

A Noble-Metal-Free Catalyst Derived from Ni-Al Hydrotalcite for Hydrogen Generation from N₂H₄·H₂O Decomposition**

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Storing hydrogen safely and efficiently is one of the major technological barriers preventing the widespread application of hydrogen-fueled cells, such as proton exchange membrane fuel cells (PEMFCs). Hydrous hydrazine (N₂H₄·H₂O) is considered as a promising liquid hydrogen storage material owing to the high content of hydrogen (7.9%) and the advantage of CO-free H₂ produced.^[1] In particular, hydrous hydrazine offers great potential as a hydrogen storage material for some special applications, such as unmanned space vehicles and submarine power sources, where hydrazine is usually used as a propellant.

The decomposition of hydrazine proceeds by two typical reaction routes:^[2]



Reaction (2) not only decreases the yield of H₂ but also complicates the separation process of products, because the ammonia by-product would poison the Nafion membrane and the fuel-cell catalysts. Thereby, it is of crucial importance to develop a highly selective catalyst over which the reaction proceeds only by pathway (1) at low temperatures. To this end, Xu and co-workers^[3] synthesized a series of nickel-containing bimetallic nanoparticles, including Ni-Rh, Ni-Pt, and Ni-Ir, which showed high H₂ selectivity at room temperature. Nevertheless, the incorporation of noble metals to nickel greatly increased the cost of catalysts. In a subsequent study by Xu and co-workers,^[4] Ni-Fe nanoparticles were

employed as catalysts for this reaction. However, the nanoparticles were only active at 70 °C, and addition of 0.5 mol L⁻¹ NaOH was necessary for the high selectivity. Moreover, the practical application of colloidal nanoparticles will raise significant problems, such as mass production, handling, stability, separation, and recyclability. Therefore, from the viewpoint of practical applications, a supported base metal catalyst is a preferred choice owing to its low cost, good mechanical stability, and easy separation from the reaction medium.

Herein, using a Ni-Al hydrotalcite-like compound (Ni-Al-HT) as the precursor, we obtained a highly dispersed nickel catalyst that presented 100% conversion of N₂H₄·H₂O and up to 93% selectivity to H₂ for the decomposition of N₂H₄·H₂O at ambient temperature. To our knowledge, this is the first report in which supported base metal catalysts show such high selectivity towards the formation of H₂.

It is well-known that supported noble metal catalysts, especially iridium catalysts, are very active for the decomposition of hydrazine. Compared with Ir, Ni is less active.^[5] Accordingly, to obtain a high activity over Ni catalysts, a very high loading of Ni is required while maintaining a high degree of dispersion. Hydrotalcite-like compounds have been demonstrated to be excellent precursors for the preparation of highly dispersed and high-loading metal catalysts.^[6] Herein, we synthesized binary Ni-Al-HT with interlayer CO₃²⁻ anions by a co-precipitation method.^[7] After reduction in a H₂ atmosphere at 500 °C, the sample was transformed into a highly dispersed Ni/Al₂O₃ nanocatalyst (denoted as Ni-Al₂O₃-HT). The molar ratio of Ni to Al, determined by ICP analysis, was 3:1. The BET surface areas of the Ni-Al-HT precursor and the derived Ni-Al₂O₃-HT catalyst were 248 m² g⁻¹ and 179 m² g⁻¹, respectively. The reduced Ni-Al₂O₃-HT catalyst was then transferred into deionized water without exposure to air and used for reaction without further treatment. The reaction was initiated by introducing N₂H₄·H₂O into the reactor containing the catalyst. Gaseous products released during the reaction were measured volumetrically and analyzed on-line with a gas chromatograph.^[8] The selectivity to H₂ was evaluated based on Equations (1) and (2). For comparison, a traditional supported Ni/Al₂O₃ catalyst was also prepared by the impregnation method with the same amount of Ni loading (denoted as 78 wt % Ni/Al₂O₃-IMP). The synthesis details can be found in the Supporting Information.

Powder X-ray diffraction patterns (Figure 1a) illustrate the crystalline nature of the layered double hydroxide (LDH) structure of hydrotalcite. No other crystalline phases were detected, thus suggesting the high purity of the precursor.

