Testing catalytic activity of ruthenium(III) acetylacetonate in the presence of trialkylphosphite or trialkylphosphine in hydrogen generation from the hydrolysis of sodium borohydride

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ABSTRACT

Catalytic activity of Ru(acac)$_3$ in the presence of different phosphorus compounds (P(OMe)$_3$, P(OPh)$_3$, PPh$_3$ and dppe) was investigated for the first time in the hydrolysis of NaBH$_4$. Phosphorus compound, usually known as poison in catalysis, is involved in the formation of a species which has higher catalytic activity in comparison with Ru(acac)$_3$ alone. Varying the phosphorus compound affects the catalytic activity and lifetime of the catalyst as well as the kinetics and the activation parameters of the hydrolysis of NaBH$_4$. For all of the phosphorus compounds, the hydrogen generation was found to be zero-order with respect to the substrate concentration and first-order regarding the catalyst concentration. The catalyst system with P(OMe)$_3$ shows the highest catalytic activity and provides the largest total turnover number (TTON = 20,700 over 72 h) in the hydrolysis of NaBH$_4$. The highest activation energy and enthalpy values were obtained for the catalyst with dppe ($E_a = 59 \pm 2$, $\Delta H^{\#} = 60 \pm 2$ kJ/mol) while the lowest values were found for the catalyst system with PPh$_3$ ($E_a = 46 \pm 2$, $\Delta H^{\#} = 43 \pm 1$ kJ/mol).

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1. Introduction

A recent study [1] has shown that ruthenium(III) acetylacetonate acts as catalyst at room temperature in the hydrolysis of sodium borohydride [2–7], which has been considered as hydrogen storage material in the use of renewable energy sources [8] on the way towards sustainable energy future [9–12].

$$NaBH_4(aq) + 2H_2O(l) \xrightarrow{Ru(acac)_3} NaBO_2(aq) + 4H_2(g) \qquad (1)$$
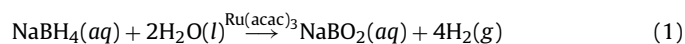
Although there has been no indication of the formation of bulk ruthenium metal during the catalytic hydrolysis of NaBH$_4$ in the presence of Ru(acac)$_3$ [1], the issue of homogeneous/heterogeneous catalysis has been addressed by performing poisoning experiments [13]. A poisoning experiment with trimethylphosphite, P(OMe)$_3$, has been used to prove that the hydrolysis of NaBH$_4$ catalyzed by Ru(acac)$_3$ is a homogeneous catalysis [1]. Indeed, addition of 1 equivalent P(OMe)$_3$ per ruthenium into the system has been shown to inhibit the catalytic activity of Ru(acac)$_3$ in the hydrolysis of NaBH$_4$ [1]. However, observation of the reaction for a longer time shows a sudden increase in the hydrogen generation rate after a certain period of time. This phenomenon is nicely illustrated in Fig. 1 which shows the plot of hydrogen volume versus time for the hydrolysis of NaBH$_4$ catalyzed by Ru(acac)$_3$. When 2 equivalents of P(OMe)$_3$ per ruthenium are added to the reaction solution containing 450 mM NaBH$_4$ and 2 mM Ru(acac)$_3$ in 50 mL H$_2$O–THF solution, the hydrogen generation rate was practically stopped (or reduced to the level of self-hydrolysis). However, the catalytic hydrolysis of NaBH$_4$ restarts at an unexpectedly high rate in a certain period of time (75 min in this case) after addition of P(OMe)$_3$. This observation indicates the formation of a new ruthenium species involving P(OMe)$_3$, which is obviously much more active than the Ru(acac)$_3$ catalyst itself in the hydrolysis of NaBH$_4$. Observation of the unexpected catalytic activity of the ruthenium species involving a molecule known to be poison in catalysis prompted us to investigate the catalytic activity of Ru(acac)$_3$ in the presence of different phosphorus compounds. Here we report the results of a kinetic study on the catalytic hydrolysis of NaBH$_4$ in the presence of ruthenium(III) acetylacetonate and a phosphorus compound: trimethylphosphite, triphenylphosphite, triphenylphosphine, or 1,2-bis(diphenylphosphino)ethane (Fig. 2).

