# A Mild, Highly Efficient Addition of Alkynes to Aldehydes Catalyzed by Titanium Dioxide-Supported Silver Nanoparticles

Min Yu,<sup>a</sup> Yong Wang,<sup>a</sup> Weijiang Sun,<sup>a</sup> and Xiaoquan Yao<sup>a,\*</sup>

 <sup>a</sup> Department of Applied Chemistry, School of Material Science and Engineering, Nanjing University of Aeronautics and Astronautics, Nanjing 210016, People's Republic of China Fax: (+86)-25-5211-2626; phone: (+86)-25-5211-2902; e-mail: yaoxq@nuaa.edu.cn

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**Abstract:** Titanium dioxide-supported silver nanoparticles were utilized as a highly efficient catalyst for the addition of terminal alkynes to aldehydes to prepare propargylic alcohols with the promotion by triphenylphosphine. Both a significant support effect and a ligand effect were observed in the catalytic reaction. With this protocol, various propargylic alcohol derivatives were synthesized from aldehydes and terminal alkynes in good to excellent yields. Furthermore, the catalyst could be recovered and reused effectively without obvious reduction in catalytic activity.

**Keywords:** ligand promotion; propargylic alcohols; silver nanoparticles; support effects

Propargylic alcohols are of considerable interest in organic synthesis because they are useful precursors for the synthesis of various important core structures in organic chemistry, such as indenes, furans, pyrroles, thiophene, triazoles,  $\alpha$ ,  $\beta$ -unsaturated aldehydes, and ketones, et al.<sup>[1]</sup> Recently, several different methods for preparing propargylic alcohols have been reported. Compared with the classical method using metal acetylides, an alternative and more atom-economical approach involves the catalytic addition of terminal alkynes to aldehydes. Recently, Carreira and co-workers developed a Zn(OTf)<sub>2</sub>-catalyzed addition of alkynes to aliphatic aldehydes.<sup>[2]</sup> Shibasaki et al. reported a catalytic alkynylation of aldehydes and ketones with InBr<sub>3</sub> or In(OTf)<sub>3</sub> as catalyst.<sup>[3]</sup> Li and his coworkers reported a RuCl<sub>3</sub>/InCl<sub>3</sub>-catalyzed alkynylation of aldehydes in water,<sup>[4]</sup> and then, a silver(I) phosphine complex-catalyzed reaction was also reported.<sup>[5]</sup>

Recently, much attention has been attracted to the use of nanoparticles as catalysts in organic reactions,<sup>[6]</sup> because their intriguing properties are different from those of their corresponding bulk materials. Metal nanoparticles have a characteristic high surface area that translates into more active sites per unit area, and can maximize the reaction rates and minimize consumption of the catalyst. Because of their easy preparation and relative stabilities in air, the nanoparticles of coinage metals, such as copper, silver and gold, were widely reported, and there are many excellent examples on their applications as catalysts in organic reactions. In comparison with many examples using copper<sup>[7]</sup> or gold nanoparticles<sup>[8]</sup> as catalysts, there are only a few reports on the use of silver nanoparticles (Ag NPs) as catalyst, and in most cases, Ag NPs worked as dehydrogenation catalysts.<sup>[9]</sup> Few reports were concerned with the construction of carbon-carbon bonds or carbon-hetero bonds.<sup>[10]</sup> Very recently, we observed that carbon-supported Ag NPs could be used as catalyst for a highly efficient annulation of 2-(1-hydroxy-3-arylprop-2-ynyl)phenols to prepare the key intermediate of aurones with the promotion of phosphine ligands, which was also the first example about the ligand effect on Ag NPs.<sup>[11]</sup>

Herein, we wish to report a highly efficient addition of alkynes to aldehydes catalyzed by  $TiO_2$ -supported Ag nanoparticles (Ag/TiO<sub>2</sub>), in which both a significant support effect and a ligand effect were observed. The catalyst showed much higher catalytic activities than the reported Ag (I)-phosphine complex,<sup>[5]</sup> and gave good to excellent yields for a variety of aldehydes and terminal alkynes. Furthermore, the catalyst could be recovered and reused effectively, no obvious reduction on catalytic activity was observed for several recycles.