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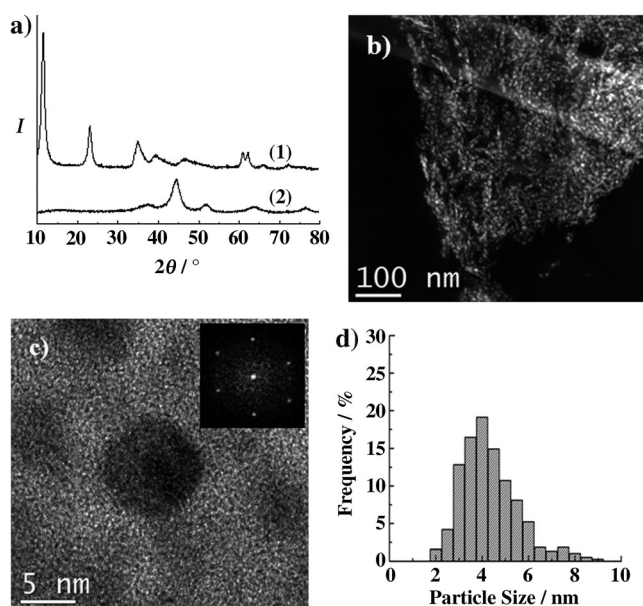


Figure 1. a) XRD patterns of: (1) Ni-Al-HT structure; (2) Ni-Al₂O₃-HT reduced at 500 °C. b) HAADF image for Ni-Al₂O₃-HT reduced at 500 °C. c) HRTEM image (inset: SAED) for a single particle. d) Histogram of the Ni particle size distribution.

After reduction, the major diffraction peak with a 2θ value of 44.5° can be indexed to the (111) plane of fcc Ni (PDF number 01-087-0712). The average particle size of Ni is around 4 nm, based on the Scherrer equation, indicating that the Ni-Al-HT precursor produces a well-dispersed Ni-Al₂O₃-HT catalyst, even with a very high Ni loading of around 78 wt %. Figure 1b,c show representative HAADF-STEM and HRTEM images of the Ni-Al₂O₃-HT catalyst derived from hydrothermalite. The well-dispersed Ni nanoparticles are surrounded by amorphous alumina (Supporting Information, Figure S1), suggesting they are strongly interacting with the alumina support. This can be further confirmed by the results of H₂-TPR measurement (Supporting Information, Figure S2). The reduction temperature of Ni-Al-HT is notably higher than that of Ni/Al₂O₃-IMP, indicating a much stronger interaction of the Ni component with Al₂O₃ in the former catalyst. The corresponding digital diffraction pattern demonstrates the crystalline nature of these Ni metal nanoparticles. As shown in the size distribution histogram (Figure 1d), most of the Ni particles are in the range of 3–9 nm, and no particles larger than 10 nm were observed. Among them, 64 % of Ni particles are in the range of 3–5 nm. In contrast, the average size of Ni particles of the 78 wt % Ni/Al₂O₃-IMP catalyst is around 38 nm (Supporting Information, Figure S3). The H₂ chemisorption measurement also demonstrates that the Ni-Al₂O₃-HT has a much larger H₂ uptake than the 78 wt % Ni/Al₂O₃-IMP catalyst ($702 \mu\text{mol g}^{-1}$ vs. $124 \mu\text{mol g}^{-1}$), which is in agreement with the conclusions from XRD and HAADF-STEM.

The catalytic performance of the Ni-Al₂O₃-HT catalyst in N₂H₄·H₂O decomposition for H₂ generation was examined and compared with the 78 wt % Ni/Al₂O₃-IMP sample. The Ni-Al₂O₃-HT catalyst shows much higher activity and selec-

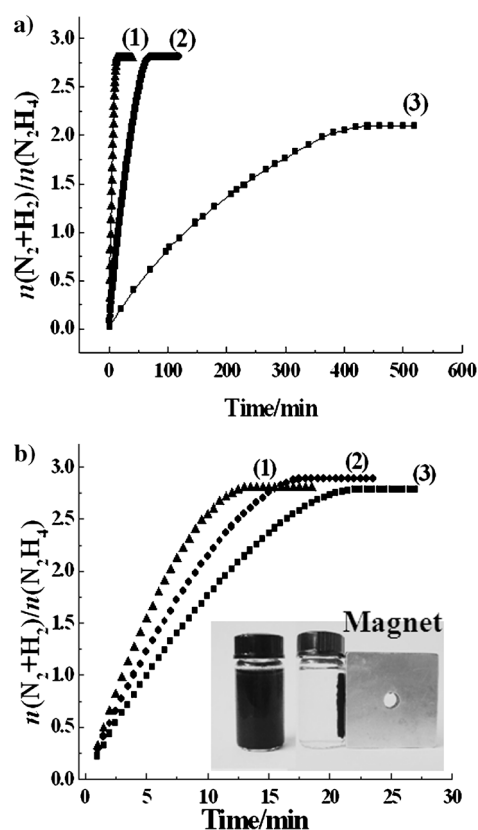


Figure 2. a) $n(\text{N}_2+\text{H}_2)/n(\text{N}_2\text{H}_4)$ versus time for Ni-Al₂O₃-HT and 78 wt % Ni/Al₂O₃-IMP at different reaction temperatures: (1) Ni-Al₂O₃-HT at 50 °C; (2) Ni-Al₂O₃-HT at 30 °C; (3) 78 wt % Ni/Al₂O₃-IMP at 30 °C. b) $n(\text{N}_2+\text{H}_2)/n(\text{N}_2\text{H}_4)$ versus time for Ni-Al₂O₃-HT at 50 °C: (1) the second time; (2) the fifth time; (3) the tenth time. Inset: magnetic separation of the catalyst after reaction.

