

Direct C–C Cross-Coupling of Secondary and Primary Alcohols Catalyzed by a γ -Alumina-Supported Silver Subnanocluster

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The construction of C–C bonds is of fundamental importance in organic synthesis. Generally, alcohols are not used as starting materials, despite their wide availability, owing to the poor leaving-group ability of the hydroxide ion. There are great disadvantages associated with one of the most conventional methods, the coupling of enolate derivatives with alkyl halides, including the use of strong bases, the large amount of weight lost with the leaving group of the alkylating agent (the atom efficiency of the process is thus lower than desired), and the generation of waste. On these grounds, much attention has been focused on the strategy of hydrogen autotransfer in the construction of C–C or C–N bonds through the use of alcohols as benign alkylating agents.^[1–6] This class of reaction is based on the dehydrogenation–hydrogenation cycle of the platinum-group metal (PGM) catalysts. One of the most successful examples, the α alkylation of methyl ketone derivatives with alcohols, proceeds by oxidation of the alcohol to an intermediate carbonyl compound, followed by condensation with the ketone to yield an α,β -unsaturated carbonyl derivative, which is finally reduced with the metal hydride to give the corresponding carbonyl compound.^[4] Several reports have demonstrated the advanced process, the β alkylation of secondary alcohols with primary alcohols under the catalysis of Ru and Ir complexes.^[6] $[\text{RuCl}_2(\text{dms})_4]$ (dms = dimethyl sulfoxide),^[6d] $[(p\text{-cymene})\text{Ru}(\text{NHC})]$ complexes (NHC = N-heterocyclic carbene ligand),^[6f] and $[\text{Ir}(\text{Cp}^*\text{IrCl}_2)_2]$ ^[6e] (Cp^* = pentamethylcyclopentadienyl) are among the few catalysts that catalyze the reaction without any hydrogen acceptor or donor; however, the catalytic turnover numbers (TONs) are low, a large amount of a strong base is required (200–300 mol % of KOH or NaOtBu), and the catalysts are difficult to synthesize, expensive, and unable to be reused. In the only related example of heterogeneous catalysis by Pd/C, a large amount of a sacrificial hydrogen acceptor is required (500 mol % of 1-dodecene).^[6b] From an environmental and an economic viewpoint, a direct C–C cross-coupling of secondary alcohols with primary alcohols in the presence of an inexpensive (PGM-free) heterogeneous catalyst and a catalytic amount of a weak base and without sacrificial agents would be most desirable.

Gold nanoparticles supported on inorganic oxides have attracted increased interest in the past few years as catalysts for a number of reactions.^[4i,7] For example, various supported gold catalysts have been reported to show catalytic activity similar to or higher than that of PGM-based catalysts for the oxidation of alcohols to carbonyl compounds.^[4h,7b–e] Numerous fundamental studies showed that the unexpected activity of gold catalysts is related to the particle size, the degree of coordinative unsaturation of the gold atoms, and the cooperation of gold and the support surface. It is to be expected that silver, as a less expensive Group IB metal, may be used for the design of PGM-free catalysts through optimization of the metal-particle size and the support material. Although silver has been a popular element in the research field of cluster synthesis,^[8] surprisingly few attempts have been made to develop catalysis by silver clusters or nanoparticles.^[9–15] Hydrotalcite-supported silver nanoparticles developed by Mitsudome et al.^[14] and γ -alumina-supported silver clusters ($\text{Ag}/\text{Al}_2\text{O}_3$) reported by our research group^[13] act as heterogeneous catalysts for the oxidant-free dehydrogenation of alcohols. Thus, silver catalysts appear to have potential as new environmentally benign C–H activation catalysts. However, further development is hindered by uncertainty in the nature of the active site. Our very recent in-depth characterization study clarified that alcohol dehydrogenation by $\text{Ag}/\text{Al}_2\text{O}_3$ proceeds by cooperation of coordinatively unsaturated silver sites and acid–base sites on the alumina surface.^[13] We envisioned that the catalyst would be applicable to the hydrogen-autotransfer strategy in the construction of C–C bonds from alcohols. Herein, we report a new and atom-economical catalytic system composed of $\text{Ag}/\text{Al}_2\text{O}_3$ as a recyclable solid catalyst and a catalytic amount of a weak base for a one-pot C–C cross-coupling reaction of secondary and primary alcohols without any sacrificial additives. Systematic structure–activity relationship studies also provided a synthetic strategy based on the use of inorganic cooperative catalysts without expensive PGM materials.

