

Novel Ni-based catalysts for hydrogen generation from hydrolysis of ammonia borane

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Abstract. Hydrogen can be regarded as the most promising clean energy in the 21st century. Up to now, hydrogen production is still a challenge for scientists. With further research, many theories of hydrogen generation have been delivered successfully. Ni-based catalysts hydrolyze ammonia borane can be simple and effective. Ammonia borane (H_3NBH_3 , AB) has the advantages of high hydrogen storage density and mild hydrogen release conditions. And in the paper, recent research achievements were reviewed on the application of Ni-based catalysts for hydrolysis of AB. It presented some kinds of catalysts with high catalysis capacities.

1. Introduction

Due to the energy crisis, we urgently need to develop new energy resources. Hydrogen is an attractive energy carrier, having high potential to replace fossil fuels. Yet, the development of a *hydrogen economy* is still hypothetical [1].

Production of H_2 is particularly problematic. Typical examples of liquid-phase hydrogen storage materials are sodium borohydride (NaBH_4) and ammonia borane in aqueous solution, hydrous hydrazine ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$) and methanoic acid (HCOOH) [1]. At room temperature, ammonia borane is a solid state with stable property and high hydrogen storage capacity. This intriguing character has driven numerous efforts to develop novel catalysts for enhanced hydrolysis efficiency of AB. Given their element abundance and recycling capability, inexpensive transition metal catalysts such as Fe, Co, and Ni have attracted considerable attention, revealing potential in prompting the hydrolytic dehydrogenation of AB [2].

Ni-based catalysts have attracted much attention due to their low cost and high abundance. Ni-based composites are investigated widely to invent the increasing requirement of expressive materials for hydrogen generation from the hydrolysis of AB.

2. Applications Of Ni-Based Composites For Hydrogeneration From Hydrolysis Of Ammonia Borane

As a good candidate of solid chemical hydrogen storage materials, ammonia borane has been concentrated on producing hydrogen among scientists. Recent catalytic hydrolysis of AB has been well studied. Qiang Xu and Manish Chandra (2006) prepared Ni-supported metal catalysts for hydrogen production via hydrolysis reaction [3]. Jun Chen *et al.* (2007) utilized $\text{Ni}_{1-x}\text{Pt}_x$ hollow spheres as catalysts for hydrogen generation from AB [4]. And then Jun Chen *et al.* (2009) made use of $\text{Pt}_x\text{Ni}_{1-x}$ nanoparticles as catalysts for hydrogen generation from AB [5]. After then, Jun Chen *et al.*



(2010) prepared out a nanoporous cobalt-tungsten-boron-phosphorus catalyst supported on Ni foam to generate hydrogen from AB [6]. SaimÖzkar *et al.* (2010) reported that the in-situ generation and catalytic activity of nickel(0) nanoclusters stabilized by poly (4-styrene sulfonic acid-Co-maleic acid), PSSA-Co-MA, in the hydrolysis of ammonia borane [7]. Fangyi Cheng *et al.* (2013) reported that nanoporous Ni-based catalysts hydrolysed ammonia borane [8]. Jing Liang and co-workers (2014) showed that carbon-supported Ni₃B nanoparticles as catalysts had more potential advantages than cobalt borides [9]. NurettinSahiner and SemaYildiz (2014) synthesized Ni nanoparticles inside cryogel network. The obtained p(4-VP)-Ni cryogel composite was used as catalyst system for producing H₂ from the hydrolysis of AB [10]. In the paper, table 1 presents the progress of some scientists.

Table1. Applications of Ni-based catalysts for hydrogen generation from hydrolyzing ammonia borane(AB)

