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Selective hydrogenation of α,β-unsaturated carbonyl compounds on silica-supported copper nanoparticles†

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Silica-supported copper nanoparticles prepared *via* surface organometallic chemistry are highly efficient for the selective hydrogenation of various α,β-unsaturated carbonyl compounds yielding the corresponding saturated esters, ketones, and aldehydes in the absence of additives. High conversions and selectivities (>99%) are obtained for most substrates upon hydrogenation at 100–150 °C and under 25 bar of H_2.

Hydrogenation reactions are key industrial processes to prepare fuels,[1] agrochemicals,[2] fine chemicals,[3] and pharmaceuticals.[4] Currently, one-quarter of all synthetic drugs on the market require at least one hydrogenation step in their synthesis.[2] Several organic reaction intermediates are based on compounds with α,β-unsaturated carbonyl groups that constitute an essential class of chemicals,[4] giving access to the corresponding hydrogenated products, employed in the food, flavor, and fragrance industries,[4–6] as well as in the pharmaceutical industry.[7]

The selective hydrogenation of the carbon–carbon double bond in α,β-unsaturated carbonyl compounds still remains challenging due to the competing hydrogenation of the carbonyl groups, over-hydrogenation or even de-oxygenation reactions. Molecular compounds based on noble metals (Ru,[8] Rh,[9] Ir,[10] Pd,[11–13] and Pt[14]) are mostly used as hydrogenation catalysts with selectivities >90% when specific ligands such as bulky phosphines are used.[8,9,15] However, these ligands typically sacrifice activity for selectivity. Non-noble metals complexes such as Fe^{II}/Na_2EDTA[16] or copper hydride complexes, such as $[(Ph_3P)CuH]_6$, also known as the Stryker reagent,[17] have also been successfully used as selective hydrogenation catalysts for α,β-unsaturated carbonyl compounds. While the homogenous systems favor high conversion and selectivities, catalyst separation and regeneration processes can be problematic and costly.[18]

Alternatively, heterogeneous catalysts, mostly based on precious metals, have been used for this transformation.[3,19] For instance, Pd nanoparticles supported on carbon in the presence of acetic acid or tri-*n*-butylamine hydrogenate α,β-unsaturated aldehydes, ketones, and esters with selectivities >80%.[20] Addition of a second metal that acts as a poison generally improves selectivity. In this context, Pb has been largely used as a Pd poison with or without quinoline for selective hydrogenation in the so-called Lindlar catalyst.[21,22] Sn,[23] Bi,[21] B,[24] and Zn[12] can also be employed as poisons for Pd and other noble metal catalysts. Noteworthily, the use of copper chromite also results in the quantitative conversion of unsaturated ketones, esters, and carboxylic acids to their corresponding selective α,β-hydrogenated products.[25] While acceptable selectivities are reported, the use of toxic additives makes these heterogeneous catalysts less appealing.

Most heterogeneous hydrogenation catalysts are based on supported metal nanoparticles and are prepared by wet impregnation[26] or co-precipitation.[26] The preparative method often leads to broad particle size distribution, associated with numerous active sites and often poorer selectivity. In contrast, surface organometallic chemistry (SOMC) has emerged as a powerful method to prepare small and narrowly distributed supported nanoparticles, including copper.[27–29] Herein we show that silica-supported copper nanoparticles prepared by SOMC are particularly efficient heterogeneous catalysts for the selective hydrogenation of carbon–carbon double bonds of α,β-unsaturated carbonyl compounds, without the need for additives such as ligands or promoter elements.

A Cu/SiO_2 catalyst was prepared by grafting $[Cu(OtBu)]_4$ on silica partially dehydroxylated at 700 °C followed by treatment under H_2 at 500 °C,[28,30] yielding small and narrowly distributed copper particles of 3.2 ± 0.8 nm (see ESI† for experimental details). With a metal loading of 5.9 wt%, H_2 chemisorption data show that 0.114 μmol $Cu_{surface}$ g^{-1} is the active and accessible metallic surface corresponding to a dispersion of 15%. We then explored their activity in the hydrogenation of α,β-unsaturated carbonyl compounds, which was performed under 25 bar of H_2 and at 150 °C for 15 hours, using (10 mg) of Cu/SiO_2 (0.57 μmol of Cu) and 0.5 mmol of substrate in 3 mL of toluene.

