

## Reduction of phenylacetylenes using Raney Ni-Al alloy, Al powder in the presence of noble metal catalysts in water

Ummei Rayhan,<sup>a,b</sup> Zannatul Kowser,<sup>a</sup> Md. Nurul Islam,<sup>b</sup> Carl Redshaw,<sup>c</sup> and Takehiko Yamato<sup>a,\*</sup>

<sup>a</sup> Department of Applied Chemistry, Faculty of Science and Engineering, Saga University, Honjo-machi 1, Saga 840-8502, Japan

<sup>b</sup> Department of Chemistry, Dhaka University of Engineering and Technology, Gazipur-1700, Bangladesh

<sup>c</sup> School of Mathematics and Physical Sciences, The University of Hull, Cottingham Road, Hull, Yorkshire, HU6 7RX, UK

Email: [yamatot@cc.saga-u.ac.jp](mailto:yamatot@cc.saga-u.ac.jp)

Dedicated to Prof. Kenneth Laali on the occasion of his 65<sup>th</sup> birthday

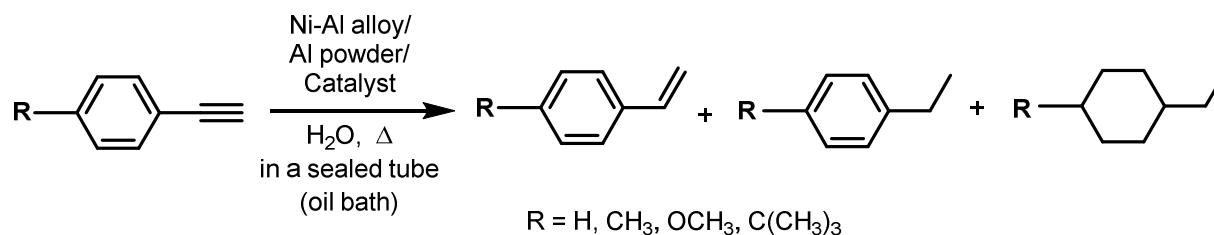
Received 07-26-2017

Accepted 11-29-2017

Published on line 12-13-2017

### Abstract

The chemoselective reduction is based on the reaction between Al either as powder or from the alloy and water which generates *in situ* hydrogen to effect the reduction of the targeted functional groups. Raney Ni-Al alloy with Al powder can reduce phenylacetylenes to the corresponding ethylbenzene (**3**) in water in excellent yield at 120 °C for 6 h in a sealed tube. In addition, the complete reduction of the aromatic ring to ethylcyclohexane required 60 °C for 12 h with Raney Ni-Al alloy, Al powder in the presence of Pt/C. Appropriate selection of reaction conditions allowed the selective preparation of ethylbenzene as well as ethylcyclohexane from phenylacetylene.



**Keywords:** Reduction, phenylacetylene, Raney Ni-Al alloy, noble metal catalyst, Al powder, water, cyclohexane ring

## Introduction

Addition of hydrogen to aromatic alkynes is one of the important transformations in synthetic organic chemistry. Catalytic hydrogenation using hydrogen gas or hydride transfer agents is commonly employed for this transformation. Numerous hydrogenation reactions have been reported, for which the active catalysts commonly employed include systems based on metals such as Pd, Rh, Ru, Ni, Pt, Ir, Os, V, Fe, and Nb.<sup>1</sup> There is particular interest in the use of Pd given its excellent performance in the selective hydrogenation of alkynes.<sup>2</sup> Nowadays, isolated single atom Pd sites in intermetallic nanostructures are used for high catalytic selectivity in the semihydrogenation of alkynes and light mediated preparation of palladium nanoparticles as catalysts for alkyne *cis*-semihydrogenation.<sup>3,4</sup> It is found that *N,N*-dimethylformamide (DMF) can act as a hydride source in nickel-catalyzed asymmetric hydrogenation of  $\alpha,\beta$ -unsaturated esters.<sup>5</sup> Also a Hantzsch amido dihydropyridine has been reported as a transfer hydrogenation reagent for  $\alpha,\beta$ -unsaturated ketones while pyridine derivatives were reduced via borane-catalyzed transfer hydrogenation reaction with ammonia-borane.<sup>6,7</sup> Recently, use of a copper catalyst as a monophasic catalytic system and silica-supported copper nanoparticles have been employed for the selective semireduction of alkynes.<sup>8,9</sup> In another study, a nonclassical Co-H<sub>2</sub> system was used to assess the effect of hydrogen spin on isomerization and E-selectivity in an alkyne semihydrogenation reaction.<sup>10</sup> Moreover, rationally tuned micropores within enantiopure metal-organic frameworks for highly selective separation of acetylene and ethylene as well as tuning the gate opening pressure of metal-organic frameworks (MOFs) for the selective separation of hydrocarbons have appeared in the literature.<sup>11-12</sup> Microporous metal-organic framework with dual functionalities for highly efficient removal of acetylene from ethylene/acetylene mixtures have also been reported. In addition, a microporous metal-organic framework for highly selective separation of acetylene, ethylene and ethane from methane at room temperature has been reported.<sup>13,14</sup>

