

Distinct Promotive Effects of 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) on Polymer Supports in Copper-Catalyzed Hydrogenation of C=O Bonds

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Abstract: An amidine base-containing polymer, polystyrene-bound 1,8-diazabicyclo[5.4.0]undec-7-ene (PS-DBU), proved to serve as a prominent catalyst support. The combined use of selected copper salts with PS-DBU in the catalytic hydrogenation of acetophenone qualifies DBU as beneficial to generate catalytically active species and stabilize them on the polymer. Catalyst preparation and characterization reveal that the active copper species is in a low-valent state and the nanosized particles possibly grow on the amidine structure. The high immobilization ability of PS-DBU almost entirely prohibited copper leaching to the product over six cycles of hydrogenation and catalyst recovery. The copper catalyst attached to PS-DBU specifically promotes the hydrogenation of various ketones and aldehydes under 10 atm of H₂ at 90 °C to afford alcoholic products in satisfactory yields.

Introduction

The utilization of first-row transition metal hydrides as hydrogenation catalysts has attracted widespread attention in both industrial and academic research fields. The earth-abundant and inexpensive elements are promising for industrial-scale implementation; in addition, characteristic aspects of the non-precious metals arouse scientific interest towards novel catalyst design.^[1] In this context, Mn, Fe, Co, Ni, Cu, and Zn complexes have been utilized for catalytic hydrogenation of unsaturated bonds, especially in carbonyl compounds,^[2–7] as modeled after a number of matured Ru complexes.^[8] Besides, (supported) metal particles based on Fe^[9] and Cu^[10] have been emerged as an active area of research.

Since the trailblazing development of Stryker's reagent,^[11] Cu hydrides with phosphine ligands and their precursors have been known to offer a versatile option for hydrogenation

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catalysts amenable to broad unsaturated functionalities.^[12] Selective transformations like alkynes to Z-alkenes,^[13] aldehydes/ketones to alcohols,^[5c,6] and 1,4-reduction of α , β -unsaturated carbonyl compounds^[6e,11] have been demonstrated by these phosphine–Cu systems. NHC–Cu complexes (NHC = *N*-heterocyclic carbene) have also emerged as a new family of hydrogenation catalysts for the semi-reduction of alkynes.^[14]

Recently, we reported that a range of Cu salts can be utilized as catalyst precursors for the hydrogenation of carbon dioxide in organic the presence of а strong base 1.8diazabicyclo[5.4.0]undec-7-ene (DBU).^[15] Along with a primary role in trapping the formic acid product as its salt, DBU behaves as a ligand to form a DBU-Cu species; this opens up the catalytic application of Cu complexes in formate synthesis.^[16] Moreover, we isolated the first DBU-Cu species [(dbu)₂Cul] that also exhibited hydrogenation activity. Subsequently, Appel's group reported that a tridentate phosphine-Cu(I) complex, [(triphos)Cu(CH₃CN)][PF₆] (triphos 1,1,1-= tris(diphenylphosphinomethyl)ethane), effectively catalyzed CO₂ hydrogenation, particularly in the presence of DBU.^[17a] A ligand exchange experiment with the triphos complex revealed that among a range of nitrogen bases, DBU exhibited the highest to copper. The resulting DBU-Cu species, affinity [(triphos)Cu(dbu)]⁺, was proposed to be involved in the H₂ activation step with the aid of the non-rigid coordination of DBU; this led to the formation of the Cu hydride, [(triphos)Cu(H)]. Further implications were very recently discussed based on the structural and thermodynamic studies of phosphine-coordinated Cu hydride intermediates.[17b]

Separately from the ancillary effect of dissociable DBU on the heterolytic activation of H₂, the engagement of the DBUcoordinated Cu species in the hydrogenation step remains controversial. We envisioned that the amidine structure would uniquely evoke catalytic activity through its coordination, thus acting as indispensable ligands for novel Cu-based hydrogenation catalysts. Utilization of polymer-bound DBU as the anchoring ligand will help to unravel whether amidine coordination is essential for actualizing the catalytic potential of Cu. Herein, we disclose how the polystyrene-bound DBU (PS-DBU, Figure 1) immobilizes the Cu precursors on the amidine structure and how the Cu-containing polymer serves as a recyclable catalyst for the hydrogenation of ketones and aldehydes. Supported by the integrated environment of the amidine structure, PS-DBU uniquely contributes to the formation and stabilization of active Cu species to promote hydrogenation.