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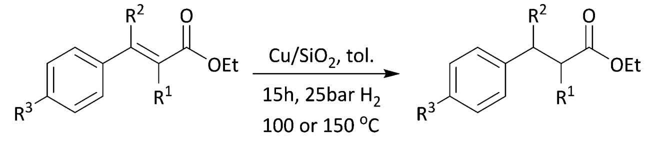
Table 1 Selective α,β-hydrogenation of cinnamate derivatives



Subst.	R^1	R^2	R^3	T (°C)	Conv. (%)	Sel. (%)
1	–H	–H	–H	150	> 99	> 99
2	$–CH_3$	–H	–H	150	> 99	> 99
3	–H	$–CH_3$	–H	150	< 1	—
4	–H	–H	–Cl	150	20	> 99
5	–H	–H	$–CH_3$	150	36	> 99
6	–H	–H	$–OCH_3$	150	86	> 99[a]
7	–H	–H	$–NO_2$	150	> 99	> 99[b]
7	–H	–H	$–NO_2$	100	> 99	> 99[c]

Besides α,β-hydrogenation: [a] Aromatic ring is fully hydrogenated. [b] Nitro group reduced to amine and ester to alcohol. [c] Nitro group reduced to amine.

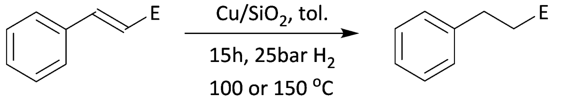
First, the hydrogenation of cinnamate derivatives was evaluated (**1–7**) with various substituents on the olefin and aromatic moieties (Table 1). The carbon–carbon double bond of the parent cinnamate (**1**) is selectively hydrogenated (> 99%).[31] This reactivity is in sharp contrast to what is observed for (i) the corresponding silica-supported Pt nanoparticles that yield the hydrogenated alcohol or (ii) silica-supported nickel nanoparticles and Cu/ZnO/Al_2O_3 that show no significant conversion under the same reaction conditions. It is noteworthy that having an additional methyl substituent in the α-position (**2**) does not affect catalysis and provides the hydrogenated product with 99% selectivity on complete conversion.[32] Having a methyl substituent in the β-position (**3**) is however detrimental, with a conversion of < 1%.[33]

Addition of functional groups to the *para*-position of the aromatic ring (**4–7**) affects the conversion, while selectivity remains unchanged (> 99%): the addition of an electron withdrawing group (*i.e.*, chloro) significantly decreases the conversion (20% – **4**), but conversions seem less influenced when functional groups are electron donating, such as methyl (36% – **5**) or in particular methoxy (86% – **6**). If a nitro group is present in the *para* position as in (**7**), complete conversion is reached; although the nitro and the ester groups are both reduced to their corresponding amine and alcohol. However, decreasing the reaction temperature to 100 °C leaves the ester group untouched; still, the nitro group is reduced.[33]

Besides cinnamates, the hydrogenation of unsaturated ketone, aldehyde, carboxylic acid, and amide derivatives, as well as allylic alcohols, was also investigated (**8–13**, Table 2). At 150 °C, all the substrates were fully converted. While a high selectivity (99%) for α,β-hydrogenation was observed for (**10–12**), the substrates with ketone and aldehyde functionalities, (**8**) and (**9**), were converted to the hydrogenated alcohol. Nevertheless, at 100 °C exclusively high selectivities of 83% and 90% in α,β-hydrogenation for (**8**) and (**9**) were achieved, respectively. The corresponding allylic alcohol **13** was also selectively hydrogenated.

The hydrogenation of coumarin (**14**), an important class of lactones, was also explored. However, at 150 °C, hydrogenation yielded allylbenzene(III), probably *via* formation of the corresponding saturated ester and pyran derivatives (Scheme 1), evidenced by GC-MS. Decreasing the reaction temperature to 100 °C provides high selectivity (> 99%) for the desired product(I) at complete conversion.