tivity (Figure 2a); the reaction was complete within 70 min at 30 °C and the H₂ selectivity was up to 93 % (Table 1). In contrast, the 78 wt % Ni/Al₂O₃-IMP catalyst exhibited a much lower activity, with a total reaction time of 440 min. This result is consistent with the poor dispersion of Ni. It should be noted that the H₂ selectivity was only 66 %. When the reaction temperature was raised to 50 °C, N₂H₄·H₂O was converted completely within 13 min over the Ni-Al₂O₃-HT catalyst and the selectivity still maintained at 93 %. Gas chromatographic analysis reveals that the H₂/N₂ molar ratio was 1.95 on the Ni-Al₂O₃-HT and 1.72 on the 78 wt % Ni/Al₂O₃-IMP, respectively, with a corresponding selectivity of 93 % and 67 % (Supporting Information, Figure S4). This ratio remained constant during the whole reaction process, which is in good agreement with H₂ selectivity obtained from the volumetric observation. On further increasing the reaction temperature from 50 °C to 80 °C, the reaction was complete within 5 min but the selectivity was reduced to 82 % (Supporting Information, Table S1), demonstrating that a higher temperature was unfavorable for Reaction (1) but the reaction took place faster than that at lower temperatures. The apparent activation energy for the reaction was about $(49.3 \pm 3.2) \text{ kJ mol}^{-1}$ (Supporting Information, Figure S5), which is very similar to the previously reported values for the catalytic decomposition

Table 1: Ni particle size after reduction, catalytic activity and selectivity, and amount of CO₂ desorbed during TPD of the corresponding Ni-Al₂O₃-HT and Ni/Al₂O₃-IMP catalysts.

Catalysts	Reaction temperature [°C]	Average size of Ni [nm]	Reaction time ^[d] [min]	Selectivity [%]	Total amount of CO ₂ desorption [μmol (g Al ₂ O ₃) ⁻¹]	Strong basic sites [μmol (g Al ₂ O ₃) ⁻¹]	Weak basic sites [μmol (g Al ₂ O ₃) ⁻¹]
Ni-Al ₂ O ₃ -HT	50	4.0	13	93	414	328	86
Ni-Al ₂ O ₃ -HT	30	4.0	70	93	414	328	86
Ni-Al ₂ O ₃ -HT (2:1) ^[a]	30	3.2	64	92	350	259	91
78 wt % Ni/Al ₂ O ₃ -IMP	30	38.2	440	66	104	33	71
20 wt % Ni/Al ₂ O ₃ -IMP	30	4.0	160	59	166	48	118
K-Ni-Al ₂ O ₃ -HT ^[b]	30	—	86	96	998	845	153
K-20 wt % Ni/Al ₂ O ₃ -IMP ^[c]	30	—	290	76	653	376	277

[a] The molar ratio of Ni/Al was 2:1. [b] The mass percent of K for K-Ni-Al₂O₃-HT was 0.23 %. [c] The mass percent of K for K-20 wt % Ni/Al₂O₃-IMP was 2.92 %. [d] The time for complete conversion of N₂H₄·H₂O.

of gaseous N₂H₄.^[9] The reaction rate per unit mole of active metal over this Ni-Al₂O₃-HT catalyst was about 2.0 h⁻¹, which is even comparable to the NiPt alloy nanoparticles.^[3d] The recyclability of the Ni-Al₂O₃-HT catalyst was also tested. There was no significant decrease in H₂ selectivity from the second to tenth runs (Figure 2b), though the rate of reaction decreased slightly. The slight decrease in reaction rate is due to the formation of small amounts of ammonia rather than the growing crystallite size. Another advantage for potential application is that the catalyst is easily separated from the reaction medium owing to the magnetic property of Ni particles (inset of Figure 2b).

This is the first report that Ni catalyst can catalyze the complete decomposition of N₂H₄·H₂O at room temperature. The freshly reduced Ni-Al₂O₃-HT catalyst exhibited desired activity and selectivity for N₂H₄·H₂O decomposition, which shows the potential for it to be a candidate to replace noble metals for this reaction. Moreover, the passivated catalyst was totally inactive for this reaction at 30 °C. An IR spectrum of adsorbed CO (Supporting Information, Figure S6) shows that for the fresh catalyst, there is a main band appearing at 2059 cm⁻¹, which is typical for CO linear adsorption on metallic Ni; however, there is no CO adsorption observed on the passivated surface, which is probably due to surface oxidation of Ni particles. This result supports the idea that the high catalytic activity of this Ni-Al₂O₃-HT catalyst originates from the metallic Ni.

