Ni-polymer Nanogel Hybrid Particles: A New Strategy for Hydrogen Production from
the Hydrolysis of Dimethylamine-Borane and Sodium Borohydride

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Abstract Efficient non-precious metal catalysts are crucial for hydrogen production from borohydride compounds in aqueous media via hydrogen atoms in water. A method for preparing magnetic polymer nanoparticles is developed in this study based on the chemical deposition of nickel onto hydrophilic polymer nanogels. High-resolution transmission electron microscopic and XPS analyses show that Ni exists mainly in the form of NiO in nanogels. Excellent catalytic activities of the nanoparticles are demonstrated for hydrogen generation from the hydrolysis of dimethylamine-borane and sodium borohydride in which the initial turn-over frequencies (TOF) are 376 and 1919 h⁻¹, respectively. Kinetic studies also reveal an Arrhenius activation energy of 50.96 kJ/mol for the hydrolysis of dimethylamine-borane and 47.82 kJ/mol for the hydrolysis of sodium borohydride, which are lower than those catalyzed by Ru metal. Excellent reusability and the use of water for hydrogen production from dimethylamine-borane provide the additional benefit of using a hybrid catalyst. The principle illustrated in the present study offers a new strategy to explore polymer-transition metal hybrid particles for hydrogen energy technology.

Keywords: hydrogen energy; dimethylamine-borane; sodium borohydride; nickel; nanogel.

1. Introduction

In recent years, hydrogen energy has been seen to be an ideal energy source due to its zero carbon emission and high heat of combustion compared with traditional fossil fuels, and hence, hydrogen has attracted enormous attention [1-3]. A hybrid energy system based on renewable energy sources (solar and wind) coupled with hydrogen technology is technically feasible for stand-alone electricity and heat supply for household applications [4,5]. In the field of mobile device applications, proton exchange membrane hydrogen fuel cells can power unmanned aerial vehicles or submarine vehicles [6,7]. From the application point of view, the safe generation of hydrogen is a prerequisite. Hydride compounds, such as sodium borohydride (NaBH_4) and dimethylamine-borane (abbreviated as DMAB) $[(\text{CH}_3)_2\text{NHBH}_3]$, are appropriate materials due to their high efficiency of H_2 production, high stability, and nontoxicity. Their prices are much lower than that of ammonia-borane.

In theory, 1 mole of NaBH_4 can produce 4 moles of H_2 by using hydrogen atoms in water (see Eq. (1)):

while the hydrolysis of DMAB produces 3 moles of H_2 per mole by using 2 moles of water (see Eq. (2)):

Self hydrolysis of DMAB and NaBH_4 is quite slow; however, the reaction can be

greatly accelerated with an appropriate catalyst [3]. Previous studies have shown that catalysts, such as Pt, Ru, Rh, Pd, Ni, Co, Fe [1,8-22], or various metal alloys [23-27] can be used for H₂ production from the hydrolysis of NaBH₄. For H₂ production from DMAB, noble metals, such as Pd, Ru, Rh, Ir, Pt and Re, have been investigated for the catalytic dehydrogenation of DMAB [28-34]; however, these reactions were mostly conducted in neat organic media, where only 1 mole of H₂ per mole of DMAB could be generated. In addition, the limited reserves and high cost of noble metal catalysts have impeded their wide applications. Therefore, it is very important to develop efficient non-precious metal catalysts that are suitable for H₂ production in aqueous media.

To take the advantage of the hydrogen atoms in water, we report here the hydrolysis of DMAB catalyzed by magnetic nickel particles in aqueous solutions. For optimal performance, the Ni particles are prepared by chemical deposition onto hydrophilic polymer nanogel particles without palladium metal activation. Combining the properties of solids and fluids, nanogels (usually in the tens to hundreds of nanometers in diameter) have swellable, porous structures in water or organic solvent and their chemical functionality and interaction with metals can be tailored [35]. A comparison with H₂ production from NaBH₄ solutions is also made for the hybrid catalyst system.

