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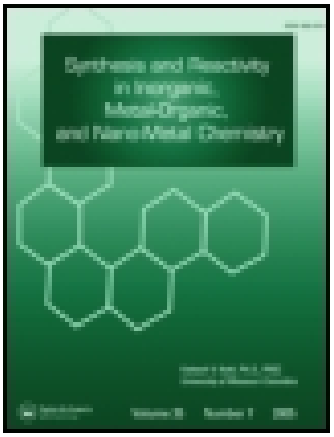

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In-Situ Formed Ruthenium(0) Nanoparticles Supported on TiO_2 Catalyzed Hydrogen Generation from Aqueous Ammonia-Borane Solution at Room Temperature under Air

Nihayet Konuş[a], Yaşar Karataş[a] & Mehmet Gulcan[a]
[a] Department of Chemistry, Science Faculty, Yüzüncü Yıl University, Van, 65080, Turkey

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In-Situ Formed Ruthenium(0) Nanoparticles Supported on TiO_2 Catalyzed Hydrogen Generation from Aqueous Ammonia-Borane Solution at Room Temperature under Air

Nihayet Konuş, Yaşar Karataş, Mehmet Gulcan*

Department of Chemistry, Science Faculty, Yüzüncü Yıl University, Van, 65080, Turkey

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* Corresponding Author: mehmetgulcan@yyu.edu.tr;

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ABSTRACT

Herein, we report that TiO_2 supported ruthenium nanoparticles ($Ru(0)/TiO_2$) during the hydrolysis of starting with $RuCl_3/TiO_2$ precatalyst, which act as highly active, long-lived and reusable nanocatalyst in the hydrogen generation from the hydrolysis of ammonia-borane (NH_3BH_3) at room temperature. The resulting $Ru(0)/TiO_2$ catalyze hydrogen generation from the hydrolysis of ammonia-borane with an initial turnover frequency (TOF) value of 200 min^{-1} at 25 ± 0.1 °C. More importantly, $Ru(0)/TiO_2$ are stable enough to be isolated and bottled as solid material, which can be reused as active catalyst under the identical conditions of the first run.

Keywords: Ruthenium; Nanoparticles; Titanium(IV) Oxide; Ammonia-Borane; Hydrogen

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INTRODUCTION

Hydrogen is a globally accepted clean energy carrier, which could overcome the world energy problem and slim down the environmental pollution caused by using fossil fuels as energy source.[1] However, the safe and efficient storage of hydrogen is still one of the trickiest problems in the "Hydrogen Economy".[2] Because of this concern, there has been a rapidly growing interest for the development of solid hydrogen storage materials that provide the combination of high volumetric/gravimetric storage capacity, adequate kinetics, reversibility, low cost and low toxicity, as the majority of them are impractical for the current high-pressure and cryogenic hydrogen storage systems.[3, 4] In this context, boron based chemical hydrides[56-7] and B-N adducts[891011-12] have been tested as solid hydrogen storage materials. Among these solid materials, ammonia-borane (AB; NH_3BH_3) seems to be much better suited for this purpose due to its high gravimetric hydrogen storage capacity (19.6 % wt), non-toxicity, low molecular weight (30.7 $g.mol^{-1}$) and inclination for bearing protic (N–H) and hydridic (B–H) hydrogens, which can be 'discharged' and 'recharged' in different chemical transformations.[13] The hydrolytic dehydrogenation of AB generates 3 equiv. of H_2 (per mole of AB) at room temperature (RT) under air only in the presence of suitable catalyst (**1**).[8,13,14,-15]

$$\mathbf{NH_3BH_3 + 2H_2O \xrightarrow[\text{at RT under air}]{\text{catalyst}} NH_4BO_2 + 3H_2}$$

Regardless of the difficulty in recycling of the (meta)borate anion, the hydrogen evolution from the catalytic hydrolysis of ammonia-borane has some features, which make it capable for prospective applications; (*i*) AB has high solubility in water (33.6 g NH_3BH_3/100 g H_2O),[16] (*ii*) it occurs at appreciable rate only in the presence of a suitable catalyst at room temperature, (*iii*)

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the catalytic hydrolysis of AB is exothermic (ΔH = -155.97 kJ/mol).[17] Since the hydrolytic dehydrogenation occurs only in the presence of a suitable catalyst, many transition metals or their compounds have been tested as catalyst for this important reaction.[18] Although, homogeneous catalysts have already showed notable activities in the hydrolysis of AB,[1920-21] the current effort has been focused on the employment of heterogeneous catalysts because of their considerable advantages in the catalytic reactions including simple product separation and catalyst recovery.[22] Among the heterogeneous catalysts Rh,[23, 24] Pt[23, 24] and Ru [25, 26] metals provide significant catalytic activities in the hydrolysis of AB.

Of particular importance, ruthenium based heterogeneous catalysts[26-**Error! Bookmark not defined.**] can catalyze the hydrolytic dehydrogenation of AB under mild conditions with acceptable rates at 3 equiv. of H_2 (per mole of AB) generation. Unfortunately, most of them used in these schemes suffer from difficult isolation,[26, 27, 28] low activity,[29, 30, 31] low stability,[27,28] and time consuming synthesis procedures.[26, 28, 32, 33] Therefore, the development of a simply prepared, highly active and reusable catalyst that operates under mild conditions remains a difficult challenge in the catalytic hydrolysis of AB.

In this study, we report our results on the *in-situ* generation of ruthenium(0) nanoparticles supported on TiO_2, hereafter referred to as Ru(0)/TiO_2, and their notable catalytic performance in terms of the activity, lifetime and reusability in the hydrolytic dehydrogenation of AB at room temperature under air. Ru(0)/TiO_2 can simply and reproducibly be prepared by the liquid phase impregnation of $RuCl_3$ on TiO_2 matrix, followed by their *in-situ* AB reduction during the hydrolysis of AB. After a short induction time period, the resulting Ru(0)/TiO_2 catalyzes the dehydrogenation of aqueous AB solution at room temperature with an *initial* turnover frequency

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(TOF) of 200 min^{-1}. Moreover, Ru(0)/TiO_2 were also found to be long-lived catalyst, which provide 60000 total turnovers in hydrogen generation from the hydrolysis of ammonia-borane over 17 h before deactivation. More importantly, Ru(0)/TiO_2 feature notable resistance against agglomeration and leaching throughout the catalytic runs. In fact, when the isolated Ru(0)/TiO_2 are reused, they retain 65 % of their *initial* activity even at 5th reuse in the hydrolytic dehydrogenation of AB.

EXPERIMENTAL

Materials

Titanium(IV) oxide (TiO_2, ≥99 %), ruthenium(III) chloride trihydrate ($RuCl_3.3H_2O$), ammonia-borane (NH_3BH_3, 97 %), D_2O and $BF_3\cdot(C_2H_5)_2O$ were purchased from Sigma-Aldrich. Deionized water was distilled with a water purification system (Thermo Scientific Barnsted Nanopure System). All glassware and Teflon-coated magnetic stir bars were cleaned with acetone, followed by copious rinsing with doubly deionized water under ultrasonication, and finally dried in an oven at 423 K.