Over a century ago Paul Sabatier developed nickel-catalyzed hydrogenation as one of the most commonly applied procedures for organic synthesis.<sup>15,16</sup> The use of complex hydrides as reducing reagents causes many environmental concerns. Catalytic hydrogenation is widely considered to be an environmentally benign process while both heterogeneous and homogeneous alternatives are popular in industry.<sup>17-23</sup> Hydrogen is an explosive gas and its production through steam reforming is a highly energy-intensive (700-1000 °C) process and it also causes considerable emission of carbon dioxide, a well-known greenhouse gas.<sup>24</sup> So the current method of production of hydrogen cannot be considered to be environmentally-friendly. Therefore, the overall environmental impact of catalytic hydrogenation cannot be considered negligible. Nowadays, heterogeneous catalysts are being used for the selective reduction of condensed *N*-heterocycles using water both as a solvent and a hydrogen source.<sup>25</sup> More recently, the application of a heterogeneous catalyst in combination with microwave irradiation has been employed as an environmentally benign tool for some contemporary organic syntheses.<sup>26,27</sup> Based on the application of Raney-type Ni-Al alloy in aqueous medium as the hydrogen source as well as solvent, the selective reduction of ketones and reductive amination of carbonyl compounds has been reported.<sup>28,29</sup>

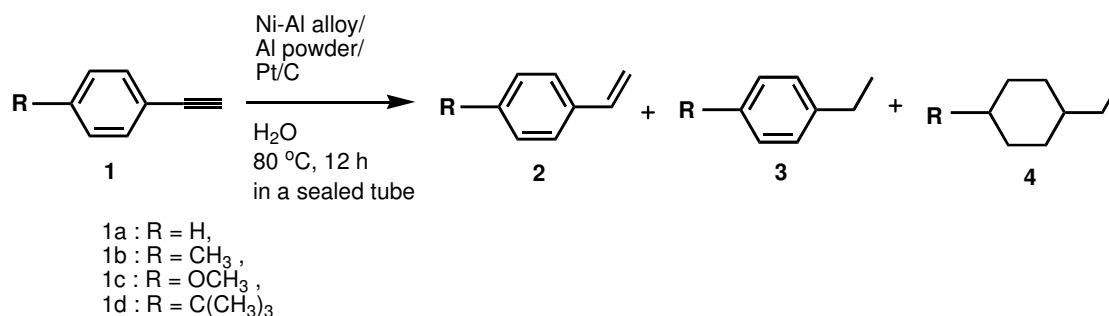
Tashiro *et al.* have pioneered the use of various metal-Al alloys (Ni-Al, Co-Al, Cu-Al, Fe-Al) in water for the reduction of aryl ketones to the corresponding alcohols or alkane derivatives. Raney Ni-Al alloy in water was found to be a good reducing agent for the reduction of aromatic ketones and aldehydes to the corresponding cyclohexane derivatives, but a large amount of alloy was employed in these studies.<sup>30</sup> Thereafter, under microwave irradiation, the reduction of acetophenones was performed using Raney Ni-Al alloy in water. Also reported were the reductive reactions of a series of aromatic ketones with noble metal catalysts such as Rh, Ru, Pd or Pt along with added Al powder in water in a sealed tube.<sup>31,32</sup> Raney Ni-Al was found to be very

efficient in the reduction of various aromatic compounds as well as for dechlorination of mono and dichlorobiphenyls to the corresponding hydrocarbon derivatives. In the absence of any organic solvents under milder reaction conditions, dilute sodium or potassium hydroxide solutions were applied to accelerate the reduction systems.<sup>33–36</sup> Recently, reduction or the oxido-reduction reaction of cinnamaldehyde and its derivatives with Ni-Al alloy and Al powder in water was also reported.<sup>37</sup>

The utilization of water as a chemical reagent is an essential aspect of Green Chemistry.<sup>38</sup> Water as a solvent for organic reactions has many advantages over the use of other organic solvents include among others cost, safety, simplicity of operation and most importantly its benign environmental nature.<sup>39–41</sup> More recently, the Pd/C-Al-water-facilitated selective reduction of a broad variety of functional groups and Pd/C catalyzed hydrogenolysis of dibenzodioxocin lignin model compounds using silanes and water as a hydrogen source has been reported.<sup>42,43</sup> Also, water has been used as a stoichiometric H or D atom donor for tetrahydroxydiboron-mediated palladium-catalyzed transfer hydrogenation and deuteration of alkenes and alkynes.<sup>44</sup> In addition, hydrogenations and deuterium labeling has been carried out with Al-based metal alloys under aqueous conditions.<sup>45</sup> Previously, we reported the reduction of carbonyl compounds by Raney Ni-Al alloy and Al powder in the presence of noble metal catalysts in water.<sup>46</sup> Herein, we illustrate a simple reduction method for the alkyne group as well as an aromatic ring using commercially available Raney Ni-Al alloy and Al powder in the presence of a noble metal catalyst (Pt/C, Pd/C, Ru/C or Rh/C) in water in a sealed tube.