With the cross-coupling of 2-bromobenzaldehyde (1a) and phenylacetylene (2a) as prototype, Ag NPs were prepared and examined as catalyst. Obviously,

Table 1. Ag NPs-catalyzed addition of 2-bromobenzaldehyde (1a) and phenylacetylene (2a).<sup>[a]</sup>

CHO Br	+	Cat. ligand, base solvent	CH=	
1a	2a		3a	

Entry	Catalyst (mol%)	Ligand (mol%)	Base (mol%)	Solvent	Conditions	Result <sup>[b]</sup> [%]
1	Ag NPs (10)	_	( <i>i</i> -Pr) <sub>2</sub> NEt (40)	water	100°C, 24 h	N.D.
2	Ag NPs (10)	Cy <sub>3</sub> P (10)	$(i-Pr)_2 NEt (40)$	water	100°C, 24 h	49
3	Ag NPs (10)	$Cy_{3}P(10)$	$Et_{3}N$ (40)	water	100°C, 24 h	63
4	Ag NPs (10)	$Cy_{3}P(10)$	$Na_2CO_3$ (40)	water	100°C, 24 h	37
5	Ag NPs (10)	bipyridine (10)	$Et_{3}N(40)$	water	100°C, 24 h	16
6	Ag NPs (10)	DPPP (10)	$Et_{3}N(40)$	water	100°C, 24 h	35
7	Ag NPs (10)	DPPE (10)	$Et_{3}N(40)$	water	100°C, 24 h	31
8	Ag NPs (10)	<b>DPPF</b> (10)	$Et_{3}N(40)$	water	100°C, 24 h	42
9	Ag NPs (10)	<b>DPPB</b> (10)	$Et_{3}N(40)$	water	100°C, 24 h	59
10	Ag NPs (10)	$PPh_3(10)$	$Et_{3}N(40)$	water	100°C, 24 h	77
11	Ag NPs (10)	$PPh_3(10)$	$Et_{3}N(40)$	THF	70°C, 24 h	N.D.
12	Ag NPs (10)	$PPh_3$ (10)	$Et_{3}N(40)$	toluene	110°C, 24 h	N.D.
13	Ag NPs (10)	$PPh_3(10)$	$Et_{3}N(40)$	water/toluene	100°C, 24 h	7
14	Ag NPs (10)	$PPh_3(10)$	$Et_{3}N(40)$	water/CH <sub>2</sub> Cl <sub>2</sub>	40°C, 24 h	5
15	Ag NPs (1)	$PPh_3$ (10)	$Et_{3}N(40)$	water	100°C, 24 h	59
16	Ag NPs (5)	$PPh_3$ (10)	$Et_{3}N(40)$	water	100°C, 24 h	85
17	Ag NPs (20)	$PPh_3$ (10)	$Et_{3}N(40)$	water	100°C, 24 h	81
18	Ag NPs (5)	$PPh_3(10)$	$Et_{3}N(40)$	water	60°C, 24 h	89
19	Au NPs (5)	$PPh_3$ (10)	$Et_{3}N(40)$	water	60°C, 24 h	10
20	Cu NPs (5)	$PPh_3(10)$	$Et_3N(40)$	water	60°C, 24 h	41

<sup>[a]</sup> *Reaction conditions:* **1a** (1 mmol), **2a** (3 equiv.), catalyst, ligand, base, solvent (3 mL) were heated under nitrogen for 24 h. <sup>[b]</sup> Isolated yield.