Characterization

TEM samples were prepared by dropping one drop of dilute suspension on copper coated carbon TEM grid and the solvent was then evaporated at room temperature under reduced pressure (10^{-3} torr). The conventional TEM was carried out on a JEOL JEM-200CX transmission electron microscopes operating at 120 kV. The ruthenium content of Ru(0)/TiO_2 was determined by inductively coupled plasma atomic emission spectroscopy (ICP-OES; ULTIMA 2-HORIBA Jobin-Yvon) after the powdered sample was completely dissolved in the mixture of HNO_3:HCl with a 1:3 ratio. XPS analysis was performed on a Kratos AXIS ultra imaging X-ray photoelectron spectrometer using monochromatic Al Kα radiation (1486.6 eV, the X-ray tube working at 15 kV, 350 W and pass energy of 23.5 keV). At the end of the hydrolysis reaction, the resulting solutions were filtered and the filtrates were collected for ^{11}B NMR analysis. ^{11}B NMR spectra were recorded on a Bruker Avance DPX 400 with an operating frequency of 128.15 MHz. D_2O and $BF_3\cdot(C_2H_5)_2O$ were used as a lock and an external reference, respectively.

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Preparation of ruthenium(III) supported on titanium(IV) oxide (Ru^{3+}/TiO_2) precatalyst and the general procedure for the in-situ generation of $Ru(0)/TiO_2$ during the hydrolytic dehydrogenation of ammonia-borane

Ruthenium(III) cations were introduced onto TiO_2 support by the liquid phase impregnation in a 10 ml aqueous solution that contains 100 mg of TiO_2 and 2.6 mg $RuCl_3.3H_2O$ for 12 h at room temperature. The sample was then filtered by suction filtration using a Whatman-1 filter (Ø = 9 cm), washed three times with 100 mL of deionized water to remove chloride ions, and dried at 353 K in the oven. The *in-situ* formation of $Ru(0)/TiO_2$ and the concomitant hydrolytic dehydrogenation of AB were performed in a typical jacketed, three-necked reaction flask thermostatted at 25 ± 0.1 °C and connected to the water-filled cylinder glass tube. In a typical experiment, 123 mg of Ru^{3+}/TiO_2 (with 0.66 % wt Ru loading corresponding to 8.0 μmol Ru) was weighted and placed into a reaction flask containing a new 5/16 in. × 5/8 in. stir bar. Next, 10.0 mL of 100 mM AB solution was added to the reaction flask and the reaction timer was started (t = 0 min). Hydrogen gas generation from the catalytic reaction solution was followed using a typical water-filled gas buret system and recording the displacement of the water level in the gas buret until no more hydrogen evolution was observed. When no more hydrogen generation was observed, the experiment was stopped, the reactor was disconnected from the water-filled tube, and the hydrogen pressure was released and a small aliquot from the reaction solution in the culture tube was withdrawn for ^{11}B NMR analysis.

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Isolability and reusability of Ru(0)/TiO_2 in the hydrolytic dehydrogenation of ammonia-borane

After the first run of the catalytic hydrolysis of 100 mM AB in 10 mL H_2O starting with 123 mg of Ru^{3+}/TiO_2 (8.0 μmol Ru) at 25 ± 0.1 °C, the catalyst was isolated by suction filtration, washed three times with 20 mL of deionized water, and dried under N_2 gas purging at room temperature then transferred into the glove box. The dried samples of Ru(0)/TiO_2 were weighted and used again in the hydrolytic dehydrogenation of 100 mM AB in 10 mL H_2O and the same procedure was repeated up to 5th catalytic cycle. The results were expressed as percentage of the retained *initial* catalytic activity of Ru(0)/TiO_2 in the hydrolysis of AB versus number of catalytic runs.

Catalytic lifetime of Ru(0)/TiO_2 in the hydrolytic dehydrogenation of ammonia-borane

The catalytic lifetime of Ru(0)/TiO_2 formed *in-situ* during the hydrolytic dehydrogenation of AB was determined by measuring total turnover number (TTO). This experiment was started with 123 mg of Ru^{3+}/TiO_2 (8.0 μmol Ru) precatalyst in a 20 mL solution of 100 mM AB. When all the AB in the solution was completely hydrolyzed, more AB was added and the reaction was continued in this way until no hydrogen gas evolution was observed.

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RESULTS AND DISCUSSION

In-situ generation of Ru(0)/TiO_2 during the hydrolysis of AB starting with Ru^{3+}/TiO_2 precatalyst at room temperature under air

Ruthenium nanoparticles supported on titanium(IV) oxide (Ru(0)/TiO_2) were prepared by the liquid phase impregnation of Ru^{3+} ions onto TiO_2, followed by the *in-situ* reduction of ruthenium(III) cations in the Ru^{3+}/TiO_2 precatalyst during the hydrolytic dehydrogenation of AB. The evolution of Ru(0)/TiO_2 and associated hydrolysis of AB can be followed by monitoring the changes in hydrogen pressure, which was then converted into the equivalent H_2 per mole of AB, using the known 3:1 H_2/AB stoichiometry (**1**). Fig. 1 shows the equivalent hydrogen generated per mole of AB versus time plot for the hydrolytic dehydrogenation of AB starting with Ru^{3+}/TiO_2 precatalyst at room temperature under air. The formation kinetics of Ru(0)/TiO_2 catalyst can be obtained by using the catalytic hydrolysis of AB as the reporter reaction,[34,35] (Scheme 1), in which P is the added precatalyst (Ru^{3+}/TiO_2) and Q is the growing supported ruthenium nanoparticles (Ru(0)/TiO_2). The catalytic hydrolysis of AB will straightforwardly report and intensify the amount of Ru(0)/TiO_2 catalyst, Q, present if the rate of AB hydrolysis is fast in comparison to the ruthenium(0) nanoparticles formation rate. Sigmoidal kinetic can be seen in Fig. 1 fits well by the Finke-Watzky two-step nucleation and autocatalytic growth mechanism of nanoparticles formation.[36,37] The surveillance of a sigmoidal hydrogen generation curve and its stimulated fit to the slow, continuous nucleation P→Q (rate constant k_1) followed by autocatalytic surface growth P+Q→2Q (rate constant k_2) kinetics is strongly declarative of the

Figure 1

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formation of a metal(0) nanoparticles catalyst from a precatalyst in the presence of a reducing agent.[34-37] The rate constants determined from the nonlinear least-squares curve fit from Fig. 1 are k_1 = 9.68×10^{-2} min^{-1} and k_2 = 90.11 M^{-1}. min^{-1} (the mathematically required correction has been made to k_2 for the stoichiometry factor of 83.3, as described elsewhere,[34] but not for the "scaling factor"; that is, no correction has been made for the changing number of Ru atoms on the growing metal surface).