We prepared a series of supported silver catalysts with the same silver content (5 wt %) and similar silver-particle size, but with a variety of metal oxide supports: Ag/MO_x -5 ($\text{MO}_x = \text{CeO}_2, \text{MgO}, \text{ZrO}_2, \text{Al}_2\text{O}_3, \text{SiO}_2$). Characterization of these catalysts by X-ray absorption fine structures (XAFS) analysis showed that silver clusters with a mean particle size of 0.8–3.0 nm are the main silver species on these catalysts (see below). Ag K-edge X-ray absorption near-edge structures (XANES) of the silver-supported catalysts are clearly different from that of Ag_2SO_4 (as a reference compound for ionic Ag^+ species surrounded by oxygen atoms), but rather similar to that of Ag powder, which indicates that silver species in these samples are in a reduced state (see Figure S1 in the

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Supporting Information). Ag K-edge extended X-ray absorption fine structure (EXAFS) analysis (see Figures S1 and S2 and Table S1 in the Supporting Information) showed that the Ag–Ag coordination numbers for all the catalysts (5.8–10) are lower than that for bulk silver (12). For Ag/Al₂O₃-5, an Ag–Ag shell with a coordination number of 5.8 and a bond distance of 0.287 nm was observed. By using the coordination numbers of the Ag–Ag contribution in EXAFS analysis and the model of Jentys,^[16] the average size of the metallic silver species was determined. The result (see Table S2 in the Supporting Information) shows that the mean size of the silver clusters on each oxide support is in the region of a few nanometers to subnanometers (CeO₂: 0.9 nm, MgO: 3.0 nm, ZrO₂: 1.8 nm, Al₂O₃: 0.8 nm, SiO₂: 0.9 nm).

The C–C cross-coupling reaction of 1-phenylethanol (**1a**) with benzyl alcohol (**2a**) was chosen as the model reaction for the optimization of catalytic activity and selectivity. First, the reaction was tested with various transition-metal catalysts and Cs₂CO₃ (100 mol %). 1,3-Diphenylpropan-1-one (**3a**) was the main C–C cross-coupling product (Table 1). The initial rate of

Table 1: Reaction of 1-phenylethanol (**1a**) with benzyl alcohol (**2a**).^[a]

$ \begin{array}{c} \text{OH} \\ \\ \text{Ph}-\text{CH}-\text{CH}_3 \\ \mathbf{1a} \end{array} + \begin{array}{c} \text{Ph}-\text{CH}_2-\text{OH} \\ \mathbf{2a} \end{array} \xrightarrow[115^\circ\text{C}, 48\text{ h}]{\text{catalyst (0.1 g)} \\ \text{Cs}_2\text{CO}_3 (100\text{ mol}\%)} \begin{array}{c} \text{O} \\ \\ \text{Ph}-\text{CH}-\text{CH}_2-\text{Ph} \\ \mathbf{3a} \end{array} $			
Entry	Catalyst- <i>x</i> ^[b]	Conversion of 1a [%]	Yield of 3a [%]
1	Ag/Al ₂ O ₃ -1	98	72
2	Ag/Al ₂ O ₃ -3	100	78
3	Ag/Al ₂ O ₃ -5	100	80
4	Ag/Al ₂ O ₃ -10	100	68
5	Ag/Al ₂ O ₃ -50	100	49
6	Au/Al ₂ O ₃ -1	100	45
7	Pt/Al ₂ O ₃ -1	9	1
8	Rh/Al ₂ O ₃ -1 ^[c]	91	17
9	Ru/Al ₂ O ₃ -5	100	19
10	Pd/Al ₂ O ₃ -3	100	36
11	Cu/Al ₂ O ₃ -8 ^[c]	51	17
12	Pd/C-5	100	54

[a] The reactions were carried out with **1a** (1 mmol) and **2a** (1 mmol) in toluene (2 mL). The conversion of **1a** and the yield of **3a** were determined by GC. [b] *x* is the metal loading (wt %). [c] Reaction time: 72 h.

formation of **3a** was also measured under conditions under which conversion was below 30 % (result not shown). Of the various alumina-supported transition-metal catalysts tested, Ag/Al₂O₃-5 gave the best results, with the highest yield of **3a** and the highest reaction rate. The yield of **3a** was higher with the Ag/Al₂O₃ catalyst with an Ag loading of 5 wt % than with Ag/Al₂O₃ catalysts with other Ag loadings. The activity was strongly dependent on the nature of the support material. A series of silver-cluster catalysts supported on various metal oxides were tested (Figure 1). The use of Ag/Al₂O₃-5 led to the highest yield of **3a** and the highest rate of formation of **3a**. With the standard catalyst, Ag/Al₂O₃-5, the reaction conditions were optimized for the reaction of equimolecular amounts of 1-phenylethanol and benzyl alcohol through variation of the base, temperature, and solvent (see Table S3 in the Supporting Information). First, the nature of