there was no reaction with pure Ag NPs as catalyst (entry 1, Table 1). Considering the ligand effect observed previously in our reported Ag NPs-catalyzed annulation,<sup>[11]</sup> a catalytic amount of phosphine ligand was added to improve the reaction. To our delight, the reaction then proceeded successfully with the promotion of 10 mol% of Cy<sub>3</sub>P, and propargylic alcohol 3a was obtained by 49% of yield (entry 2). This result suggested that the phosphine ligand triggered the catalytic reaction. The detailed conditions were then examined, such as base (entries 3 and 4), ligands (entries 5–10), solvents (entries 11–14), the loading of Ag NPs (entries 15–17) and temperature (entry 18). Thus, the combination of Ag NPs/PPh<sub>3</sub> with 0.4 equivalents of Et<sub>3</sub>N in water was found to be the best of choice, and up to 89% yield was achieved. It should be mentioned here that PPh<sub>3</sub> was more effective than Cy<sub>3</sub>P which was reported as the best ligand in silver(I) phosphine complex-catalyzed reaction.<sup>[5]</sup> With the optimized conditions, Au NPs and Cu NPs were also tested in the reaction instead of Ag NPs. However, lower conversions were observed in both of cases. (entry 18 vs. entries 19 and 20).

The nature of the support materials proved to be an important influential factor for the catalytic activities of nanoparticles in the previous reports.<sup>[12]</sup> Considering further improvement of the reaction as well as convenience in handling and storage, a variety of metal oxide-supported Ag NPs, with same silver content (10 wt%) and similar particle size, were prepared and examined as catalyst in the coupling reaction (Table 2).<sup>[13]</sup>

It can be seen from Table 2 that the best result was achieved with Ag/TiO<sub>2</sub>-10 (Ag=10 wt%) as catalyst. The catalytic activity was increased significantly and up to 97% yield was achieved in the presence of TiO<sub>2</sub> (entries 4 and 5 in Table 2 *vs.* entry 18 in Table 1). To the best of our knowledge, this is also the first example of the use of TiO<sub>2</sub>-supported Ag NPs as catalyst to construct carbon-carbon bonds; such supported Ag NPs were only reported as a photocatalyst previous-ly.<sup>[14]</sup>

The supported catalyst could be separated and recovered conveniently by centrifugation from the reaction mixture, and then, new solvent, substrate and fresh phosphine ligand were added to set up a new reaction. Following this procedure, the catalyst was recycled effectively for two times without an obvious decrease in yields or catalytic activities (Table 2, entries 6 and 7). It is worthwhile to mention that the reaction could be carried out without air exclusion, which gave the same result as the reaction under a ni-

**Table 2.** Coupling of 2-bromobenzaldehyde (1a) and phenylacetylene (2a) catalyzed by supported Ag NPs.<sup>[a]</sup>



1	$Al_2O_3$	60°C, 24 h	76	
2	$CeO_2$	60°C, 24 h	63	
3	SiO <sub>2</sub>	60°C, 24 h	80	
4	$TiO_2$	60°C, 24 h	96	
5	TiO <sub>2</sub>	60 °C, 12 h	97	
6 <sup>[c]</sup>	TiO <sub>2</sub>	60 °C, 12 h	95	
7 <sup>[d]</sup>	TiO <sub>2</sub>	60 °C, 12 h	93	
8 <sup>[e]</sup>	TiO <sub>2</sub>	60 °C, 12 h	97	
9 <sup>[e]</sup>	TiO <sub>2</sub>	r.t., 36 h	95	

[a] *Reaction conditions:* **1a** (1 mmol), **2a** (3 equiv.), catalyst (5 mol% of silver), PPh<sub>3</sub> (10 mol%), Et<sub>3</sub>N (40 mol%), and water (3 mL) were mixed and heated under nitrogen.

<sup>[b]</sup> Isolated yield.

<sup>[d]</sup> The catalyst was reused for the second time.

<sup>[e]</sup> The reaction was carried out in air.

trogen atmosphere (Table 2, entry 8 *vs.* entry 5). Furthermore, an excellent yield was also achieved at room temperature after a prolonged reaction time (Table 2, entry 9).