After the generation of 3 equiv. of H_2, the resulting Ru(0)/TiO_2 were simply isolated by filtration and ^{11}B NMR spectrum of the aliquot taken from the reaction solution showed that the formation metaborate (δ = 8.7 ppm, s).[38] Fig. 2 show TEM images of Ru(0)/TiO_2, which reveals that the formation of ruthenium(0) nanoparticles on TiO_2 with an average diameter of 5.51 ± 0.91 nm (Fig. 2(c)). The oxidation state of ruthenium in the Ru(0)/TiO_2 sample was also investigated by X-ray photoelectron spectroscopy (XPS). The high resolution XPS spectrum (Fig. 3) of Ru(0)/TiO_2 shows a prominent peak at 462 eV, which can readily be assigned to Ru(0) $3p_{3/2}$,[39] thus revealing that the reduction of Ru^{3+} species during the hydrolysis of AB.

Figure 2

Figure 3

The effect of ruthenium loading on the catalytic activity of Ru(0)/TiO_2 in the hydrolytic dehydrogenation of AB

The effect of ruthenium loading (wt %) on the catalytic activity of *in-situ* generated Ru(0)/TiO_2 in the hydrolytic dehydrogenation of AB was investigated by performing a series of experiments for the catalytic AB hydrolysis starting with Ru^{3+}/TiO_2 precatalysts with different ruthenium loadings in the range of 0.25 – 3.60 wt %. Fig. 4(a) shows the variation in the observed *initial* TOF values with respect to the ruthenium loadings (% wt). The trend in the catalytic activities of Ru(0)/TiO_2 with different Ru loadings mirrors the accessibility of ruthenium(0) nanoparticles supported on TiO_2 by the substrate.

Figure 4

The best catalytic activity (TOF = 200 min^{-1}) is obtained by using Ru^{3+}/TiO_2 precatalyst containing 0.66 wt % Ru, in which the *in-situ* generated ruthenium(0) nanoparticles exist mostly on the surface and readily accessible. The small size of Ru(0)/TiO_2 containing 0.66 wt% Ru may be another reason for its high activity. In fact, TEM image taken from Ru(0)/TiO_2 sample with 3.60 wt % Ru loading (Fig. 4(b)) indicates the existence of larger ruthenium(0) nanoparticles and agglomerates on the surface of TiO_2 support. It should also be noted that, TOF value provided by our Ru(0)/TiO_2 catalyst is the apparent lower limit as it is not corrected for the amount of ruthenium that is on the surface of the Ru(0)/TiO_2[40,41] but it is still comparable with the majortiy of the previous ruthenium based catalysts tested in the same reaction (*see* Table 1).

Table 1

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Initial kinetic studies and the determination of activation energy (Ea) for the in-situ generated Ru(0)/TiO_2 catalyzed hydrolytic dehydrogenation of AB

Fig. 5(a) presents the plot of mol of H_2 generated per mole of AB versus time for the catalytic dehydrogenation of AB starting with different concentrations of Ru in water at 25 ± 0.1 °C. As expected from an *in-situ* formed catalyst, a linear hydrogen generation starts with induction period and continues until the generation of 3 equiv. of H_2. The dehydrogenation rate, determined from the nearly linear portion of the plots, increases with the catalyst concentration. Plotting the dehydrogenation rate versus ruthenium concentration (both on logarithmic scales) gives a straight line with a slope of 0.72 (Fig. 5(b)).

Figure 5

That is, an apparent first-order dependence on the catalyst concentration is observed. The deviation from the first-order kinetics with respect to catalyst concentration might be due to the initial stage deactivation of some ruthenium nanoparticles by the borate anion $[BO_2]^-$, which acts as a catalyst poison by significantly decreasing the accessibility of active sites.[42]

The effect of the substrate concentration on the hydrolytic dehydrogenation rate was also studied by performing a series of experiments starting with variation of the *initial* concentration of AB while keeping the catalyst concentration constant at 25 ± 0.1 °C. Fig. 6(a) shows the volume of H_2 generated versus time for the hydrolytic dehydrogenation of AB starting with different concentrations of AB at constant Ru concentration. In a substrate concentration higher than 90 mM, the catalytic dehydrogenation of AB appears to be zero-order in the substrate

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concentration, while at lower substrate concentration; one observes first-order dependence (Fig. 6(b)).

Figure 6

The activation energy for the *in-situ* generated Ru(0)/TiO_2 catalyzed hydrolytic dehydrogenation of AB was also determined by using the temperature dependent kinetic data shown in Fig. 7(a). The observed rate constants were calculated from the nearly linear portions of the curves at different temperatures and used for the construction of Arrhenius (Fig. 7(b)) plot, which gives us the activation energy of Ea = 87.4 kJ/mol for the *in-situ* generated Ru(0)/TiO_2 catalyzed hydrolytic dehydrogenation of AB.

Figure 7

Reusability of the in-situ generated Ru(0)/TiO_2 in the hydrolytic dehydrogenation of AB

The isolability and reusability of Ru(0)/TiO_2, as two crucial measures in heterogeneous catalysis, were also tested in the hydrolytic dehydrogenation of AB. After the generation of 3 equiv. of H_2 per AB and formation of Ru(0)/TiO_2 starting with Ru^{3+}/TiO_2 precatalyst in the first run, the catalyst was simply isolated by suction filtration then dried in vacuo and bottled under inert atmosphere. When reused the isolated Ru(0)/TiO_2 were found to be still highly active in the hydrolytic dehydrogenation of AB. They retain > 65 % of their initial catalytic activity even at the 5th catalytic run, with the generation of 3 equiv. H_2 per mole AB (Fig. 8(a)).

The reusability performance of Ru(0)/TiO_2 is also better than some of the previously reported Ru catalysts; laurate[27] and PSSA-*co*-MA[28] stabilized ruthenium(0) nanoparticles and ruthenium(0) nanoparticles supported on carbon[32] and carbon nanotube[33] tested in this reaction (*see* Table 1). The decrease in the activity of Ru(0)/TiO_2 can be explained by the agglomeration of surfactant-free ruthenium(0) nanoparticles on the surface of TiO_2 into some extent as evidenced by the representative TEM image of Ru(0)/TiO_2 sample harvested from the 5th catalytic run (Fig. 8(b)).

Figure 8

More importantly, the leaching tests performed by ICP-OES analyses of Ru in the filtrate collected from each cycles confirm that ruthenium(0) nanoparticles are not leaching into the reaction solution from TiO_2 support. A control experiment was also performed to show that the hydrolytic dehydrogenation of AB is completely stopped by the removal of Ru(0)/TiO_2 from the reaction solution.

Catalytic lifetime of the in-situ generated Ru(0)/TiO_2 in the hydrolytic dehydrogenation of AB

In a catalyst lifetime experiment started with Ru^{3+}/TiO_2 precatalyst, the *in-situ* generated Ru(0)/TiO_2 were found to provide total turnover number (TTON) 60000 in the hydrolytic dehydrogenation of AB over 15 h before deactivation. An *initial* TOF value of 200 min^{-1} was obtained; however, the *average* TOF value was calculated to be 100 min^{-1}. The observation that the TOF value decreases as the reaction proceeds indicates the deactivation of the ruthenium(0) nanoparticles catalyst. Moreover, it should be noted that the *in-situ* formed Ru(0)/TiO_2 provide approximately 45-fold higher TTON than the bulk ruthenium(0) metal formed *in-situ* during the hydrolysis of AB started with support-free $RuCl_3$ (TTON = 2000)[27] under the same conditions.

