

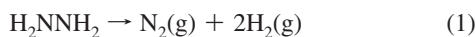
Room-Temperature Hydrogen Generation from Hydrous Hydrazine for Chemical Hydrogen Storage

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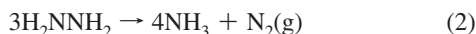
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Finding efficient hydrogen storage materials remains one of the most difficult challenges on the way to a “hydrogen economy” society, even after several decades of exploration. Its solution requires breakthroughs in material performance coming from wide-ranging innovative basic research that looks beyond the storage materials currently known.^{1,2} Anhydrous hydrazine, H₂NNH₂, is a liquid at room temperature and has a hydrogen content as high as 12.5 wt %.³ Recent studies, mostly on the reactions of hydrazine highly diluted in inert gases such as argon, have shown that hydrazine can be decomposed in two ways: complete decomposition,



and incomplete decomposition,

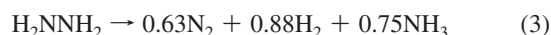


The reaction pathways depend on the catalyst used and the reaction conditions.^{4–9} However, anhydrous hydrazine (>98%) is explosive when exposed to a metal catalyst, making it difficult to apply safely. Hydrous hydrazine, such as hydrazine monohydrate, H₂NNH₂·H₂O, which also contains a large amount of hydrogen (7.9 wt %), is much safer. Therefore, hydrous hydrazine might be a promising hydrogen carrier for storage and transportation that has the distinct advantages of easy recharging, the availability of the current infrastructure of liquid fuels for recharging, and the production of only nitrogen (which does not need recycling) in addition to hydrogen. In this context, the development of efficient and selective catalysts for H₂ generation from hydrous hydrazine is of critical importance. Herein we report that Rh nanoparticles (NPs) act as an active and appreciably selective catalyst that can readily facilitate hydrous hydrazine decomposition to hydrogen under ambient conditions.

Rh NPs were rapidly generated as a black suspension by mixing aqueous rhodium(III) nitrate (0.1 M) and sodium borohydride (0.125 M) solutions. After the absence of gas evolution from the solution was verified, hydrazine monohydrate (1:10 Rh/N₂H₄ molar ratio) was introduced, resulting in the release of 1.5 equiv of gases in 180 min (Figure 1), which were identified by mass spectrometry to be H₂ and N₂ (Figure 2). It was found that the $n(\text{N}_2 + \text{H}_2)/n(\text{N}_2\text{H}_4)$ ratio of 1.5 remained unchanged as the Rh/N₂H₄ ratio decreased from 1:10 to 1:100, corresponding to an increase in hydrazine concentration from 0.5 to 5.0 M, while the time required for completion of the reaction increased (Figure S1 in the Supporting Information).¹⁰ It should be noted that the absence of an NH₃ signal does not rule out the generation of NH₃, since NH₃ is highly soluble in water. To clarify this question, ¹⁵N NMR spectra were recorded, and the results (Figure S2) showed a gradual decrease in the hydrazine signal intensity ($\delta = -332$ ppm) during the course of reaction in the presence of Rh(0) NPs, accompanied by the growth of a newly generated signal at $\delta = -376$ ppm, which can be assigned to ammonia dissolved in water.¹⁰ Consequently,

the absence of the hydrazine signal for the spent solution sample indicates the full consumption of hydrazine.

On the basis of the observed release of 1.5 equiv of H₂ and N₂ gases, the selectivity of hydrazine decomposition toward H₂ and N₂ (via reaction 1) is calculated to be 43.8%. That is, under our experimental conditions, the whole hydrazine decomposition reaction catalyzed by Rh(0) NPs can be formulated as



The volumetric observation is in good agreement with the mass spectrometric result (Figure 2), which shows a H₂/N₂ ratio of 1.3. The H₂/N₂ ratio, which is 1.2, 1.1, and 1.3 at $n(\text{N}_2 + \text{H}_2)/n(\text{N}_2\text{H}_4) = 0.25, 0.5,$ and 1.5, respectively, remains almost constant as the reaction proceeds, indicating that the competing pathways (1) and (2) proceed at the same time; eq 3 reflects the total reaction over the whole time course. As one can infer from literature reports, the complete decomposition reaction presumably is initiated by the coordination of hydrazine to the metal surface, after which oxidative insertion of the metal via N–H bond activation occurs.^{7,9,11} An abundance of NH adsorbed on the metal surface^{7,9} or the stabilization of metal-bound HN=NH as a transient intermediate is crucial and leads to the release of N₂ and H₂ by selective activation of the N–H bond over the N–N bond on the metal surface.¹¹

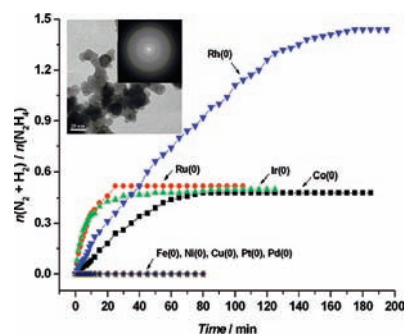


Figure 1. Time-course plots for the decomposition of hydrazine in aqueous solutions in the presence of different metal NPs (metal/N₂H₄ = 1:10) at 298 K. The inset shows a TEM image of Rh(0) NPs and the corresponding SAED pattern. Scale bar, 20 nm.