2. Experimental

2.1. Materials

Potassium persulfate, N-isopropyl acrylamide (NIPAM), 2-acrylamide-2-methyl propanesulfonic acid (AMPS), N-tert-butyl acrylamide (NtBAM), methylene-bis-acrylamide (MBAM), sodium potassium tartrate ($C_4H_4O_6KNa$), NaOH, $NiSO_4 \cdot 7H_2O$, DMAB aqueous solution (10.0 wt% concentration) and $NaBH_4$ were purchased from Aladdin Reagent Company (Shanghai) in analytical grade. All of these chemical compounds were used as received, without further purification.

2.2. Preparation of polymer nanogel-supported Ni particles

In a typical synthesis, NIPAM (1.13 g), AMPS (0.104 g), NtBAM (0.254 g), MBAM (0.046 g) and potassium persulfate (0.053 g) were dissolved in water (50 mL) in a three-necked flask with a N_2 gas inlet and a reflux condenser. N_2 gas was bubbled through the mixture with stirring for 20 min to remove oxygen. The mixture was stirred in a water bath at 70 °C. After 5 h, the precipitation polymerization reaction was completed, and copolymer nanogel particles of P(NIPAM-co-AMPS-co-NtBAM) were obtained for the subsequent experiments.

Fifteen milliliters of the above copolymer aqueous dispersions and 1.39 g of $NiSO_4 \cdot 7H_2O$ in 35 mL of water were mixed in a beaker. After stirring for 15 h, the mixture was filtered by a 100-nm pore-sized polyethersulfone membrane filter and then washed three times with distilled water. Next, the Ni^{2+} impregnated copolymer nanogel was dispersed in water (40 mL) and then mixed with $NaBH_4$ (0.10 g in 10 mL H_2O) for 15 h for reduction, resulting in Ni-modified gel particle seeds.

Electroless Ni plating was performed after the Ni-modified gel particle seeds were added to a Ni-complex electroless plating bath with sodium potassium tartrate

(6.5 g), NaOH (3 g), NiSO₄•7H₂O (2.39 g) and NaBH₄ (0.3 g). The mixture was mechanically stirred for 2 h at 90°C. After the reaction, the nanospheres were filtered and dried under vacuum, yielding a black catalyst.

2.3. Catalytic activities of the nanogel-supported Ni particles for H₂ production from NaBH₄

The catalysis reactions were performed in a procedure similar to that of our previous report [36]. Briefly, the nanogel supported catalyst was mixed with 0.095 g of NaBH₄ in a flask that was tightly sealed and positioned in a thermostat bath. Water (50 mL) was charged into the flask by using a syringe. The volume of the H₂ generated was recorded by using an upside-down graded cylinder charged with water, in which the gas can replace the water at different times. The slope of the H₂ volume versus time in the initial linear section can be used to determine the H₂ production rate (k).

2.4. Catalytic activities of the polymer nanogel-supported Ni particles for the hydrolysis of DMAB

The catalysts were mixed with 16 mL of water in a three-necked flask that was tightly sealed and placed in a thermostat bath. Four milliliters of a DMAB aqueous solution was charged into the flask through a syringe to fully reduce the Ni metal. After the reaction, the catalyst was dispersed in 18 mL of water in a 50°C water bath after centrifuging the solution. Next, 2.0 mL of a DMAB aqueous solution was added. The H₂ gas produced thereafter was recorded by using a procedure similar to the above-described measurement of H₂ production from NaBH₄.

The H₂ generation rate was also measured at different solution temperatures (from 308.15 to 328.15 K for NaBH₄ and from 313.15 to 333.15 K for DMAB) to determine the activation parameters involved in the catalytic hydrolysis reaction. The measurement was also undertaken with different amounts of the catalyst (0.002, 0.004, 0.008, and 0.012 g for NaBH₄ and 0.020, 0.025, 0.030, and 0.040 g for DMAB) and different concentrations of DMAB (81, 162, 324, and 486 mM). For the recyclability test, the catalyst was collected by centrifuging from the reaction solutions, washed thoroughly in water, and then used for the next round.

2.5. Characterization of the nanogel-supported Ni particles

The catalyst was investigated using a JEM-2100 electron microscope at an acceleration voltage of 200 kV. The hydrodynamic diameters were measured using a Nanophox dynamic light scattering analyzer (Sympatec GmbH, Germany). The Ni contents were analyzed using a Prodigy XP ICP atomic emission spectrometer (Leeman Labs, USA). K-ALPHA X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific Company) analysis was performed to identify the oxidation state of nickel on the surface of the catalyst.