2. Experimental

2.1. Materials

Ruthenium(III) acetylacetonate, Ru(acac)$_3$, (97%), sodium borohydride, NaBH$_4$, (98%), trimethylphosphite, P(OMe)$_3$, triphenylphoshine, PPh$_3$, and 1,2-bis(diphenylphosphino)-ethane, dppe,

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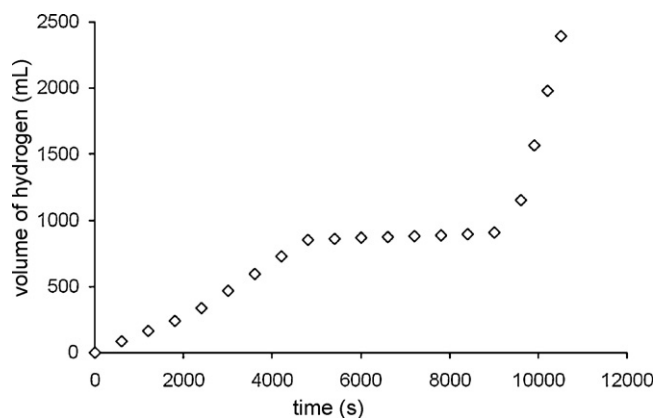*E-mail address:* sozkar@metu.edu.tr (S. Özkar).

Fig. 1. Plot of the volume of hydrogen generated versus time for the hydrolysis of NaBH$_4$ at 25 °C in 50 mL THF/water (1/9) solution starting with [NaBH$_4$] = 450 mM, [Ru(acac)$_3$] = 2 mM, and trimethylphosphite ([P(OMe)$_3$] = 4 mM) added in 80 min after the start of reaction. The addition of trimethylphosphite first stops the reaction completely. The reaction restarts at a faster rate in 75 min after the addition of P(OMe)$_3$.
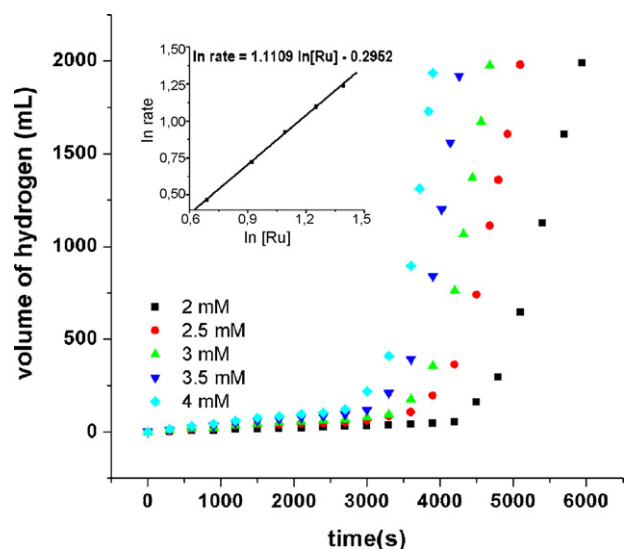

Fig. 2. The volume of H$_2$ versus time plots during the hydrolysis of NaBH$_4$ solution (450 mM) catalyzed by Ru(acac)$_3$ and 2 equivalents of P(OMe)$_3$ in different ruthenium concentration at 25 °C. The inset shows the plot of rate versus ruthenium concentration, both in logarithmic scale.

were purchased from Aldrich®, and triphenylphosphite, P(OPh)$_3$, tetrahydrofuran, THF, were purchased from Merck®. All glassware and Teflon-coated magnetic stir bars were cleaned with acetone, followed by copious rinsing with distilled water before drying at 150 °C in oven for a few hours.

2.2. Equipment

The experimental setup [14] used for performing the hydrolysis of NaBH$_4$ and measuring the hydrogen gas generated from the reaction consists of a 75 mL jacketed reaction flask containing a Teflon-coated stir bar 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 (RL6 LAUDA water bath). A graduated glass tube (50 cm in height and 2.5 cm in diameter) filled with water was connected to the reaction flask to measure the volume of the hydrogen gas to be evolved from the reaction.