Catalysts	Dosage	Catalytic time/min	AB	Temp.	H ₂ values	References
Ni/γ-Al ₂ O ₃	0.18ml	65	10ml	293K	28.7ml	Xu Q *et al.2006
Ni _{0.88} Pt _{0.12}	12mg	28	50ml	293K	24mmol	Chen J* et al. 2007
Ni hollow sphere	12mg	120	50ml	293K	5mmol	Chen J* et al. 2007
Ni powder	12mg	20	50ml	293K	1mmol	Chen J* et al. 2007
Ni _{0.88} Pt _{0.12} hollow	20mg	88	50ml	293K	165mmol	Chen J* et al. 2007
Spheres(5.0wt.%) Pt _{0.65} Ni _{0.35}	9mg	2	10ml(0.5wt%)	298K	94ml	Chen J* et al. 2009
Co-W-B-P/Ni foam (W=5)	5.5mg	5	8ml(0.5wt%)	303K	84ml	Chen J* et al. 2011
PSMA-Ni	3mM	9	100mM	298K	100ml	Özkar S* et al.2011
Ni _{0.5} Fe _{0.5}	17mg	12	10ml(0.4wt%)	298K	2.75mol	Chen F Y* et al.2013
Pt ₃ Ni/C	20mg	61	31mg	296K	61ml	Yang H X* et al.2008
Ni ₃ B/C	20mg	224	31mg	296K	53ml	Yang H X* et al.2008
NiAu/C	20mg	175	31mg	296K	63ml	Yang H X* et al.2008
NiAg/C	20mg	70	31mg	296K	65ml	Yang H X* et al.2008
NiCu/C	20mg	24	31mg	296K	59ml	Yang H X* et al.2008
NiSn/C	20mg	180	31mg	296K	58ml	Yang H X* et al.2008
NiCo/C	20mg	355	31mg	296K	62ml	Yang H X* et al.2008
Co-Ni-P/Pd-TiO ₂ (M=80wt%)	25mg	45	25mg	298K	40ml	Özkar S* et al.2011
Ru ₁ @Ni _{7.5} /graphene	0.034mmol	3	8.5mmol	298K	2.875mmol	Luo W* et al.2014
Cu _{0.2} Ni _{0.8} /MCM-41	0.055mmol	5	34.30mg	293K	73ml	Lu Z H* et al.2014
rGO-Ni ₃₀ Pd ₇₀	20mg	13	2mmol	298K	76ml	Metin Ö* et al.2014
hollow Ni-SiO ₂ NPs	0.08mmol	18	1.6mmol	298K	140ml	Xu Q* et al.2009
Fe _{0.5} Ni _{0.5} Nps	0.192mmol	2.25	1.6mmol	293K	130ml	Xu Q* et al.2009
Ni@Zeolite	4.0mM	8	1mmol	298K	38ml	Özkar S* et al.2011
Ni/SiO ₂	10ml Solution	18	128mg	298K	275ml	Özkar S* et al.2010
Co-Ni-B	0.2mmol	70	1mmol	/	3mol	Jagirdar*et al.2009
Ni-Ni ₃ B	0.2mmol	158	1mmol	/	2.9mol	Jagirdar*et al.2009
Ni/ZIF-8	10mg	12	2mmol	roomTemp	140ml	Xu Q*et al.2012
Fe-Ni/PEI-GO	0.01g	15	10mg	293K	147.3ml	Lu H X*et al.2012
Ag _{0.1} @Co _{0.45} Ni _{0.45} /grapheneNPs	0.05mmol	6	1mmol	298K	3.25mmol	Luo W*et al.2013
NiNPs@3D-(N)GFs	0.018	8	2mmol	298K	6mmol	Shaabani*et al.2014
Ni _{0.85} /Pt _{0.15} hollow nanospheres	10mg	2	4mmol	298K	150ml	Yu R B*et al.2014
Ni/CNTs	13mg	4.5	1.5mmol	298K	110ml	Qin Y*et al.2016
Ni _{0.9} Mo _{0.1} /Graphene NCs	0.05mmol	0.9	1mmoll	298K	72ml	Chen X H*et al.2016
Ni _{0.74} Ru _{0.26} NPs	1mM	10	200mM	303K	130ml	Ma D L*et al.2012
Ni ₃ B	2mg	28	2mol	332K	0.85mol	Chen P*et al.2009
Ni nanoparticles	2.6mmol	6	90mg	293K	225ml	Xu Q*et al.2009

Ni/C	8.5mM	8	200mM	298K	140ml	Sun S H*et al.2009
Ni NPs	0.031mmol	6	2mmol	293K	140ml	Xu Q*et al.2012
Ni ₂ P NPs	0.054mmol	46	1.62mmol	273K	118ml	Fu W F*et al.2015

3. Summary

Hydrogen generation is urgent to be solved. Lots of Ni-based catalysts have been extensively explored for hydrogen production. Different materials are with different release hydrogen capacities. Compared with different study conditions, we will find out a high selectivity and low-cost way. Efforts should be devoted to developing methods like this. Therefore, we must understand exactly the mechanisms of catalytic hydrogen production.

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