## Results and Discussion

In order to develop an environmentally benign methodology, the reduction of phenylacetylene (**1a**) was performed by using commercially available Al powder and a noble metal catalyst in water in a sealed tube. The functional group that can undergo reduction has been assessed in terms of applicability, yields and chemoselectivity. The reduction of phenylacetylene using the heterogeneous catalysts was investigated to obtain the optimized reaction conditions, *i.e.* the effects of the reaction temperature, time, amount of catalyst and the required volume of water. As a first step, the reduction of phenylacetylene (**1a**) was carried out using only Al powder. The reaction was carried out at 60 °C for 6 h in water in a sealed tube and did not start (*ie* nothing occurred). The reaction did not proceed on increasing the reaction time up to 12 h and at a temperature of 120 °C. Then it was decided to add a noble metal catalyst such as Pt/C, Pd/C, Ru/C or Rh/C and Al powder in water in a sealed tube. Selective and complete reduction of phenylacetylene (**1a**) occurred and the results are summarized in Table 1.



**Scheme 1.** Reduction of substituted phenylacetylenes (**1a-1d**) using Raney Ni-Al, Al powder and Pt/C in H<sub>2</sub>O.

The reduction of phenylacetylene (**1a**) also occurred with high selectivity providing 83% styrene (**2a**) as the major product using Pd/C at 80 °C for 6 h (Table 1; entry 5). Finally, the reduction at 120 °C for 6 h resulted in complete reduction to ethylbenzene in a highly selective and quantitative reaction (Table 1; entry 3, 6) using both catalysts Pt/C and Pd/C. Moreover, the catalytic systems employing Ru/C and Rh/C exhibited a low selectivity for the reduction of alkyne group to the corresponding alkene and alkane groups (Table 1; entries 7, 8).

From these results, it can be concluded that Al powder alone in water is unable to generate hydrogen gas but the addition of a noble metal catalyst can produce hydrogen gas.

**Table 1.** Reduction of phenylacetylene (**1a**) using Al powder and catalyst in H<sub>2</sub>O<sup>a,b</sup>

Entry	Catalyst	Temp. (°C)	Yield (%) <sup>c</sup>		Recovery <b>1a</b>
			<b>2a</b>	<b>3a</b>	
1	none	60	0	0	100
2	Pt/C	60	33	4	63
3	Pt/C	120	0	100	0
4	Pd/C	60	74	10	16
5	Pd/C	80	83	15	2
6	Pd/C	120	0	100	0
7	Ru/C	60	1	2	97
8	Rh/C	60	17	4	79

<sup>a</sup>Substrate: 20 mg (0.20 mmol), Catalyst: 4.5 mol% (metal), Al powder: 100 mg (500 wt%), H<sub>2</sub>O: 0.5 mL.

<sup>b</sup>Conditions: time: 6 h. <sup>c</sup>The yields were determined by GLC.

Tashiro *et al.* also reduced acetophenone with a noble metal catalyst and Al powder to the corresponding ethylbenzene and cyclohexyl benzene in water at 130 °C.<sup>32</sup> Also using Raney Ni-Al alloy in water, reduction of carbonyl groups to the corresponding methylenes in high yields was performed within 2 h by Ishimoto *et al.* as was the microwave-assisted reduction of acetophenones by Miyazawa *et al.*<sup>30,31</sup> Inspired by this, we introduced Raney Ni-Al alloy into our reaction system and carried out the reduction of phenylacetylene (**1a**) for 6 h at 120 °C. A quantitative yield of ethylbenzene was obtained as complete reduction occurred under these reaction conditions (Table 2; entry 3).

**Table 2.** Reduction of phenylacetylene (**1a**) using Raney Ni-Al and Al powder in H<sub>2</sub>O<sup>a,b</sup>

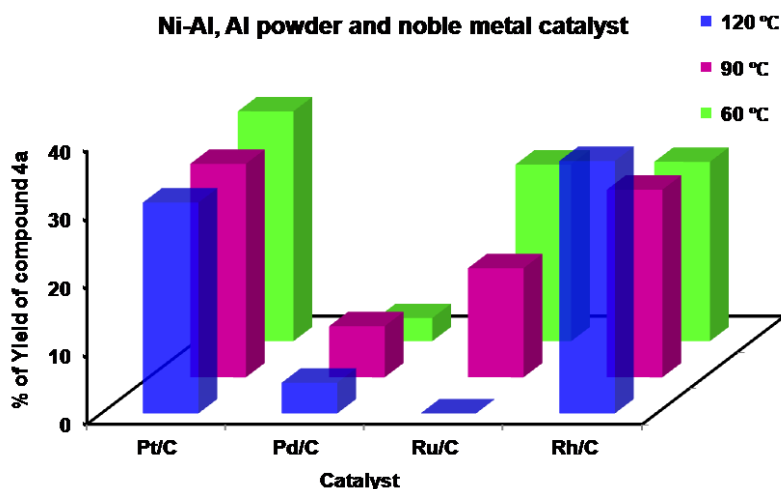
Entry	Temp. (°C)	Yield (%) <sup>c</sup>		Recovery <b>1a</b>
		<b>2a</b>	<b>3a</b>	
1	60	0	0	100
2	90	70	26	4
3	120	0	100	0

<sup>a</sup>Substrate: 20 mg (0.20 mmol), Raney Ni-Al: 100 mg (500 wt%), Al powder: 100 mg (500 wt%), H<sub>2</sub>O: 0.5 mL.

<sup>b</sup>Conditions: time: 6 h. <sup>c</sup>The yields were determined by GLC.

