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. Anhydrous hydrazine, H₂NNH₂, is a liquid at room temperature and has a hydrogen content as high as 12.5 wt %. Recent studies, mostly on the reactions of hydrazine in aqueous solutions in the presence of different metal NPs (metal/N₂H₄ ratio from 1:10 to 1:100) at 7%. It is important to note that 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:

\[
\text{H}_2\text{NNH}_2 \rightarrow 0.63\text{N}_2 + 0.88\text{H}_2 + 0.75\text{NH}_3
\]  

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(N₂ + H₂)/m(N₂H₄) = 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.

An abundance of NH adsorbed on the metal surface 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.

**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(N₂ + H₂)/m(N₂H₄) ratio remained unchanged.
In contrast, without CTAB the Rh NPs had an average particle size of \(~16 \text{ nm}\) (Figure 1 inset). Supportive of these TEM results, the BET surface area (60.02 m\(^2\) g\(^{-1}\)) of the Rh NPs modified with CTAB was considerably higher than that for their counterparts not modified with CTAB (17.08 m\(^2\) g\(^{-1}\)) (Figure S5), 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.\(^{46}\) 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 \(\text{H}_2\) and \(\text{N}_2\) 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.

References


(10) See the Supporting Information.


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