2.3. Catalytic activity of Ru(acac)$_3$ in the hydrolysis of NaBH$_4$ in the presence of different phosphorus compounds (P(OMe)$_3$, P(OPh)$_3$, PPh$_3$ or dppe)

A stock solution of 100 mM phosphorus compound in THF was prepared by dissolving 1.18 mL P(OMe)$_3$ (MW = 124.08 g/mol, d = 1.052 g/mL), 2.6 mL P(OPh)$_3$ (MW = 310.29 g/mol, d = 1.19 g/mL), 2.63 g PPh$_3$ (MW = 262.29 g/mol, 99%), or 4.00 g dppe (MW = 398.43 g/mol, 97%) in 100 mL THF. For the preparation of catalyst solution with P/Ru ratio of 0.5–5.0, an aliquot of the stock solution was diluted to 5 mL by adding THF and, then, 41 mg Ru(acac)$_3$ was added to this solution and dissolved completely by stirring the solution. Then, the solution was transferred into the reaction flask containing 852 mg (22.5 mmol) NaBH$_4$ dissolved in 45 mL water and thermostated at 25.0 ± 0.1 °C. The initial concentration of Ru(acac)$_3$ in the reaction solution was 2 mM Ru and concentration of phosphine was in the range of 1–10 mM P. The reaction was started by closing the reactor and turning on the stirrer at 1000 rpm simultaneously. The volume of hydrogen gas generated was recorded every 5 min.

Kinetics of the hydrolysis of NaBH$_4$ catalyzed by Ru(acac)$_3$ and phosphine system was studied depending on substrate concentration, catalyst concentration and the temperature. In a set of experiments, NaBH$_4$ concentration was held constant at 450 mM and Ru(acac)$_3$ concentration was varied in the range of 2, 2.5, 3, 3.5 and 4 mM, by holding P/Ru ratio at 2, at 25.0 ± 0.1 °C. The hydrogen generation was measured for each set by recording the water level in graduated glass tube, which is connected to the reaction flask, in every 2 min. In the second set of experiments, Ru(acac)$_3$ concentration was held constant at 2 by keeping P/Ru ratio at 2, while NaBH$_4$ concentration was varied in the range of 300, 600, 900, 1200 and 1500 mM at 25.0 ± 0.1 °C. In the third set of experiments, the catalytic hydrolysis of NaBH$_4$ in the presence of Ru(acac)$_3$/Phosphine system with a Ru(acac)$_3$ concentration of 2 mM and a P/Ru ratio of 2 was performed by keeping NaBH$_4$ concentration constant at 450 mM at various temperatures in the range of 20, 25, 30, 35, and 40 °C in order to obtain the activation energy (E_a), enthalpy of activation ($\Delta H^{\neq}$) and entropy of activation ($\Delta S^{\neq}$). Note that each reaction was repeated at least 3 times and the results are given as the average of values obtained in the repeated experiments.

2.4. Catalytic lifetime of ruthenium(III) acetylacetonate in the presence of different phosphorus compounds

The catalytic lifetime of Ru(acac)$_3$ with different phosphorus compounds in the hydrolysis of NaBH$_4$ was determined by measuring the total turnover number (TTO). Such a lifetime experiment was started with a 50 mL solution containing 2 mM Ru(acac)$_3$, 450 mM NaBH$_4$ and keeping mole ratios constant at P(OMe)$_3$/Ru = 2, P(OPh)$_3$/Ru = 2, PPh$_3$/Ru = 2, dppe/Ru = 1 at 25.0 ± 0.1 °C. When the conversion exceeded 75%, more NaBH$_4$ was added to the reaction solution and the reaction was continued in this way until hydrogen gas evolution was slowed down to the self-hydrolysis level.

2.5. Poisoning experiment

To determine whether the hydrolysis of sodium borohydride catalyzed by the Ru(acac)$_3$ and phosphine system is homogeneous or heterogeneous, a mercury poisoning experiment was performed [15]. To the reaction solution started with 450 mM NaBH$_4$ and 2 mM Ru(acac)$_3$ plus 4 mM P(OMe)$_3$ was added 1 equivalent of mercury per ruthenium after the 50% conversion. The hydrogen generation rate was not changed at all after the addition of mercury, indicating that the reaction is indeed a homogeneous catalysis.

