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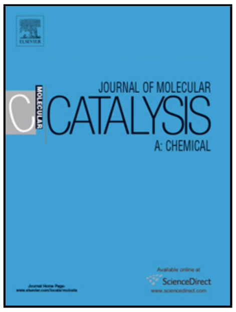

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Inverse relation between the catalytic activity and catalyst concentration for the ruthenium(0) nanoparticles supported on xonotlite nanowire in hydrogen generation from the hydrolysis of sodium borohydride

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Keywords: Sodium borohydride; Hydrogen; Hydrolysis; Ruthenium nanoparticles; Xonotlite nanowire; Inverse TOF dependence

Graphical Abstract

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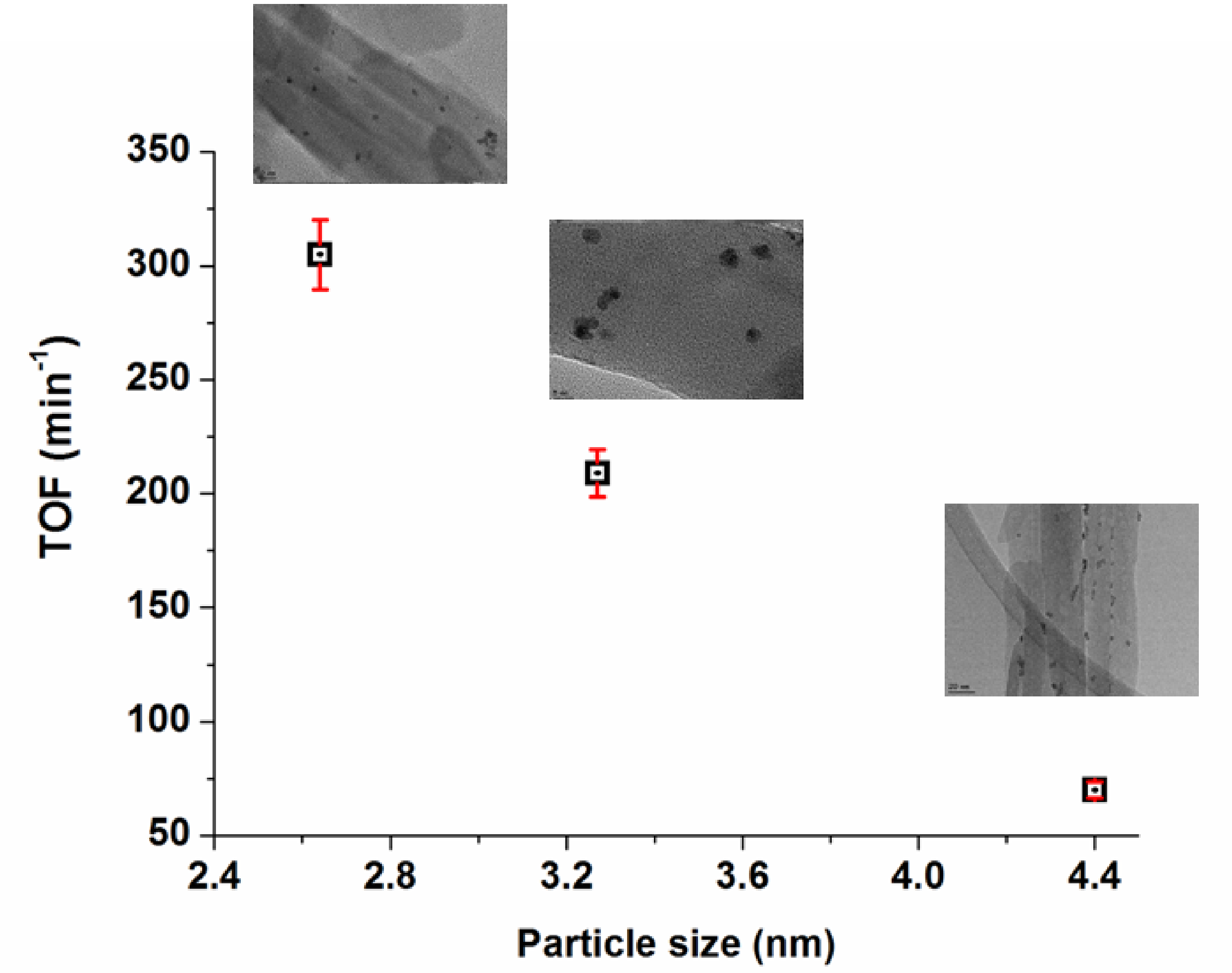

Research highlights

- Formation of ruthenium(0) nanoparticles supported on xonotlite nanowire during the hydrolysis of SB.
- Turnover frequency decreases with the catalyst concentration and particle size.
- High catalytic activity with an initial TOF of 305 min^{-1} in hydrogen generation from the hydrolysis of SB at 25 °C.
- A reusable and long-lived catalyst providing 63,100 turnovers in hydrogen generation from the hydrolysis of SB.

ABSTRACT

Ruthenium(0) nanoparticles supported on xonotlite nanowire (Ru(0)/X-NW) were prepared by the ion exchange of Ru^{3+} ions with Ca^{2+} ions in the lattice of xonotlite nanowire followed by their reduction with sodium borohydride in aqueous solution at room temperature. Ru(0)/X-NW show high catalytic activity and long life time in hydrogen generation from the hydrolysis of sodium borohydride with a turnover frequency value up to 305 min^{-1} and a total turnover number of 63,100 mol H_2 / mol Ru in hydrogen generation from the hydrolysis of sodium borohydride at 25.0 ± 0.1 °C. Moreover, the catalytic activity of Ru(0)/X-NW shows an inverse dependence on the catalyst concentration. Ru(0)/X-NW at different ruthenium concentrations were characterized by high resolution transmission electron microscopy. The results reveal that Ru(0)/X-NW have tunable particle size depending on the metal concentration. An increase in the mean particle size of ruthenium(0) nanoparticles is observed when the metal concentration increases. The smaller particle size distribution at low ruthenium concentrations exhibits higher catalytic activity in hydrogen generation from the hydrolysis of sodium borohydride. The reaction kinetics of the catalytic hydrolysis of sodium borohydride was also studied.