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CONCLUSIONS

In summary, our study of the *in-situ* generated Ru(0)/TiO_2 catalyzed hydrolytic dehydrogenation of AB has led to the following conclusions and insights: (*i*) TiO_2 supported ruthenium(0) nanoparticles, Ru(0)/TiO_2, were reproducibly prepared from the *in-situ* reduction Ru^{3+}/TiO_2 during the hydrolytic dehydrogenation of ammonia- borane at room temperature; (*ii*) The preliminary characterization of the resulting catalytic material by using ICP-OES, XPS, and TEM techniques reveal that the formation of well-dispersed ruthenium(0) nanoparticles with an average diameter of 5.51 ± 0.91 nm within TiO_2; (*iii*) Ru(0)/TiO_2 provide notable catalytic activity (lower-bound TOF_{inital} = 200 min^{-1}) among all the heterogeneous ruthenium catalysts tested in the hydrolytic dehydrogenation of AB at room temperature; (*iv*) Ru(0)/TiO_2 have great stability against to sintering and leaching, that make them highly reusable catalyst, when redispersed they retain 65 % their initial activity even at the 5th catalytic run in the hydrolytic dehydrogenation of AB with the generation of 3 equiv. of H_2 per mole of AB; (*v*) Morover, Ru(0)/TiO_2 were also found to be long-lived catalyst in the hydrolytic dehydrogenation of AB so that they provide total turnover number (TTON) 60000, which is 30-fold higher TTON than the bulk ruthenium(0) metal formed *in-situ* during the hydrolysis of AB started with support-free $RuCl_3$; (*vi*) The quantitative kinetic studies depending on the catalyst/substrate concentrations and temperature indicates that Ru(0)/TiO_2 catalyzed hydrolytic dehydrogenation of AB is first-order in catalyst concentration and zero order in AB concentration (>90 mM). The activation energy was also estimated for the *in-situ* generated Ru(0)/TiO_2 catalyzed hydrolytic dehydrogenation of AB (Ea = 87.4 kJ/mol); (*vii*) The kinetic data, collected for the Ru(0)/TiO_2 formation and concomitant hydrolytic dehydrogenation of AB fit well to the two-step mechanism for the nanoparticles formation [36, 37]: continuous nucleation P→Q (rate constant k_1) followed by autocatalytic surface growth P+Q→2Q (rate constant k_2). At this concern, after the known catalytic dehydrocoupling of DMAB in water,[43] the hydrolytic dehydrogenation of AB is the second reporter reaction takes place in water for the nanoparticles formation kinetics.

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Table Captions

Table 1. Catalyst systems (in chronological order) and their performances in terms of activation energy, activity, and reusability in the hydrolytic dehydrogenation of AB.

entry	**Pre(catalyst)**	***ex or in-situ* Formation**	**Ea** (kJ/mol)	**TOF** (min^{-1})	**Reusability (% of retaining *initial* activity)**	**Ref.**
1	Laurate Stabilized Ru NPs	*ex-situ*	47	75	53 % at 5th reuse	27
2	PSSA-*co*-MA Stabilized Ru NPs	*in-situ*	54	18	Not Demonstrated	28
3	Ru_{bulk}@C	*ex-situ*	76	113	Not Demonstrated	31
4	Ru NPs@C	*in-situ*	34	430	25 % at 5th reuse	32
5	Ru NPs@CNT	*in-situ*	33	329	41 % at 4th reuse	33
6	Ru NPs@ZK-4	*ex-situ*	28	91	85 % at 5th reuse	29
7	Ru NPs@Al_2O_3	*ex-situ*	48	83	90 % at 10th reuse	26
8	RuNPs@*micro*-HAp	*ex-situ*	58	137	92 % at 5th reuse	25
9	**RuNPs@TiO_2**	***in-situ***	**87**	**200**	**65 % at 5th reuse**	**this study**

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Figure Captions

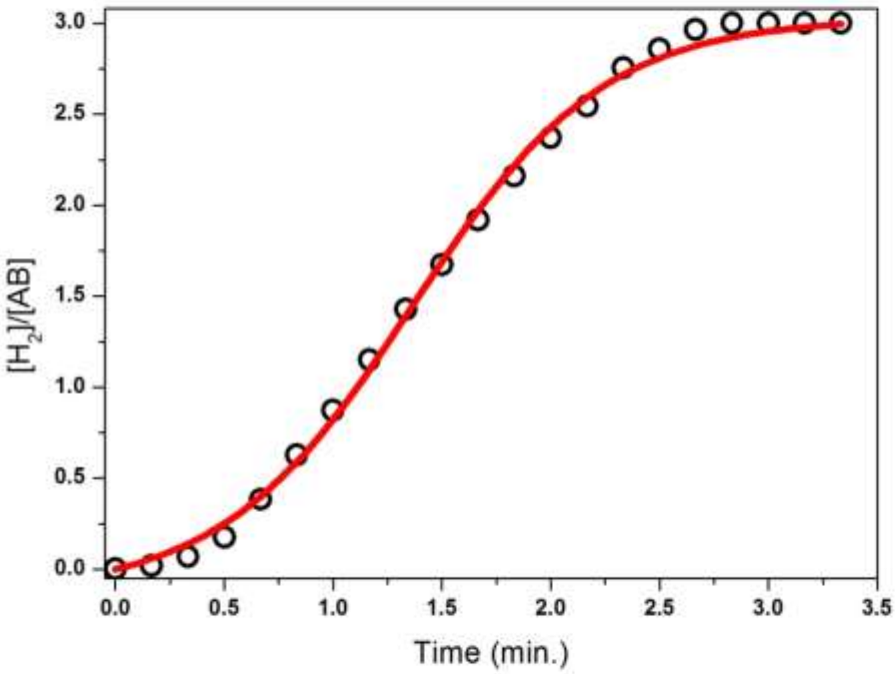

Figure 1. Plot of $[H_2]/[NH_3BH_3]$ versus time (min.) for the in-situ generated Ru(0)/TiO_2 catalyzed hydrolysis of AB starting with Ru^{3+}/TiO_2 precatalyst ([AB] = 100 mM; [Ru] = 0.8 mM in 10.0 mL H_2O) at 25 ± 0.1 ºC and its curve fit (red) to F–W two-step nucleation and autocatalytic growth mechanism ($k_1 = (9.68 \pm 0.76) \times 10^{-2}$ min^{-1}, $k_2 = (90.11 \pm 3.07)$ M^{-1}. min^{-1} and $R^2 = 0.9979$) for TiO_2 supported ruthenium(0) nanoparticles formation.