3. Results and discussion

Although the addition of 1 equivalent P(OMe)$_3$ per ruthenium inhibits the catalytic activity of Ru(acac)$_3$ in the hydrolysis of NaBH$_4$ [1], the observation of the reaction for a longer time shows a sudden increase in the hydrogen generation rate after a certain period of time (induction period, ending when the hydrogen evolution starts at a significant rate). Fig. 1 illustrates this phenomena clearly in the case of 2 equivalents P(OMe)$_3$ per ruthenium. After addition of 2 equivalents P(OMe)$_3$ per ruthenium to the reaction solution containing 450 mM NaBH$_4$ and 2 mM Ru(acac)$_3$ in 50 mL H$_2$O–THF, the hydrogen generation rate was reduced to the level of self-hydrolysis. After 75 min, the hydrogen generation restarts and continues at a rate (83 mL H$_2$/min) faster than that before the addition of P(OMe)$_3$ (11 mL H$_2$/min). Obviously, a new species involving P(OMe)$_3$ is formed during the induction period and acting as catalyst in the hydrolysis of NaBH$_4$.

Two questions needed to be addressed initially: the first question is whether this behavior is unique for P(OMe)$_3$ or other alkylphosphines show similar activities of enhancing the rate of catalytic hydrolysis of NaBH$_4$. The second issue concerns the effect of varying amount of phosphine per ruthenium on this rate enhancement. In order to answer these questions, a series of experiments were performed starting with 450 mM solution of NaBH$_4$, 2.0 mM Ru(acac)$_3$ and various amount of P(OMe)$_3$, P(OPh)$_3$, PPh$_3$ or dppe at 25 °C. In all of the experiments, a linear hydrogen generation starts after an induction period which depends on the phosphine used (Figs. S1–S4 in the Supporting Information). The rate of hydrogen generation obtained from the linear portion of curves is plotted against the mole ratio of phosphorus to ruthenium for all of the four phosphines (Fig. S5 in the Supporting Information). Inspection of the diagrams given in Fig. S5 reveals the following points: (i) All of the phosphorus compounds used lead to formation of an active species yielding an acceleration in the hydrogen generation from the hydrolysis of NaBH$_4$. (ii) However, using P(OMe)$_3$ yields the most active catalyst with ruthenium for the hydrolysis of NaBH$_4$. (iii) The rate of hydrolysis varies very slightly with the mol ratio of phosphorus to ruthenium for all of the phosphorus compounds. However, 2 equivalents of phosphorus per ruthenium were used for the further experiments with all of the phosphines. In what follows, results of the kinetic study on the hydrolysis of NaBH$_4$ catalyzed by Ru(acac)$_3$ and phosphine (2 equivalents of phosphorus per ruthenium) will be discussed.

Kinetics of the hydrolysis of NaBH$_4$ in the presence of Ru(acac)$_3$ plus P(OMe)$_3$, P(OPh)$_3$, PPh$_3$ or dppe in 2 equivalents amount per ruthenium were studied by monitoring the hydrogen evolution depending on catalyst concentration, substrate concentration, and temperature. Ruthenium(III) acetylacetonate and 2 equivalents phosphine was used for the first time as a homogeneous catalyst in the hydrolysis of NaBH$_4$. Fig. 2 shows the volume of H$_2$ versus time plots during the hydrolysis of NaBH$_4$ solution (450 mM) catalyzed by Ru(acac)$_3$ and 2 equivalents of P(OMe)$_3$ in different ruthenium concentration at 25 °C, while the same plots for the other three phosphine are given in Figs. S6–S8 in the Supporting Information. The inspection of the plots in Fig. 2 and Figs. S6–S8 reveals following points: (i) For all of the phosphines, a linear hydrogen evolution is observed after an induction period, which depends on the catalyst concentration as well as on the phosphine used. Note that the induction period ends when the hydrogen evolution starts at a measurable rate and in some cases a sharp end point is difficult to recognize because hydrogen generation increases gradually as the active species is formed. (ii) The induction period decreases with the increasing concentration of catalyst. (iii) On the contrary to this, the catalytic activity during the induction period increases with the increasing concentration of catalyst. (iv) That an increasing catalytic activity is observed throughout the induction period
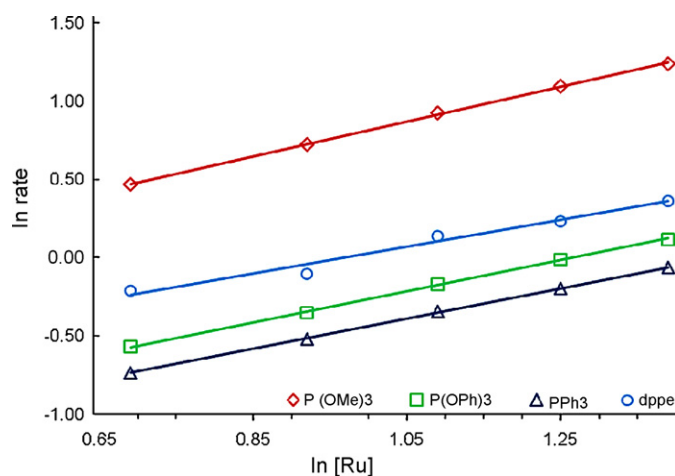