From these results, Raney Ni-Al alloy with Al powder is found to be a good reducing agent for the reduction of an alkyne group to the ethyl radical in high yield.

As the catalytic system appears to work efficiently, noble metal catalysts were introduced into the mixture of Raney Ni-Al alloy and Al powder in water to afford the complete reduction of the aromatic ring of phenylacetylene (**1a**). The reduction was examined using these catalysts at various temperatures for 6 h and the results are plotted in the following Figure 1.



**Figure 1.** Reduction of Phenylacetylene (**1a**) using Raney Ni-Al, Al powder and noble metal catalysts in water for 6 h.

From Figure 1, it is observed that the reduction of an aromatic ring using either Pd/C or Ru/C was less effective compared to systems employing Pt/C or Rh/C. The Rh/C catalyst turned out to be the most effective catalyst for this reduction, but the temperature is comparatively higher than for Pt/C. The reduction product **4a** was afforded in lower than 40% yield in both these cases. For the Pt/C catalyst, the favorable reaction temperature is 60 °C which is lower and more convenient for most organic syntheses. Consequently, the reaction time was increased from 6 h to 12 h in order to increase the yield for the reduction of the aromatic motif. The temperature was fixed at 60 °C under various catalyst combinations using Pt/C, Raney Ni-Al alloy and Al powder. The results are tabulated in Table 3.

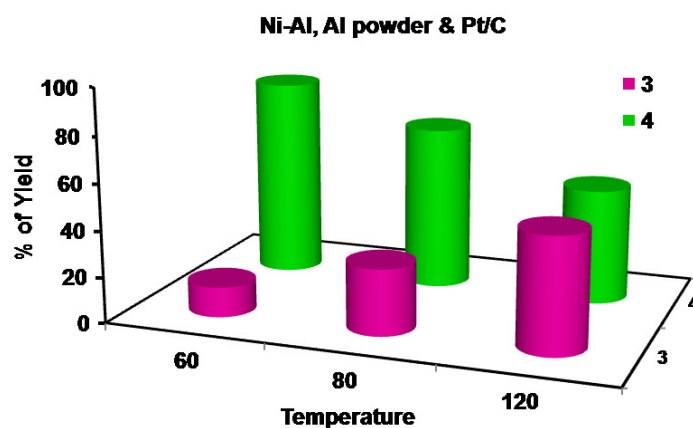
**Table 3.** Reduction of phenylacetylene (**1a**) using Raney Ni-Al, Al powder and Pt/C in H<sub>2</sub>O<sup>a,b</sup>

Entry	Catalyst	<b>2a</b>	<b>3a</b>	Yield (%) <sup>c</sup>	
				<b>4a</b>	<b>1a</b>
1	Ni-Al + Al powder	50	15	0	35
2	Ni-Al + Pt/C	62	36	0	2
3	Pt/C	0	0	0	100
4	Al powder + Pt/C	6	92	2	0
5	Ni-Al + Al powder + Pt/C	0	13	87	0

<sup>a</sup> Substrate: 20 mg (0.20 mmol), Raney Ni-Al: 100 mg (500 wt%), Al powder: 100 mg (500 wt%), catalyst: 4.5 mol% (metal), H<sub>2</sub>O: 0.5 mL. <sup>b</sup> Conditions: temp: 60 °C, time: 12 h. <sup>c</sup> The yields were determined by GLC.

At the time of treatment of phenylacetylene (**1a**) with Pt/C catalyst and Al powder for 12 h, the alkyne group was reduced to an ethyl radical in 92% yield with trace amounts of reduction of aromatic ring (Table 3; entry 4). Pt/C by itself is unable to reduce either the alkyne group or aromatic ring (Table 3; entry 3). Interestingly, Pt/C in the presence of a mixture of Raney Ni-Al and Al powder can reduce the aromatic ring of compound **4a** (87%) (Table 3; entry 5). From these results, it can be stated that Pt/C is an effective catalyst with a mixture of Raney Ni-Al and Al powder in water to generate sufficient nascent hydrogen to reduce the aromatic motif. These results clearly show that a transition-metal catalyst increases the reducing capability of Raney Ni-Al as also reported previously by our group.<sup>46</sup> Guo-Bin Liu *et al.* reported that Raney Ni-Al alloy in a dilute alkaline aqueous solution becomes a powerful reducing agent, which is highly effective in the reduction of benzophenones to the corresponding hydrocarbon derivatives without using any organic solvent.<sup>35</sup> In our case, reduction of phenylacetylene (**1a**) to the corresponding hydrocarbon derivatives is achieved in water without using any alkaline solution and under mild reaction conditions.

Next, in order to obtain higher yields of the aromatic reduction product, the reaction temperature was raised up to 120 °C using Pt/C catalyst in the presence of a mixture of Raney Ni-Al and Al powder. The results are plotted in Figure 2.



**Figure 2.** Effects of temperature on the reduction of phenylacetylene (**1a**) for 12 h.

From Figure 2, it is observed that an increase in the reaction temperature, leads to a gradual decrease in the reduction of the aromatic ring instead of improving the product yield. These results reveal that the rapid generation of hydrogen gas at higher temperature decreases the reduction reaction. A lower temperature is effective for the generation of sufficient nascent hydrogen to reduce the benzene ring. To ascertain whether ethylbenzene can function as an intermediate and produce the desired products under the reaction conditions employed, it was subjected to the same reaction conditions and 100% ethylcyclohexane was obtained.

