Highly efficient dehydrogenation of hydrazine over graphene supported flower-like Ni-Pt nanoclusters at room temperature

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Experimental

Chemicals and materials

All chemicals were commercial and used without further purification. nickel chloride hexahydrate (NiCl\textsubscript{2}·6H\textsubscript{2}O, Sinopharm Chemical Reagent Co., Ltd., ≥99%), potassium chloroplatinate (K\textsubscript{2}PtCl\textsubscript{6}, Wuhan Greatwall Chemical Co., Ltd., 99%), hydrazine monohydrate (H\textsubscript{4}N\textsubscript{2}·H\textsubscript{2}O, TCI Shanghai Co., Ltd., >98%), sodium borohydride (NaBH\textsubscript{4}, Sinopharm Chemical Reagent Co., Ltd., 96%), potassium permanganate (KMnO\textsubscript{4}, Shanghai Chemic Co., Ltd., ≥99.5%), hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}, Sinopharm Chemical Reagent Co., Ltd, ≥30%), phosphoric acid (H\textsubscript{3}PO\textsubscript{4}, Sinopharm Chemical Reagent Co., Ltd, AR), sulfuric acid (H\textsubscript{2}SO\textsubscript{4}, Sinopharm Chemical Reagent Co., Ltd, 95~98%), graphite power (Sinopharm Chemical Reagent Co., Ltd, ≥99.85%) were used as received. We use ordinary distilled water as the reaction solvent.

Graphene Oxide (GO) preparation
GO was made by a modified Hummers method [S1-S2]. In an improved synthesis of graphene oxide, a 9:1 mixture of concentrated H$_2$SO$_4$/H$_3$PO$_4$ (360:40 mL) was added to a mixture of graphite flakes (3.0 g) and KMnO$_4$ (18.0 g). The reaction was then heated to 50 °C and stirred for 12 h. The reaction was cooled to room temperature and poured onto ice (~400 mL) with 30% H$_2$O$_2$ (3 mL). The addition of 2 mL of excess H$_2$O$_2$ was followed until observation of a permanent yellow color, which indicating the complete oxidation of graphite. The resultant solution was centrifuged to obtain the product. The product was washed by deionized water, 30% diluted hydrochloric acid and absolute ethyl alcohol for many times and dried under vacuum at 25 °C.

**In situ synthesis of NiPt/graphene catalysts**

In a typical experiment, 8 mg GO were dissolved in 5 mL of water kept in a two-necked round-bottom flask. Ultrasonication was required to get a uniform dispersion. 0.7 mL potassium chloroplatinate solution (0.1 mol L$^{-1}$) and 0.3 mL nickel chloride solution (0.1 mol L$^{-1}$) was added into the flask. The resulting mixture was then reduced by 4 ml of aqueous solution containing 75.8 mg NaBH$_4$ and 80 mg NaOH with vigorous stirring at 25 °C. One neck was connected to a gas burette to monitor the volume of the gas evolution, and the other for the introduction of hydrazine monohydrate (0.1 mL, 1.96 mmol). A water bath was used to control the temperature of the reaction solution at 50 °C. The gas released during the reaction was passed through a HCl solution (1.0 M) before it was measured volumetrically. The selectivity towards H$_2$ generation (X) can be calculated using eqn (3)
\[ X = \frac{(3\lambda - 1)}{8} \quad [\lambda = \frac{n(H_2 + N_2)}{n(H_2NNH_2)}] \quad (3) \]

In order to optimize the reaction condition for catalytic dehydrogenation of hydrazine, the molar ratio of Ni/Pt varied from 1:9, 3:7, 5:5, 7:3, 9:1 in different reaction trials, when the molar ratio of metal to hydrazine was kept as a constant of 0.010. The temperatures were varied from 25 to 60 \(^\circ\)C, to obtain the activation energy (\(E_a\)). 

(metal/N_2H_4\cdotH_2O = 0.005)

Sets of experiments were performed for comparison. Ni/graphene and Pt/graphene were performed in the same way as NiPt/graphene, and a physical mixture of 30\% Ni/graphene and 70\% Pt/graphene is used for testing the catalytic in hydrazine dehydrogenation. The mixture of \(Ni_3Pt_7\) and graphene is following the analogous process.

**Different support**

Sets of experiments with different support (such as SiO\(_2\), PVP and carbon black) were performed at room temperature (25\(\pm\)0.2 \(^\circ\)C). All the experiments were performed in the same way as described in the section 2.3.

