

(Supporting Information)

Room Temperature Hydrogen Generation from Hydrous Hydrazine for Chemical Hydrogen Storage

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Experimental

General. Commercial chemicals were used as received for catalyst preparation and hydrazine decomposition experiments. Hydrazine monohydrate ($\text{H}_2\text{NNH}_2 \cdot \text{H}_2\text{O}$, 99%), sodium borohydride (NaBH_4 , 99%), hexadecyltrimethyl ammonium bromide (CTAB, 95%), $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ (99.98%), and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (95%) were obtained from Aldrich. K_2PtCl_4 (98%), PdCl_2 (99.9%), $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (95%), IrCl_3 (97%), $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (99.5%), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (99.9%), and CuCl_2 (95%) were purchased from Wako. $\text{Rh}(\text{NO}_3)_3$ was obtained from Cica Reagent.

Instrumentation. Mass analysis of the generated gases was performed using a Balzers Prisma QMS 200 mass spectrometer. Powder X-ray diffraction (XRD) studies were performed on a Rigaku RINT-2000 X-ray diffractometer ($\text{Cu K}\alpha$) for the synthesized Rh(0) nanoparticles (NPs). Scanning electron microscope (SEM, Hitachi S-5000), scanning transmission electron microscope (STEM) and transmission electron microscope (TEM, FEI TECNAI G²) equipped with energy dispersed X-ray detector (EDS) were applied for the detailed microstructure information. Transmission electron microscope (TEM) and selected area electron diffraction (SAED) images were observed on Hitachi H-9000NA. The SEM, TEM and SAED samples were prepared by depositing few droplets of the nanoparticle suspension onto the amorphous carbon coated copper

grids, which were dried in argon atmosphere. The surface area measurements were performed by N₂ adsorption at liquid N₂ temperature using an automatic volumetric adsorption equipment (Belsorp II), for which the samples were pre-treated at 453 K for 5.0 h under vacuum. The pH measurements were performed using a Cyberscan pH 1100 instrument. ¹⁵N NMR spectra were recorded on a JEOL JNM-AL400 spectrometer at an operating frequency of 40.40 MHz. Liquid samples were contained in 5.0-mm-o.d. sample tubes, in which coaxial inserts containing CD₃CN (¹⁵N, δ -134.00 ppm) as an external reference and a lock were placed.

Preparation of Rh(0) NPs. 0.058 g of rhodium(III) nitrate was dissolved in 2.0 mL of distilled water to get a transparent yellow solution, to which 2.0 mL of 0.125 M NaBH₄ aqueous solution was rapidly added. Immediately a black suspension of Rh(0) NPs was formed, which was stirred for 15 min before use for the catalytic reaction.

Preparation of Pt(0), Pd(0), Ir(0), Ru(0), Fe(0), Co(0), Ni(0), and Cu(0) NPs. In general the same process as for the synthesis of Rh(0) NPs was adopted, using respective metal chlorides, K₂PtCl₄ (0.083 g), PdCl₂ (0.035 g), IrCl₃ (0.058 g), RuCl₃·xH₂O (0.041 g), FeCl₂·4H₂O (0.040 g), CoCl₂·6H₂O (0.047 g), NiCl₂·6H₂O (0.047 g), CuCl₂ (0.026 g), in place of the rhodium(III) salt.

Preparation of Rh(0) NPs with CTAB. In a typical synthetic method, rhodium(III) nitrate (0.058 g or 0.029 g) or chloride (0.027 g) along with 0.105 g of CTAB is dissolved in 2.0 mL of distilled water, and stirred for 10 min to get a transparent yellow (NO₃⁻) or orange

(Cl⁻) solution. To this solution 2.0 mL of 0.125 M NaBH₄ aqueous solution is rapidly added and instantly a black foamy suspension of Rh(0) NPs was formed, which was stirred for 15 min before use for the catalytic reactions.

Preparation of Ir(0), Ru(0), and Co(0) NPs with CTAB. A similar procedure as for Rh(0) NPs was adopted, using respective metal chloride salts in place of the rhodium(III) salt.