Fig. 3. Plot of hydrogen generation rate versus ruthenium concentration, both in logarithmic scale, in the hydrolysis of NaBH$_4$ catalyzed by Ru(acac)$_3$ plus 2 equivalents of phosphine. [NaBH$_4$] = 450 mM, [Ru] = 2.0 mM, T = 25 °C. The equation for the trend line is ln(rate) = 1.1109 ln[Ru] − 0.2952 for P(OMe)$_3$; ln(rate) = 0.9942 ln[Ru] − 1.2578 for P(OPh)$_3$; ln(rate) = 0.9674 ln[Ru] − 1.4053 for PPh$_3$; ln(rate) = 1.0821 ln[Ru] − 1.0734 for dppe.

in each case is indicative of the formation of active species from the reaction of Ru(acac)$_3$ and phosphine during the induction time. (v) Both the induction period and catalytic activity during the induction period show dependency on the phosphine compound: the longest induction period and the lowest activity during the induction period are observed with the P(OMe)$_3$; the shortest induction period is observed for the system with P(OPh)$_3$. (vi) After the induction period, the rate of hydrogen evolution, obtained from the slope of the linear portion of plots, increases with the increasing catalyst concentration as shown in Fig. 3. For all of the phosphine compounds, the hydrogen evolution rate shows first-order dependency on the ruthenium concentration. In other words, the hydrolysis of NaBH$_4$ is first-order with respect to the catalyst concentration.

In the second set of experiments, NaBH$_4$ concentration was varied in the hydrolysis of NaBH$_4$ catalyzed by Ru(acac)$_3$ and 2 equivalents of phosphine per ruthenium by keeping ruthenium concentration constant at 2.0 mM at 25.0 °C. For all the phosphine compounds, the rate of hydrogen evolution was found to be almost independent of the substrate concentration in the range of 0.30–1.5 M NaBH$_4$ (Figs. S9–S12 in the Supporting Information). This indicates that the hydrolysis of NaBH$_4$ is zero-order with respect to the substrate concentration, at least in the range of 0.30–1.5 M NaBH$_4$, in the presence of Ru(acac)$_3$ plus 2 equivalents of phosphine.

Next, the hydrolysis of NaBH$_4$ was performed at various temperature in the presence of Ru(acac)$_3$ and 2 equivalents of phosphine. Fig. 4 shows the plots of hydrogen volume versus time in the hydrolysis of NaBH$_4$ starting with a solution containing 450 mM NaBH$_4$ and 2.0 mM Ru(acac)$_3$ plus 2 equivalents of P(OMe)$_3$ per ruthenium at different temperatures, while the same plots for the other three phosphines are given in Figs. S13–S15. It is obvious that the induction period and catalytic activity during the induction time depend not only on the phosphine used but also on the temperature. The induction period is getting shorter while the activity during the induction time increases with the increasing temperature for all of the four phosphorus compounds used. The values of rate constant for the hydrogen evolution, obtained from the linear part of the plots in Fig. 4 and Figs. S13–S15, were used to attain the activation parameters for the catalytic hydrolysis of NaBH$_4$ by using either Arrhenius (the insets in Fig. 4 and Figs. S13–S15) or Eyring plots (Figs. S16–S19 in the Supporting Information). Table 1 lists the values of rate constant k in (mol

Table 1

The values of rate constant k in $(mol\ H_2)(mol\ Ru)^{-1}\ s^{-1}$ at five different temperatures and the activation parameters (E_a in $kJ\ mol^{-1}$, A, $\Delta H^{\#}$ in $kJ\ mol^{-1}$, and $\Delta S^{\#}$ in $J\ mol^{-1}\ K^{-1}$) for the hydrolysis of $NaBH_4$ catalyzed by $Ru(acac)_3$ plus 2 equivalents phosphine per Ru starting with a solution of 450 mM $NaBH_4$ and 2 mM Ru.