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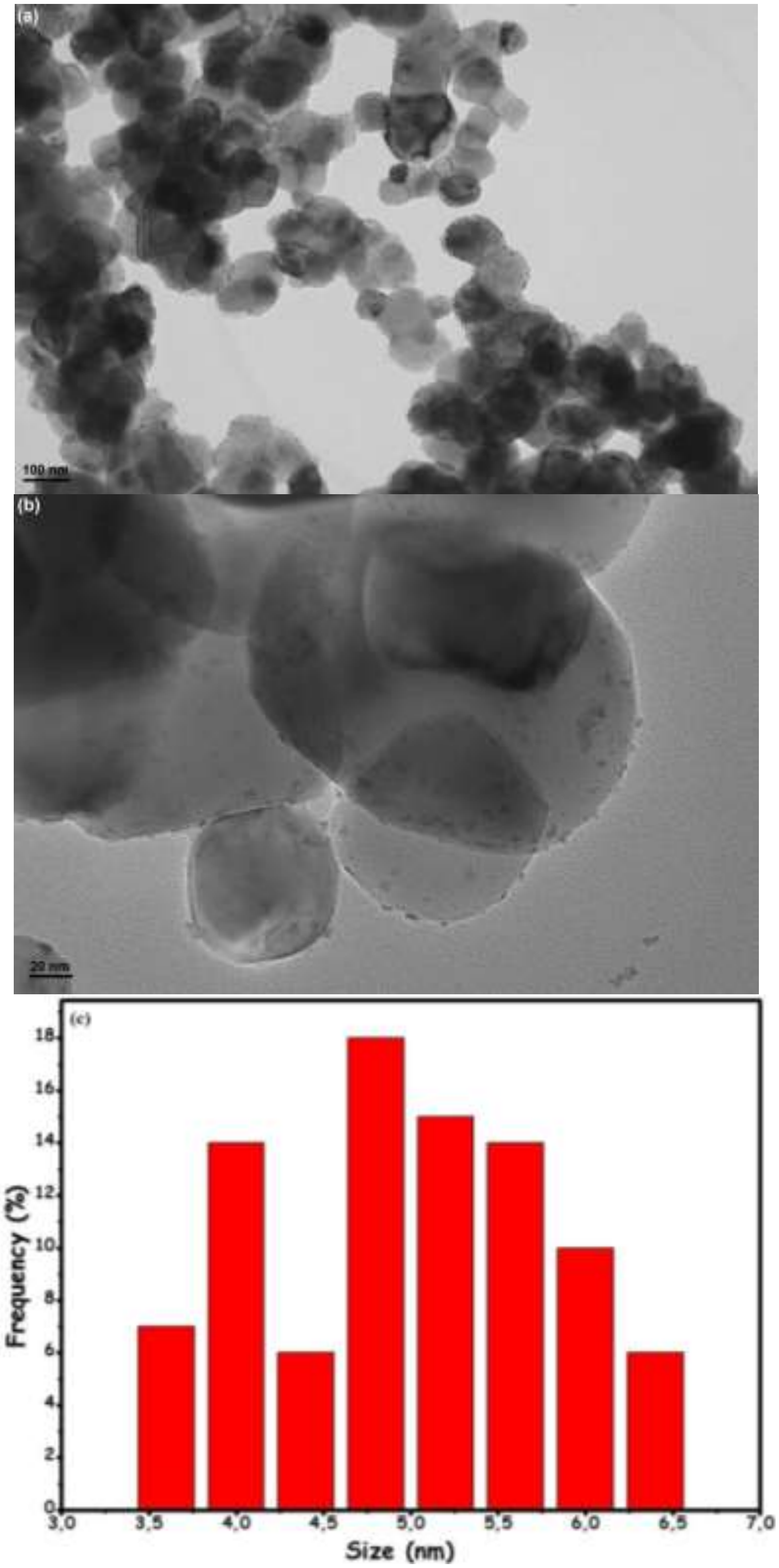

Figure 2. (a-b) TEM images (in different magnifications) of Ru(0)/TiO_2 formed in-situ during the hydrolytic dehydrogenation of AB starting with Ru^{3+}/TiO_2 precatalyst ([AB] = 100 mM, [Ru] = 0.8 mM in 10.0 mL H_2O) at room temperature under air **(c)** corresponding size histogram of Ru(0)/TiO_2.

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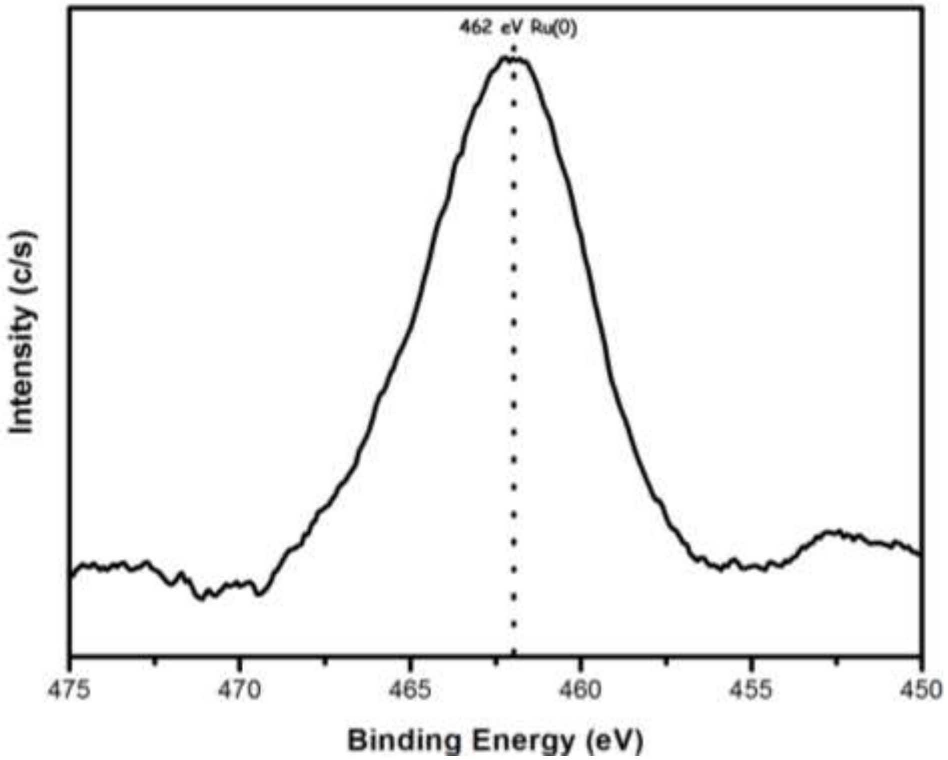

Figure 3. High resolution X-ray photoelectron spectrum of Ru(0)/TiO_2 formed in-situ during the hydrolytic dehydrogenation of AB.