Introduction

Hydrogen has attracted great interest as a globally accepted clean energy carrier. However, secure storage and effective release of hydrogen are very important in the application of hydrogen energy [1]. Among the chemical hydrides tested as hydrogen storage materials for onboard applications [2], sodium borohydride ($NaBH_4$, SB) has been one of the most promising candidates due to its high stability in alkaline solution, non-flammability, non-toxicity in nature, and high hydrogen storage capacity of 10.8 wt% [3]. The hydrolysis of sodium borohydride releases 4 equivalents of H_2 per mole of sodium borohydride according to the equation 1 [4].

$$NaBH_4(aq) + 2H_2O(l) \xrightarrow{\text{catalyst}} NaBO_2(aq) + 4H_2(g) \qquad (1)$$

Since the hydrolysis occurs only in the presence of a suitable catalyst [5] many transition metal nanoparticles including cobalt, nickel, ruthenium, palladium and platinum have been tested as catalyst for this industrially important reaction [6]. Among them, ruthenium is one of the most efficient catalysts in hydrogen generation from the hydrolysis of sodium borohydride [7,8]. Since ruthenium(0) nanoparticles encapsulated in cavities of the zeolite Y support with 3-dimensional confinement have been reported to show the highest catalytic activity in hydrogen generation from the hydrolysis of sodium borohydride [9,10], metal nanoparticles supported on the surface of nanowires are also expected to provide high catalytic activity in the same reaction. However, there exist no report on the use of one-dimensional support for the metal nanoparticles catalyst in the hydrolysis of sodium borohydride. Our recent report [11] has shown that ruthenium(0) nanoparticles supported on xonotlite nanowire ($Ca_6(Si_6O_{17})(OH)_2$, X-NW) [12,13] provide high catalytic activity (a turnover frequency value up to 135 min^{-1}) and unprecedented catalytic lifetime (TTO = 134,100) in hydrogen generation from the hydrolysis of ammonia borane at 25.0 ± 0.1 ºC. These results prompted us to test these ruthenium(0) nanoparticles supported on xonotlite nanowire, Ru(0)/X-NW as catalyst in hydrogen generation from the hydrolysis of sodium borohydride. Indeed, we observed that Ru(0)/X-NW are also highly active and long lived catalyst in this reaction. They provide a turnover frequency value up to 305 min^{-1} and 63,100 turnovers in hydrogen generation from the hydrolysis of sodium borohydride at 25.0 ± 0.1 °C before deactivation. Furthermore, we observed an inverse relation between the catalytic activity (turnover frequency, TOF) and the concentration of ruthenium catalyst. Since the true TOF is expected to be constant for a given metal containing catalyst in a given reaction under specified conditions [14], understanding this inverse relation between the TOF and precatalyst concentration is important. The use of Ru(0)/X-NW as catalyst in hydrogen generation from the hydrolysis of sodium borohydride provides a unique opportunity to investigate the inverse relation between the TOF and ruthenium concentration in terms of increasing particle size. Thus, we were able to report the results of the first investigation on the decrease in catalytic activity with the increasing catalyst concentration in hydrogen generation from the hydrolysis of sodium borohydride.

Experimental section

Materials

$RuCl_3$‡ $3H_2O$, $Ca(NO_3)_2$‡ $4H_2O$, Na_2SiO_3‡ $9H_2O$, and $NaBH_4$ were purchased from Aldrich. Milli-Q System was used to obtain deionized water. All glassware and Teflon-coated magnetic stir bars were cleaned with acetone, followed by copious rinsing with water before drying at 150 − C.

Characterization

Transmission electron microscopy (TEM) was performed on a JEM-2100F (JEOL) microscope operating at 200 kV. Samples were examined at magnification between 100 and 400 K. The details for the characterization of Ru(0)/X-NW can be seen in our recent study [11].

Preparation of xonotlite nanowire [$Ca_6(Si_6O_{17})(OH)_2$]

Xonotlite nanowire (X-NW) was prepared by following the procedure described elsewhere [15]. $Ca(NO_3)_2$‡ $4H_2O$ and Na_2SiO_3‡ $9H_2O$ were dissolved in water in two separate flasks to obtain 0.5 M solution for each. The calcium nitrate solution was added dropwise into the sodium silicate solution at room temperature under stirring to obtain a white suspension. The Ca/Si molar ratio was kept at 1.0. The suspension was transferred into the Teflon-lined stainless-steel autoclave and heated at 200 − C for 24 h. After cooling down to room temperature, the suspension was filtered and washed with water and anhydrous ethanol for three times, respectively. The liquid residue was removed by vacuum filtration, and the remaining xonotlite nanowires were dried at 120 − C for 24 h.

Preparation of ruthenium(III) ion exchanged xonotlite nanowire (Ru^{3+}/X-NW)

Ruthenium(III) cations were introduced onto the xonotlite nanowires by ion exchange of 400 mg xonotlite nanowires in 100 mL aqueous solution of $RuCl_3 \cdot 3H_2O$ (21.83 mg). The slurry was stirred at room temperature for 3 days. The solid Ru^{3+}/X-NW was isolated by centrifugation and washed with 100 mL of water. The solid remnant was dried under vacuum (10^{-3} Torr) at 80 °C.

In situ formation of ruthenium(0) nanoparticles supported on xonotlite nanowire (Ru(0)/X-NW) and concomitant catalytic hydrolysis of SB

Ruthenium(0) nanoparticles supported on xonotlite nanowire were in situ generated from the reduction of Ru^{3+}/X-NW during the catalytic hydrolysis of sodium borohydride by following the procedure as described elsewhere [11]. Before starting the catalyst formation and concomitant catalytic hydrolysis of sodium borohydride, a 20 mL jacketed reaction flask with a Teflon-coated stir bar was placed on a magnetic stirrer (Heidolph MR-301) and thermostated to 25.0 ± 0.1 °C by circulating water through its jacket from a constant temperature bath. Then, a graduated glass tube (60 cm in height and 3.0 cm in diameter) filled with water was connected to the reaction flask to measure the volume of the hydrogen gas generated from the hydrolysis of sodium borohydride. Next, desired amount of Ru^{3+}/X-NW (1.37 wt.% Ru) powder was dispersed in 10 mL water in the reaction flask thermostated at 25.0 ± 0.1 °C. Then, sodium borohydride (38.6 mg, 1.0 mmol) was added into the flask and the reaction mixture was stirred at 1000 rpm. After a short induction period, ruthenium(0) nanoparticles were formed and the concomitant hydrolysis of sodium borohydride started. The volume of hydrogen gas evolved was measured by recording the displacement of water level every 1 min at constant atmospheric pressure of 693 Torr. The reaction was stopped when no more hydrogen evolution was observed. All the hydrogen volume data were corrected by subtracting the self hydrolysis data of sodium borohydride to obtain the volume of hydrogen generated only from the catalytic hydrolysis.

Determination of apparent activation energy for the hydrolysis of sodium borohydride catalyzed by Ru(0)/X-NW

In a typical experiment, the hydrolysis reaction was performed starting with 10 mL of 100 mM sodium borohydride solution and 10 mg Ru^{3+}/X-NW (1.37 wt.% ruthenium, [Ru] = 0.135 mM) at various temperatures of 25, 30, 35, 40, 45 °C to determine the apparent activation energy.

Determination of the catalytic lifetime of Ru(0)/X-NW in the hydrolysis of sodium borohydride

The catalytic lifetime of Ru(0)/X-NW in the hydrolysis of sodium borohydride was determined by measuring the total turnover number (TTO). Such a lifetime experiment was started with a 100 mL solution containing 0.135 mM Ru(0)/X-NW and 30 mM sodium borohydride at 25.0 ± 0.1 °C. When all the sodium borohydride present in the solution was completely hydrolyzed, more sodium borohydride was added and the reaction was continued in this way until no more hydrogen evolution was observed.