In order to further understand the effect of the acid-base characteristics of the support, the initial rate of reaction  $(\text{mmol g}^{-1} \text{ catalyst})$  was plotted as a function of the electronegativity of the metal species in the support material, which has been used as a parameter of acidity of metal oxides (Figure 1). The Ag NPs supported on TiO<sub>2</sub>, which have suitable acidic sites, showed the highest catalytic activity. The sup-



**Figure 1.** Initial rate of reaction ( $mmol g^{-1}$  catalyst) *versus* the electronegativity of the support cations.



**Figure 2.** TOF based on the total Ag atoms *versus* the loading of Ag on  $TiO_2$  catalysts.

port with strong basic character (CeO<sub>2</sub>) and that with an acidic character (SiO<sub>2</sub>) are not suitable for the reaction. Use of Al<sub>2</sub>O<sub>3</sub>, which has both acidic and base groups, also resulted in a low activity. We proposed that suitable acidic sites on the silver-TiO<sub>2</sub> surface might facilitate the binding of aldehyde, and accelerate the addition of silver acetylide to the carbonyl group.

In many examples on heterogeneous catalysis, the loading of a metal species onto the support is one of key factors to influence the reaction.<sup>[15]</sup> Thus, several catalyst samples with different silver loadings on  $TiO_2$  were prepared and examined in the coupling reaction of **1a** and **2a**. The turnover frequency based on the total Ag atoms (TOF) was then plotted as a function of the silver loading (Figure 2). 10 wt% (Ag/TiO<sub>2</sub>-10) was found as the most suitable loading amount for this reaction.

To further understand the nature of the Ag NPscatalyzed reaction, a "hot separation" experiment was designed and carried out:<sup>[16]</sup> the solid catalyst was removed from reaction mixture by centrifugation after 2 h heating at 60 °C, and then, the residue was stirred at the same temperature for another 10 h. No further increase in conversion was observed (Scheme 1). This result indicated that the reaction should take place on the surface of the solid catalyst rather than by the presence of soluble silver-phosphine complex in the solution.

Therefore, the scope of the reaction was investigated with a series of aldehydes and terminal alkynes under the optimized condition, and good to excellent yields were achieved for most substrates (Table 3). It is worthy to note that even a tri-substituted aldehyde (1e) could also react very well with various terminal alkynes. Eight new propargylic alcohols were synthesized. However, with benzaldehyde (1f) as substrate, lower conversion and isolated yield were observed. This result might suggest that the absence of the neighbouring groups on the benzene ring decreased

<sup>&</sup>lt;sup>[c]</sup> The catalyst was reused for the first time.



ΗQ

Scheme 1. The "hot separation" experiment.

**Table 3.** Ag/TiO<sub>2</sub>-10-catalyzed addition of alkynes to aldehydes.<sup>[a]</sup>

	R <sup>I</sup> + R'	$-= \begin{array}{c} Ag/TiO_2-10 \\ PPh_{3,} Et_3N \\ water, 60 \ ^{\circ}C \end{array} \begin{array}{c} CF \\ R \end{array}$	! <i>≡</i> {}} <sub>R'</sub>
	1 2		3
Entry	Aldehyde	Acetylene	Yield <sup>[b]</sup> [%]
1	CHO Br 1a	2a	<b>3a</b> , 97
2	<b>1</b> a	-{	<b>3b</b> , 98
3	<b>1</b> a	H <sub>3</sub> CO-	<b>3c</b> , 97
4	CHO CI 1b	<u>ک</u> 2a	<b>3d</b> , 90
5	1b	-{	<b>3e</b> , 88
6	1b	H <sub>3</sub> CO-	<b>3f</b> , 83
7	1b	CI	<b>3g</b> , 93
8	F 1c	<u>ک</u> 2a	<b>3h</b> , 91
9	CHO CF <sub>3</sub> 1d	2a	<b>3i</b> , 89
10	1d	-{	<b>3j</b> , 85
11	1d	H <sub>3</sub> CO-	<b>3k</b> , 73
12	F Br 1e	<u>ک</u> 2a	<b>3I</b> , 92
13	1e	H <sub>3</sub> CO-	<b>3m</b> , 85
14	CHO	<u>ک</u> 2a	<b>3n</b> , 45 (71% conversion)
15	CHO 1g	2a	<b>30</b> , 34 (63% conversion)

<sup>[a]</sup> Reaction conditions: 1 (1 mmol), 2 (3 equiv.), Ag/TiO<sub>2</sub>-10 (5 mol%), PPh<sub>3</sub> (10 mol%), Et<sub>3</sub>N (40 mol%), and water (3 mL) were mixed and stirred at 60 °C for 12 h.