3. Results and discussion

3.1. Characterization of the polymer nanogel-supported Ni particles

Nanogel-supported Ni particles were prepared by a novel electroless plating process in which the activation of the polymer nanogel particles was achieved by impregnation in a Ni salt solution that replaced traditional noble metal seeding,

followed by chemical reduction. The polymer nanogel particles were prepared by precipitation polymerization of N-isopropyl acrylamide, 2-acrylamide-2-methyl propanesulfonic acid, and N-tert-butyl acrylamide. The Ni-deposited nanogel particles were analyzed using transmission electron microscopy (TEM). Fig. 1(a) shows that nickel is highly dispersed in the polymer nanogel particles (black areas in the image). The average size of the copolymer nanogels before electroless plating is 210 nm, while that after plating is approximately 225 nm. Introduction of nickel does not dramatically expand or shrink the size of the nanogel particles, which is suggestive of the highly porous nature of the nanogels in water. Nickel metal is continuously spread throughout the nanogel particles because of the sufficient number of pores that are present in the hydrophilic particles. Dynamic light scattering characterization of the Ni-embedded nanogel particles in water shows that their hydrodynamic diameters are approximately 411.9 nm, which are larger than those shown in the TEM image because the nanogels swell in water during the light scattering analysis. This result also implies that the surface area characterization of the gel particles in vacuum may not reflect the actual surface areas in the aqueous phase reactions.

For further characterization of the Ni metals in the nanogel particles, their lattice images were obtained by using high-resolution TEM. Fig. 1(b) shows that the lattice spacings of the Ni in the copolymer gel particles are 0.205 nm, which correspond quite well to those of nickel oxide (NiO) (0.208 nm, 200 plane, referring to XRD card 03-065-6920). The lattice spacings are only slightly contracted by 1.44%, which can be interpreted in terms of a lattice stress [37].

The Ni contents in the polymers before and after electroless plating were analyzed by ICP-AES according to the following steps. A certain amount of the particles was mixed with concentrated HCl (37%, 30 mL) for 30 min at 60 °C, followed by centrifugation. The Ni contents in the solution were measured by ICP-AES analysis. The results show that the Ni loading in the polymers is 0.498 wt% after the impregnation (seeding) step and 10.92 wt% after the electroless plating step. The Ni impregnation step can effectively promote Ni loading in the ensuing electroless plating, although Ni-loading from the impregnation is low. Without this seeding step, no deposition is achieved in the polymer nanogel.

The oxidation state of nickel in the nanogel was analyzed by XPS. Fig. 2 shows that there are obvious peaks at 855.6 and 873.1 eV, which are the $2p_{3/2}$ and $2p_{1/2}$ electron binding energies, respectively. These binding energies are close to those of bulk NiO or NiO nanoparticles [38]. Furthermore, obvious shake-up (satellite) peaks can be found in the region at 861.1 and 879.4 eV, further confirming the presence of paramagnetic NiO because neither Ni(0) nor the square-planar Ni(II) complex gives satellite peaks [39]. There are weak peaks at 852.2 and 869.4 eV, which are $2p_{3/2}$ and $2p_{1/2}$ binding energies of Ni(0), respectively. Therefore, the nickel in the catalyst is mainly in the form of NiO, with a minor amount of Ni(0).

3.2. Kinetics of the hydrolysis of DMAB catalyzed by the nanogel-supported Ni particles

As shown in Table 1, in the absence of the catalyst, the hydrolysis of DMAB essentially does not proceed, with a poor H₂ yield of 1.88% in 160 min. Upon adding

the Ni-nanogel catalyst, the H₂ evolution starts immediately, with a turnover frequency (TOF, defined as the amount of H₂ generated per moles of catalyst per unit time) of 376 h⁻¹ in the initial 9 min linear regime (see Fig. 3 and Table 2). The Pd/C catalyst had a TOF value of *ca.* 75 h⁻¹ for the hydrolysis of DMAB (also see Table 2) [3]. In organic solvents, the dehydrogenation reaction of DMAB catalyzed by such precious metals as Ru, Rh, Pd, or Ir has TOF values ranging from only 4.2 to 137 h⁻¹ [29,31] because only 1 mole of H₂ can be generated from each mole of DMAB.

