Supporting Information

Synthesis and Property of Helwingia-Structured Nickel Nitride/Nickel Hydroxide Nanocatalyst in Hydrazine Decomposition

Shirin Norooz Oliaee, Changlin Zhang, Sang Youp Hwang, Harry M. Cheung, and Zhenmeng

Peng*

Department of Chemical and Biomolecular Engineering, The University of Akron, Akron, Ohio

44325, United States

Experimental

Materials

Nickel acetate tetrahydrate (Ni(CH$_3$CO$_2$)$_2$.4H$_2$O, 98%), nickel acetylacetonate (Ni(acac)$_2$, 95%), and anhydrous hydrazine (N$_2$H$_4$, 98%) were purchased from Sigma-Aldrich. hexamethylenetetramine (HMT, C$_6$H$_{12}$N$_4$, 99%) was obtained from Acros Organics. Chloroform (CHCl$_3$, 99.9%) was purchased from Fisher Scientific. Hydrogen (H$_2$, 99.999%), and ammonia (NH$_3$, 99.995%) gases were obtained from Praxair.

Preparation of catalysts

Typically, 2 mmol of nickel acetate and 4 mmol of HMT were dissolved in 35 mL of deionized water under vigorous stirring for 30 min. The mixture was transferred into a 40 mL Teflon-lined autoclave, sealed and heated at 120 °C for 12h. After cooling down to room temperature, the sample was collected by centrifugation and washed with water and ethanol for several times. The final product was obtained by drying the sample at 60 °C overnight. For preparing the H-Ni$_3$N/Ni(OH)$_2$, the Ni(OH)$_2$ nanosheets were heated to 250 °C with a rate of 5 °C/min under flowing NH$_3$ for 20 h. Then the system was cooled down to room temperature under flowing NH$_3$, and the product was collected.

10 wt.% Ni/C was prepared for catalytic performance comparison. It was prepared by dissolving $Ni(acac)_2$ precursor in $CHCl_3$ and impregnating it on carbon support, followed by calcination in air at 300 °C for 1 h and then reduction in H_2 at 300 °C for 1 h.

Characterization

Transmission electron microscopy (TEM) images of catalyst samples were characterized by a JEOL JEM-1230 microscope operated at 120 kV. High-resolution TEM (HRTEM) of individual H-$Ni_3N/Ni(OH)_2$ was taken using a FEI Tecnai G2 F20 microscope operated at 200 kV. The X-ray diffraction (XRD) patterns were recorded on a Bruker AXS Dimension D8 X-Ray diffractometer with Cu Kα radiation source. X-ray photoelectron spectroscopy (XPS) was carried out using a PHI VersaProbe II Scanning XPS Microprobe with Al-K α line excitation source.

Catalytic property test

The experiments were conducted in a semi-batch flask reactor containing 3 mL of water and 30 mg of catalyst. The reaction temperature was controlled using an oil bath. Under magnetic stirring, the reaction was initiated by injecting designated amount of N_2H_4 into the reactor. The amount of generated gas was measured using an airtight gas burette after either or not passing through an ammonia trap. The initial mass activity ($r'_{N2+H2,0}$) was calculated using the following equation:

$$r'_{N2+H2,0} = \frac{1}{W}\frac{dn(N_2+H_2)}{dt}\bigg|_{t=0} = \frac{n(N2H4)0}{W} \frac{d\frac{n(N_2+H_2)}{n(N_2H_4)}}{dt}\bigg|_{t=0}$$

Eq. S1

Where $n(N_2H_4)_0$ is initial mole of hydrazine and W is the total mass of catalyst used and $d[n_{(N2+H4)}/n_{(N2H4)}]/dt$ is obtained by differentiation of the time-course plots.

The overall H_2 selectivity value was determined based on the measured amount of gases using the following equation:

$$Selectivity = \frac{1}{8}(3\frac{n(N_2+H_2)}{n(N_2H_4)} - 1)$$

Eq. S2

The gas effluent was also analyzed using an online gas chromatograph equipped with TCD detector (GC, Shimadzu GC-2014) by flowing Ar carrier gas at 100 sccm through the flask reactor, which carried the gas products to the GC. The flask was been purged with Ar to remove air before hydrazine decomposition. The peak areas for H_2 and N_2 gases were calibrated with standard gas mixture with H_2/N_2 ratio of 2:1.
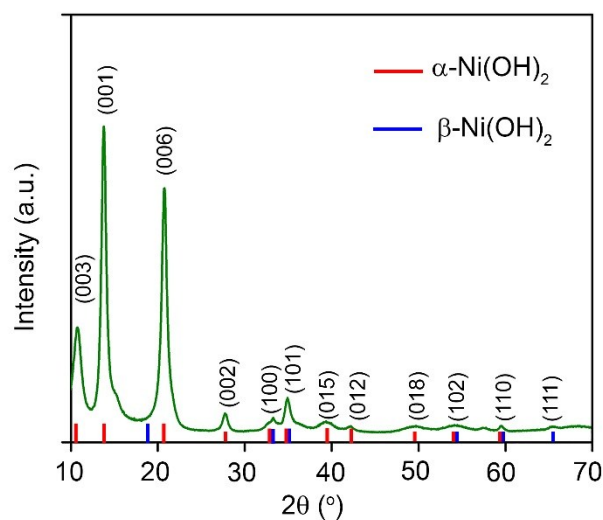