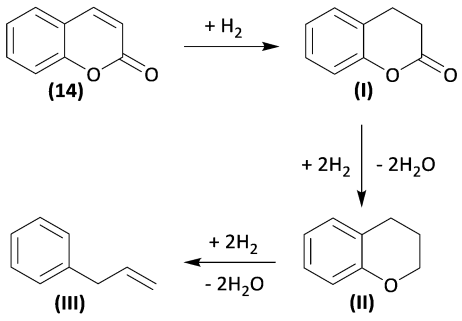
Table 2 Selective α,β-hydrogenation of cinnamyl substrates



Subst.	E	T (°C)	Conv. (%)	Sel. (%)
8	$–COCH_3$	100	> 99	83
9	–CHO	100	> 99	90
10	–COOH	150	> 99	> 99
11	$–CONH_2$	150	> 99	> 99
12	$–CON(CH_2CH_3)_2$	150	> 99	> 99
13	$–CH_2OH$	150	> 99	> 99

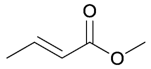
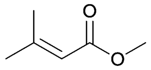
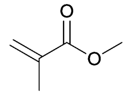
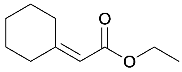
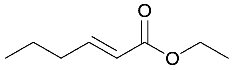
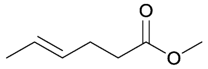
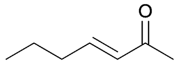
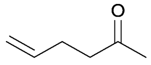
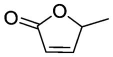
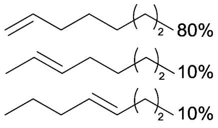
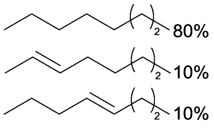
The hydrogenation of acrylate derivatives (**15–19**) was also investigated; they all exhibited high conversions and selectivities (> 99%), independent of the methyl substituent position (Table 3). Highly encumbered derivatives bearing methylenecyclohexane (**18**) or longer alkyl chains like (**19**) are also selectively hydrogenated with good conversions. Note that hydrogenation also occurs selectively when the unsaturation is more remote from the ester groups as in (**20**), but the conversion is lower (88%) under similar reaction conditions. This shows that copper prefers to hydrogenate electron-deficient olefins. For ketones, whether conjugated or not such as (**21**) and (**22**), the carbonyl is partially hydrogenated to the corresponding alcohol at 150 °C. The selectivity is hardly improved at 100 °C (**21**), as the ketone group to alcohol transformation also occurs at lower temperatures. The α-angelica lactone (**23**), a relevant intermediate of biomass, is only hydrogenated with low selectivity, due to competitive oligomerization and decarboxylation pathways, which also take place at 100 °C.[34] Note that in a mixture of unfunctionalized olefins, which contains 1-nonene (80%), 2-nonene (10%), and 4-nonene (10%) (**24**) – only the terminal olefin was hydrogenated at 100 °C, while no conversion was observed for internal olefins.

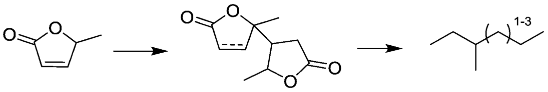
Finally, recycling tests using ethyl cinnamate have been carried out: no deactivation was observed during the first 3 cycles, while additional recycling tests show a decrease of conversion by *ca.* 5% in the two subsequent cycles. Catalytic tests performed after hot filtration on cycles 1, 3, and 5 show no activity in the filtered solution, consistent with active supported nanoparticles and not



Scheme 1 Possible reaction path of (**14**).

Table 3 Selective α,β-hydrogenation of carbonyl compounds

Subst.		T (°C)	Conv. (%)	Sel. (%)
15		150	>99	83
16		150	>99	90
17		150	>99	>99
18		150	>99	>99
19		150	>99	>99
20		150	88	>99
21		150	>99	<1
22		100	>99	84
23[a]		100	10	<1
24				100



[a] Reaction path of α-angelica lactone.

species in solution. In addition, no copper (<0.01% wt) is detected in solution according to elemental analysis, consistent with the absence of leaching (see ESI† for details). Finally, TEM carried out after the catalytic tests shows small and narrow copper particles of 3.2 ± 0.6 nm identical to the fresh catalyst, suggesting that the loss of activity may be due to poisoning of the surface site upon cycling.