Results and Discussion

Xonotlite nanowire (X-NW) was prepared by following the procedure described elsewhere [15]. Fig. 1 exhibits the SEM image, SEM-EDX spectrum and TEM images of xonotlite nanowire indicating that (i) xonotlite nanowire has an average diameter of 36 nm and length of 1.4 μm, and (ii) there is no impurity detected in addition to the framework elements of xonotlite nanowire (Ca, Si, O). Ruthenium(0) nanoparticles supported on xonotlite nanowire (Ru(0)/X-NW) were *in situ* generated from the reduction of ruthenium(III) ions impregnated on X-NW during the hydrolysis of sodium borohydride at room temperature. When sodium borohydride is added to the suspension of xonotlite nanowire containing ruthenium(III) ions, both reduction of ruthenium(III) to ruthenium(0) and hydrogen release from the hydrolysis of sodium borohydride occur concomitantly. The progress of ruthenium(0) nanoparticles formation and concomitant hydrolysis of sodium borohydride was followed by monitoring the change in H_2 pressure which was then converted into the equivalent H_2 per mole of sodium borohydride, using the known 4:1 H_2/SB stoichiometry (Eq. (1)). Fig. 2, shows the plot of equivalent H_2 generated versus time for the hydrolysis of $NaBH_4$ starting with Ru^{3+}/X-NW precatalyst (0.406 mM Ru) and 100 mM $NaBH_4$ in 10 mL aqueous solution at 25.0 ± 0.1 °C. After a short induction period of 2 min, the hydrogen generation starts and continues almost linearly until the release of 4 equiv. H_2 per mole of $NaBH_4$. The observation of an induction period and a sigmoidal shape of dehydrogenation curve indicates the formation of ruthenium(0) nanoparticles with a two-step, nucleation plus autocatalytic growth mechanism [16,17]. Formation kinetics of the $Ru(0)_n$ nanoparticle catalyst can be obtained using the hydrogen release from the hydrolysis of $NaBH_4$ as reporter reaction [18] given in Scheme 1, where P is the added precursor Ru^{3+}/X-NW and Q is the growing $Ru(0)_n$ nanoparticles on the surface of xonotlite nanowire. The hydrogen generation from the hydrolysis of $NaBH_4$ will accurately report on and amplifies the amount of $Ru(0)_n$ nanoparticle catalyst Q present if the dehydrogenation rate is fast in comparison to the rate of nanoparticles formation. Sigmoidal kinetics can be seen in Fig. 2 and fit well by the Finke–Watzky two-step, nucleation, and autocatalytic growth mechanism of nanoparticle formation [16]. The observation of a sigmoidal dehydrogenation curve and its curve-fit to the slow, continuous nucleation, $P \rightarrow Q$ (rate constant k_1) followed by autocatalytic surface growth, $P + Q \rightarrow 2Q$ (rate constant k_2) kinetics are very strong evidence for the formation of metal(0) nanoparticles catalyst from a soluble transition-metal complex in the presence of reducing agent [16]. The rate constants determined from the nonlinear least-squares curve-fit in Fig. 2, given below, are $k_1 = 1.82 \times 10^{-2}$ min^{-1} and $k_2 = 0.089 \times 10^{2}$ M^{-1} min^{-1}. The mathematically required correction has been made to k_2 for the stoichiometry factor of 246 as described elsewhere [17] but not for the “scaling factor”; that is no correction has been made for the changing the number of Ru atoms on the growing metal surface [17]. The large value of k_2/k_1 ratio (4.92×10^{2} M^{-1}) is indicative of the high level kinetic control in the formation of ruthenium(0) nanoparticles from the reduction of the precursor ruthenium(III) ions on the surface of xonotlite nanowire (rate constants k_2 and k_1 were calculated according to the kinetic model equation described elsewhere [11]).

Ru(0)/X-NW was isolated from the reaction solution by centrifugation, copious washing with water, and drying under vacuum (10^{-3} Torr) at 80 °C and characterized by ICP-OES, XRD, SEM, SEM-EDX, TEM, XPS and the N_2 adsorption–desorption technique (See our recent study [11] for the details of the catalyst characterization). It is noteworthy that XPS analysis shows the existence of ruthenium(0) in the samples studied.

Hydrogen generation from the hydrolysis of sodium borohydride catalyzed by Ru(0)/X-NW

A control experiment was performed to check whether xonotlite nanowire show any catalytic activity in the hydrolysis of sodium borohydride before starting the investigation on the catalytic activity of Ru(0)/X-NW. In a control experiment starting with 1.0 mmol SB and 10 mg powder of xonotlite nanowire in 10 mL water at 25.0 ± 0.1 °C or 45.0 ± 0.1 °C, no hydrogen generation was observed in 1 h at both temperatures. This observation indicates that the hydrolysis of sodium borohydride does not occur at an appreciable rate in the presence of xonotlite nanowire in the temperature range used in this study. Ruthenium(0) nanoparticles supported on xonotlite nanowire, Ru(0)/X-NW, are found to be highly active catalyst in hydrogen generation from the hydrolysis of sodium borohydride yielding 4.0 equivalent H_2 gas per mol of SB in the same temperature range.

Fig. 3a shows the plots of equivalent H_2 gas generated per mole of sodium borohydride versus time during the catalytic hydrolysis of 100 mM SB solution using Ru(0)/X-NW with a loading of 1.37% wt Ru in different ruthenium concentration at 25.0 ± 0.1 °C. In each of the experiments, hydrogen evolution starts immediately without induction period and continues almost linearly until the consumption of sodium borohydride present in the solution. The hydrogen generation rate was determined from the linear portion of each plot in Fig. 3a and plotted versus the initial concentration of ruthenium, both in logarithmic scale, in Fig. 3c. This plot gives straight line with a slope of 0.40 indicating that the order of the catalytic hydrolysis of sodium borohydride is 0.40 with respect to the ruthenium concentration. Since all the hydrogen volume versus time plots are linear, it is conceivable that the hydrogen evolution is zero order with respect to sodium borohydride concentration.