	T (K)	P(OMe)$_3$	P(OPh)$_3$	PPh$_3$	dppe
	293	0.329 ± 0.0066	0.162 ± 0.0032	0.214 ± 0.0032	0.326 ± 0.0007
	298	0.468 ± 0.0130	0.228 ± 0.0046	0.309 ± 0.0049	0.502 ± 0.008
k	303	0.918 ± 0.0183	0.324 ± 0.0065	0.421 ± 0.0064	0.722 ± 0.011
	308	1.25 ± 0.025	0.467 ± 0.0093	0.521 ± 0.0170	1.28 ± 0.044
	313	1.60 ± 0.032	0.610 ± 0.0122	0.742 ± 0.0280	1.60 ± 0.062
E_a		58 ± 2	52 ± 2	46 ± 2	59 ± 2
A		7.49×10^9	1.87×10^8	3.43×10^7	2.48×10^{10}
$\Delta H^{\#}$		56 ± 2	48 ± 2	43 ± 1	60 ± 2
$\Delta S^{\#}$		-64 ± 4	-95 ± 5	-109 ± 6	-50 ± 3

$H_2)(mol\ Ru)^{-1}\ s^{-1}$ at five different temperatures, Arrhenius activation energy E_a in $kJ\ mol^{-1}$, activation enthalpy $\Delta H^{\#}$ in $kJ\ mol^{-1}$, and activation entropy $\Delta S^{\#}$ in $J\ mol^{-1}\ K^{-1}$ for the hydrolysis of $NaBH_4$ catalyzed by $Ru(acac)_3$ plus 2 equivalents of phosphine per ruthenium starting with a solution of 450 mM $NaBH_4$ and 2 mM ruthenium for all of the four phosphine compounds. For the catalyst with P(OMe)$_3$ both the activation energy $(57.8 \pm 3\ kJ\ mol^{-1})$ and the activation enthalpy $(55.4 \pm 3\ kJ\ mol^{-1})$ are very close to the values reported for $Ru(acac)_3$ alone (58.2 and 55.7 kJ mol^{-1}) [1], respectively. Compared to the values of $Ru(acac)_3$ [1], the ruthenium catalysts involving P(OPh)$_3$ or PPh$_3$ provide lower activation energy and enthalpy values, while the dppe catalyst has slightly higher values for both activation energy and enthalpy. The higher activation energy and enthalpy for the ruthenium–dppe catalyst may be attributed to the additional stability of complex in ground state due to the chelate effect [16,17]. It is worth to note that the activation entropy has large negative value for all of the phosphines, indicating that the mechanism for the catalytic hydrolysis of $NaBH_4$ has an associative nature in the transition state [18,19].

A mercury poisoning experiment was performed in order to show whether the hydrolysis of $NaBH_4$ catalyzed by $Ru(acac)_3$ and phosphine system is homogeneous or heterogeneous [15]. The hydrogen generation rate in the system comprising $Ru(acac)_3$ and 2 equivalents of P(OMe)$_3$ per ruthenium was not affected by the addition of 1 equivalent of mercury to the reaction solution after 50% conversion of $NaBH_4$. This observation indicates unequivocally that the catalytic reaction is indeed homogeneous.

The system comprising $Ru(acac)_3$ and 2 equivalents of phosphine per ruthenium appears to be stable and long-live catalyst in the hydrolysis of $NaBH_4$. Lifetime of the catalyst was measured by
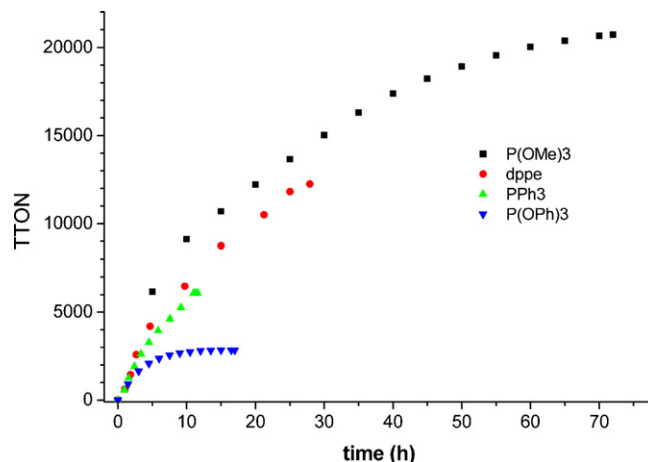
Fig. 5. Plots of total turnover number versus time for hydrogen generation from the hydrolysis of $NaBH_4$ catalyzed by $Ru(acac)_3$ and 2 equivalents of phosphine per ruthenium at 25.0 °C for all of the phosphines.