Figure S1. XRD pattern of as-synthesized Ni(OH)$_2$ nanosheets.
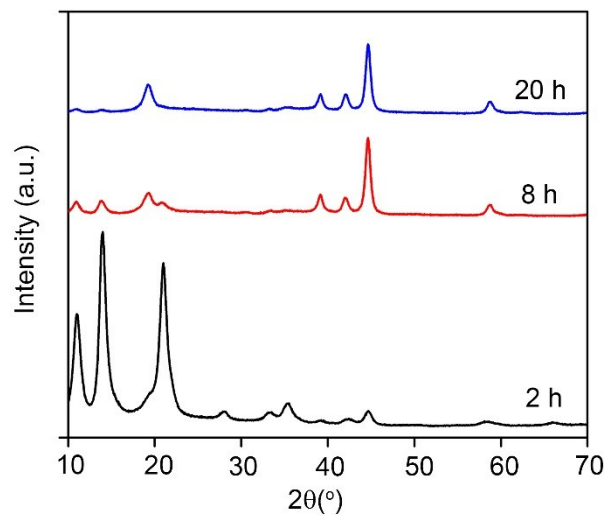
Figure S2. XRD pattern of the H-Ni$_3$N/Ni(OH)$_2$ prepared under NH$_3$ at 250 °C for different reaction time.
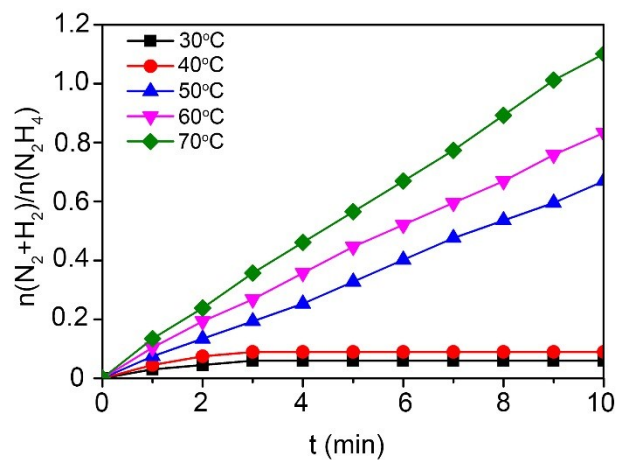

Figure S3. Time-course plot at different temperatures using 10 wt.% Ni/C catalyst with initial hydrazine concentration of 0.1 M and 1 M NaOH solution.
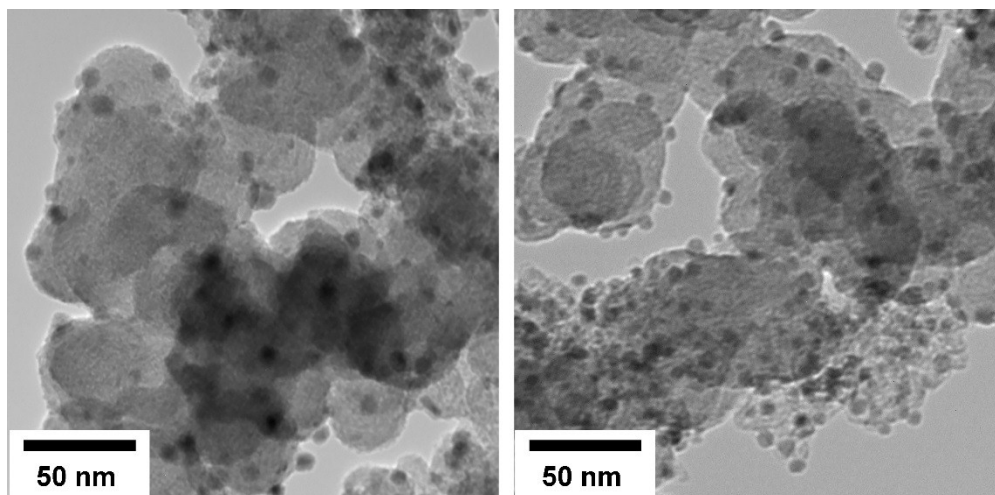
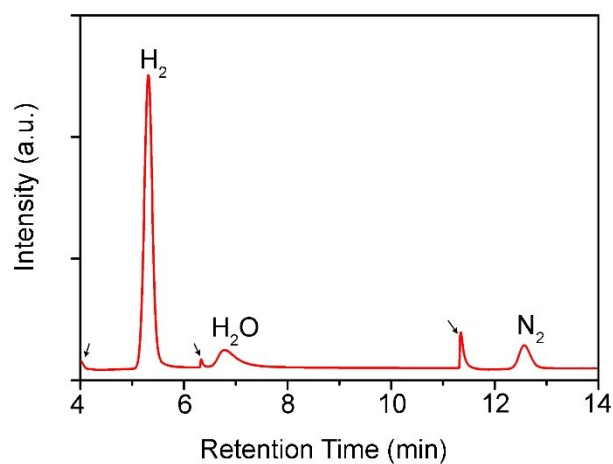**Figure S4.** TEM of (a) fresh and (b) 2-day old 10 wt.% Ni/C.

