

## Efficient and Chemoselective Reduction of Olefins Catalyzed by Fe<sub>3</sub>O<sub>4</sub> Nanoparticles using Hydrazine Hydrate<sup>†</sup>

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Olefin reduction is one of the most fundamental reactions in organic synthesis. Most common reduction methods used in the laboratories include the use of heterogeneous metal catalysts such as Pd/C, Rh/C, Pt/C, and Raney nickel in the presence of hydrogen gas. As an alternative to the metal-catalyzed hydrogenation, hydrazine mediated olefin reduction has been known for almost one hundred years.<sup>1</sup> The use of hydrazine as a hydrogen source in the olefin reduction gives the advantage of avoiding the use of a flammable gas and expensive metal catalysts. In the hydrazine-mediated hydrogenation of olefins, it is generally accepted that double bonds are reduced by diimide (NH=NH), which is generated from hydrazine *via* oxidation.<sup>2</sup>

Over the past several decades, many methods of olefin reduction using diimide precursors have been reported. Although hydrazine decomposition is known to occur even in the absence of oxidants,<sup>3</sup> many strategies have been employed to facilitate the oxidation of hydrazine to diimide. First, instead of hydrazine itself, hydrazine derivatives or diimide precursors such as sodium- or potassium hydrazide, toluenesulfonic hydrazide, azodiformate, or azodicarboxylic acid have been used.<sup>4</sup> Second, additives such as oxygen or hydrogen peroxide and other oxygen equivalent systems have been used often with copper salt, mercury oxide, or potassium ferricyanide.<sup>5</sup> Recently, a broad range of olefin substrates was tested for hydrazine hydrate-mediated reduction with a metal catalyst or through a combination of sodium bromate and acetic acid.<sup>6</sup> From evaluation of literature over several decades, it appears that *controlling the speed of diimide generation from hydrazine is a key element* in successful diimide-mediated olefin reduction. Herein, we report on the efficient method of olefin reduction using iron oxide nanoparticles as an extremely convenient and recyclable catalyst. Being the most abundant metal on earth, iron is one of the most readily available and environmentally friendly metals. However, there have been scarce reports on simple olefin reduction methods using hydrazine hydrate in the presence of iron oxide catalyst under neutral conditions.

Generally, magnetically separable catalysts are regarded as one of the most promising heterogeneous catalysts due to

their simple recycling process.<sup>7</sup> Among them, magnetic nanoparticles have attracted much attention because they show good dispersibility and allow for an easy recovery after use.<sup>8</sup> Herein, we report on the utilization of commercially available Fe<sub>3</sub>O<sub>4</sub> nanoparticles (<50 nm, Aldrich<sup>®</sup>) as convenient and practical olefin reduction catalysts.

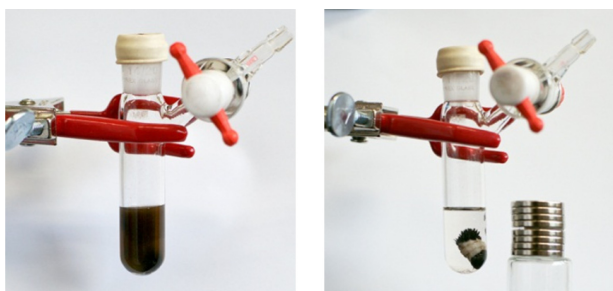
First, we examined the catalytic activity of the Fe<sub>3</sub>O<sub>4</sub> nanoparticles taking the reduction of styrene to ethylbenzene as a test reaction (Table 1). Progress of each reaction was monitored after 16 h. As can be seen in Table 1, even though the reduction of styrene with hydrazine hydrate proceeded without the Fe<sub>3</sub>O<sub>4</sub> nanoparticle catalysts in EtOH at rt (45% yield) and even more (70% yield) at 80°C (entries 1 and 2, respectively), clearly the presence of Fe<sub>3</sub>O<sub>4</sub> nanoparticle catalysts (40 mol %) enhanced the reaction rate of the reduction under otherwise the same reaction conditions and drove the reaction to completion within 16 h (entry 3). The reaction rate appeared to be dependent upon the amount of Fe<sub>3</sub>O<sub>4</sub>; the reaction using 20 mol % of catalyst was slightly slower than that with 40 mol %, and it took 18 h to complete the reaction (entry 4). Though there is little reactivity

**Table 1.** Optimization of reaction conditions in the reduction of styrene<sup>a</sup>

Entry	Fe <sub>3</sub> O <sub>4</sub> (mol %)	Hydrazine (equiv)	Solvent	Temp (°C)	Yield (%) <sup>b</sup>
1	-	8	Ethanol	rt	45
2	-	8	Ethanol	80	70
<b>3</b>	<b>40</b>	<b>8</b>	<b>Ethanol</b>	<b>80</b>	<b>99</b>
4 <sup>c</sup>	20	8	Ethanol	80	99
5	40	8	Ethanol	rt	48
6	40	4	Ethanol	80	81
7	40	8	Cyclohexane	80	10
8	40	8	Toluene	80	42
9	40	8	Benzene	80	11
10	40	8	1,4-Dioxane	80	18
11	40	8	DMF	80	27

<sup>a</sup>All reactions were carried out with 1.0 mmol styrene in 6.0 mL of solvent for 16 h unless otherwise noted. <sup>b</sup>Yields were determined through GC analyses. <sup>c</sup>The reaction was complete in 18 h.