determining the total turnover number (TTON) in hydrogen generation from the hydrolysis of $NaBH_4$. Fig. 5 shows the plot of total turnover number versus time for hydrogen generation from the hydrolysis of $NaBH_4$ catalyzed by $Ru(acac)_3$ and 2 equivalents of phosphine per ruthenium at 25.0 °C for all of the phosphines. The TTON values for the catalyst system with P(OMe)$_3$, P(OPh)$_3$, PPh$_3$, or dppe are 20,700 (over 72 h), 2850 (over 17 h), 6080 (over 12 h), and 12,250 (over 28 h), respectively, in the hydrolysis of $NaBH_4$ at 25.0 °C. The highest values of turnover frequency (TOF) for the catalyst with P(OMe)$_3$, P(OPh)$_3$, PPh$_3$, or dppe are 38.4, 17.8, 13.2, and 16.4 $(mol\ H_2)(mol\ Ru)^{-1}\ (min)^{-1}$, respectively, at 25.0 °C. Compared to the TTON value of 1200 for the sole $Ru(acac)_3$, all the phosphines caused a remarkable increase in the lifetime of the homogeneous catalyst. In particular, the system with P(OMe)$_3$ provides the highest number of turnovers and the highest turnover frequency. That the dppe provides TTON and TOF values higher than those of PPh$_3$ is attributable to the stability of the complex due to the chelate effect [20].

4. Conclusion

In summary, our study on the catalytic system comprising $Ru(acac)_3$ plus various phosphine in the hydrolysis of $NaBH_4$ leads to the following conclusions and insights, some of which were previously unavailable: (i) $Ru(acac)_3$ is acting as homogeneous catalyst also in the presence of various phosphine: P(OMe)$_3$, P(OPh)$_3$, PPh$_3$ or dppe. (ii) Catalytic activity of $Ru(acac)_3$ in the hydrolysis of $NaBH_4$ is enhanced in the presence of phosphorus compound. (iii) A new species is formed from the reaction of $Ru(acac)_3$ and phosphine during the induction period. (iv) The new complex of ruthenium with phosphine is a more active homogeneous catalyst than the parent
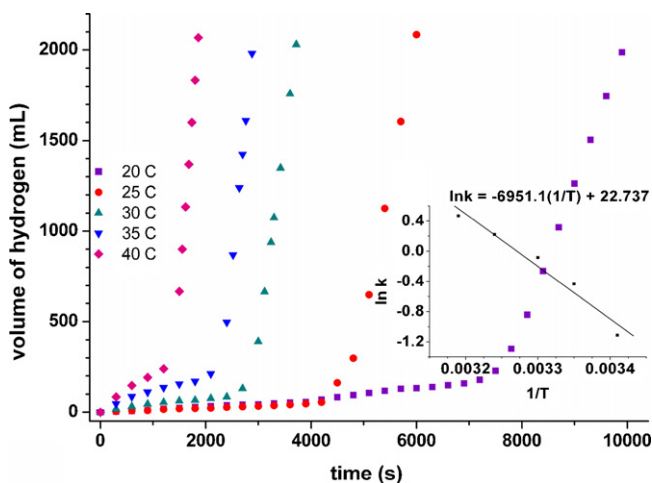
Fig. 4. Plots of hydrogen volume versus time in the hydrolysis of $NaBH_4$ starting with a solution containing 450 mM $NaBH_4$ and 2.0 mM $Ru(acac)_3$ plus 2 equivalents of P(OMe)$_3$ per ruthenium at different temperatures. The inset shows the Arrhenius plot.