From the above, the mixture of Raney Ni-Al and Al powder emerged as the best reducing agent for the reduction of the alkyne functional group. To observe the effect of substituents, different types of 4-substituted phenylacetylenes were treated with the reducing agent and the results are shown in Table 4. A series of 4-substituted phenylacetylenes (**1a–1d**) were investigated under the same reaction conditions. In the case of methyl-, methoxy- and *tert*-butyl-phenylacetylene, a temperature of only 60 °C is sufficient for the reduction of the alkyne group (Table 4; entries 2–4). Indeed, only temperature variation *versus* substituent effect was observed. The substituent effect in this case is to modify the reactivity of the substrate leading to reaction at a low temperature. In fact, this could be a clue in understanding the reaction mechanism.

**Table 4.** Reduction of substituted phenylacetylenes (**1a–1d**) to afford compound **3** using Raney Ni-Al and Al powder in H<sub>2</sub>O<sup>a,b</sup>

Entry	Substrate ( <b>1</b> )	Temp. (°C)	Yield (%) <sup>c</sup> <b>3</b>
1	H	120	100[65]
2	CH <sub>3</sub>	60	100
3	OCH <sub>3</sub>	60	100
4	C(CH <sub>3</sub> ) <sub>3</sub>	60	98

<sup>a</sup> Substrate: 20 mg (0.20 mmol), Raney Ni-Al: 100 mg (500 wt%), Al powder: 100 mg (500 wt%), H<sub>2</sub>O: 0.5 mL. <sup>b</sup> Conditions: time: 6 h. <sup>c</sup> The yields were determined by GLC.

Addition of Pt/C to the mixture of Raney Ni-Al and Al powder was found to create the best catalyst system for the reduction of the aromatic ring at 60 °C for 12 h. For the methyl substituted derivative, a 93% yield of the reduction of the aromatic ring was obtained with both *cis* and *trans* products. Unfortunately, for the methoxy and *tert*-butyl derivatives, yields of products were less at 78 and 63%, respectively. For the methoxy containing compound, **4a** was obtained which indicates that cleavage of the C-O bond had occurred. Clearly, this strong reducing agent not only reduces the aromatic ring but also cleaves the polar C-O bond. The presence of the bulky *tert*-butyl group matters for that derivative, as it cannot approach parallel to the metal surface to give the targeted product in high yield. From these substituent effects, it can be summarized that the approach of the 4-substituted phenylacetylenes (**1**) toward the highly porous surface of the Ni and Pt catalyst depends on the pattern of substituents.

**Table 5.** Reduction of substituted phenylacetylene (**1a–1d**) using Raney Ni-Al, Al powder and Pt/C in H<sub>2</sub>O<sup>a,b</sup>

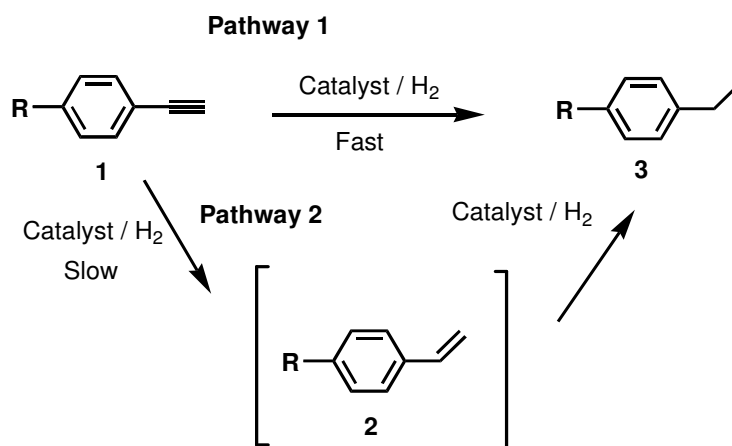
Entry	Substrate ( <b>1</b> )	Yield (%) <sup>c</sup>		Recovery <b>1</b>
		<b>3</b>	<b>4</b>	
1	H	13	87 [50]	0
2	CH <sub>3</sub>	7	93 <sup>d</sup>	0
3	OCH <sub>3</sub>	11	11( <b>4a</b> )+78( <b>4c</b> ) <sup>d</sup>	0
4	C(CH <sub>3</sub> ) <sub>3</sub>	36	63 <sup>d</sup>	0

<sup>a</sup> Substrate: 20 mg (0.20 mmol), Ni-Al: 100 mg (500 wt%), Al powder: 100 mg (500 wt%), catalyst: 4.5 mol% (metal), H<sub>2</sub>O: 0.5 mL. <sup>b</sup> Conditions: temp: 60 °C, time: 12 h. <sup>c</sup> The yields were determined by GLC. <sup>d</sup> *cis*- and *trans*-Isomers.