Figure 1. Amidine and guanidine ligands. DBU = 1,8diazabicyclo[5.4.0]undec-7-ene; PS-DBU = polystyrene-bound DBU; PS-TBD = polystyrene-bound 1,5,7-triazabicyclo[4.4.0]dec-5-ene.

Results and Discussion

Initially, the catalytic hydrogenation of acetophenone (1a) as a model substrate, using Cu salts with PS-DBU (1.8 mmol/g), was investigated. The reaction was conducted with a substrate/Cu ratio of 100/1 in methanol under 10 atm of H_2 at 90 °C for 20 h, described as the first run in Scheme 1. When Cu(OAc)₂, a potent Cu source in CO₂ hydrogenation,^[15] was tested in the reaction, 1-phenylethanol (2a) was selectively formed in 80% yield. A heterogeneous reaction mixture comprising a colorless liquid phase and a dark red-brown solid phase was formed. After filtration under Ar, the polymer residue was washed with methanol, dried in vacuo, and then reused for the second run as depicted in Scheme 1. A slightly higher activity (87% yield) than that of the first run indicates that the polymer residue is an active catalyst for the hydrogenation reaction. Sufficient immobilization of the Cu catalyst on the polymer support was corroborated by a control experiment in which no hydrogenation took place in the absence of Cu salts (Table 1, entry 2). Intrigued by these results, we performed screening experiments for the Cu source as summarized in Table 1. In contrast to the result afforded by Cu(OAc)₂ (entry 1), Cu(OAc) and CuCl₂ did not exhibit any catalytic activity in both the first and second runs (entries 3 and 4). Notably, hydrogenation with CuCl proceeded in 76% yield in the second run, although the first run was unsuccessful (entry 5). This clearly indicates an induction period preceding the onset of catalytic activity after immobilization of Cu on the polymer.^[18] Similar behavior was observed during the treatment of Cu(OTf)₂ and Cu(OTf)(toluene)_{0.5} (entries 6 and 7). The screening tests indicated that the mononuclear Cu(II) complex, Cu(acac)₂, was the best Cu source to afford 2a quantitatively in both runs (entry 8). Considering the differences in catalytic performance, the structure of the precursory Cu salts should be intimately related to the ease of formation of the active species. That is, molecular Cu sources such as Cu(acac)₂ and Cu(OAc)₂ are beneficial for attachment to PS-DBU whereas the oligomeric or polymeric Cu sources are likely to exhibit limited hydrogenation activity. The ratio of Cu(acac)₂ to DBU on the PS support was found to have non-negligible influence on the catalytic activity (entries 8-10).

The addition of a stoichiometric amount of DBU on the PS to the Cu moles resulted in modest yields, possibly due to the insufficient immobilization of the Cu precursor; no less than two equivalents of DBU units provided efficient catalytic activity.



Scheme 1. The sequence of catalytic hydrogenation and catalyst recovery.

Table 1. Hydrogenation of 1a with Cu salts in the presence of PS-DBU. ¹²	a]
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Entry	Cu salt	Yield [%] ^[b]		
		The 1st run	The 2nd run	
1	Cu(OAc) ₂	80	87	
2	None	<1	<1	
3	Cu(OAc)	<1	<1	
4	CuCl ₂	<1	<1	
5	CuCl	<1	76	
6	Cu(OTf) ₂	<1	7	
7	Cu(OTf)(toluene) _{0.5}	<1	14	
8	Cu(acac) ₂	>99	>99	
9 ^[c]	Cu(acac) ₂	60	59	
10 ^[d]	Cu(acac) ₂	>99	>99	

[a] Reaction conditions: 1a (2.00 mmol), Cu salt (0.02 mmol), PS-DBU (0.04 mmol-DBU units), CH₃OH (2.0 mL), H₂ (10 atm), 90 °C, 20 h. [b] Determined by ¹H NMR. [c] PS-DBU (0.02 mmol-DBU units). [d] PS-DBU (0.06 mmol-DBU units).