The turnover frequency (TOF) value for hydrogen generation from the hydrolysis of sodium borohydride (100 mM) at 25.0 ± 0.1 °C was determined from the hydrogen generation rate in the linear portion of each plot given in Fig. 3a. The TOF value of Ru(0)/X-NW catalyst (Table 1) is as high as 305 min^{-1} (mol H_2/(mol Ru×min)) which corresponds to 1110 mL $H_2/(\text{min}\times g_{cat})$ in the hydrolysis of sodium borohydride at 25.0 ± 0.1 °C. Turnover frequency decreases with the increasing initial concentration of ruthenium in the Ru(0)/X-NW catalyst, down to a value of 35 min^{-1} for the 0.542 mM Ru. An inverse relation between the TOF and ruthenium concentration was observed (Fig.3b) and ascribed to the increasing size of ruthenium(0) nanoparticles. In fact, inverse relationship between the apparent turnover frequency and the concentration of precatalyst or catalyst has been reported for different reactions with different catalysts such as hydrogenation by cobalt(III) acetylacetonate [19], alcohol oxidation by palladium(II) acetate [20], hydrogenation of styrene by osmium [21], Heck reaction by palladium [22,23], heterolysis by cobalt [24], cyclohexene hydrogenation by iridium [25], and methanolysis by rhodium [26]. With one exception of iridium hydrogenation catalyst [25], in all the reports the inverse relationship has been ascribed to the increasing size of nanoparticles. However, only in the case of methanolysis of ammonia borane catalyzed by rhodium nanoparticles, experimental evidence has been provided showing that the decrease in catalytic activity with the increasing catalyst concentration is due to the increasing particles size [26]. Herein we also report that in hydrogen generation from the hydrolysis of sodium borohydride catalyzed by ruthenium(0) nanoparticles, the inverse relation between the TOF and catalyst concentration is in fact due to increasing particle size of Ru(0)/X-NW. Fig. 4 shows the TEM images of Ru(0)/X-NW at different ruthenium concentration along with the associated particle size histogram. The particle size for

Ru(0)/X-NW at three different ruthenium concentrations were determined and given in Table 1. Expectedly, size of ruthenium(0) nanoparticles increases as ruthenium concentration increases while the TOF value decreases in the same direction (Fig. 5). The TOF value of Ru(0)/X-NW in hydrogen generation from the hydrolysis of sodium borohydride decreases as the particle size of the ruthenium(0) nanoparticles increases with the increasing initial concentration of ruthenium (Fig. 5a and Fig. 5b). However, when the TOF values are corrected for the number of ruthenium atoms on the surface of nanoparticle, calculated as described elsewhere [25,27], the inverse relation between the catalytic activity and the size of nanoparticles becomes less perceptible (Table 1). This also indicates that the inverse relation between the catalytic activity and the concentration of ruthenium is indeed a size issue.

Catalytic activity of Ru(0)/X-NW in hydrolysis of sodium borohdyride at room temperature can be compared to that of other reported catalysts such as Co-NP-B-MA (TOF= 48 min^{-1}) [28], PVP/Ru-Pd NPs (TOF= 762 min^{-1}) [29], Ni(0) nanoclusters stabilized on PVP (4250 mL H_2/ ($min×g_{cat}$)) [30], Co-B embedded on B thin film (3375 mL H_2/ ($min×g_{cat}$) [28], acetate stabilized Ru(0) nanoclusters (96,800 mL H_2/ ($min×g_{cat}$)) [31].

Finally, we performed the catalytic hydrolysis of sodium borohydride in the presence of Ru(0)/X-NW at constant $NaBH_4$ (100 mM in 10 mL) and ruthenium (0.135 mM Ru) concentrations at various temperatures in the range of 25-45 °C in order to obtain the apparent activation energy (E_a). The rate constant for the hydrogen generation reactions was calculated from the slope of the linear part of each hydrogen evolution per mole of sodium borohydride versus time plot prepared at various temperatures (Fig. 6a). The apparent activation energy calculated from the slope of the regression line (Fig. 6b) is $E_a = 75 \pm 2$ kJ/mol. The apparent activation energy for the hydrolysis of sodium borohydride catalyzed by Ru(0)/X-NW is comparable with the literature values reported for various catalysts such as Ni(0) nanoclusters stabilized on PVP (E_a = 48 kJ/mol) [30], hydrogen phosphate stabilized Ni(0) NPs (E_a = 54 kJ/mol) [32], acetate stabilized Ru(0) nanoclusters (E_a = 41 kJ/mol) [31], Fe-Co NPs (E_a = 35.6 kJ/mol) [33], 5 wt % Pt/carbon black (E_a = 44 kJ/mol) [28], 10 wt% Pd/carbon black (E_a = 52 kJ/mol) [28], Co-NP-B-MA (E_a = 30 kJ/mol) [28], Co–La–Zr–B nano allloy (E_a = 60 kJ/mol) [34], PVP/Ru-Pd NPs (E_a = 52 kJ/mol) [29], Ni(0)/ Zeolite (E_a = 64 kJ/mol) [35]. It is noteworthy that there is no obvious relation between apparent activation energy value and catalytic activity of a catalyst.

Catalytic lifetime of Ru(0)@X-NW was determined by measuring the total turnover number (TTO) in hydrogen generation from the hydrolysis of sodium borohydride. A catalyst lifetime experiment starting with 10 mg Ru(0)@X-NW in 50 mL of solution of sodium borohydride (100 mM) at 25.0 ± 0.1 °C reveals a minimum of 63,100 turnovers over 101 h in hydrogen generation from the hydrolysis of sodium borohydride before deactivation of the catalyst (Fig. 7). The deactivation of Ru(0)/X-NW catalyst can be attributed to a decrease in the accessibility of active sites of ruthenium nanoparticles due to the passivation of metal surface by metaborate ions which accumulate in solution as the reaction proceeds. In addition, the increase in viscosity of the solution as the reaction proceeds might hinder the diffusion of sodium borohydride, which results in decreasing the catalytic activity [36]. In fact, Ru(0)/X-NW could not be separated from the reaction medium after the lifetime experiment because of the difficulties arising from the high viscosity of reaction medium due to the accumulating metaborate ion. It was impossible to separate small amount of the catalyst (10 mg) from the highly viscous reaction medium containing more than 1 gram BO_2^- ion.

Although it is difficult to propose a specific reason to explain the high activity and long lifetime of Ru(0)/X-NW catalyst, the factors making contribution to the stability include the nature of supporting material (such as surface area, porosity, structure), the identity of metal (generally ruthenium provides high stability), the preparation method of catalysts (such as impregnation, ion exchange method) and the metal-support interactions. In our case, the main contribution to the high stability of Ru(0)/X-NW catalyst is likely from the preparation technique used for the ruthenium(0) nanoparticles: The ruthenium(III) ions are ion-exchanged with calcium(II) ions of the X-NW and then reduced by sodium borohydride whereby the cation-vacancies are re-occupied by sodium ions. In this way, the integrity of support is maintained after nanoparticle formation on the surface of X-NW. The favorable interaction of ruthenium(0) nanoparticles with the surface of support might also provide significant contribution to the high activity and long life time of Ru(0)/X-NW catalyst.

Hydrolysis of sodium borohydride reaction was continued until hydrogen gas evolution was slowed down to the self-hydrolysis level. Self-hydrolysis of sodium borohydride occurs even at ambient temperature at much slower rates compared to the hydrolysis catalyzed by Ru(0)/X-NW. Under our experimental conditions, the self-hydrolysis of sodium borohydride liberates nearly 12 mL of H_2 gas in 1 h while the catalytic hydrolysis of sodium borohydride in the presence of Ru(0)/X-NW can generate 182 mL H_2 gas in 1 h at 25.0 ± 0.1 °C. The self-hydrolysis of sodium borohydride is slow but not negligible, and therefore, we have taken it into account during the catalytic life time test. Note that all the hydrogen volume data were corrected by subtracting the self hydrolysis data of $NaBH_4$ in order to obtain the volume of hydrogen generated only from the catalytic reaction.