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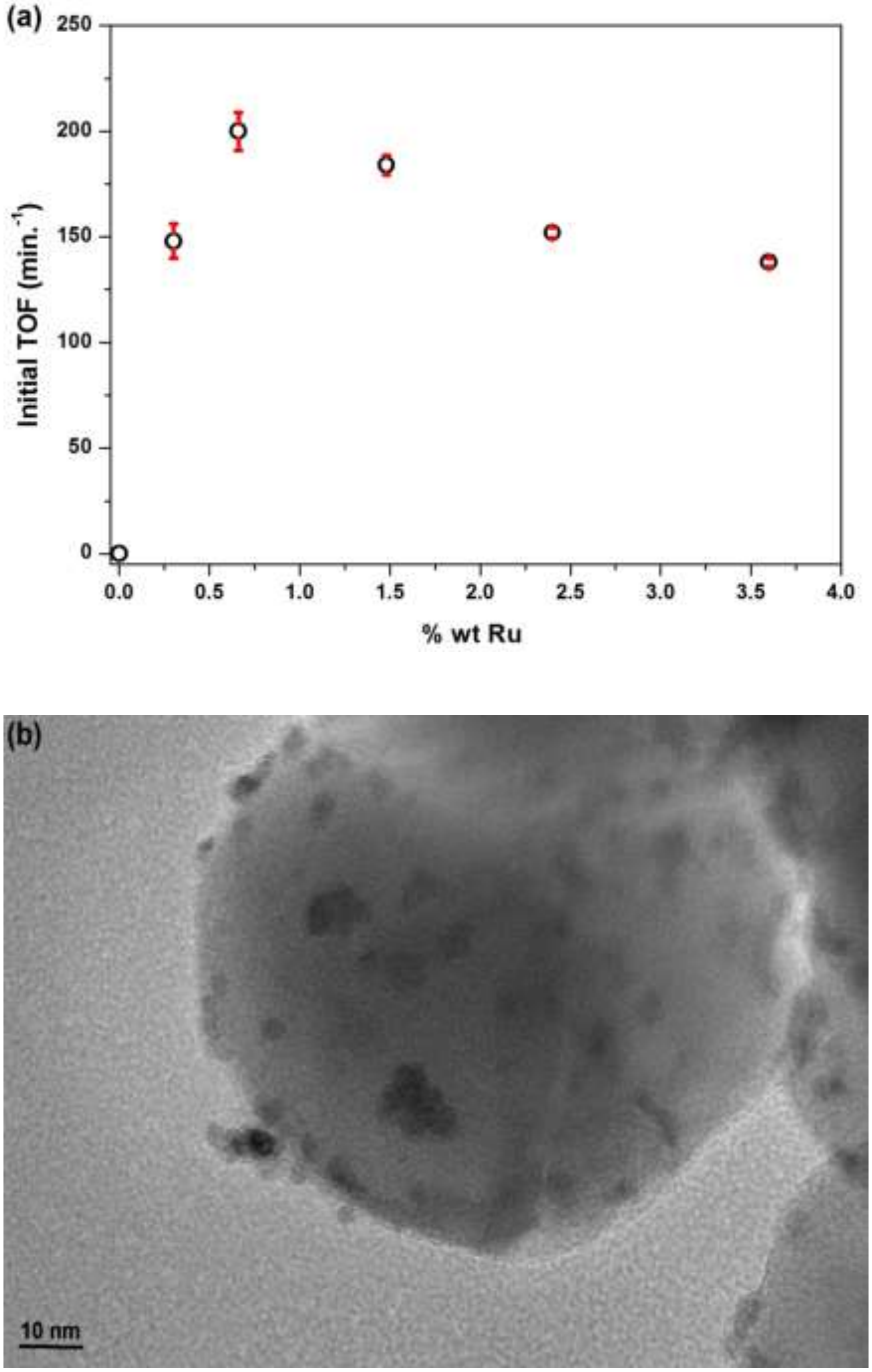

Figure 4 (a) Plot of initial TOF values versus Ru loadings (wt %) for the catalytic hydrolysis of AB, **(b)** TEM image of Ru(0)/TiO_2 formed in-situ during the hydrolytic dehydrogenation of AB

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starting with Ru^{3+}/TiO_2 precatalyst with 3.6 wt % Ru loading ([AB] = 100 mM, [Ru] = 0.8 mM in 10.0 mL H_2O) at room temperature under air.

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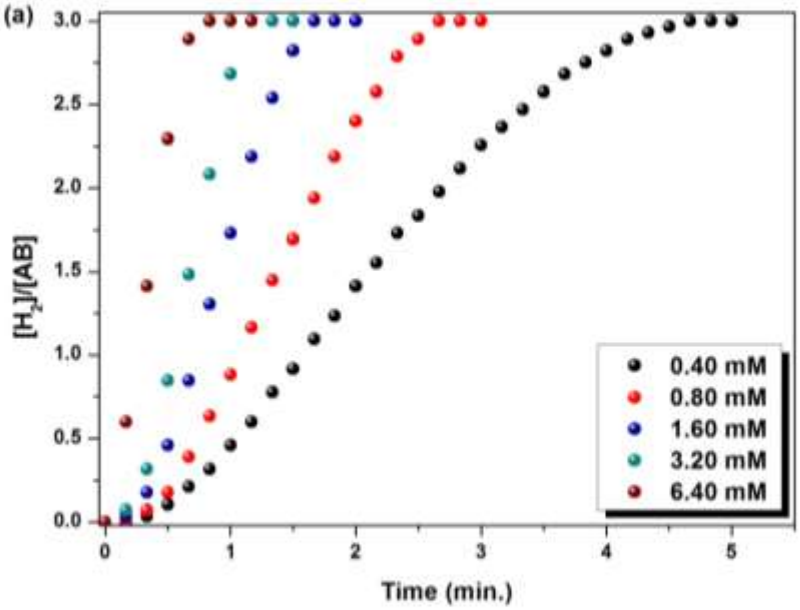

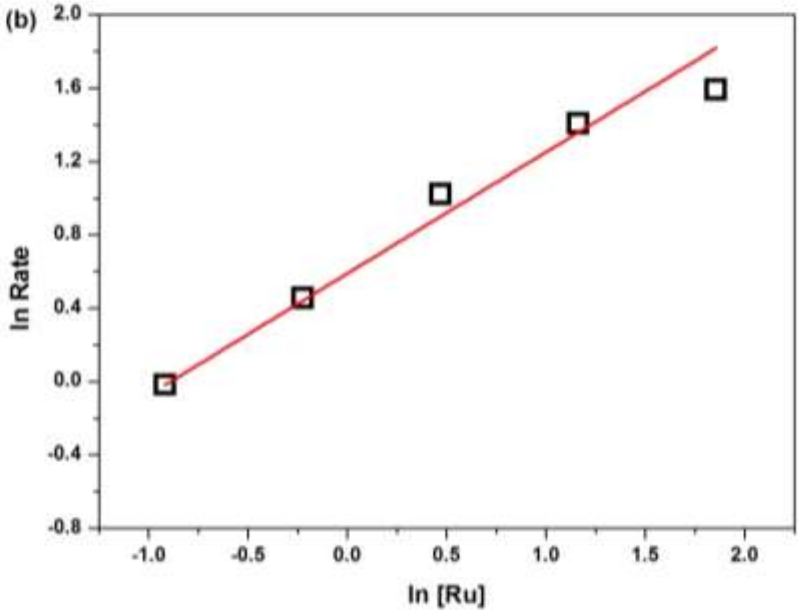

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Figure 5 (a) Plot of generation of equivalent H_2 per NH_3BH_3 versus time (min.) for the hydrolytic dehydrogenation of AB starting with Ru^{3+}/TiO_2 precatalyst (in all [AB] = 100 mM in 10.0 mL H_2O) at different ruthenium concentrations as given on the graph at 25 ± 0.1 ºC, **(b)** ln(rate) versus ln([Ru]) graph ($y = 0.588 + 0.72\,x$ and $R^2 = 0.9984$).