complex itself in the hydrolysis of $NaBH_4$ even at room temperature. (v) The variation in the ratio of phosphine to ruthenium does affect the catalytic activity slightly. A phosphorus to ruthenium molar ratio of 2 appears to have usually high activity and therefore was used in the further experiments with all of the phosphines. (vi) The hydrolysis of $NaBH_4$ catalyzed by $Ru(acac)_3$ plus 2 equivalents of phosphine per ruthenium is first-order with respect to the catalyst concentration and zero-order with respect to the substrate concentration. (vii) Addition of phosphine to $Ru(acac)_3$ solution leads to the formation of a more active catalyst. In the case of $P(OMe)_3$, the species formed is a highly active and long-live catalyst providing 20,700 turnovers in the hydrolysis of $NaBH_4$ over 72 h at room temperature. (viii) Increasing catalyst concentration and applying higher temperature lead to a decrease in the induction time and an increase in the formation rate of active catalyst.

The addition of a phosphorus compound leads to a remarkable increase in the rate of catalytic hydrogen generation from the hydrolysis of $NaBH_4$ in the presence of $Ru(acac)_3$. There are indications for the formation of a new ruthenium complex containing phosphine compounds, which is much more active than the parent ruthenium complex in the hydrolysis of $NaBH_4$. All the issues regarding the characterization of active catalyst and its formation from the $Ru(acac)_3$ and a phosphorus compound under the reducing conditions will be extensively studied in an ongoing work.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2009.05.022.

References

[1] E. Keçeli, S. Özkar, J. Mol. Catal. A: Chem. 286 (2008) 87.
[2] A. Züttel, Naturwissenschaften 91 (2004) 157.
[3] S.C. Amendola, P. Onnerud, M.T. Kelly, P.J. Petillo, G.L. Sharp, M. Binder, J. Power Sources 85 (2000) 186.
[4] S.C. Amendola, J.M. Janjua, N.C. Spencer, M.T. Kelly, P.J. Petillo, G.L. Sharp, M. Binder, Int. J. Hydrogen Energy 25 (2000) 969.
[5] J.Y. Lee, H.H. Lee, J.H. Lee, D.M. Kim, J.H. Kim, J. Electrochem. Soc. 149 (2002) 603.
[6] H.I. Schlesinger, H.C. Brown, A.B. Finholt, J.R. Gilbreath, H.R. Hockstra, E.K. Hydo, J. Am. Chem. Soc. 75 (1953) 215.
[7] B.H. Liu, Z.P. Li, J. Power Sources 187 (2009) 527.
[8] E. Fakıoglu, Y. Yürüm, T.N. Veziroglu, Int. J. Hydrogen Energy 29 (2004) 1371.
[9] Basic Research Needs For the Hydrogen Economy, Report of the Basic Energy Sciences Workshop on Hydrogen Production, Storage and Use, May 13–15, 2003, Office of Science, U.S. Department of Energy, www.sc.doe.gov/bes/hydrogen.pdf.
[10] Annual Energy Outlook, 2005 With Projections To 2025, Energy Information Administration, February 2005, www.eia.doe.gov/oiaf/aeo/pdf/0383(2005).pdf.
[11] J. Turner, G. Sverdrup, K. Mann, P.G. Maness, B. Kroposki, M. Ghirardi, R.J. Evans, D. Blake, Int. J. Energy Res. 32 (2008) 379.
[12] I.A.C. Report, Lighting the Way Towards a Sustainable Energy Futures, Interacademy Council, Amsterdam, 2007.
[13] C.M. Hagan, J.A. Widegren, P.M. Maitlis, R.G. Finke, J. Am. Chem. Soc. 127 (2005) 4423.
[14] M. Zahmakiran, S. Özkar, J. Mol. Catal. A: Chem. 258 (2006) 95.
[15] J.A. Widegren, R.G. Finke, J. Mol. Catal. A: Chem. 198 (2003) 317.
[16] M. Amirnasr, R. Houriet, S. Meghdadi, J. Therm. Anal. Calorim. 67 (2002) 523.
[17] E. Prasad, R.A. Flowers, J. Am. Chem. Soc. 124 (2002) 6357.
[18] K.A. Connors, Theory of Chemical Kinetics, VCH Publishers, New York, 1990.
[19] M.V. Twigg, Mechanisms of Inorganic and Organometallic Reactions, Plenum Press, New York, 1994.
[20] S. Maechling, M. Zaja, S. Blechert, Adv. Synth. Catal. 347 (2005) 1413.