As shown in Fig. 7, Ru(0)/X-NW provide an unprecedented TTO value for hydrogen generation from the hydrolysis of sodium borohydride as compared to other catalysts such as hydrogen phosphate stabilized Ni(0) NPs (TTO= 1450), acetate stabilized Ru(0) nanoclusters (TTO= 5170) [31], Ni(0) nanoclusters stabilized on PVP (TTO = 8700) [30], Ni(0)/ Zeolite (TTO=19,400) [35].

Conclusion

In summary, ruthenium(0) nanoparticles supported on xonotlite nanowire (Ru(0)/X-NW) show high catalytic activity and long life time providing an initial turnover frequency of 305 min^{-1} and 63,100 turnovers over 101 h in hydrogen generation from the hydrolysis of sodium borohydride at 25.0 ± 0.1 °C. Most interestingly, an inverse relation between the catalytic activity of Ru(0)/X-NW and the catalyst concentration is observed for this hydrolysis reaction. The decrease in turnover frequency with the increasing concentration of ruthenium was shown to due to the increase in particle size with the increasing catalyst concentration. The mean particle size of Ru(0)/X-NW, formed from the reduction of Ru^{3+}/X-NW during the hydrolysis of sodium borohydride at room temperature, increases with the increasing initial ruthenium concentration. Thus, the size of ruthenium(0) nanoparticles supported on xonotlite nanowire can be tuned by varying the initial concentration of precatalyst. As the mean particle size increases, the fraction of catalytically active ruthenium atoms on the surface over the total ruthenium atoms decreases, so does the catalytic activity.

The facile preparation, high catalytic activity, high stability, and long life time of ruthenium(0) nanoparticles supported on the surface of xonotlite nanowires make them promising candidate to be exploited as catalyst in releasing hydrogen from the hydrolysis of sodium borohydride which has been considered as hydrogen storage materials for portable application systems.

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Figure Captions:

Figure 1 (a) SEM image, (b) SEM-EDX spectrum, (c) and (d) TEM images of xonotlite nanowire with two different magnifications.

Figure 2 Plot of equivalent H_2 generated versus time for the hydrogen generation from the hydrolysis of sodium borohydride starting with 30 mg Ru^{3+}/ X-NW (with a loading of 1.37 wt% Ru) as catalyst and 1.0 mmol $NaBH_4$ in 10 mL of aqueous solution at 25.0 ± 0.1 °C. The sigmoidal curve fits well to the two-step mechanism for the ruthenium(0) nanoparticle formation.

Figure 3 (a) mol H_2/mol $NaBH_4$ versus time graph depending on the ruthenium concentration in Ru(0)/X-NW for the hydrolysis of SB (100 mM) at 25.0 ± 0.1 °C. (b) The TOF values of the catalyst at different Ru concentrations. (c) The logarithmic plot of hydrogen generation rate versus the Ru concentration; ln(rate) = 0.40 ln[Ru] + 1.87.

Figure 4 TEM images of Ru(0)/X-NW for (a) 0.0135 mM Ru, (b) 0.0338 mM Ru, (c) 0.203 mM Ru (the TEM images were taken from the samples harvested after the hydrolysis of sodium borohydride) and Histograms showing particle size distribution of (d) 0.0135 mM Ru (mean diameter: 2.64 ± 0.09 nm), (e) 0.0338 mM Ru (mean diameter: 3.27 ± 0.15 nm), (f) 0.203 mM Ru (mean diameter: 4.40 ± 0.40 nm)

Figure 5 (a) The plots of TOF and particle size of Ru(0)/X-NW versus the ruthenium concentration, (b) The plot of TOF versus the particle size of Ru(0)/X-NW for hydrogen generation from the hydrolysis of sodium borohydride at 25.0 ± 0.1 °C.

Figure 6 (a) The evolution of equivalent hydrogen per mole of SB versus time plot for the hydrolysis of SB starting with Ru(0)/X-NW (0.135 mM Ru) and 100 mM SB at various temperatures. (b) The Arrhenius plot for the Ru(0)/X-NW catalyzed hydrolysis of SB. In*k*= -8959.66(1/T) + 31.06.

Figure 7 The variation in turnover number (TON) and turnover frequency (TOF) during the catalytic lifetime experiment performed starting with 10 mg Ru(0)/X-NW (ruthenium loading = 1.37% wt Ru, and [Ru] = 0.0271 mM) in 50 mL solution of sodium borohydride at 25.0 ± 0.1 °C.

Scheme 1 Illustration of the hydrogen release from the catalytic hydrolysis of sodium borohydride as reporter reaction: P is the precursor Ru^{3+}/X-NW and Q is the growing Ru(0)n nanoparticles on the surface of xonotlite nanowire.

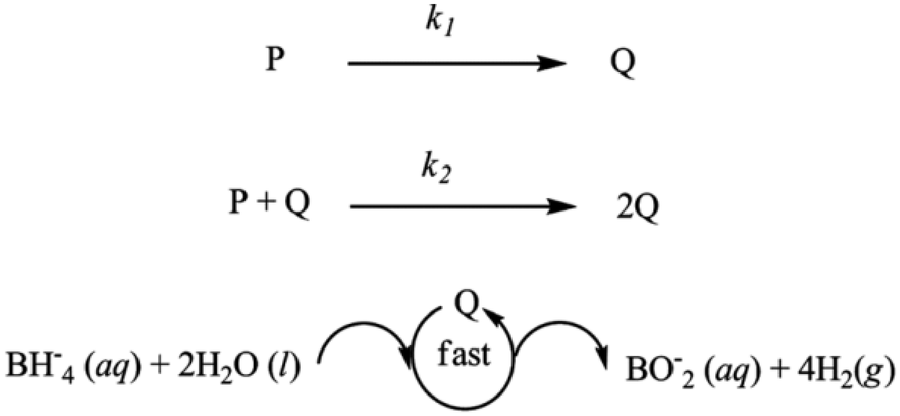


Table 1 The apparent turnover frequency (TOF_{app}=mol H_2×mol Ru^{-1}×min^{-1}), the corrected turnover frequency ($TOF_{corrected}$, the value corrected for the surface atoms), and the particle size of Ru(0)/X-NW with standard deviation in parentheses depending on the ruthenium concentration ([Ru]) of the catalyst in hydrogen generation from the hydrolysis of sodium borohydride at 25.0 ± 0.1 °C. [a] TOF_{app} values were calculated from the total ruthenium content without correction by the fraction of active sites.[b] $TOF_{corrected}$ values were determined by estimating the fraction of surface atoms which were calculated from the ratio of number of surface Ru atoms to the total number of Ru atoms. The total number of Ru atoms in a nanoparticle was estimated by using the equation given elsewhere [24], $n = (N_0 \rho(4/3)\pi(D/2)^3)/W$, where n = number of Ru atoms, $N_0 = 6.022 \times 10^{23}$ mol^{-1}, ρ = room-temperature density of ruthenium (12.45 g/cm^3), D = diameter of ruthenium nanoparticles, W= atomic weight of ruthenium (101.07 g/mol). The number of surface Ru atoms was estimated from full-shell "magic number" approach described elsewhere [24]. From these calculations, the percentage surface atoms were found as 42%, 36% and 27% for the Ru nanoparticles with average diameters of 2.64 nm, 3.24 nm and 4.4 nm, respectively. The TOF_{app} is divided by the surface fraction to obtain the $TOF_{corrected}$ value.