Fig. 3 shows the time-dependent volumes of H₂ generated from the hydrolysis of DMAB starting with a different mass of the catalyst (0.02, 0.025, 0.03, and 0.04 g) at 50°C. The H₂ production rate increases with the catalyst mass. The slope of the H₂ production in the linear section of the initial 9 min can be used to quantify the catalyst activities in Fig. 3. Thus, the initial rates of H₂ production (*k*, in mL min⁻¹) and the TOF values calculated from the amount of H₂ generated per moles of catalyst per hour are listed in Table 1. The *k* value increases with the amount of catalyst, whereas the TOF reaches the maximum (376 h⁻¹) at a catalyst mass of 0.030 g. The use of additional catalyst may lead to the decrease of the catalytic efficiency; therefore, all of the hydrolysis reactions of DMAB are hereafter performed with 0.030 g of the catalyst with a high yield. The inset in Fig. 3 shows the plot of the initial H₂ production rate (*k*, in mL min⁻¹) versus the [Ni] concentration on a double logarithmic scale. A slope of 1.0864 in the inset shows that the reaction is nearly first order in terms of the Ni concentration.

Fig. 4 shows the effect of the DMAB concentration (81, 162, 324, and 486 mM)

in the hydrolysis of DMAB. The volume of H₂ evolved increases along with the DMAB concentration. The inset in Fig. 4 shows the plot of the initial H₂ production rate (k , in mL min⁻¹) versus the DMAB concentration on a double logarithmic scale. A slope of 0.2332 in the inset indicates that the hydrolysis of DMAB catalyzed by the Ni-nanogel catalyst is nearly zero-order with respect to the DMAB concentration.

The following rate equation can be obtained from the data in Figs. 3 and 4,

$$\text{Rate} = -\frac{3 \, d[(\text{CH}_3)_2\text{NHBH}_3]}{dt} = \frac{d[\text{H}_2]}{dt} = k[\text{Ni}]^{1.0864}[(\text{CH}_3)_2\text{NHBH}_3]^{0.2332} \quad (3)$$

Fig. 5 shows time-dependent volumes of H₂ generated in the hydrolysis of DMAB catalyzed by the Ni-nanogel catalyst at different temperatures ranging from 313.15 K to 333.15 K at a fixed amount of catalyst (0.030 g) and DMAB concentration (162 mM). The initial hydrolysis rate (slope k) was determined from the slope of the H₂ generation in the first 9-min region at each temperature. As shown in Fig. 5, the hydrolysis rate (k) clearly increases with the temperature. The activation parameters (activation energy, activation entropy, and activation enthalpy) for the hydrolysis of DMAB were calculated from $\ln k$ versus $1/T$ plot and $\ln(k/T)$ versus $1/T$ plot (see Fig. 6, top panel) according to the following Arrhenius and Eyring equations, respectively,

$$\ln k = \ln A - \left(\frac{E_a}{RT} \right) \quad (4)$$

$$\ln \left(\frac{k}{T} \right) = \ln \left(\frac{k_B}{h} \right) + \frac{\Delta S}{R} - \frac{\Delta H}{R} \left(\frac{1}{T} \right) \quad (5)$$

where T is the absolute temperature (K), R is the gas constant (8.314 JK⁻¹ mol⁻¹), E_a is the activation energy, k is the rate constant, h is the Planck constant (6.626×10⁻³⁴ J

s), k_B is the Boltzmann constant ($1.381 \times 10^{-23} \text{ J K}^{-1}$), ΔS is the activation entropy and ΔH is the activation enthalpy.

The activation energy (E_a) for the hydrolysis of DMAB catalyzed by the Ni-nanogel catalyst is determined to be $50.96 \text{ kJ mol}^{-1}$, while the obtained activation enthalpy and entropy are $48.28 \text{ kJ mol}^{-1}$ and $-78.45 \text{ J mol}^{-1}\text{K}^{-1}$, respectively. The negative entropy implies that the activation fashion in the rate-determining step is possibly composed of the addition of water to the DMAB molecule (associative mechanism). The activation energy is much lower than that of the recently reported Ru nanoparticles for the hydrolysis of DMAB, which is 92.4 kJ mol^{-1} (Table 2) [29].