Though the actual overall yield seems relatively low, one of the most important advantages of this method is that the reaction can be carried out in water which is cheap, readily available and the most environmentally benign solvent. Besides, water serves as an economic source of hydrogen, and as a result no extra hydride or addition of hydrogen is required. Moreover, this is also conducted without the need of any additional strong base. Probably, the noble metal catalysts and Ni of the alloy readily adsorb hydrogen to facilitate the effective reduction of the substrates. The reaction does not also produce any harmful by-products. The only by-product is Al(OH)<sub>3</sub>, which is a non-toxic and an easily recyclable material. The reaction does not require a high

pressure of hydrogen, which is advantageous given the explosive nature of hydrogen that also requires the use of high pressure reaction vessels.

The reaction mechanism of reduction is not yet well understood. Water as a solvent may play an important role in the creation of the catalytic surface (Figure 3).<sup>34</sup> From the substituent effect (Table 4), it was observed that an electron donating substituent could increase the electronic density on the triple bond. This means the first species that is being trapped by the alkyne moiety could be a proton.



**Figure 3.** Proposed reaction pathways for the reduction of phenylacetylenes (**1**).

Being rich in  $\pi$ -electrons, both alkyne group and aromatic ring are adsorbed on the surface of the active Ni metal and react with the reactive form of the hydrogen already adsorbed on the catalyst surface. In water, the Raney Ni-Al alloy reacts in an uncontrolled manner and liberates hydrogen gas which escapes unreacted from the reaction vessel. Based on the GC-MS analysis, a reaction pathway for the reduction of phenylacetylene can be proposed.<sup>47</sup> The reduction of triple bond to a single bond directly in pathway **1** and the single bond is afforded via the intermediate styrene (**2**) as shown in pathway **2**. The intermediate compound **2** only forms when Pd/C is used with Al powder (Table 1; entry 5) and the mixture of Raney Ni-Al alloy with Pt/C (Table 3; entry 2) under mild reaction conditions. These results indicate that pathway **2** is a relatively slower route compared to pathway **1**.

## Conclusions

Raney Ni-Al alloy along with Al powder in water is an effective reducing agent for the reduction of an alkyne group under mild reaction conditions. In addition, the presence of Pt/C in the mixture of Raney Ni-Al alloy together with Al powder in water can further reduce an aromatic ring. The nature of the reduction product formed was found to be strongly influenced by the reaction temperature, time, volume of water and also the amount of catalyst employed. Moreover, the reduction capability of para substituted phenylacetylenes depends on the substituents present. The reduction of the aromatic ring produces both *cis* and *trans* products but the stereochemistry of the cyclohexyl substituted compound has not yet been established. Overall, this reduction is operationally simple, *i.e.* no harsh reaction conditions such as elevated temperatures, high pressures, a hydrogen atmosphere, an inert gas atmosphere, highly alkaline media or any special apparatus are required. Finally, the readily commercially available Raney Ni-Al alloy in water provides yet another very important protocol for the reduction of aromatic compounds.



## Experimental Section

**General.** All melting points are uncorrected.  $^1\text{H}$  NMR spectra were recorded at 300 MHz on a Nippon Denshi JEOL FT-300 NMR spectrometer in  $\text{CDCl}_3$  with  $\text{Me}_4\text{Si}$  as an internal reference. IR spectra were measured as KBr pellets on a Nippon Denshi JIR-AQ20M spectrometer. Mass spectra were obtained on Shimadzu GCMS-QP5050A Ultrahigh Performance Mass Spectrometer AOC-20I, 100 V using a direct-inlet system. G.L.C. analyses were performed by Shimadzu gas chromatograph, GC-2010.

**General procedure for reduction of aromatic compounds.** The mixture of a substrate (20 mg, 0.20 mmol) (Wako), Raney Ni-Al alloy (500 wt%), Al powder (500 wt%) (53-150  $\mu\text{m}$ , 99.5%) (Wako) and Pt/C, Pd/C, Ru/C or Rh/C (20 mg) (4.5 mole % metal) was added to water (0.5 mL) (Wako distilled water). After heating the mixture at 60–120  $^\circ\text{C}$  for 6-12 h, it was cooled to room temperature. The solution was then diluted with 1 mL water and stirred overnight at room temperature in a sealed tube. After 24 h, the solution was extracted with diethyl ether (3  $\times$  2 mL) as per the reported procedure.<sup>37</sup> The combined organic layers were dried over anhydrous  $\text{MgSO}_4$  and filtered through a porous cotton plug followed by concentrating in vacuum to afford the corresponding reduction product. The yields were determined by GLC analysis using the standard compound (1,2,3,4-tetrahydronaphthalene), and the products were identified by GC-MS.

## Acknowledgements

This work was conducted under the Cooperative Research Program of “Network Joint Research Center for Materials and Devices (Institute for Materials Chemistry and Engineering, Kyushu University)”. The EPSRC is thanked for the financial support in the form of a travel grant to CR.

## Supplementary Material

Electronic Supplementary Information (ESI) is available: For the details of the GC and GC-MS data.

