybdate dihydrate),  $40\text{ g L}^{-1}$  sodium hypophosphite monohydrate as reducing agent,  $10\text{ g L}^{-1}$  ammonium fluoride as buffer and  $20\text{ g L}^{-1}$  trisodium citrate dihydrate as stabilizer. When the concentration of sodium molybdate dihydrate ranged from 0.5 to  $0.9\text{ g L}^{-1}$ , the total concentration of metal salts and the weight ratio of  $\text{CoSO}_4/\text{NiSO}_4$  remained  $25\text{ g L}^{-1}$  and 9:1, respectively. The pH 9 was easily controlled by the addition of ammonia solution and the thickness of the coating was controlled by the deposition time. The process was optimized at  $90\text{ }^\circ\text{C}$ .

### Catalyst characterization

The morphologies and sizes of the catalysts were characterized using field-emission scanning electron microscopy (FE-SEM, JEOL JSM-6700F). The atomic ratio of Co, Ni, Mo and P in the coatings was analyzed by energy dispersive X-ray spectroscopy (EDS, Oxford instrument INCA). The crystal structures of the Co–Ni–Mo–P/ $\gamma\text{-Al}_2\text{O}_3$  and  $\gamma\text{-Al}_2\text{O}_3$  were observed by X-ray diffraction (XRD, Rigaku D-max- $\gamma\text{A}$  XRD with Cu  $k\alpha$  radiation,  $\lambda = 1.54178\text{ \AA}$ ) from  $5^\circ$  to  $85^\circ$ . The specific surface area of the sample was measured by Brunauer–Emmett–Teller (BET, Micromeritics instrument ASAP-2020) nitrogen adsorption-desorption method. The surface electronic state was analyzed by X-ray photoelectron spectroscopy (XPS) using Perkin–Elmer PHI 550 spectrometer with Al  $K\alpha$  (1486.6 eV) as the X-ray source. The composition and loading of the supported catalysts were confirmed by inductively coupled plasma atomic emission spectrometer (ICP-AES, Leeman PROFILE SPEC).

### Hydrogen generation measurement

In the hydrogen generation experiments, 20 mL mixed solution of 7 wt.%  $\text{NaBH}_4$  and 10 wt.%  $\text{NaOH}$  was placed in a sealed flask immersed in a thermostatic bath and the solution temperature was kept at  $45\text{ }^\circ\text{C}$ . The catalysts ( $1.5\text{ g Co–Ni–Mo–P}/\gamma\text{-Al}_2\text{O}_3$ ) were placed into the reaction flask to initiate hydrolysis reaction of  $\text{NaBH}_4$ . As the reaction proceeded, the volume of water replaced by hydrogen was measured by a graduated cylinder. During the catalytic process, no stirring was adopted due to the presence of vigorous bubbles induced by the generated hydrogen. After the reaction completed, the

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