Hydrazine decomposition reaction. The reactions were carried out at room temperature using a two-necked round bottom flask with one of the flask openings connected to a gas burette. Catalytic decomposition reaction of hydrazine for the release of hydrogen (along with nitrogen) was initiated by stirring the mixture of hydrazine monohydrate (0.1 mL, 1.97 mmol), which was added by a syringe to the reaction flask, and the aqueous suspension of metal NP catalyst (prepared as described above). The gas released during the reaction was passed through a trap containing 1.0 M hydrochloric acid to ensure the absorption of ammonia, of which the volume was monitored using the gas burette. For preparing the samples for ¹⁵N NMR measurements and mass spectral analysis of the released gases the acid trap was not used.

Characterization of Rh(0) NPs. After the reaction the suspension was centrifuged (15000 rpm, 10 min, 298 K) to separate the solution and the Rh(0) NPs, which were washed twice with 5.0 mL of water, dried at 373 K for 10 h and then used for BET, powder XRD, SEM and TEM measurements.

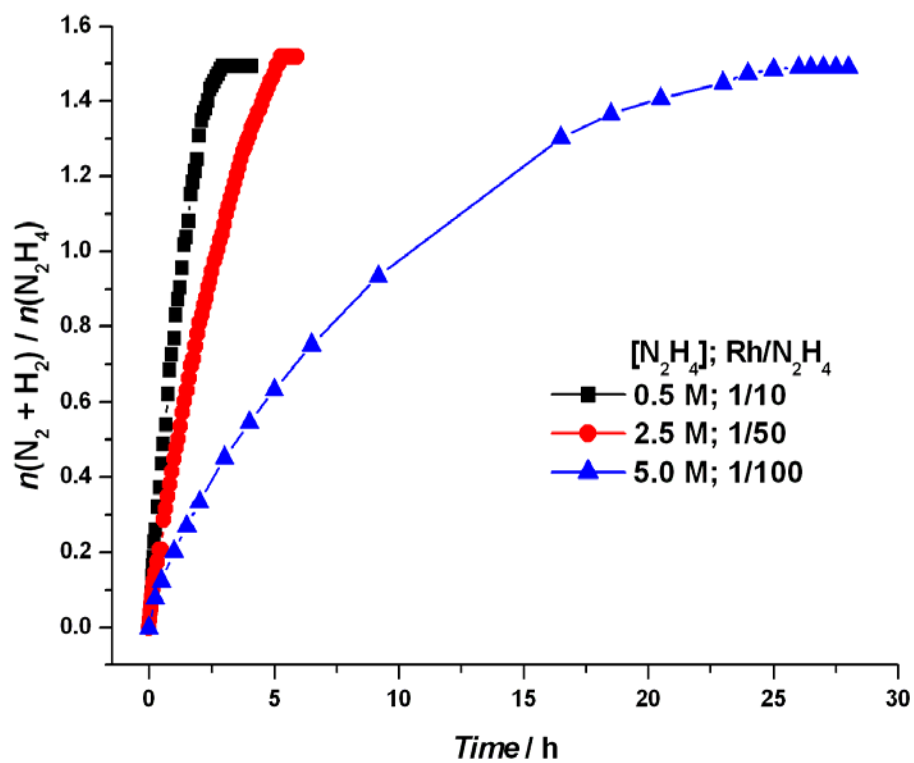


Figure S1. Time course plots for the decomposition of hydrazine in aqueous solutions in the presence of Rh(0) NPs with various hydrazine concentrations, corresponding to various Rh/N₂H₄ ratios, at 298 K.