The Cu-catalyzed hydrogenation was specifically enhanced by use of PS-DBU, as summarized in Table 2. No hydrogenation proceeded in the absence of a supporting ligand (entry 2). As an attempt to elucidate the homogeneous system, the reaction using a mixture of $Cu(acac)_2$ and 2 equivalents of PS-free DBU

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resulted in poor yield (2%) of 2a and concomitant precipitation of insoluble materials derived from Cu (entry 3). Even in the presence of an extra amount of DBU (20 equivalents/Cu), the precipitation of Cu from the reaction mixture could not be suppressed (entry 4). These experiments suggested that an active species was formed in the presence of DBU but deteriorated with rapid aggregation of the Cu atom under the reaction conditions.^[19,20] To demonstrate the effectiveness of the Cu species immobilized on the amidine structure attached to PS (i.e., PS-DBU), the combined use of DBU and non-modified PS resin was next examined (entry 5). The catalytic outcome was similar to that observed in the above-mentioned experiments without PS. Moreover, the resulting PS residue exhibited no catalytic activity (<1% yield) in the second run. The related guanidine base-containing polymer, PS-bound 1,5,7triazabicyclo[4.4.0]dec-5-ene (PS-TBD; 2.6 mmol/g), exhibited scant catalytic activity relative to PS-DBU. Based on these experimental results, we concluded that catalytic activity was uniquely exhibited in the presence of PS-DBU whose amidine structure presumably acted as the foothold. Moreover, the PS-DBU material would provide an appropriate microenvironment to stabilize active species as well as to immobilize the Cu catalyst.

Table 2. ligands. ^[a]	Cu-catalyzed h	ydrogenation of 1a wi	th amidine or guanidine
Entry	Ligand	C=N units/Cu	Yield [%] ^[b]
1	PS-DBU	2	>99
2	None	-	<1
3	DBU	2	2
4	DBU	20	3
5	DBU, PS	2	4
6	PS-TBD	2	6

[a] Reaction conditions: 1a (2.00 mmol), Cu(acac)₂ (0.02 mmol), CH₃OH (2.0 mL), H₂ (10 atm), 90 °C, 20 h. [b] Determined by ¹H NMR.

The distinctive catalytic function originating from the combination of Cu(acac)₂ with PS-DBU prompted us to prepare active immobilized catalysts. When Cu(acac)₂ was treated with two amidine unit equivalents of PS-DBU under conditions A or B (Scheme 2), a dark red-brown polymer residue formed in each case. Sufficient immobilization of the Cu source on the resulting polymers (Cu/PS-DBU A and B, respectively) was confirmed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) and CHN elemental analysis. The Cu content in Cu/PS-DBU A was determined as 0.82 mmol-Cu/g and the intrinsic Cu/DBU ratio on the polymer was 0.93/2. This indicated that 93% of Cu loaded was immobilized under these conditions. Almost the same result was observed with Cu/PS-DBU B (Scheme 2).^[21] The catalytic activity of the Cu/PS-DBU materials in hand was compared to that of the aforementioned binary system. As described in Figure 2, the time-yield curve in the hydrogenation of 1a indicated that the Cu(acac)₂/PS-DBU binary system had a relatively long induction period of ~3 h. On the other hand, the Cu/PS-DBU A catalyst displayed a smooth startup (3% yield in the initial 10 min) and the reaction was completed within 6 h. Cu/PS-DBU B displayed a slightly superior catalytic activity and hydrogenation was completed in 5 h. X-ray photoelectron spectroscopy (XPS) analysis of the preformed catalyst did not detect any Cu(II) species in catalyst B. This confirmed that the Cu precursor was reduced to Cu(0) and/or Cu(I) species through catalyst preparation. These results clearly indicate that the low-valent Cu is a catalytically active species, analogous to the reported homogeneous^[6] and heterogeneous^[10,22] hydrogenation catalysts. In addition, highangle annular dark-field scanning transmission electron microscopy (HAADF-STEM) analysis revealed that Cu/PS-DBU A and B materials comprised nano-order Cu particles as illustrated in Figure 3 [Collected images and energy dispersive X-ray (EDX) spectra in the Supporting Information].^[23] Based on the particle-size distribution of Cu/PS-DBU A, the average size was determined as 25.0 nm. Cu/PS-DBU B had a rather narrow range of particle sizes; however, the average particle size was comparable to that of catalyst A. Notably, the particle size and distribution did not alter after the sixth run of hydrogenation and catalyst recovery (vide infra).^[24] Although the active species in the hydrogenation reaction is obscure at this stage, PS-DBU characterized by strong stabilization of the nanoparticles is supposed to contribute to the catalyst robustness.