3.3. Reusability of the nanogel-supported Ni in the hydrolysis of DMAB

To measure the recyclability of the Ni-nanogel catalyst in the hydrolysis of DMAB, the catalyst was collected by centrifuging and re-dispersing in water to conduct the next catalytic run under the same conditions. As illustrated in Fig. 7 (top panel), the conversion in percentage over nine runs changes little after the complete release of H_2 in each of the catalytic runs, and the catalytic activity for the reaction time of 30 min decreases very slowly. The catalytic activities retain 91% of their initial activity at the sixth run and 79% of their initial activity at the ninth run in the hydrolysis of DMAB. This observation indicates that the catalyst can provide a good durability and life time, an important performance for practical applications.

3.4. Kinetics of the hydrolysis of NaBH_4 catalyzed by the nanogel-supported Ni particles

Previous reports have shown that the noble metals of Ru, Rh, and Pd [1,8-10] or

light transition metals of Ni and Co [11-17] could be used for H₂ production from the hydrolysis of NaBH₄. Fig. 8 shows the time-dependent volumes of H₂ generated from the hydrolysis of NaBH₄ catalyzed by the nanogel-supported Ni. The H₂ production process slows down in the final stage of the reaction, partly because of the formation of the by-product; however, this effect does not hinder the reusable performance of the catalyst. Catalysts with masses of 0.002, 0.004, 0.008 and 0.012 g were compared in the hydrolysis of NaBH₄ (0.095 g in 50 g of water) at 45°C (see Fig. 8). The H₂ generation rates (k , in mL min⁻¹) measured from the slopes of the initial production lines and the TOF values are listed in Table 3. In analogy to the hydrolysis of DMAB, the k value of the hydrolysis of NaBH₄ increases with the amount of the catalyst. The inset in Fig. 8 illustrates the plot of the H₂ generation rate (k) versus [Ni] on a logarithmic scale. The slope of 0.5889 in the inset confirms that there is a deviation from the first-order kinetics with respect to the Ni concentration, which might be attributed to the adsorption (and/or deactivation) on the Ni surface by the [BO₂]⁻ by-product. The value of TOF reaches its highest value (1919 h⁻¹) at a catalyst mass of 0.004 g, which is higher than the value for the Ru or Co catalyst in the hydrolysis of NaBH₄ (see Table 4). Therefore, all of the hydrolysis reactions of NaBH₄ in the following experiments are performed with 0.004 g of the catalyst.

The time-dependent volumes of H₂ generated were analyzed for the hydrolysis of NaBH₄ (0.095 g in 50 g of water) in the first 9 min at different temperatures varying from 308.15 K to 328.15 K with the same catalyst amount of 0.004 g. The slopes (k) measured from the H₂ generation rates at different temperatures were used for the

Arrhenius plot and Eyring graph (see Fig. 6 bottom panel). An activation energy (E_a) of 47.82 kJ mol⁻¹, activation enthalpy of 45.17 kJ mol⁻¹, and activation entropy of -90.92 J mol⁻¹K⁻¹ were obtained. The E_a value is lower than that of the Co metal, noble metal Ru, or Raney Ni (see Table 4) [40-43].

3.5. Reusability of the nanogel-supported Ni in the hydrolysis of NaBH₄

The reusability of the nanogel-supported Ni was tested in the hydrolysis of NaBH₄ collected by centrifuging the catalyst. As shown in Fig. 7 (bottom panel), the conversion in percentage of the catalyzed hydrolysis of NaBH₄ after eight runs is approximately 91.6±1.3%. The percentage of the catalytic activity has a slow trend of decline, but still retains at 75% of their initial catalytic activity at the eighth run in the hydrolysis of NaBH₄.

4. Conclusions

This study provides a novel approach for H₂ production from the hydrolysis of dimethylamine-borane and sodium borohydride by nanogel particle-supported Ni catalysts. Compared to most of the reactions conducted in neat organic media, which generate only 1 mole H₂ per mole of DMAB, the H₂ production catalyzed by the current Ni catalysts produces 3 moles of H₂ per mole of DMAB by using hydrogen atoms in water. The obtained Ni catalysts have activities that are higher than those of the Ru and Co catalysts for the hydrolysis of dimethylamine-borane and sodium borohydride. The strong interaction between Ni and the nanogels leads to good durability and recyclability. The catalyst is also recoverable by a magnet, which

simplifies the workup process. The principle and strategy described in this study is generally applicable, and it is expected that more types of nanogel supported transition metals, such as Fe, Co, and Cu, as well as their alloys, should be investigated and explored in the future for H₂ generation.