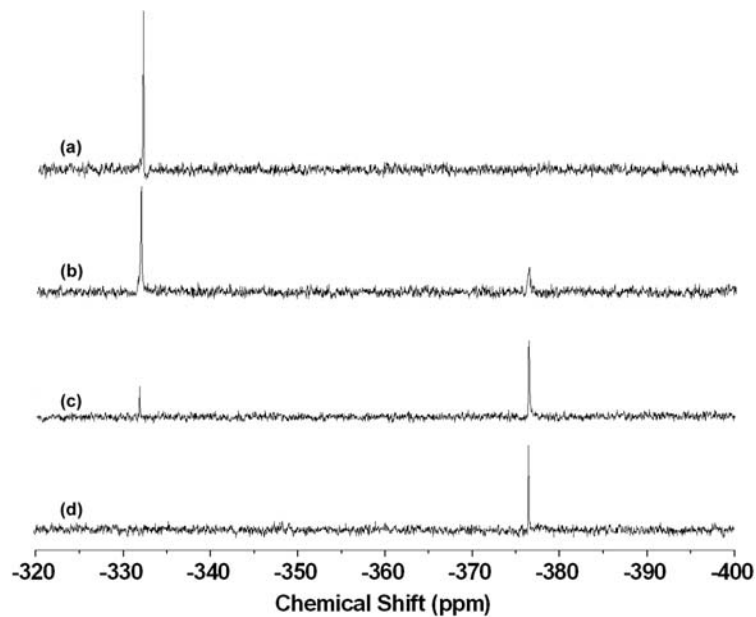


Figure S2. ^{15}N NMR spectra (298 K, referenced to CD_3CN , δ -134 ppm) of (a) aqueous hydrazine solution (5.0 M), (b and c) after the reaction (8 and 16 h) of (a), and (d) after the completion ($n(\text{N}_2+\text{H}_4)/n(\text{N}_2\text{H}_4) = 1.5$) of hydrazine decomposition reaction (26 h) of (a) in the presence of Rh(0) NPs ($\text{Rh}/\text{N}_2\text{H}_4 = 1/100$).

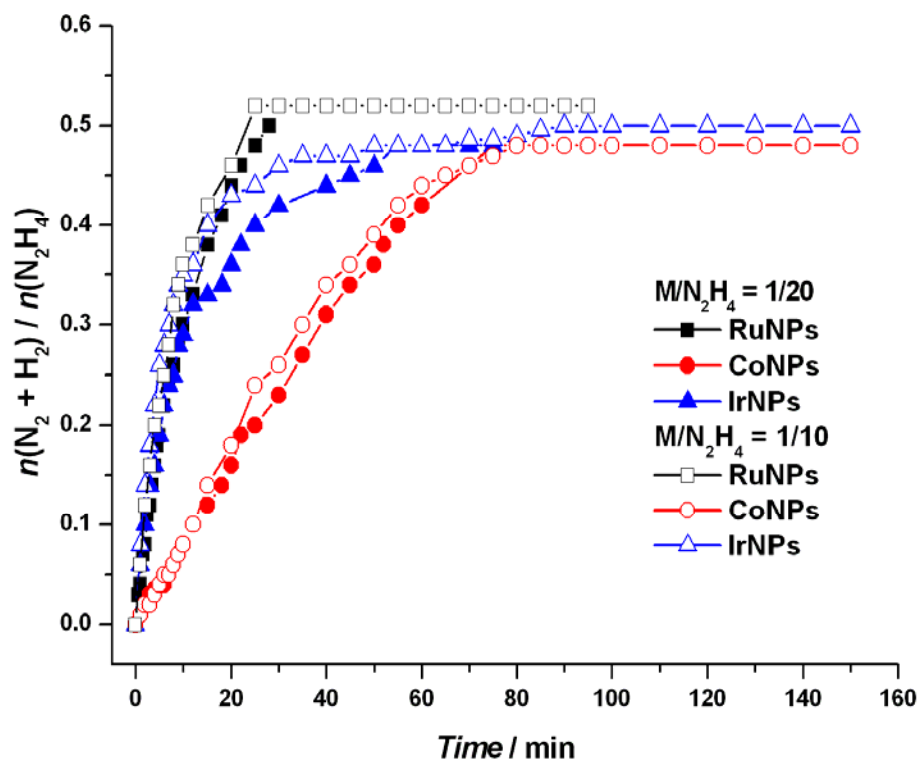


Figure S3. Time course plots for the decomposition of hydrazine in aqueous solutions in the presence of different metal NPs with metal/N₂H₄ molar ratios of 1/10 and 1/20 at 298 K.