C	l(acac) _e +	PS-DBU	H ₂ (10 atm)	1. filtration 2. wash with Cl 3. dry in vacuo	H₃OH	PS-DBU
		10-000	CH ₃ OH (5 mL)		P 00/1	0-000
[C	u] = 0.1 M u/DBU units	= 1/2	A : 90 °C, 20 h B : 130 °C, 4 h	1		
-	conditions	Cu conter	nt DBU conten	It ratio of	yield of	

[mmol-Cu/g]^a [mmol-DBU/g]^b Cu/DBU units immobilized Cu

0.93/2

93

В	0.83	1.76	0.94/2	94		
^a Determined by ICP-AES. ^b Determined by CHN elemental analysis.						

1.77

Scheme 2. Preparation of Cu-immobilized PS-DBU

0.82

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Figure 2. Time-yield curves of the hydrogenation of 1a.



Figure 3. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image of Cu/PS-DBU: a) Cu/PS-DBU A, b) Cu/PS-DBU A after six cycles of hydrogenation and catalyst recovery, c) Cu/PS-DBU B.

The hydrogenation reaction proved to be strongly influenced by the solvent (Table 3). Among the alcohols (entries 1-3), methanol proved to be the optimal solvent; ethanol also provided a satisfactory yield. Aprotic solvents afforded rather low yields (<5% in 5 h; entries 4-6). Since the reduction of 1a was hampered under the pressure of Ar instead of H₂ in the methanol

solution (entry 7), we concluded that this catalyst system does not involve a transfer hydrogenation mechanism. The Cu/PS-DBU catalyst was operative under a milder temperature (60 °C) to afford 99% yield in 20 h (entry 8). When a tenfold increase in the substrate/catalyst ratio was employed with a prolonged reaction time of 50 h, the maximum turnover number (TON) reached ~1000 (97% yield; entry 9). This is comparable to other homogeneous Cu catalysts.^[6] The Cu/PS-DBU catalyst also allows a lower catalyst loading than that observed for other heterogeneous Cu catalysts.^[22]

Table 3.	Solvent and co	nditions effect	in hydrogenati	on of 1a . ^[a]	
Entry	Solvent	1a /Cu	Temp [°C]	Time [h]	Yield [%] ^[b]
1	СН₃ОН	100	90	5	>99
2	Ethanol	100	90	5	96
3	2-Propanol	100	90	5	33
4	CH ₃ CN	100	90	5	2
5	THE	100	90	5	<1
6	Toluene	100	90	5	<1
7 ^[c]	CH ₃ OH	100	90	5	<1
8	CH ₃ OH	100	60	20	99
9	CH₃OH	1000	90	50	97
[a] <i>Rea</i> (Cu), sol NMR. [c	c <i>tion conditions.</i> vent (2.0 mL), ł] Conducted uno	• 1a (2.00 mi H₂ (10 atm), 6 Ier Ar (10 atm	mol), Cu/PS-D 60–90 °C, 5–56) instead of H ₂	BU B (0.02- 0 h. [b] Dete	-0.002 mmol- rmined by ¹ H
To durabil examir The re solid re similar After s of 1a ,	confirm the ity and leach ned in reitera cycling study esidue after e work-up pro ubsequent re hydrogenatic	reliable imn ning of Cu tion of hyd / was carri each run w cedure to submission n was per biosted to	nobilization from the progenation a ied out with as reused for catalyst pre- to another formed for 4	on PS-DB polymer su and catalys Cu/PS-DI or the next paration (S portion of t 4 h and th	U, catalyst upport was at recovery. BU A . The cycle in a Scheme 2). the solution the resulting