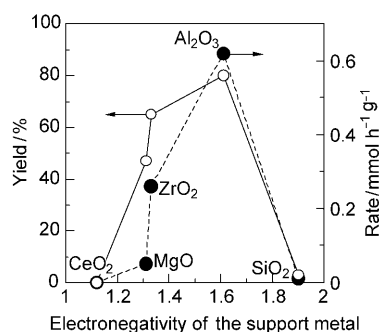


Figure 1. Yield (○) and formation rate (●) of **3a** versus the electronegativity of the support cation.

the base was investigated. The yield of **3a** was only 1 % in the absence of a base. A number of alkaline carbonates were tested; the conversion of the secondary alcohol and the yield of the product (**3a**) increased with increasing basicity of the carbonate in the following order: Li₂CO₃ < Na₂CO₃ < K₂CO₃ < Cs₂CO₃. This result suggests that the alcohol-dehydrogenation and aldol-condensation steps demand stronger basic sites. However, lower conversion and lower yields were observed when the stronger bases KOH and NaOH were used than with Cs₂CO₃. Among the bases tested, Cs₂CO₃ was found to be the most suitable. The catalytic activity was affected by the amount of Cs₂CO₃ added; a quantity of 20 mol % was enough to give the optimal yield. In toluene, the reaction rate increased as the temperature was raised from 80 to 115 °C. Studies on the effect of the solvent revealed that solvents with a higher boiling point were more effective. Under the optimized conditions (Ag/Al₂O₃-5 (4 mol %), Cs₂CO₃ (20 mol %), toluene (2 mL), 115 °C), alcohols **1a** and **2a** were converted completely within 48 h, and **3a** was formed in 80 % yield along with a small amount of acetophenone (3 %; see Figure S3 in the Supporting Information for a time-conversion profile). To the best of our knowledge, this is the first successful PGM-free catalyst for the C–C cross-coupling of secondary and primary alcohols.

The reaction was stopped completely by the removal of Ag/Al₂O₃-5 from the reaction mixture: After the reaction mixture had been stirred for 2 h (yield: 14 %), the catalyst was removed by centrifugation at 100 °C. The reaction did not proceed further when the filtrate was heated at 115 °C for 46 h. This result excludes a possible contribution of homogeneous catalysis by leached silver species.

We also studied the reuse of the Ag/Al₂O₃-5 catalyst. The catalyst can be separated readily from the reaction mixture by simple filtration. For each successive use, the filtered catalyst was washed with water to remove Cs₂CO₃, subjected to calcination in air at 600 °C for 10 min, and then reduced with H₂ at 150 °C for 5 min. After this treatment, the activity of the recovered catalyst was comparable to that observed for the first run (Table 2, entry 1). To the best of our knowledge, Ag/Al₂O₃ is the first recyclable catalyst for the C–C cross-coupling of secondary alcohols with primary alcohols without sacrificial agents.

Compound **3a** was obtained in good yield (74 %) with a small amount of Ag/Al₂O₃-1 (0.092 mol %) at 145 °C (see

Table S3 in the Supporting Information), and the total turnover number (TON) based on the total Ag content was 800. This value is larger than those reported for a related process, the β alkylation of **1a** with **2a** in the presence of homogeneous PGM catalysts:^[6d–f] TON = 164 for [Cp*Ir], TON = 95 for [(*p*-cymene)Ru(NHC)], TON = 48 for [RuCl₂(dmsO)₄]. If one takes into account that these homogeneous systems required a strong base, such as KOH or NaOtBu, Ag/Al₂O₃ shows higher activity for the C–C coupling of **1a** with **2a** under milder conditions.

With suitable reaction conditions established, we investigated the scope of the reaction with a series of secondary and primary alcohols (Table 2). The reactions of **1a** with

Table 2: Ag/Al₂O₃-5-catalyzed reaction of primary and secondary alcohols.^[a]