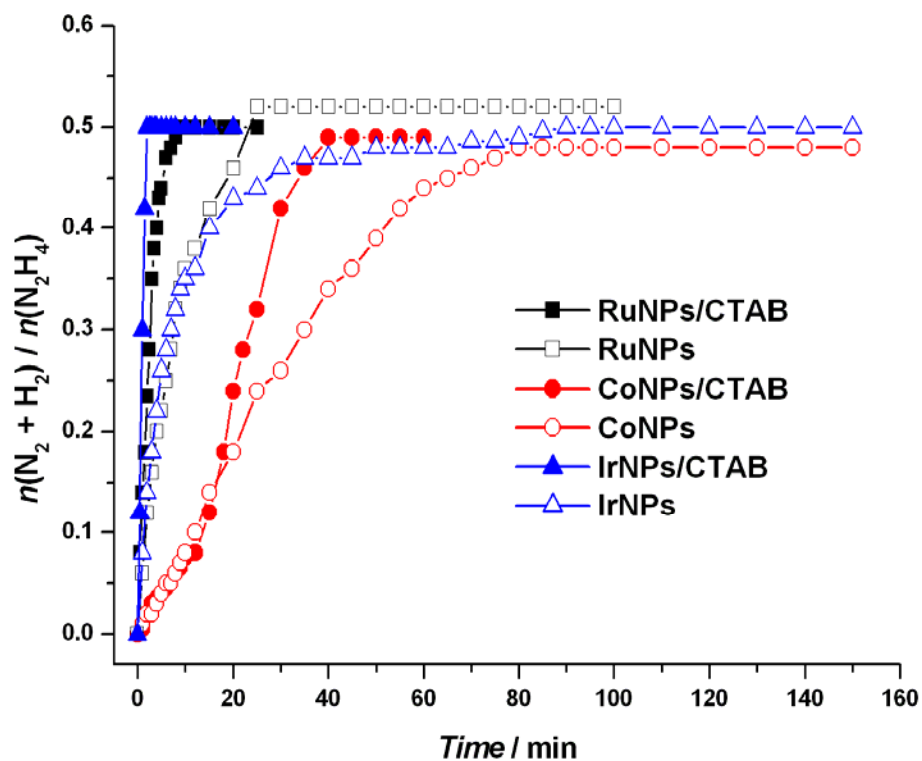


Figure S4. Time course plots for the decomposition of hydrazine in aqueous solutions in the presence of different metal NPs (metal/ $\text{N}_2\text{H}_4 = 1/10$) prepared with and without CTAB at 298 K.