<sup>†</sup>This paper is dedicated to Professor Eun Lee on the occasion of his honourable retirement.



**Figure 1.** Magnetic separation of Fe<sub>3</sub>O<sub>4</sub> catalyst after the reaction.

**Table 2.** Recycling of Fe<sub>3</sub>O<sub>4</sub> nanoparticle catalyst in the reduction of styrene<sup>a</sup>

Run	Time	Yield (%) <sup>b</sup>
1		99
3		99
5	16 h	99
7		99
10		99

<sup>a</sup>All reactions were carried out with 1.0 mmol of styrene in 6.0 mL EtOH at 80 °C. <sup>b</sup>Yields were determined through GC analyses.

difference in the reactions using either 20 or 40 mol % catalysts in the case of styrene, sterically more hindered olefins proceeded with noticeably increased reactivity with 40 mol % catalyst, therefore we chose 40 mol % catalyst as a part of our standard reaction conditions (*vide infra*). Reaction at room temperature proceeded very slowly (entry 5) and reaction with 4 equiv hydrazine hydrate was a little slower than that with 8 equiv hydrazine hydrate, giving 81% yield at 16 h (entry 6). When the reaction was performed in a non-polar solvent such as cyclohexane, toluene or benzene at 80 °C, a lower yield was observed presumably due to the lower dispersibility of the iron oxide nanoparticles in the nonpolar solvents (entries 7-9). Even when a polar aprotic solvent such as DMF was used, a low yield was observed (entry 11). Therefore, we chose ethanol as an optimal solvent for olefin reduction.

With the optimized reaction conditions in hand, we examined the recycling capacity of the Fe<sub>3</sub>O<sub>4</sub> nanoparticle catalyst in the reduction of styrene.<sup>9</sup> After completion of the reaction, the catalyst was collected with an external magnet and the solution was decanted (Fig. 1) and then directly analyzed with gas chromatography. The remaining catalyst was washed with ethanol (5 mL × 2), dried under vacuum, and reused for the next cycle of the reaction, and the results are summarized in Table 2. Each reaction was complete in 16 h and the catalyst showed no loss of reactivity up to 10 recycles. Figure 2 shows TEM images of Fe<sub>3</sub>O<sub>4</sub> catalyst before use and after 10<sup>th</sup> run. They appear almost unchanged in their size and shape.

Based on the results in Table 2, we examined the substrate scope of the reduction protocol (Table 3). Most of mono- and di-substituted olefins, whether they are aliphatic or aromatic, were reduced to the corresponding saturated compounds in excellent yields. Reduction of mono-

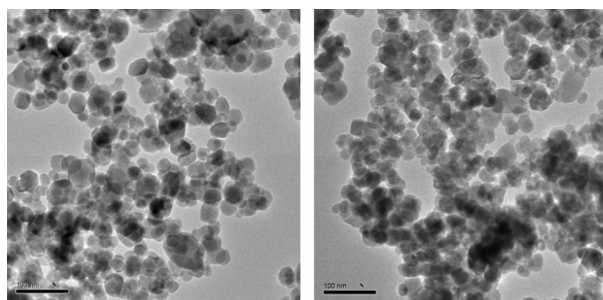
**Table 3.** Substrate scope of Fe<sub>3</sub>O<sub>4</sub> catalyzed olefin reduction<sup>a</sup>

$$\text{R}_1 \text{---} \text{C}(\text{R}_2) \text{=C}(\text{R}_3) \xrightarrow[80\text{ }^\circ\text{C}]{\text{Fe}_3\text{O}_4, \text{Hydrazine}} \text{R}_1 \text{---} \text{C}(\text{R}_2) \text{---} \text{C}(\text{R}_3)$$

Entry	Substrate	Product	Time (h)	Yield (%) <sup>b</sup>
1			36 (37)	80 <sup>c</sup> (87) <sup>d</sup>
2			2	99
3 <sup>e</sup>			48	65 <sup>e</sup>
4			14	99
5			6	99
6			5	93
7			17	99
8			21	99
9			13	99
10			6	99
11			7	99
12			28	99
13			36	21 <sup>f</sup>