To confirm the reliable immobilization or durability and leaching of Cu from the pol examined in reiteration of hydrogenation and The recycling study was carried out with C solid residue after each run was reused for similar work-up procedure to catalyst prepare After subsequent resubmission to another po of 1a, hydrogenation was performed for 4 h liquid phase was subjected to ICP-MS analysis to determine the contents of the released Cu. The catalytic activity of each run was evaluated by turnover frequency (TOF, h⁻¹).^[25] As presented in Figure 4, the product yields ranged from 85 to 94% and the turnover frequency (TOF) values were almost constant (21.3-23.0 h⁻¹). No noticeable loss in catalytic activity was observed during the six cycles. In each cycle, Cu contamination in the hydrogenation product was undetectable (<1 ppm). This indicated that the strong coordination of PS-DBU to Cu effectively suppressed leaching into the solution phase.



Figure 4. Catalyst recycling experiments using recovered Cu/PS-DBU catalyst **A**, showing yields of **2a** (bars) and turnover frequency (TOF, points). Reaction conditions: **1a**/Cu = 100, [**1a**] = 1.0 M in CH₃OH, P_{H^2} = 10 atm, T = 90 °C, t = 4 h.

The robust immobilized catalyst on PS-DBU has broad substrate tolerance. Cu/PS-DBU B was used to explore the substrate scope under a substrate/catalyst ratio of 100/1, under 10 atm H₂, at 90 °C (Table 4). As with **1a**, sterically hindered ketone 1b was smoothly reduced to afford the corresponding secondary alcohol (entry 2). The cyclopropyl group remained intact in the reaction of cyclopropyl phenyl ketone (1c), giving the desired product with complete selectivity (entry 3). 2'-Methylacetophenone (1d) was slightly less reactive (entry 4), possibly due to steric hindrance (87% yield in 20 h). In contrast, the substrates bearing a methyl substituent at the meta or para position to the acetyl group (1e and 1f, respectively) were completely hydrogenated within 20 h (entries 5 and 6). Aryl ketones bearing an electron withdrawing (1g) or donating group (1h and 1i) were also hydrogenated in excellent yields within 20 h, regardless of their electronic properties (entries 7-9). In addition, a primary amino group was uneventfully applied to the Cu/PS-DBU system. An aliphatic ketone (1j) was accessible to the corresponding secondary alcohol (>99% yield in 15 h; entry 10). Similarly, aldehydes (1k-m) including substituted furfural were smoothly converted into the corresponding primary alcohol within 6 h (entries 11-13). Since chromone was converted to a mixture of 4-chromanone and 4-chromanol, chemoselectivity for α,β -unsaturated carbonyl compounds is relatively low for the Cu/PS-DBU catalyst, while some heterogeneous hydrogenation catalysts directed toward 1,2-selective reduction have been reported.^[26] Regarding the entries where the reaction was completed, the hydrogenation products were easily isolated with satisfactory purities and yields (88-98%) after filtration and concentration, as a result of the additive-free heterogeneous system.

	Table 4. Hydrogenation of carbonyl compounds with a Cu/PS-DBU catalyst. ^[a]						
Entry Substrate Product Time Yield	Entry	Substrate		Product	Time	Yield	

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[a] Reaction conditions: 1 (2.00 mmol), Cu/PS-DBU B (0.02 mmol-Cu), CH₃OH (2.0 mL), H₂ (10 atm), 90 °C. [b] Determined by ¹H NMR. [c] Isolated yield in parenthesis.