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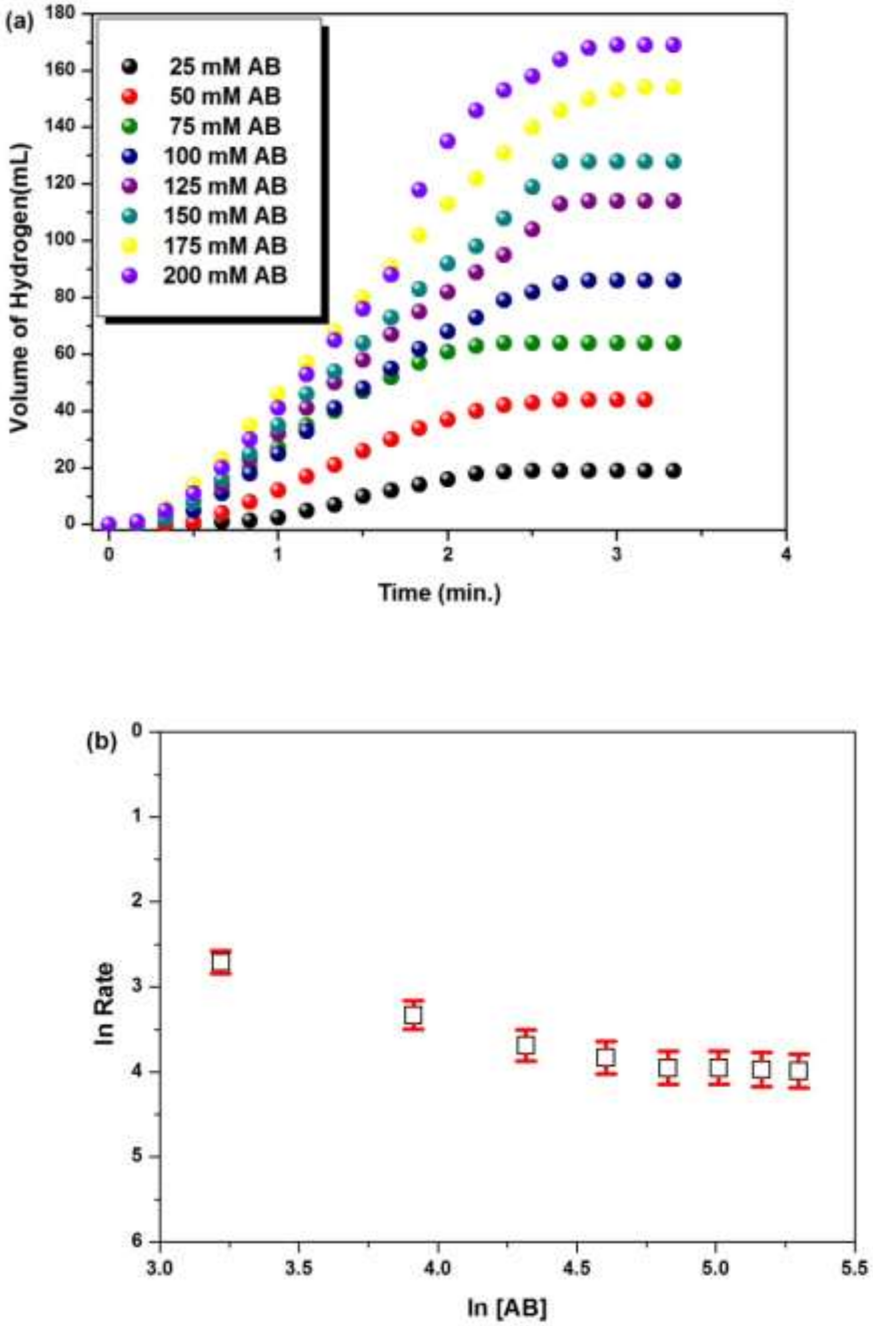

Figure 6 (a) Plot of volume of H_2 generated versus time (min.) for the hydrolytic dehydrogenation of AB starting with Ru^{3+}/TiO_2 precatalyst (in all [Ru] = 0.8 mM in 10.0 mL

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H_2O) at different AB concentrations as given on the graph at 25 ± 0.1 ºC, **(b)** ln(rate) versus ln([AB]) graph.

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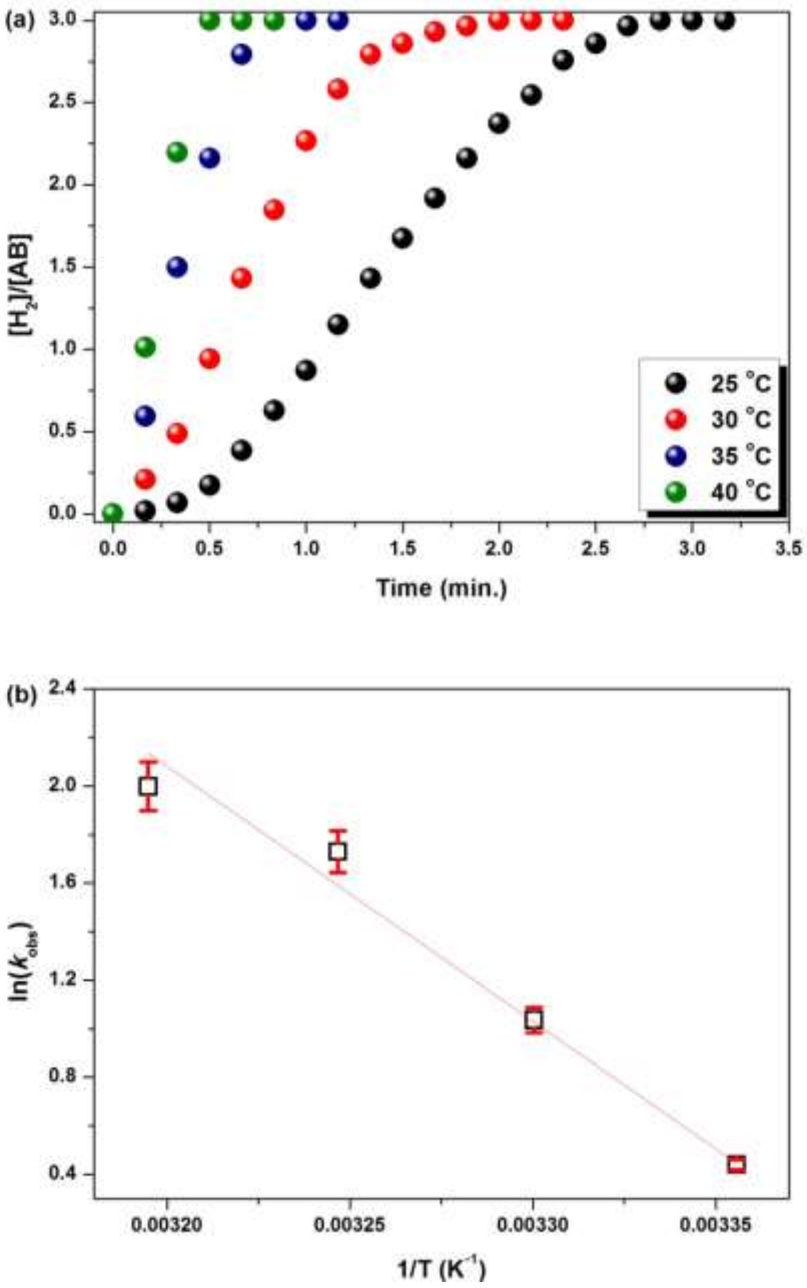