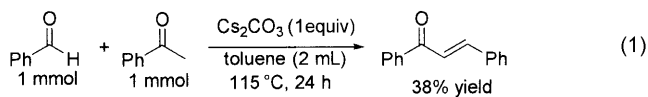
$\text{R}^1\text{CH(OH)CH}_3 + \text{R}^2\text{CH}_2\text{OH} \xrightarrow[115^\circ\text{C, 48 h}]{\text{Ag/Al}_2\text{O}_3\text{-5 (4 mol\%)} \\ \text{Cs}_2\text{CO}_3 \text{ (20 mol\%)}} \text{R}^1\text{CH}_2\text{CH(R}^2\text{)CH}_2\text{CH}_2\text{R}^2$				
Entry	R ¹	R ²	Conversion [%]	Yield [%]
1	Ph	Ph	100 (100, ^[b] 100 ^[c])	80 (77, ^[b] 78 ^[c])
2	Ph	MeOC ₆ H ₄	100	73
3	Ph	MeC ₆ H ₄	100	72
4	Ph	FC ₆ H ₄	100	67
5	Ph	<i>t</i> Bu	100	74
6	Ph	2-pyridyl	100	70
7	Ph	2-furyl	100	81
8	MeC ₆ H ₄	Ph	100	79
9 ^[d]	MeC ₆ H ₄	2-furyl	100	79
10 ^[e]	Ph	<i>n</i> Pr	100	67
11 ^[e]		Ph	100	65
12 ^[e]		<i>n</i> Pr	100	51

[a] The reactions were carried out with the two alcohols (1 mmol each) in toluene (2 mL). The conversion of the secondary alcohol and the yield of the product were determined by GC. [b] The catalyst had been recycled once. [c] The catalyst had been recycled twice. [d] Reaction time: 72 h. [e] The reaction was carried out in *p*-xylene at 145 °C.

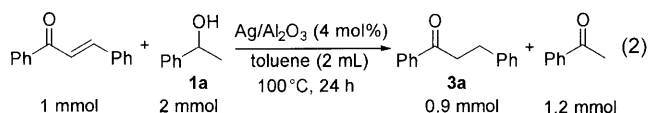
benzyl alcohols with an electron-donating or an electron-withdrawing substituent proceeded in moderate to good yield (Table 2, entries 2–5). The catalyst was applicable to the conversion of heterocyclic alcohols containing oxygen and nitrogen atoms, whereby the desired products were formed in good yields (Table 2, entries 6, 7, and 9). The reaction of **1a** with an aliphatic primary alcohol and the reaction of an aliphatic secondary alcohol with **2a** or *n*-propanol gave the corresponding products in moderate yields (51–67%; Table 2, entries 10–12). Unfortunately, the reaction of 2-octanol with 1-octanol in toluene at 115 °C resulted in higher selectivity for ester formation.

To obtain information about the reaction mechanism, we studied the aldol condensation of the ketone derived from **1a** with the aldehyde derived from **2a** and the transfer hydrogenation of the resulting α,β -unsaturated ketone. The reac-

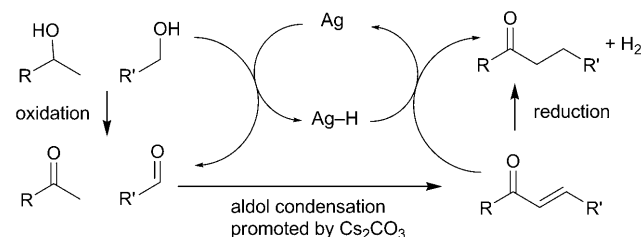
tion of acetophenone with benzaldehyde in the presence of Cs₂CO₃ (100 mol%) at 115 °C for 24 h gave 1,3-diphenyl-2-propen-1-one in 38% yield [Eq. (1)]. When the transfer



hydrogenation of 1,3-diphenyl-2-propen-1-one with **1a** (1.0 equiv) as a hydrogen donor was carried out in the presence of Ag/Al₂O₃-5 at 100 °C for 24 h, **3a** was formed in 87% yield [Eq. (2)].



On the basis of these results, we propose a mechanism for the Ag/Al₂O₃-catalyzed C–C cross-coupling of secondary alcohols with primary alcohols (Scheme 1): The reaction begins with the oxidation of the primary and secondary



Scheme 1. Proposed mechanism for the C–C coupling reaction.

alcohol to the corresponding aldehyde and ketone with the generation of a silver hydride species.^[13] A base-mediated cross-aldol condensation then occurs between the aldehyde and the ketone to give an α,β -unsaturated ketone, which undergoes selective transfer hydrogenation of the C=C bond with the silver hydride species to give the product. The hydride species generated in the alcohol-dehydrogenation step are consumed in the final reduction step. We examined the relationship between relative rates and the Brown–Okamoto parameters for the reactions of **1a** with benzyl alcohols with an electron-donating or an electron-withdrawing substituent (see Figure S4 in the Supporting Information). Reactions with a series of different benzylic alcohols were catalyzed by Ag/Al₂O₃-5; the order of reactivity for the benzyl alcohol was *p*-CH₃O > *p*-CH₃ > *p*-H > *p*-Cl. There is a fairly good linearity between log(*k*_X/*k*_H) and σ^+ , with a negative slope ($\rho = -1.57$, $r^2 = 0.91$). This result suggests that the transition state of the rate-determining step involves a positive charge at the α carbon atom adjacent to the phenyl ring. For the alcohol-dehydrogenation reaction, we showed previously that the silver cluster is responsible for the rate-

determining cleavage of the C α –H bond of the alkoxide species.^[13] Therefore, the C–H cleavage of the alkoxide by the silver cluster may be the rate-determining step in the present C–C coupling reaction.