[Ru] mM	**TOF_{app} (min^{-1})[a]**	**Particle size (nm) (standard deviation)**	**$TOF_{corrected}$ (min^{-1})[b]**
0.0135	305	2.64 (0.96)	726
0.034	209	3.24 (0.95)	581
0.068	105	-	-
0.135	79	-	-
0.203	70	4.40 (1.40)	259
0.271	48	-	-
0.406	41	-	-
0.542	35	-	-

Fig.1

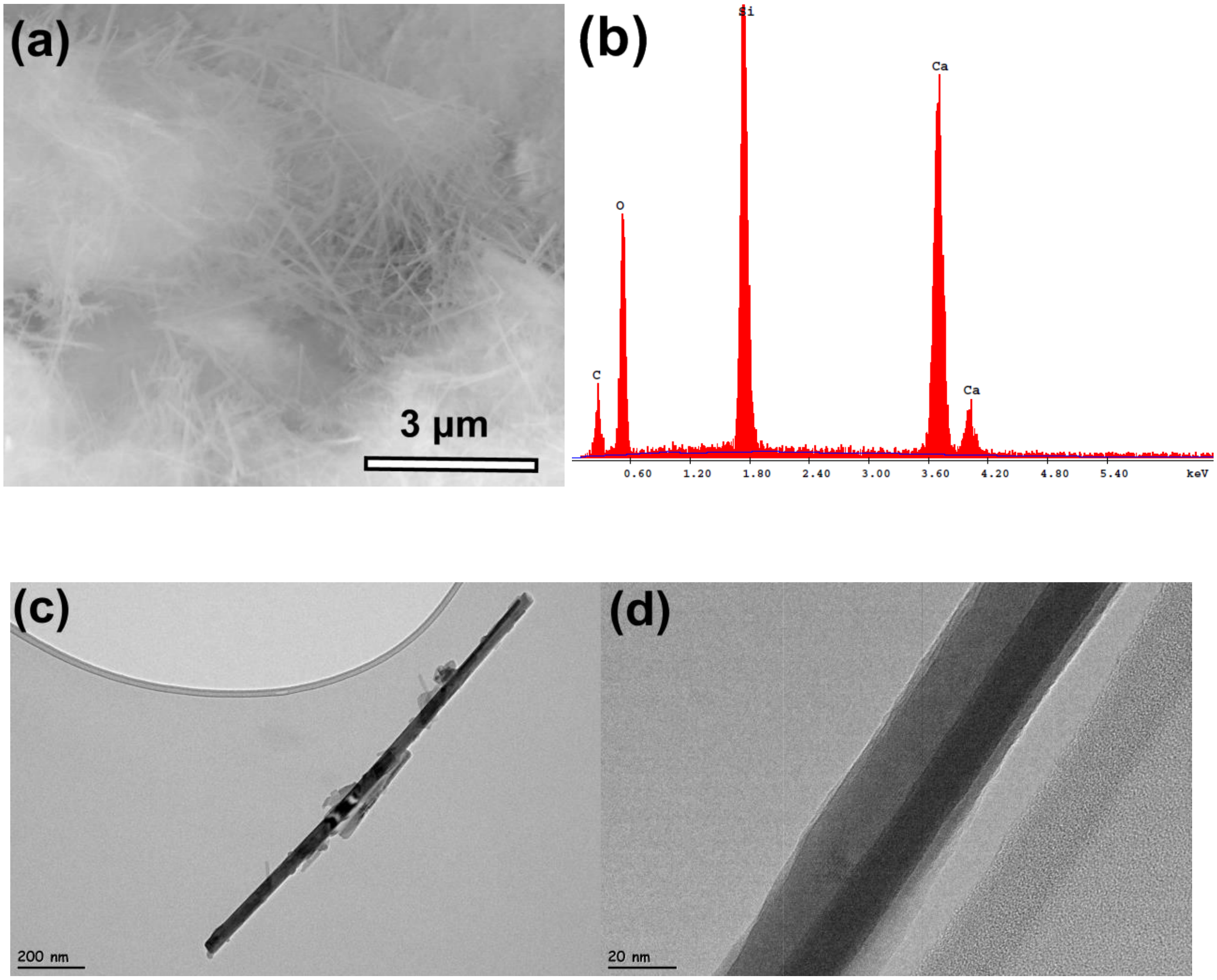

(a)
3 μm
(b)
Si
Ca
O
C
Ca
0.60
1.20
1.80
2.40
3.00
3.60
4.20
4.80
5.40
keV
(c)
200 nm
(d)
20 nm

Fig.2

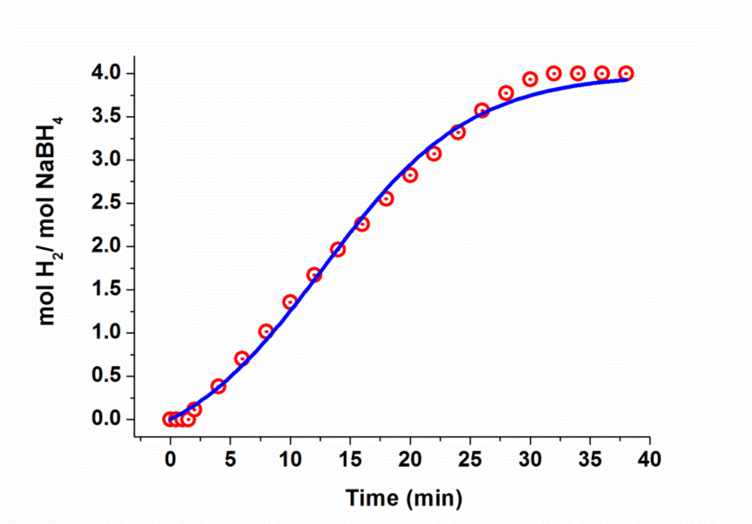

mol H_2/ mol $NaBH_4$
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
5
10
15
20
25
30
35
40
Time (min)