Figure 7 (a) Plot of generation of equivalent H_2 per NH_3BH_3 versus time (min.) for the hydrolytic dehydrogenation of AB starting with Ru^{3+}/TiO_2 precatalyst (in all [AB] = 100 mM, [Ru] = 0.8 mM in 10.0 mL H_2O) at different temperatures as given on the graph, **(b)** Arrhenius plot ($y = 35.724 - 10513\,x$ and $R^2 = 0.9859$).

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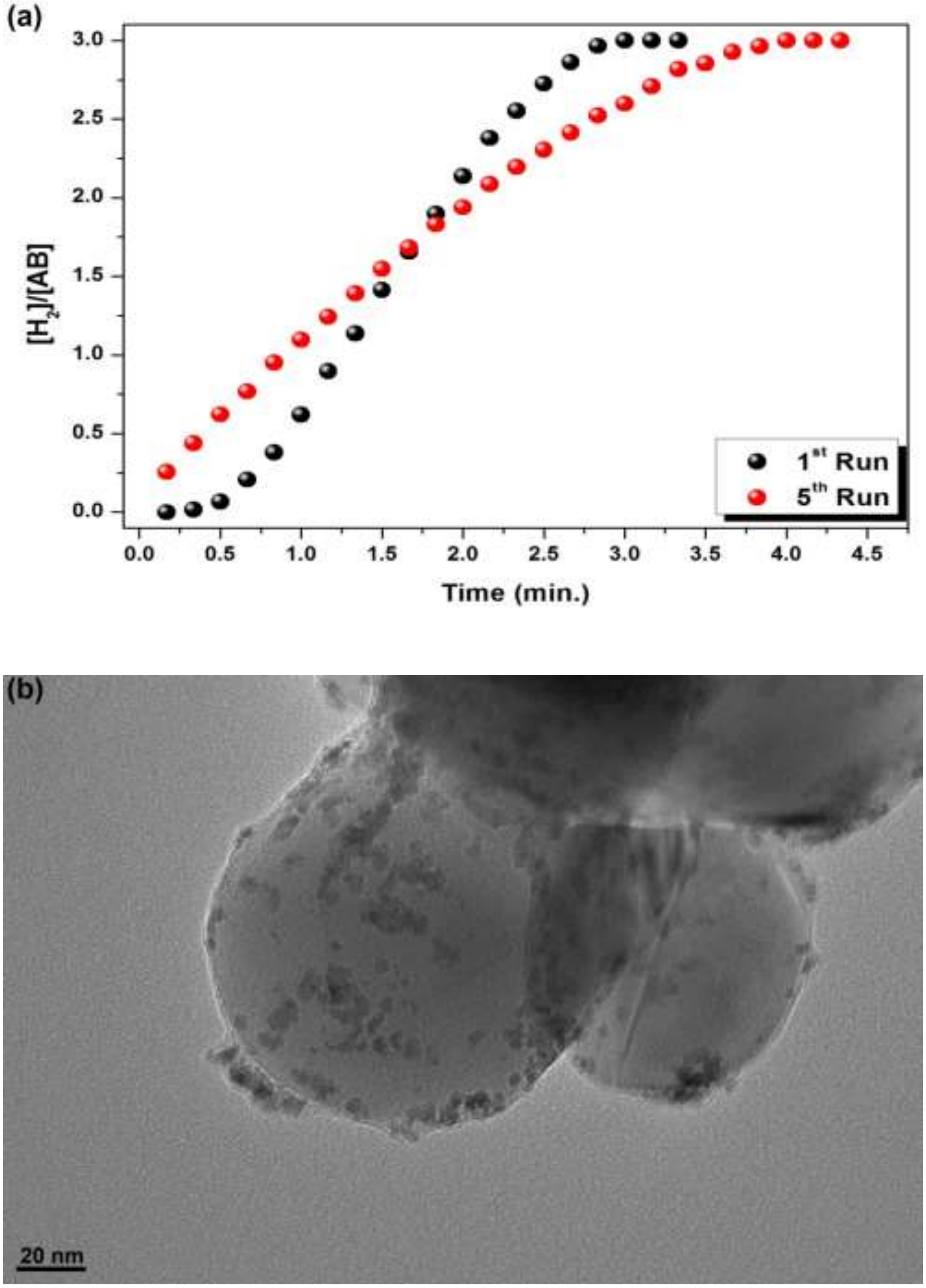

Figure 8 **(a)** Plot of generation of equivalent H_2 per NH_3BH_3 versus time (min.) for the first and fifth catalytic runs of the *in-situ* generated Ru(0)/TiO_2 catalyzed hydrolytic dehydrogenation of

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AB ([AB] = 100 mM; [Ru] = 0.25 mM in 10.0 mL H_2O), **(b)** TEM image of Ru(0)/TiO_2 harvested from the fifth catalytic run.

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$$\mathbf{P} \xrightarrow{k_1} \mathbf{Q}$$

$$\mathbf{P + Q} \xrightarrow{k_2} \mathbf{2Q}$$

$$n\mathbf{Ru^{3+} / TiO_2} \xrightarrow[\mathbf{NH_3BH_3 + H_2O}]{k_1} \mathbf{Ru(0)_n / TiO_2}$$

$$\mathbf{Ru^{3+} / TiO_2 + Ru(0)n / TiO_2} \xrightarrow[\mathbf{NH_3BH_3 + H_2O}]{k_2} \mathbf{Ru(0)_{n+1} / TiO_2}$$

Scheme 1. Minimalistic, two-step nanoparticles nucleation then autocatalytic surface growth mechanism[34-37] for *in-situ* generated Ru(0)/TiO_2 during the hydrolytic dehydrogenation of AB starting with Ru^{3+}/TiO_2 precatalyst at room temperature under air.

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