It should be noted that a much lower H₂ selectivity (only 66 %) was observed over the 78 wt % Ni/Al₂O₃-IMP catalyst. We tentatively attribute this to Ni particle size difference (4 nm versus 38 nm), considering that Ni catalysts are structure-sensitive for N-H cleavage in NH₃ decomposition.^[10] To confirm this proposition, we prepared a Ni/Al₂O₃-IMP catalyst with a mean particle size of 4 nm by lowering the metal loading to 20 wt %. However, the selectivity to H₂ on the impregnated sample was still very low (around 59 %), which is even lower than the 78 wt % Ni/Al₂O₃-IMP catalyst, indicating that the difference in Ni particle size may not be the only reason for the H₂ selectivity. In fact, by varying the molar ratio of Ni/Al and reduction temperature, the particle sizes of Ni-Al₂O₃-HT catalysts can be tuned (Supporting Information, Table S2). Interestingly, there were no significant changes in the selectivity to H₂ when varying the Ni particles size in the

range from 3 to 9 nm, while only the reaction rate increased with the reducing of Ni particle size.

A quantitative measure of the number and strength of basic sites was obtained by a CO₂-TPD experiment (Supporting Information, Figure S7 and Table 1). The number of basic sites on Ni-Al₂O₃-HT was clearly larger than that on the impregnated sample. In fact, there are two kinds of basic sites, strong and weak, and the major difference lies in the number of strongly basic sites. By comparing 20 wt % Ni/Al₂O₃-IMP and Ni-Al₂O₃-HT catalysts, which have quite different H₂ selectivity (Supporting Information, Figure S8), we found that the latter catalyst contained many more strong basic sites. Therefore, it is reasonable to speculate that the strong basic sites contribute to the increased H₂ selectivity. To further investigate the influence of the basicity of the catalyst, a small amount of potassium was deliberately introduced to both the Ni-Al₂O₃-HT and Ni/Al₂O₃-IMP catalysts. As expected, the K-promoted catalyst with stronger basicity did exhibit an increase of H₂ selectivity from 93 % to 96 % for Ni-Al₂O₃-HT and 59 % to 76 % for Ni/Al₂O₃-IMP. Noticeably, with decreased Ni loading, there was also an increase in the weak basicity of the sample owing to the increased content of Al₂O₃, but this was not accompanied by increase in selectivity.

The decomposition reaction of N₂H₄·H₂O consists of several elementary reactions, including the cleavage of N-N and N-H bonds. If the N-N bond firstly breaks to produce ·NH₂ radical, it is much easier to produce ammonia instead of hydrogen because further N-H bond cleavage needs more energy than the combination of ·NH₂ and H· to form NH₃.^[11] The Ni-Al₂O₃-HT catalyst exhibits much higher selectivity to H₂, which is quite different from other metal catalysts (10 % for cobalt, 5 % for iridium). This unique selectivity to H₂ can be explained by facilitating the dissociation of N-H bond over Ni-based catalyst.^[5b,12] KOH has been reported to be a promoter for selective cracking of the N-H bond in N₂H₄ decomposition.^[2e,4] Therefore, the stronger basicity of the Ni-Al₂O₃-HT leads to a highly selective catalyst for production of H₂ from the decomposition of N₂H₄·H₂O. On the other hand, the selectivity of the Ni-Al₂O₃-HT was significantly higher than that of the K-promoted Ni/Al₂O₃-IMP sample, even though the latter catalyst contained large amounts of strong basic sites. This may be related to the strong metal support interaction (SMSI), as expected from the peculiar textural

property that is typical of hydrotalcite-derived material. Therefore, it is likely that the high H_2 selectivity of Ni- Al_2O_3 -HT originates from the cooperative action of the small Ni particle size and strong basic sites located nearby.

In summary, a supported Ni catalyst with a high loading and good dispersion, prepared by using Ni-Al hydrotalcite-like compounds as precursors, exhibits 100% conversion and 93% H_2 selectivity for the decomposition of $N_2H_4 \cdot H_2O$ at room temperature. This unique catalysis is due to the cooperation of Ni nanoparticles and strong basic sites. This Ni-Al hydrotalcite derived catalyst could be a promising candidate to replace noble metals for the catalytic decomposition of $N_2H_4 \cdot H_2O$ and for hydrogen generation under ambient conditions.

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