Fig. 3

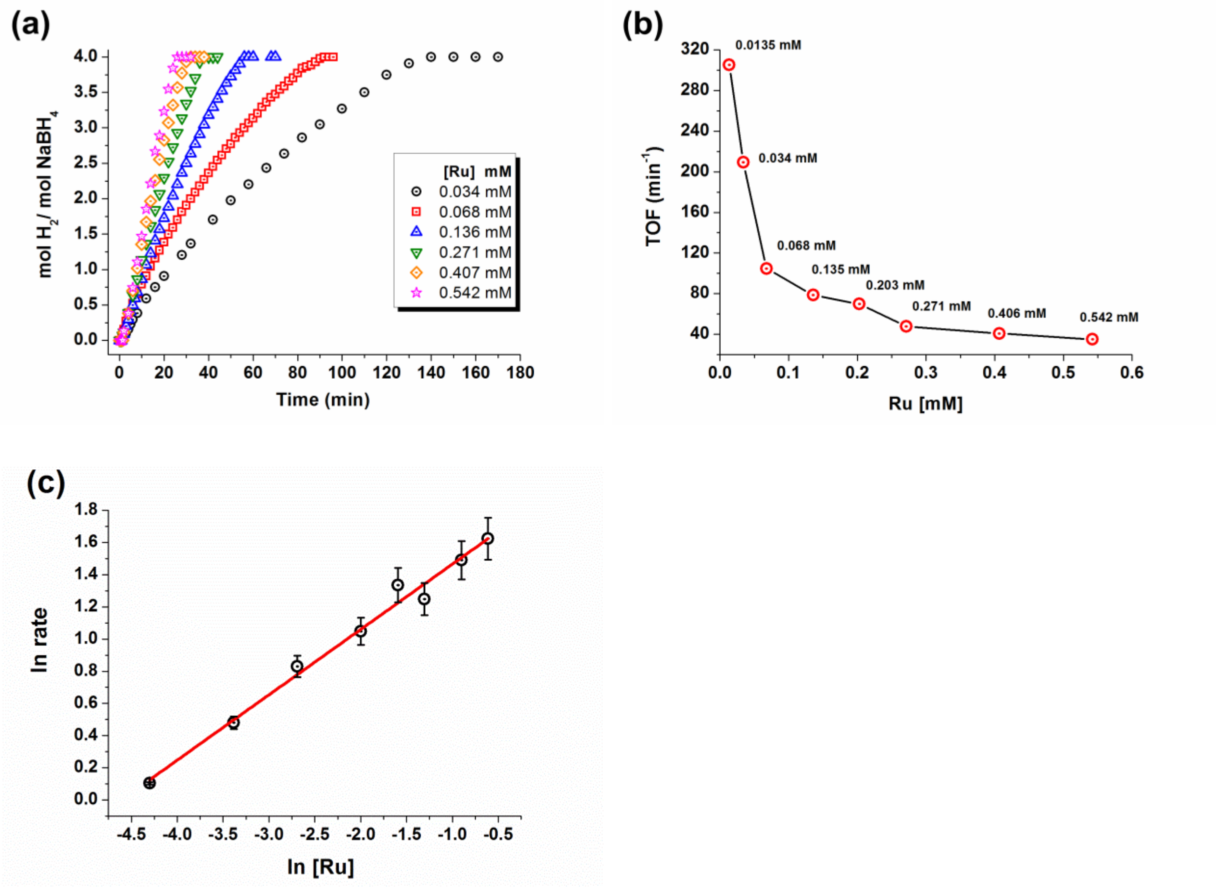

(a)
mol H$_2$ / mol NaBH$_4$
Time (min)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
0
20
40
60
80
100
120
140
160
180
[Ru] mM
0.034 mM
0.068 mM
0.136 mM
0.271 mM
0.407 mM
0.542 mM
(b)
TOF (min^{-1})
Ru [mM]
40
80
120
160
200
240
280
320
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.0135 mM
0.034 mM
0.068 mM
0.135 mM
0.203 mM
0.271 mM
0.406 mM
0.542 mM
(c)
ln rate
ln [Ru]
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
-4.5
-4.0
-3.5
-3.0
-2.5
-2.0
-1.5
-1.0
-0.5