<sup>a</sup>All reactions were carried out with 1.0 mmol of olefin and 40 mol % Fe<sub>3</sub>O<sub>4</sub> catalyst in 6.0 mL EtOH at 80 °C unless otherwise noted. <sup>b</sup>Yields were determined through GC analyses. <sup>c</sup>Excess (20 equiv) hydrazine was used. <sup>d</sup>Reaction was carried out with 2 mL benzene as a co-solvent. <sup>e</sup>No *cis*-stilbene was detected from GC analysis. <sup>f</sup>Excess (12 equiv) hydrazine was used.

substituted olefins proceeded extremely well (entries 4-6). Both *cis*- and *trans*-di-substituted olefins as well as 1,2-disubstituted olefin were reduced efficiently (entries 1-2, 7-11, and 12), although the reduction of *trans*-stilbene was much slower than *cis*-stilbene (entries 1 and 2, respectively). The low reactivity of the *trans*-stilbene may be due to lower solubility of the olefin and addition of benzene as a co-solvent slightly increased the yield (entry 1). Triple bond was also reduced fully to the saturated bond (entry 3), although it took a long time. It is of particular note that no significant amount of side product formation was observed



**Figure 2.** TEM images of  $\text{Fe}_3\text{O}_4$  nanoparticle before use (left) and after 10 times of use (right)

**Table 4.** Different reactivity between *cis*- and *trans*-stilbene and *cis*-stilbene and 1,2-diphenylacetylene<sup>a</sup>

Entry	Substrate	Time (h)	Products (%) <sup>b</sup>
1	<i>cis</i> -stilbene	2	99
	<i>trans</i> -stilbene		2.6
2	<i>cis</i> -stilbene	2	99
	1,2-diphenylacetylene		1.6

<sup>a</sup>All reactions were carried out using 1.0 mmol of unsaturated compounds with 40 mol %  $\text{Fe}_3\text{O}_4$  and 8 equiv hydrazine hydrate in 6.0 mL EtOH and 2 mL benzene at 80 °C. <sup>b</sup>Yields were determined through GC analyses.

in the reactions of compounds containing other reducible functional groups such as *O*-allyl, *O*-benzyl, and halogen groups (entries 5-8). Reduction of di-substituted cyclic olefins proceeded smoothly in 6-7 h to furnish excellent yields of products (entries 10 and 11). Complete reduction of 1,1-disubstituted olefin was observed in 28 h (entry 12), although the reduction of tri-substituted olefin was quite slow even in the presence of 12 equiv hydrazine hydrate, furnishing only 21% yield after 36 h (entry 13).

To investigate if different reactivities between *cis*- and *trans*-olefins and between *cis*-olefin and alkyne can be utilized in the reduction of one unsaturated compound over another, we have investigated a set of reactions including *cis*- and *trans*-stilbenes, and another set including *cis*-stilbene and diphenylacetylene (Table 4). As shown in Table 4, it was found that a very selective reduction of *cis*-stilbene was possible in the presence of either *trans*-stilbene or 1,2-diphenylacetylene.

In conclusion, we have shown that efficient olefin reductions can be accomplished using hydrazine hydrate in presence of  $\text{Fe}_3\text{O}_4$  nanoparticle catalysts at 80 °C in refluxing EtOH. Under the optimized conditions, styrene was converted to ethylbenzene in >99% yield in 16 h and various mono- and di-substituted alkenes and alkynes were efficiently reduced to the corresponding alkanes. Using this reduction conditions, alkenes were reduced to the corresponding alkanes with excellent chemoselectivities in the presence of other reducible functional groups such as halogen, *O*-allyl and *O*-benzyl groups. Considering that the reaction conditions involve no flammable gas and produce no hazardous waste, the system offers an efficient way to a practical reduction conditions for mono- and di-substituted olefins.

## Experimental Section

A general procedure for the recycling of  $\text{Fe}_3\text{O}_4$  catalyst in olefin reductions: To an oven-dried, two-necked 25 mL round-bottom flask equipped with a magnetic stir bar and a reflux condenser,  $\text{Fe}_3\text{O}_4$  (92 mg, 0.40 mmol) and ethanol (6.0 mL) were added, and the mixture was sonicated in an ultrasonic bath for 1 minute under  $\text{N}_2$  atmosphere. Styrene (1.0 mmol) and hydrazine monohydrate (380  $\mu\text{L}$ , 8 equiv) were added. Then the reaction mixture was stirred at 80 °C under argon atmosphere until the reaction was completed. After magnetic separation of the catalyst (see Fig. 2), the remaining solution was decanted, then directly analyzed with gas chromatography. The remaining catalyst was washed with ethanol (5 mL  $\times$  2), dried under vacuum, and reused for the next cycle of the reaction.

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