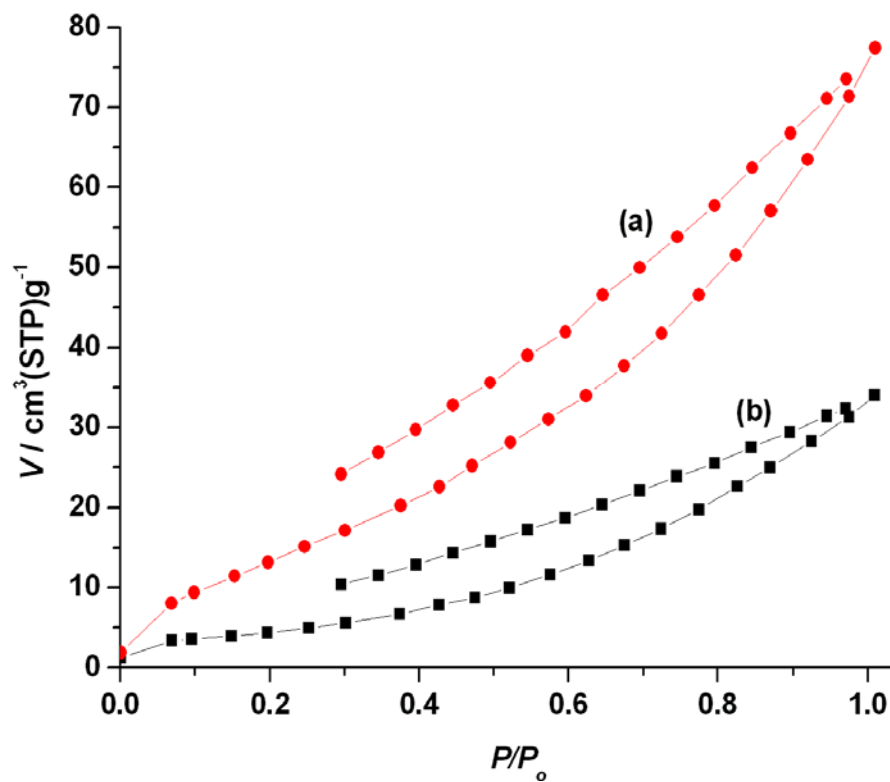


Figure S5. Nitrogen sorption-desorption isotherms at 77 K ($P_0 = 1.0$ atm) for the Rh(0) NPs prepared (a) with and (b) without CTAB.

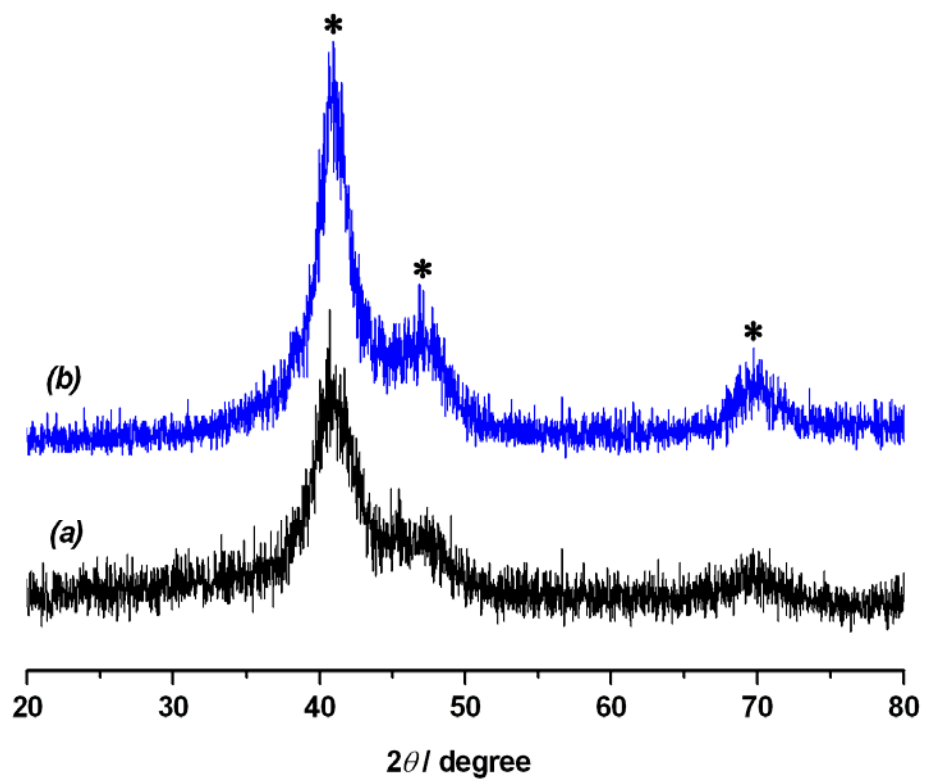


Figure S6. Powder X-ray diffraction profiles for the Rh(0) NPs obtained from $\text{Rh}(\text{NO}_3)_3$ (a) with and (b) without CTAB.