## References

1. Niu, M.; Wang, Y.; Li, W.; Jiang, J.; Jin, Z. *Catal. Commun.* **2013**, *38*, 77–81.  
<https://doi.org/10.1016/j.catcom.2013.04.015>
2. López, N.; Vargas-Fuentes, C. *Chem. Commun.* **2012**, *48*, 1379–1391.  
<https://doi.org/10.1039/C1CC14922A>
3. Feng, Q.; Zhao, S.; Wang, Y.; Dong, J.; Chen, W.; He, D.; Wang, D.; Yang, J.; Zhu, Y.; Zhu, H.; Gu, L.; Li, Z.; Liu, Y.; Yu, R.; Li, J.; Li, Y. *J. Am. Chem. Soc.* **2017**, *139*, 7294–7301.  
<https://doi.org/10.1021/jacs.7b01471>
4. Mäsing, F.; Nüsse, H.; Klingauf, J.; Studer, A. *Org. Lett.* **2017**, *19*, 2658–2661.  
<https://doi.org/10.1021/acs.orglett.7b00999>
5. Guo, S.; Zhou, J. *Org. Lett.* **2016**, *18*, 5344–5347.  
<https://doi.org/10.1021/acs.orglett.6b02662>
6. Arman, S. A. V.; Zimmet, A. J.; Murray, I. E. *J. Org. Chem.* **2016**, *81*, 3528–3532.  
<https://doi.org/10.1021/acs.joc.6b00041>
7. Zhou, Q.; Zhang, L.; Meng, W.; Feng, X.; Yang, J.; Du, H. *Org. Lett.* **2016**, *18*, 5189–5191.

- <https://doi.org/10.1021/acs.orglett.6b02610>
8. Whittaker, A. M.; Lalic, G. *Org. Lett.* **2013**, *15*, 1112–1115.  
<https://doi.org/10.1021/ol4001679>
  9. Fedorov, A.; Liu, H.-J.; Lo, H.-K.; Copéret, C. *J. Am. Chem. Soc.* **2016**, *138*, 16502–16507.  
<https://doi.org/10.1021/jacs.6b10817>
  10. Tokmic, K.; Fout, A. R. *J. Am. Chem. Soc.* **2016**, *138*, 13700–13705.  
<https://doi.org/10.1021/jacs.6b08128>
  11. Xiang, S.-C.; Zhang, Z.; Zhao, C.-G.; Hong, K.; Zhao, X.; Ding, D.-R.; Xie, M.-H.; Wu, C.-D.; Das, M. C.; Gill, R.; Thomas, K. M.; Chen, B. *Nat. Commun.* **2011**, *2*, 204.  
<https://doi.org/10.1038/ncomms1206>
  12. Nijem, N.; Wu, H.; Canepa, P.; Marti, A.; Balkus, K. J.; Thonhauser, T.; Li, J.; Chabal, Y. J. *J. Am. Chem. Soc.* **2012**, *134*, 15201–15204.  
<https://doi.org/10.1021/ja305754f>
  13. Hu, T.-L.; Wang, H.; Li, B.; Krishna, R.; Wu, H.; Zhou, W.; Zhao, Y.; Han, Y.; Wang, X.; Zhu, W.; Yao, Z.; Xiang, S.; Chen, B. *Nat. Commun.* **2015**, *6*, 7328.  
<https://doi.org/10.1038/ncomms8328>
  14. He, Y.; Zhang, Z.; Xiang, S.; Fronczek, F. R.; Krishna, R.; Chen, B. *Chem. -Eur. J.* **2012**, *18*, 613–619.  
<https://doi.org/10.1002/chem.201102734>
  15. Sabatier, P.; Senderens, J. B. *Compt. Rend.* **1899**, *128*, 1173.
  16. Sabatier, P.; *La Catalyse en Chimie Organique* **1913**, Catalysis in Organic Chemistry (Translated by Reid E. E.); Van Norstrand: Princeton NJ, **1922**, 923.
  17. Nishimura, S. *Handbook of Heterogeneous Catalytic Hydrogenation for Organic Synthesis*; Wiley: New York, 2001.
  18. Blaser, H.-U.; Malan, C.; Pugin, B.; Spindler, F.; Steiner, H.; Studer, M. *Adv. Synth. Catal.* **2003**, *345*, 103–151.  
<https://doi.org/10.1002/adsc.200390000>
  19. Kulkarni, A.; Török, B. *Curr. Org. Synth.* **2011**, *8*, 187–207.  
<https://doi.org/10.2174/157017911794697295>
  20. Noyori, R. *Angew. Chem. Int. Ed.* **2002**, *41*, 2008–2022.  
[https://doi.org/10.1002/1521-3773\(20020617\)41:12<2008::AID-ANIE2008>3.0.CO;2-4](https://doi.org/10.1002/1521-3773(20020617)41:12<2008::AID-ANIE2008>3.0.CO;2-4)
  21. Girard, C.; Kagan, H. B. *Angew. Chem. Int. Ed.* **1998**, *37*, 2922–2959.  
[https://doi.org/10.1002/\(SICI\)1521-3773\(19981116\)37:21<2922::AID-ANIE2922>3.0.CO;2-1](https://doi.org/10.1002/(SICI)1521-3773(19981116)37:21<2922::AID-ANIE2922>3.0.CO;2-1)
  22. Knowles, W. S. *Angew. Chem. Int. Ed.* **2002**, *41*, 1998–2007.
  23. Blaser, H.-U.; Pugin, B.; Spindler, F.; Thommen, M. *Acc. Chem. Res.* **2007**, *40*, 1240–1250.  
<https://doi.org/10.1021/ar7001057>
  24. Press, R. J.; Santhanam, K. S. V.; Miri, M. J.; Bailey, A. V.; Takacs, G. A. *Introduction to Hydrogen Technology*, Ch. 4.1 pp 195–210, Wiley: Hoboken, NJ, 2009.
  25. Cho, H.; Török, F.; Török, B. *Org. Biomol. Chem.* **2013**, *11*, 1209–1215.  
<https://doi.org/10.1039/c2ob26903a>
  26. Daştan, A.; Kulkarni, A.; Török, B. *Green Chem.* **2012**, *14*, 17–37.  
<https://doi.org/10.1039/C1GC15837F>
  27. Bag, S.; Dasgupta, S.; Török, B. *Curr. Org. Synth.* **2011**, *8*, 237–261.  
<https://doi.org/10.2174/157017911794697321>
  28. Tomin, A.; Lazarev, A.; Bere, M. P.; Redjeb, H.; Török, B. *Org. Biomol. Chem.* **2012**, *10*, 7321–7326.