Figure S5. GC profile for gas products of hydrazine decomposition reaction using 100 mg of $Ni_3N/Ni(OH)_2$ catalyst at temperature of 60 °C and initial hydrazine concentration of 0.3 M. The small black arrows indicate the peaks due to GC channel switch, and they do not represent any chemicals. A cold trap has been used before the products enter GC.
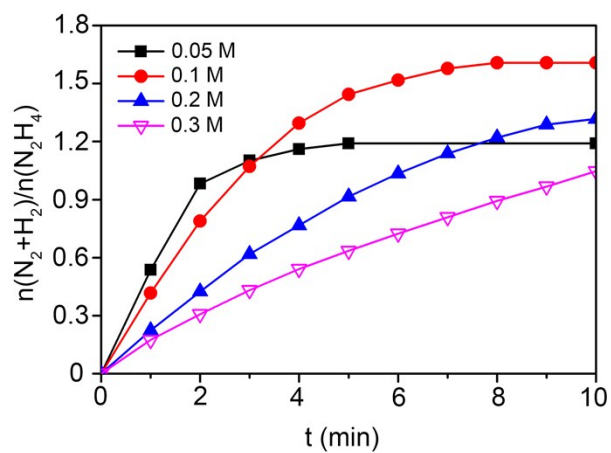
Figure S6. Time-course plot with different initial concentration of hydrazine and using the H-Ni$_3$N/Ni(OH)$_2$ catalyst at 60°C in 1 M NaOH solution.
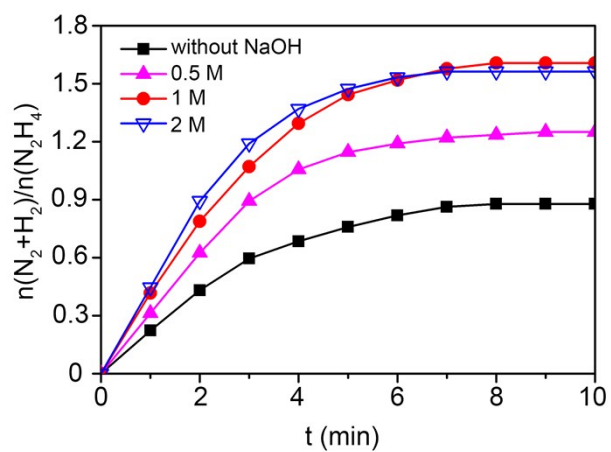

Figure S7. Time-course plot with different concentration of NaOH using the H-Ni$_3$N/Ni(OH)$_2$ catalyst at 60 °C and initial hydrazine concentration of 0.1 M.
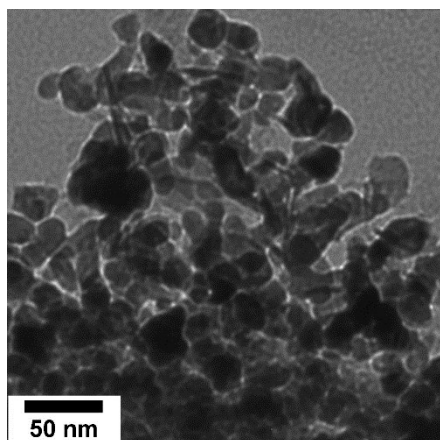
Figure S8. TEM of used H-Ni$_3$N/Ni(OH)$_2$ after hydrazine decomposition.

Table S1. Summary of literature-reported metal nitride catalysts for hydrazine decomposition.

Catalyst	Amount	Temperature (°C)	N$_2$H$_4$ Concentration	N$_2$H$_4$ Conversion%	H$_2$ Selectivity%	Ref
FeN$_x$O$_y$	0.1-0.2 g	60	~3 vol.% N$_2$H$_4$/Ar	100	NA	35
FeN$_x$	0.1-0.2 g	60	3 vol.% N$_2$H$_4$/Ar	100	Negligible at T< 400 °C	35
FeN$_x$	0.1-0.2 g	30	3 vol.% N$_2$H$_4$/Ar	97.2	NA	35
γ-Mo$_2$N	0.1-0.2 g	30	3 vol.% N$_2$H$_4$/Ar	100	Negligible at T< 400 °C	35
NbN	0.1-0.2 g	30	3 vol.% N$_2$H$_4$/Ar	Negligible	NA	35
Fe$_3$N	0.2 g	70	NA	100	NA	40
Mo$_2$N	0.04 cm^3	30	3 vol.% N$_2$H$_4$/Ar	100	Negligible at	39

					T< 400 °C	
Co$_4$N/Al$_2$O$_3$(HT)	50 mg	60	3 vol.% N$_2$H$_4$/Ar	100	NA	41
Co$_4$N/Al$_2$O$_3$(IMP)	50 mg	60	3 vol.% N$_2$H$_4$/Ar	55	NA	41