Conclusions

In summary, we demonstrated that a DBU-modified PS serves as an effective immobilization support for the Cu-catalyzed hydrogenation of C=O bonds. The combination of Cu(acac)₂ and PS-DBU was proven to be optimal for the reaction, where PS-DBU provides a suitable environment for the formation and stabilization of catalytically active Cu species. This was not observed with PS-free DBU and guanidine-modified PS-TBD. The preparation and identification of the immobilized Cu catalyst revealed that PS-DBU-based materials contain nanoscale lowvalent Cu particles, possibly grown on the amidine unit. In addition, the catalyst could be reused repetitively in hydrogenation reactions. The leaching of Cu in the hydrogenation product was negligible over six cycles. This validates the strong coordination of PS-DBU to Cu. The Cu/PS-DBU catalyst can be utilized in the hydrogenation of a variety of ketones and aldehydes even in the absence of an inorganic base, required for the well-established phosphine-Cu catalysts. Moreover, this immobilized Cu catalyst is attractive because it can be formed from readily available materials. This work opens up the potential of PS-DBU as an immobilizing support for transition metal catalysts for the first time. Other catalytic systems involving the rigid coordination of amidines to Cu species are now under development in our laboratories.

Experimental Section

General procedures for the hydrogenation of 1a

Distilled methanol (2.0 mL) was added to Cu(acac)₂ (5.2 mg, 0.02 mmol) and PS-DBU (22.2 mg) in an oven-dried 30-mL autoclave equipped with a glass insert and a magnetic stirring bar under Ar atmosphere. Degassed **1a** (240.3 mg, 2.0 mmol) was added to the resulting mixture. The autoclave was flushed with H₂ and then pressurized to 10 atm at room temperature. The reaction mixture was heated to 90 °C and stirred at a constant rate of 300 rpm for 20 h. After the reaction, the autoclave

was cooled in an ice bath and the pressure was carefully vented. An aliquot of the resulting colorless liquid phase was analyzed by ¹H NMR in CDCl₃ to confirm the formation of **2a**. The yield was determined based on the relative integration of the signal at 1.38 ppm (d, 3 H) to that at 2.09 ppm due to the methyl groups of 1,2,4,5-tetramethylbenzene used as internal standard. After filtration of the reaction mixture at room temperature and subsequent rinsing of the resulting residue with methanol (6 mL), the combined organic phase was concentrated in vacuo to afford an almost colorless oil as the analytically pure product. ¹H NMR (399.78 MHz, CDCl₃): δ = 1.50 (d, 3 H, ³*J* (H,H) = 6.4 Hz), 1.91 (brs, 1 H), 4.90 (q, 1 H, ³*J* (H,H) = 6.4 Hz), 7.26–7.30 (m, 1 H), 7.34–7.40 ppm (m, 4 H); ¹³C{¹H} NMR (100.53 MHz, CDCl₃): δ = 25.3, 70.5, 125.5, 127.6, 128.6, 145.9 ppm. These spectral data were identical to those previously reported in literature.^[27]

General procedures for the preparation of Cu/PS-DBU B

Distilled methanol (5.0 mL) was added to Cu(acac)₂ (130.9 mg, 0.50 mmol) and PS-DBU (555.6 mg) in an oven-dried 50-mL autoclave equipped with a glass insert and a magnetic stirring bar under Ar atmosphere. The autoclave was flushed with H₂ and then pressurized to 10 atm at room temperature. The reaction mixture was heated to 130 °C and stirred at a constant rate of 300 rpm for 4 h. After the reaction, the autoclave was cooled in an ice bath and the pressure was carefully vented. The reaction mixture was decanted under Ar to remove the liquid phase. The resulting dark red-brown polymer residue was washed with distilled methanol (10 mL), and dried in vacuo overnight, to afford the titled material. The Cu content in Cu/PS-DBU was determined as 0.83 mmol-Cu/g by ICP-AES analysis.

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Keywords: copper • DBU • hydrogenation • immobilization • supported catalysts

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