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Figure Captions

Fig. 1. TEM image of the nanogel-supported Ni particles (black areas) under different magnifications: (a) nickel spheres at 500 nm scale; (b) HRTEM image of nickel spheres at 5 nm scale.

Fig. 2. XPS spectrum of the nanogel-supported Ni particles in 2p electron region.

Fig. 3. Time-dependent volumes of hydrogen generated from the hydrolysis of DMAB catalyzed by Ni-nanogel catalyst with different masses of the catalyst (0.020, 0.025, 0.030, 0.040 g) at 50 °C. The inset shows the hydrogen generation rate versus the Ni concentration relationship in double logarithmic scale.

Fig. 4. Time-dependent volumes of hydrogen generated from the hydrolysis of DMAB catalyzed by the Ni-nanogel catalyst (0.030 g) with different concentrations of DMAB (81, 162, 324, 486 mM) at 50°C. Inset: plot of the initial hydrogen production rate (k , in mL min^{-1}) versus DMAB concentration in double logarithmic scale.

Fig. 5. Time-dependent volumes of hydrogen generated from the hydrolysis of DMAB (162 mM) catalyzed by Ni-nanogel catalyst (0.030 g) at different temperatures ranging from 313.15K to 333.15K.

Fig. 6. Logarithm of the initial hydrogen production rate ($\ln k$) versus $1/T$ plot (solid squares) and $\ln(k/T)$ versus $1/T$ plot (solid circles) for the hydrolysis of DMAB (top panel) and that of NaBH_4 (bottom panel) catalyzed by Ni-nanogel at different temperatures.

Fig. 7. The percentage of conversion and catalytic activity versus catalytic runs by Ni-nanogel catalyst. Top panel: hydrolysis of DMAB catalyzed at 50°C; bottom panel: hydrolysis of NaBH₄ catalyzed at 45°C.

Fig. 8. Time-dependent volumes of hydrogen generated from the hydrolysis of NaBH₄ (0.095 g in 50 g of water) catalyzed by Ni-nanogel catalyst with different masses of the catalyst (0.002, 0.004, 0.008, 0.012 g) at 45°C. The inset shows the hydrogen generation rate versus the Ni concentration relationship in double logarithmic scale.

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Table 1. Effect of catalyst amount on the hydrolysis of DMAB

m (g)	0	0.020	0.025	0.030	0.040
k (mL/min)	0.21	4.24	6.84	8.48	9.15
V (mL)	4	180	184	199	190
Reaction time (min)	160	54	42	30	30
TOF (h ⁻¹)	-	271	363	376	300
Yield (%)	1.88	84.51	86.38	93.43	89.20

Table 2. Comparison of the TOF and E_a of various catalysts for the hydrolysis of dimethylamine-borane

Catalyst	TOF (h ⁻¹)	E_a (kJ/mol)	Ref.
Ru(0) nanoparticles	500	92.4	29
Pd/C	75	ud	3
NiSO ₄ /Na ₂ MoO ₄	2.8	ud	33
NiSO ₄ /Na ₂ WO ₄	4.2	ud	34
NiSO ₄ /KReO ₄	3.6	ud	34
Ni-nanogel	376	50.96	This study

Note: ud denotes undetermined

Table 3. Effect of catalyst amount on the hydrolysis of NaBH₄

m (g)	0	0.002	0.004	0.008	0.012
k (mL/min)	1.30	2.64	5.28	7.05	7.66
V (mL)	75	191	204	206	209
Reaction time (min)	140	300	105	58	40
TOF (h ⁻¹)	-	1840	1919	1280	933
Yield (%)	33.33	84.89	90.67	91.56	92.89

Table 4. Comparison of the TOF and E_a of various catalysts for the hydrolysis of sodium borohydride

Catalyst	TOF (h ⁻¹)	E_a (kJ/mol)	Ref.
Raney Ni	-	63	40
Intrazeolite Co	250	55 ± 2	41
Ru(acac) ₃	792	59 ± 2	42
PAA-Co	183	58 ± 2	43
Ni-nanogel	1919	47.82	This study

TOC Graphic