<sup>[b]</sup> Isolated yield.

the combination between the substrates and the surface of catalysts (entry 14 vs. entries 1–13). The weaker combination with catalyst surface might also

result in the poorer conversion and yield for aliphatic aldehyde substrate 1g (entry 15). Unless otherwise specified, all of the reactions were carried out in air.

In summary, titanium dioxide-supported silver nanoparticles (Ag/TiO<sub>2</sub>) were utilized as a highly effective and recyclable catalyst for the coupling of aldehydes and terminal alkynes in the presence of catalytic amounts of PPh<sub>3</sub> in water. In the reaction, significant support and ligand effects were observed. This result has provided a new approach to develop novel catalytic reactions by coinage metal nanoparticles. The detailed mechanism, the effect of particle size and supports as well as the scope of the reaction are currently under further investigations.

## **Experimental Section**

All experiments were carried out in air. Flash column chromatography was performed over silica gel 200–300 mesh. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were acquired at 300 MHz and 75 MHz, respectively, and referenced to the internal solvent signals. HR-MS were obtained from Shanghai Institute of Organic Chemistry, CAS.

#### Synthesis of Silver Nanoparticles (Ag NPs) Catalyst

In a 100-mL round-bottom flask equipped with a stir bar and fitted with a rubber septum placed in a preheated oil bath at 60 °C, trisodium citrate dehydrate (Na<sub>3</sub>Cit·2 H<sub>2</sub>O, 0.1 M, 5 mL) and polyvinylpyrrolidone (PVP, average MW: 40,000, 100 mg) were added. After stirring at 60 °C for 15 min, aqueous silver nitrate solution (0.01 M, 25 mL) was added by dropwise over a period of 15 min, and stirred vigorously for 5 h in order to ensure the reduction was finished completely. The solution turned to blue-black color which is the characteristic color of silver nanoparticles. The silver nanoparticles were separated by centrifugation, and then the precipitate was washed with distilled water (3×10 mL), ethanol (3×5 mL) and ether (3×5 mL) successively. The residue was then dried in vacuum at 40 °C overnight.

#### Synthesis of Metal Oxide (MO)-Supported Silver Nanoparticle Catalyst

The preparation of Ag/Al<sub>2</sub>O<sub>3</sub>, Ag/SiO<sub>2</sub>, Ag/CeO<sub>2</sub>, Ag/TiO<sub>2</sub> followed the procedure described in ref.<sup>[10b]</sup> Ag/MO<sub>x</sub>-10 (Ag=10 wt%, MO<sub>x</sub>=Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, CeO<sub>2</sub>, TiO<sub>2</sub>) catalysts were prepared by impregnating the support with an aqueous solution of silver nitrate followed by evaporation to dryness at 80 °C. Before each catalytic or spectroscopic experiment, the precursor was calcined in air at 600 °C for 1 h, followed by reduction in H<sub>2</sub> at 300 °C for 10 min. The material was cooled to room temperature under an H<sub>2</sub> atmosphere.

#### General Procedure for Coupling of Alkyne and Aldehyde (Table 3, entry 1)

2-Bromobenzylaldehyde (**1a**, 117  $\mu$ L, 1 mmol), phenyacetylene (**2a**, 313  $\mu$ L. 3 mmol), Ag/TiO<sub>2</sub>-10 (54.0 mg, 0.05 mmol, 5 mol%), PPh<sub>3</sub> (26.2 mg, 0.1 mmol, 10 mol%), Et<sub>3</sub>N (54  $\mu$ L, 0.4 mmol, 40 mol%), and 3 mL of distilled water were added into a 15 mL Schlenk tube in atmosphere, and then, were stirred at 60 °C for 12 h. The mixture was extracted by ether  $(3 \times 3 \text{ mL})$ . The extraction was then dried with anhydrous sodium sulfate and concentrated by rotary evaporation. The residue was purified by flash column (10:1 hexanes and EtOAc) to give **3a**; yield: 97%.

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