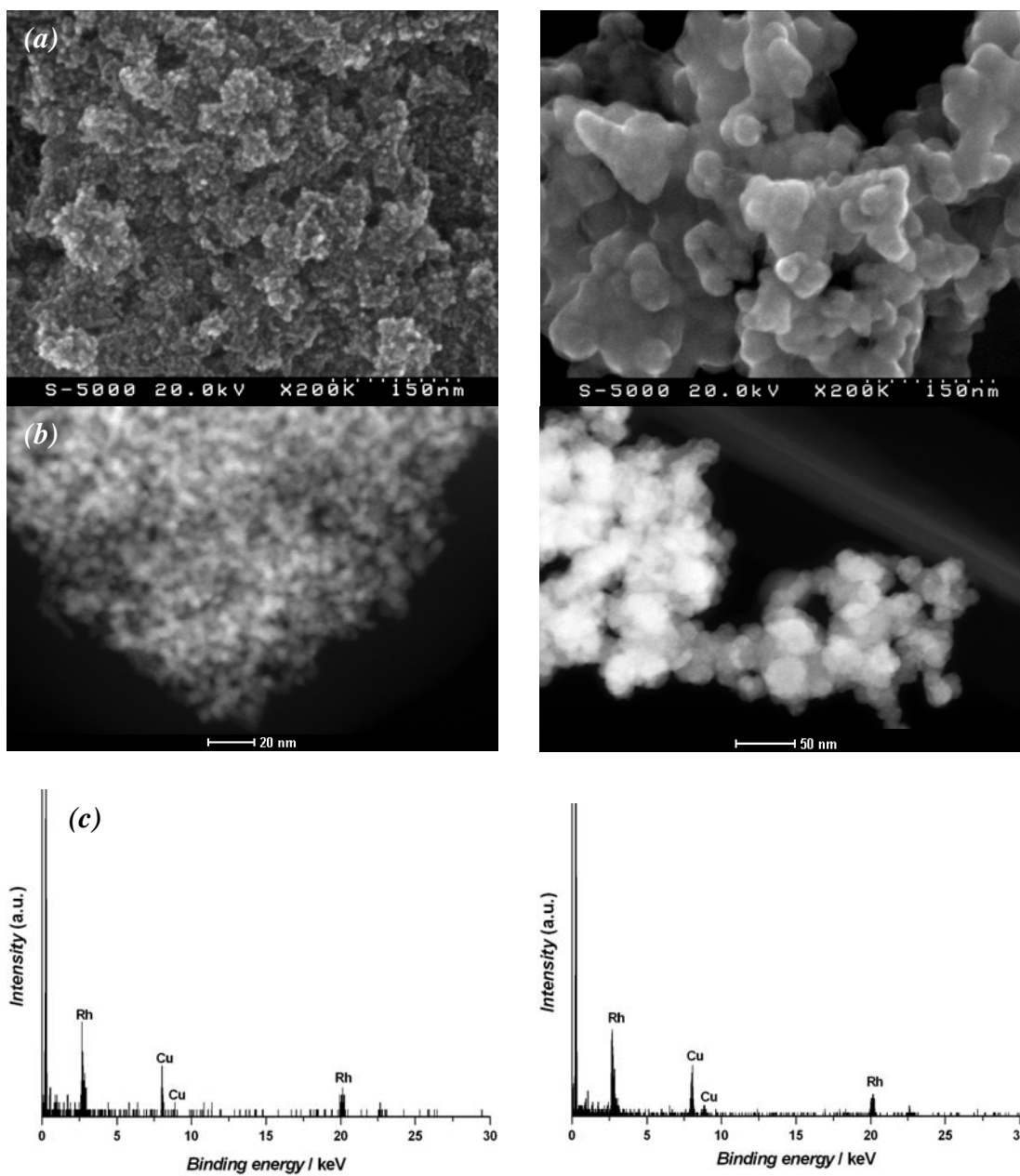


Figure S7. (a) SEM, (b) STEM micrographs, and (c) EDS spectra of Rh(0) NPs obtained with (left) and without (right) CTAB. Cu signals in EDS are from Cu grids.