Fig.4

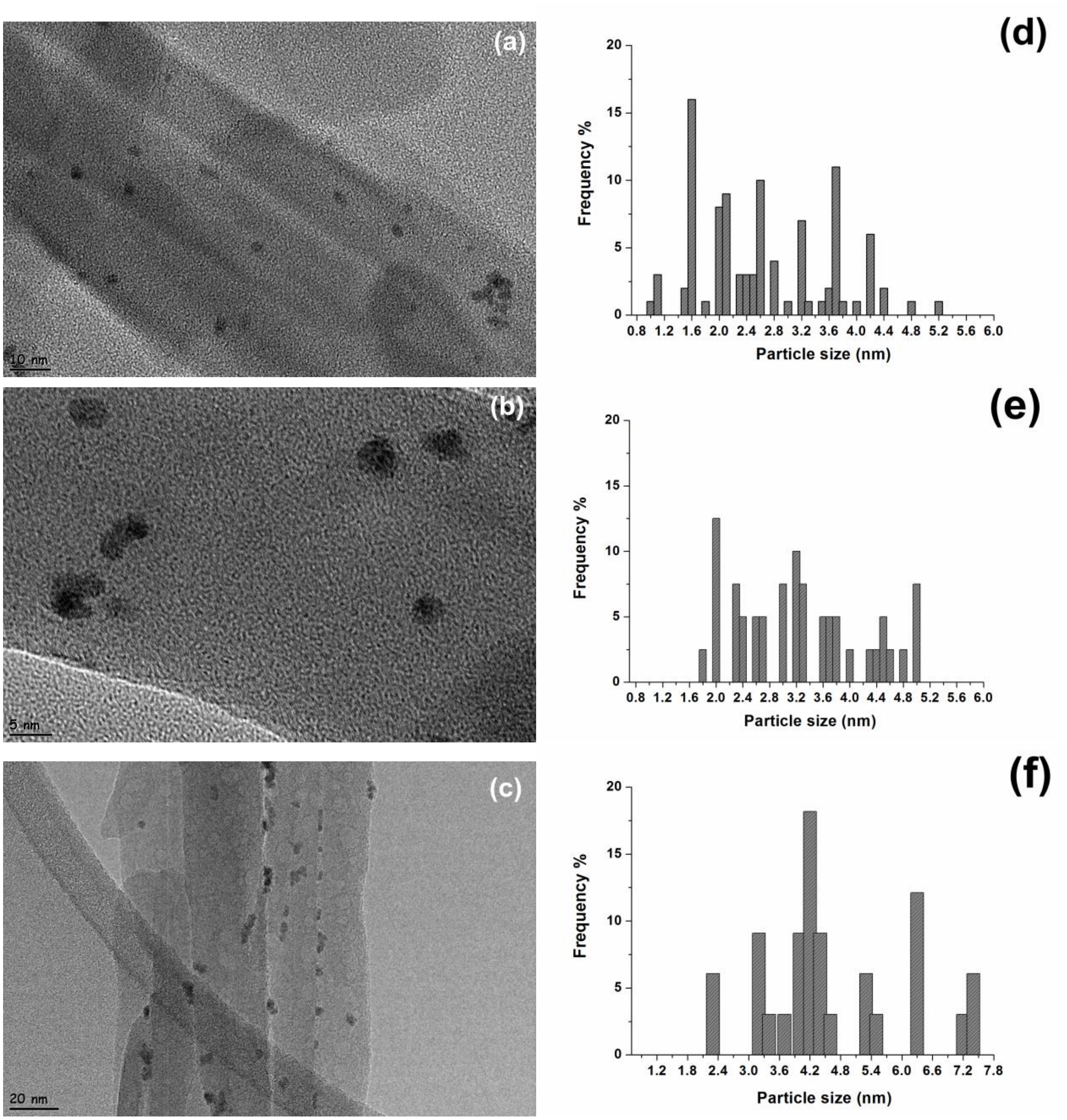

(a)
10 nm
(b)
5 nm
(c)
20 nm
(d)
Frequency %
20
15
10
5
0
0.8 1.2 1.6 2.0 2.4 2.8 3.2 3.6 4.0 4.4 4.8 5.2 5.6 6.0
Particle size (nm)
(e)
Frequency %
20
15
10
5
0
0.8 1.2 1.6 2.0 2.4 2.8 3.2 3.6 4.0 4.4 4.8 5.2 5.6 6.0
Particle size (nm)
(f)
Frequency %
20
15
10
5
0
1.2 1.8 2.4 3.0 3.6 4.2 4.8 5.4 6.0 6.6 7.2 7.8
Particle size (nm)

Fig.5

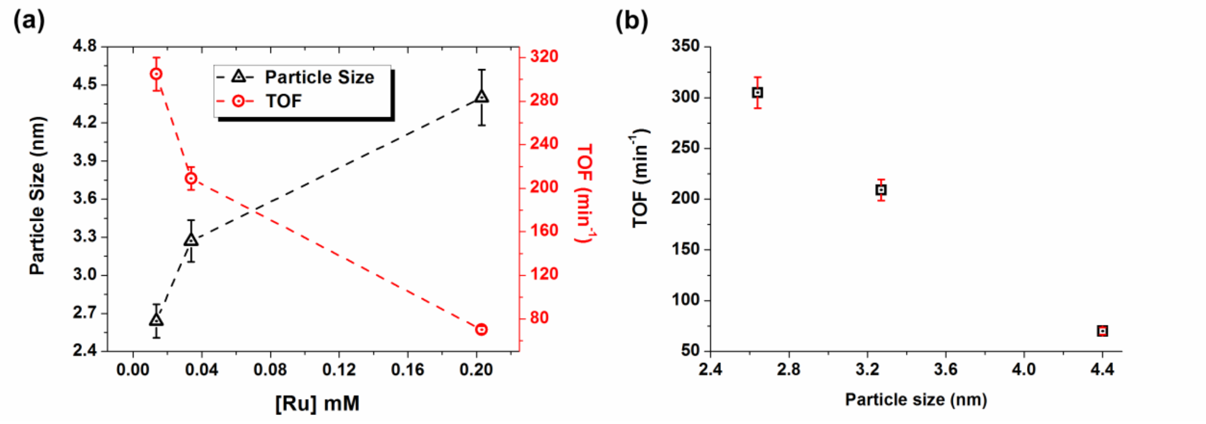

(a)
Particle Size (nm)
4.8
4.5
4.2
3.9
3.6
3.3
3.0
2.7
2.4
0.00
0.04
0.08
0.12
0.16
0.20
[Ru] mM
TOF (min^{-1})
320
280
240
200
160
120
80
Particle Size
TOF
(b)
TOF (min^{-1})
350
300
250
200
150
100
50
2.4
2.8
3.2
3.6
4.0
4.4
Particle size (nm)

Fig.6

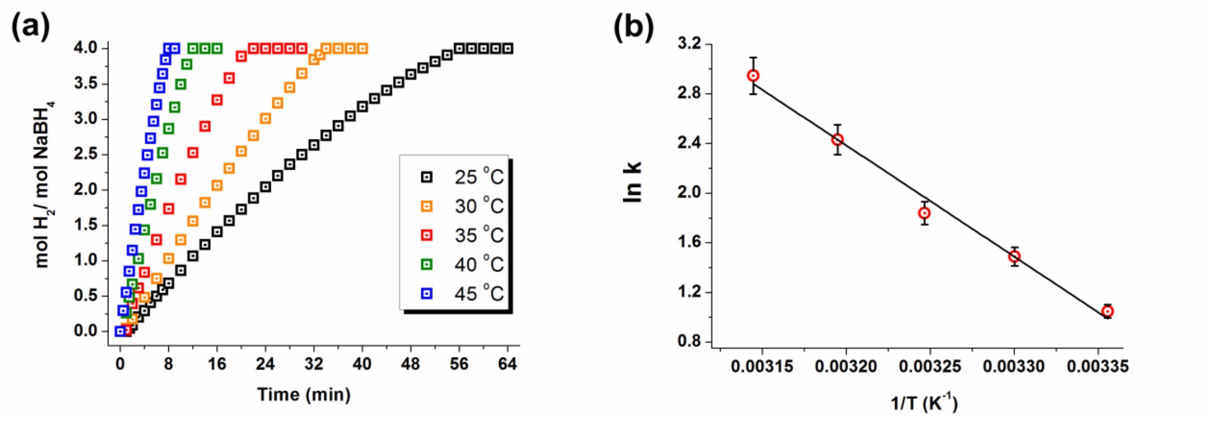
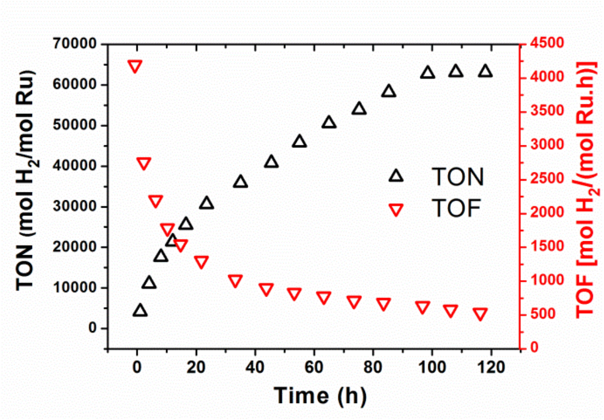

(a)
mol H_2 / mol $NaBH_4$
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
8
16
24
32
40
48
56
64
Time (min)
25 °C
30 °C
35 °C
40 °C
45 °C
(b)
ln k
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.00315
0.00320
0.00325
0.00330
0.00335
1/T (K^{-1})

Fig.7


70000
60000
50000
40000
30000
20000
10000
0
TON (mol H_2/mol Ru)
4500
4000
3500
3000
2500
2000
1500
1000
500
0
TOF [mol H_2/(mol Ru.h)]
0
20
40
60
80
100
120
Time (h)
TON
TOF