**Characterization**

The morphologies and sizes of the samples were observed by using a Titan G2 60-300 Probe Cs Corrector HRSTEM/Tecnai G20 U-Twin transmission electron microscope (TEM) equipped with an energy dispersive X-ray detector (EDX) at an acceleration voltage of 200 kV. Powder X-ray diffraction (XRD) patterns were measured by a Bruker D8-Advance/PANalytical X’Pert Pro X-ray diffractometer.
using Cu Ka radiation source (λ = 0.154178 nm) with a velocity of 1° min⁻¹. FTIR spectra were collected at room temperature using a Thermo FTIR-iS10 instrument with KBr discs in the 400-4000 cm⁻¹ region. Raman spectra were carried out with a confocal Raman microscope (Renishaw, RM-1000) at 514.5 nm excitation wavelength. MS of the generated gases were collected by using a Ametek Dycor mass spectrometer under Ar atmosphere. X-ray photoelectron spectroscopy (XPS) measurement was performed with a Kratos XSAM 800 spectrophotometer.

References:


Figure captions

Figure S1. (left) The HAADF-STEM image for Ni₃Pt₇/graphene. (right) The EDX elemental mapping of the Ni₃Pt₇/graphene.

Figure S2. Raman spectra of GO and Ni₃Pt₇/graphene.

Figure S3. FTIR spectra of GO and Ni₃Pt₇/graphene.

Figure S4. MS profile for the gases released from the decomposition reaction of hydrazine in aqueous NaOH solution (0.5 M) over Ni₃Pt₇/graphene (metal/N₂H₄•H₂O = 0.005) under an argon atmosphere at 25 °C.

Figure S5. (a) Time course plots for hydrogen generation by the decomposition of hydrazine by Ni₃Pt₇/graphene at 25°C, 40°C, 50°C and 60°C. (b) Plot of ln k versus 1/T during the hydrazine decomposition over Ni₃Pt₇/graphene at different temperatures. (metal/N₂H₄•H₂O = 0.005)

Figure S6. The XPS spectra of (a) Pt and (b) Ni in Ni₃Pt₇/graphene before (0 s) and after (514.8 s and 1017.5 s) argon sputtering.

Figure S7. Durability test of Ni₃Pt₇/graphene and for decomposition of hydrazine in aqueous NaOH solution (0.5 M) at 25°C (metal/N₂H₄•H₂O = 0.005). Additional aliquots of hydrazine monohydrate were subsequently introduced into the reaction vessel after the completion of the last runs.
Figure S4

(a) Pt 4f\textsubscript{5/2} and Pt 4f\textsubscript{7/2} intensity (a.u.) vs. binding energy (eV)

(b) Ni 2p\textsubscript{1/2} intensity (a.u.) vs. binding energy (eV)

Figure S5

H\textsubscript{2} and N\textsubscript{2} intensity (a.u.)

Figure S6

(a) Reaction rate vs. time (min)

(b) lnk vs. 1/T

Activation Energy

Er=49.36kJ mol\textsuperscript{-1}
Table S1. Comparison of activities and Ea of different catalysts for hydrogen generation by H$_2$NNH$_2$$\cdot$H$_2$O decomposition.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>T (℃)</th>
<th>TOF(h$^{-1}$)</th>
<th>Ea(kJ/mol)</th>
<th>Reference</th>
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<tr>
<td>G4-OH(Pt$<em>{12}$Ni$</em>{48}$)</td>
<td>70</td>
<td>240</td>
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<tr>
<td>NiFe</td>
<td>70</td>
<td>6.6</td>
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<td>Ni$_3$Pt$_7$/graphene</td>
<td>50</td>
<td>416</td>
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<td>This study</td>
</tr>
<tr>
<td>Ni$<em>{88}$Pt$</em>{12}$/MIL-101</td>
<td>50</td>
<td>350</td>
<td>55.5</td>
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<td>Ni$<em>{80}$Pt$</em>{20}$/ZIF-8</td>
<td>50</td>
<td>90</td>
<td>--</td>
<td>S6</td>
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<tr>
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<tr>
<td>Ni$<em>{0.99}$Pt$</em>{0.01}$</td>
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<td>6</td>
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<td>Raney Ni-300</td>
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<td>114</td>
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<td>NiPt$_{0.05}$/Al$_2$O$_3$</td>
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<td>16.5</td>
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<td>Ni$_3$Pt$_7$/graphene</td>
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<td>68</td>
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<td>This study</td>
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<td>Ni$<em>{0.9}$Pt$</em>{0.1}$/Ce$_3$O$_3$</td>
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<td>S15</td>
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<tr>
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