A systematic study of the influence of the size of the silver particles in Ag/Al₂O₃ in combination with spectroscopic characterization showed the nature of the active silver species. For samples with an Ag loading of 1, 3, 5, and 10 wt %, we estimated the average silver-particle size previously by EXAFS analysis.^[13] For a sample with an Ag loading of 50 wt %, the average particle size was estimated from the XRD line broadening due to Ag metal of the Ag(111) reflection at $2\theta = 38.1^\circ$ by using the Scherrer equation. The average particle size increased with silver loading (see Figure S5 in the Supporting Information). By using the mean diameter of silver clusters and the atomic diameter of silver (0.289 nm) and assuming that the supported silver clusters can be modeled as an fcc crystal lattice, the number of surface silver atoms for each catalyst was determined statistically according to the method developed by Abad et al.^[7d] The turnover frequency (TOF) per surface Ag site versus the average particle size is shown in Figure 2.

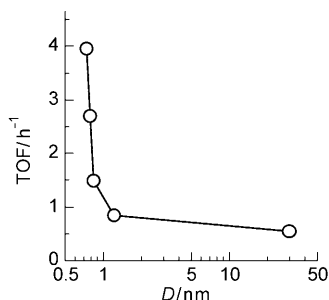


Figure 2. TOF based on the number of surface Ag atoms for the reaction of **1a** with **2a** at 115 °C versus the average particle size of Ag in Ag/Al₂O₃ catalysts (from Figure S5 in the Supporting Information).

Clearly, silver clusters with a smaller particle size have higher intrinsic activity. The relative occurrence of surface Ag atoms on faces, edges, and corners of Ag clusters with a cuboctahedral shape has been estimated by Claus and Hofmeister.^[9] The fraction of corner atoms increases dramatically when the silver-particle size is less than 2 nm. Therefore, a dramatic increase in TOF per surface Ag atom below a particle size of 2 nm (Figure 2) indicates that the present Ag/Al₂O₃-catalyzed reaction is a structure-sensitive reaction that demands coordinatively unsaturated Ag sites, such as Ag atoms at corner sites. These sites should be required for the rate-determining C–H cleavage of alkoxide species.

To investigate the effect of the acid–base characteristics of the support material, we plotted the yield of the product **3a** and the initial rate as a function of the electronegativity of the metal species in the support material (Figure 1), which has been used as a parameter for the acidity of metal oxides. The silver clusters supported on alumina, which is known to have both acidic and basic surface OH groups,^[17] had the highest catalytic activity. Supports with a strong basic character

(CeO₂ and MgO) and the support with an acidic character (SiO₂)^[18] resulted in low activity. This result suggests that both acidic and basic surface sites are necessary for this reaction. We reported a similar tendency for the oxidant-free dehydrogenation of alcohols, and established the following roles of acid and base sites.^[13] Basic sites at the silver–support interface facilitate the binding of the alcohol substrate through deprotonation to give an alkoxide intermediate on the support-oxide surface, and protic (electrophilic) OH groups adjacent to silver sites facilitate the removal of the hydride species from the silver sites to regenerate coordinatively unsaturated sites on the silver cluster. These roles of the acid–base sites on the support may be applicable to the present C–C coupling reaction, as the reaction begins with alkoxide formation, and one equivalent of H₂ is produced as a product.

In summary, we have demonstrated that an alumina-supported subnanometer-sized silver cluster acts as a recyclable heterogeneous catalyst for the hydrogen-autotransfer C–C cross-coupling of secondary and primary alcohols in the presence of a catalytic amount of the weak base Cs₂CO₃. The catalytic activity (TON) is the highest reported so far for this type of reaction. Structure–activity relationship studies and the reaction mechanism showed that the reaction proceeds by a cooperation of coordinatively unsaturated silver sites and acid–base sites on the Al₂O₃ support. The fundamental information gained from this study will enable the design of new PGM- and ligand-free processes for hydrogen-autotransfer catalysis for the environmentally benign production of chemicals.

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