- <https://doi.org/10.1039/c2ob25941a>
29. Schäfer, C.; Nişancı, B.; Bere, M. P.; Daştan, A.; Török, B. *Synthesis* **2016**, *48*, 3127–3133.  
<https://doi.org/10.1055/s-0035-1561647>
30. Ishimoto, K.; Mitoma, Y.; Nagashima, S.; Tashiro, H.; Prakash, G.K.S.; Olah, G. A.; Tashiro, M. *Chem. Commun.* **2003**, 514–515.  
<https://doi.org/10.1039/b211571a>
31. Miyazawa, A.; Tashiro, M.; Prakash, G.K.S.; Olah, G. A. *Bull. Chem. Soc. Jpn.* **2006**, *79*, 791–792.  
<https://doi.org/10.1246/bcsj.79.791>
32. Hashimoto, I.; Suzuki, H.; Ishimoto, K.; Tashiro, H.; Prakash, G. K. S.; Olah, G. A.; Tashiro, M. *Jpn. J. Deuterium Sci.* **2006**, *12*, 39–44.
33. Tsukinoki, T.; Kanda, T.; Liu, G.-B.; Tsuzuki, H.; Tashiro, M. *Tetrahedron Lett.* **2000**, *41*, 5865–5868.  
[https://doi.org/10.1016/S0040-4039\(00\)00636-5](https://doi.org/10.1016/S0040-4039(00)00636-5)
34. Liu, G.-B.; Tashiro, M.; Thiemann, T. *Tetrahedron* **2009**, *65*, 2497–2505.  
<https://doi.org/10.1016/j.tet.2009.01.052>
35. Liu, G.-B.; Zhao, H.-Y.; Zhu, J.-D.; He, H.-J.; Yang, H.-J.; Thiemann, T.; Tashiro, H.; Tashiro, M. *Synth. Commun.* **2008**, *38*, 1651–1661.  
<https://doi.org/10.1080/00397910801929762>
36. Liu, G.-B.; Zhao, H.-Y.; Dai, L.; Thiemann, T.; Tashiro, H.; Tashiro, M. *J. Chem. Res.* **2009**, 579–581.  
<https://doi.org/10.3184/030823409X12506792542783>
37. Simion, A.-M.; Arimura, T.; Simion, C. *Compt. Rend. Chimie* **2013**, *16*, 476–481.  
<https://doi.org/10.1016/j.crci.2012.11.022>
38. Anastas, P. T.; Warner, J. C. *Green Chemistry, Theory and Practice*, Oxford University Press, New York, 1998.
39. Li, C.-H.; Chan, T.-H. *Organic Reactions in Aqueous Media*; John Wiley and Sons, Inc.: New York, **1997**; pp.13-189.
40. Lubineau, A.; Auge, J.; Queneau, Y. *Synthesis* **1994**, 741–760.  
<https://doi.org/10.1055/s-1994-25562>
41. Li, C.-J. *Chem. Rev.* **1993**, *93*, 2023–2035.  
<https://doi.org/10.1021/cr00022a004>
42. Schäfer, C.; Ellstrom, C. J.; Cho, H.; Török, B. *Green Chem.* **2017**, *19*, 1230–1234.  
<https://doi.org/10.1039/C6GC03032G>
43. Subbotina, E.; Galkin, M. V.; Samec, J. S. M. *ACS Sustainable Chem. Eng.* **2017**, *5*, 3726–3731.  
<https://doi.org/10.1021/acssuschemeng.7b00428>
44. Cummings, S. P.; Le, T.-N.; Fernandez, G. E.; Quiambao, L. G.; Stokes, B. J. *J. Am. Chem. Soc.* **2016**, *138*, 6107–6110.  
<https://doi.org/10.1021/jacs.6b02132>
45. Cho, H.; Schäfer, C.; Török, B. *Curr. Org. Synth.* **2016**, *13*, 255–277.  
<https://doi.org/10.2174/1570179413999151110122145>
46. Rayhan, U.; Do, J.-H.; Arimura, T.; Yamato, T. *Compt. Rend. Chimie* **2015**, *18*, 685–692.  
<https://doi.org/10.1016/j.crci.2014.10.011>
47. Rayhan, U.; Kowser, Z; Redshaw, C.; Yamato, T. *Tetrahedron* **2016**, *72*, 6943–6947.  
<https://doi.org/10.1016/j.tet.2016.09.021>