We also examined the catalytic activities of Co, Ru, Ir, Cu, Ni, Fe, Pt, and Pd NPs under conditions analogous to those for Rh and found that the catalytic activity and selectivity strongly depend on the catalyst used (Figure 1). Release of only 0.5 equiv of gases was observed in the case of Co, Ru, or Ir, corresponding to a selectivity toward H₂ and N₂ (via reaction 1) as low as ~7%. It is noted that subsequent addition of the same amount of hydrazine after the completion of the first run resulted in additional 0.5 equiv of gases, indicating that the catalysts keep their activities and the reactant hydrazine is consumed in the reactions. It was also confirmed that the $n(\text{N}_2 + \text{H}_2)/n(\text{N}_2\text{H}_4)$ ratio remained unchanged

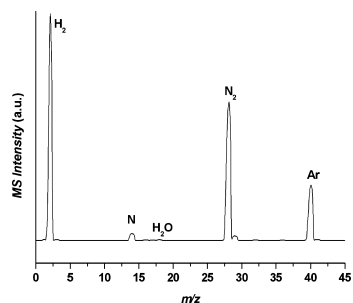


Figure 2. Mass spectral profile for the decomposition of hydrazine in aqueous solution in the presence of Rh(0) NPs ($\text{Rh}/\text{N}_2\text{H}_4 = 1:10$) under an argon atmosphere at 298 K.

as the $\text{M}/\text{N}_2\text{H}_4$ ratio ($\text{M} = \text{Co}, \text{Ru}, \text{Ir}$) decreased from 1:10 to 1:20 (Figure S3).¹⁰ In comparison with the Rh(0) NPs, the Co, Ru, and Ir NPs prefer the activation of the N–N bond to that of the N–H bond, giving rise to the formation of more ammonia. Also, the pH values for the Co, Ru, and Ir NP-catalyzed reaction media were in the range 9.9–9.7, whereas the pH value for the Rh-catalyzed reaction medium was 9.5, in agreement with the observation that more ammonia is produced in the former than the latter. Moreover, the metals Cu, Ni, Fe, Pt, and Pd are inactive for hydrazine decomposition in aqueous solution, whereas they were reported to be active for the gas-phase catalytic decomposition of hydrazine.^{4b} It is obvious that the presence of water significantly influences the activity and selectivity of the catalysts for the hydrazine decomposition.

It has been reported that surfactants might play key roles in the preparation of metal NPs.¹² The reduction of aqueous rhodium(III) nitrate with NaBH_4 in the presence of hexadecyltrimethyl ammonium bromide (CTAB) results in the formation of remarkably more active Rh(0) NPs, with which the decomposition of hydrazine was completed in only 55 and 125 min at $\text{Rh}/\text{N}_2\text{H}_4$ molar ratios of 1:10 and 1:20, respectively, with the release of 1.5 equiv of gases (Figure 3). The observed enhancement in catalytic activity of the Rh(0) NPs could be attributed to the fact that the modification of metal particles during the synthetic process could presumably control the efficacy of the catalyst.^{12,13} In addition, under the described experimental conditions, the activities of Rh(0) NPs synthesized from the rhodium(III) chloride and nitrate precursors were analogous. Similar to the case of Rh(0) NPs, the use of CTAB in the preparation of Co, Ru, and Ir NPs did not change the total volumes of the released gases but did decrease the completion time for the reactions (Figure S4).¹⁰

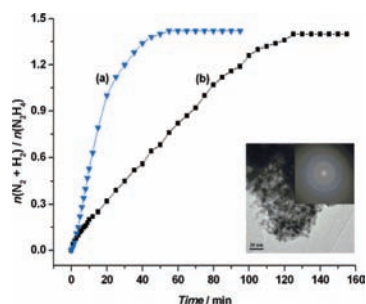


Figure 3. Time-course plots for the decomposition of hydrazine in aqueous solutions in the presence of Rh(0) NPs [$\text{Rh}/\text{N}_2\text{H}_4 =$ (a) 1:10 and (b) 1:20] prepared in the presence of CTAB at 298 K. The inset shows a TEM image of Rh(0) NPs prepared in the presence of CTAB and the corresponding SAED pattern. Scale bar, 20 nm.

A typical transmission electron microscopy (TEM) image (Figure 3 inset) illustrates that nearly monodispersed Rh(0) NPs with an average particle size of ~ 5 nm were obtained in the presence of CTAB. In contrast, without CTAB the Rh NPs had an average particle size of

~ 16 nm (Figure 1 inset). Supportive of these TEM results, the BET surface area ($60.02 \text{ m}^2 \text{ g}^{-1}$) of the Rh NPs modified with CTAB was considerably higher than that for their counterparts not modified with CTAB ($17.08 \text{ m}^2 \text{ g}^{-1}$) (Figure S5),¹⁰ indicating the size-tuning role of CTAB. The selected-area electron diffraction (SAED) patterns (Figures 1 and 3 insets) suggest that the synthesized Rh(0) NPs are crystalline in both cases. Powder X-ray diffraction (XRD, Figure S6) and energy-dispersive X-ray spectroscopy (EDS) (Figure S7) confirmed that rhodium is the exclusive component of the Rh(0) NPs.¹⁰ Hence, the observed enhanced activity of the Rh(0) NPs prepared in the presence of CTAB might be due to their smaller particle size and therefore larger catalytic surface.

In summary, we have found that Rh(0) NPs are highly active for catalytic decomposition of hydrous hydrazine to generate H_2 and N_2 under aqueous and ambient reaction conditions. The fact that the catalytic activity and selectivity strongly depend on the catalyst used inspires us to search for more efficient and selective catalysts for this promising system. The results presented here offer a new prospect for an on-board hydrogen storage system. Exploration of improving the catalytic activity and selectivity is underway.

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Supporting Information Available: Details concerning the preparation of Rh(0) NPs; their characterization by powder XRD, STEM, TEM, and EDS; and the catalytic hydrazine decomposition experiment. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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