We have shown that silica-supported Cu nanoparticles efficiently hydrogenate the olefin moiety in a large group of α,β-conjugated carbonyl compounds. Most of the 24 selected representative substrates including unsaturated esters, aldehydes, ketones, and amides, were completely converted to their corresponding saturated products with good selectivity, typically >99%, the carbonyl moiety remaining untouched in most instances. It is noteworthy that this stable and inexpensive catalyst used under mild reaction conditions achieves catalytic performances comparable to those of conventional homogeneous or heterogeneous catalysts based on noble metals.

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Conflicts of interest

There are no conflicts to declare.

References

1 K. Yan, G. Wu, T. Lafleur and C. Jarvis, *Renewable Sustainable Energy Rev.*, 2014, **38**, 663–676.
2 H. U. Blaser, C. Malan, B. Pugin, F. Spindler, H. Steiner and M. Studer, *Adv. Synth. Catal.*, 2003, **345**, 103–151.
3 H.-U. Blaser, A. Indolese, A. Schnyder, H. Steiner and M. Studer, *J. Mol. Catal. A: Chem.*, 2001, **173**, 3–18.
4 J. G. V. Alsten, M. L. Jorgensen and D. J. am Ende, *Org. Process Res. Dev.*, 2009, **13**, 629–633.
5 P. Clark, M. Poliakoff and A. Wells, *Adv. Synth. Catal.*, 2007, **349**, 2655–2659.
6 M. Rothe, *Food*, 1986, **30**, 228.
7 N. Mamidi, S. Gorai, J. Sahoo and D. Manna, *Chem. Phys. Lipids*, 2012, **165**, 320–330.
8 K. Nuithitikul and M. Winterbottom, *Catal. Today*, 2007, **128**, 74–79.
9 J. M. Grosselin, C. Mercier, G. Allmang and F. Grass, *Organometallics*, 1991, **10**, 2126–2133.
10 S. Sakaguchi, T. Yamaga and Y. Ishii, *J. Org. Chem.*, 2001, **66**, 4710–4712.
11 C. Bianchini, M. Peruzzini, E. Farnetti, J. Kašpar and M. Graziani, *J. Organomet. Chem.*, 1995, **488**, 91–97.
12 E. Keinan and N. Greenspoon, *J. Am. Chem. Soc.*, 1986, **108**, 7314–7325.
13 B. Ding, Z. Zhang, Y. Liu, M. Sugiya, T. Imamoto and W. Zhang, *Org. Lett.*, 2013, **15**, 3690–3693.
14 Z. Poltarzewski, S. Galvagno, R. Pietropaolo and P. Staiti, *J. Catal.*, 1986, **102**, 190–198.
15 T. Ohta, T. Miyake, N. Seido, H. Kumobayashi, S. Akutagawa and H. Takaya, *Tetrahedron Lett.*, 1992, **33**, 635–638.
16 M. D. Bhor, A. G. Panda, S. R. Jagtap and B. M. Bhanage, *Catal. Lett.*, 2008, **124**, 157–164.
17 W. S. Mahoney, D. M. Brestensky and J. M. Stryker, *J. Am. Chem. Soc.*, 1988, **110**, 291–293.
18 I. Vural Gürsel, T. Noël, Q. Wang and V. Hessel, *Green Chem.*, 2015, **17**, 2012–2026.
19 S. S. Mohire and G. D. Yadav, *Ind. Eng. Chem. Res.*, 2018, **57**, 9083–9093.
20 N. A. Cortese and R. F. Heck, *J. Org. Chem.*, 1978, **43**, 3985–3987.
21 J. A. Anderson, J. Mellor and R. P. K. Wells, *J. Catal.*, 2009, **261**, 208–216.
22 A. Borodziński and G. C. Bond, *Catal. Rev.*, 2006, **48**, 91–144.
23 S. Recchia, C. Dossi, N. Poli, A. Fusi, L. Sordelli and R. Psaro, *J. Catal.*, 1999, **184**, 1–4.
24 C. W. A. Chan, A. H. Mahadi, M. M.-J. Li, E. C. Corbos, C. Tang, G. Jones, W. C. H. Kuo, J. Cookson, C. M. Brown, P. T. Bishop and S. C. E. Tsang, *Nat. Commun.*, 2014, **5**, 5787.
25 H. Adkins and R. Connor, *J. Am. Chem. Soc.*, 1931, **53**, 1091–1095.
26 J. M. Thomas, *Angew. Chem., Int. Ed.*, 2009, **48**, 3390–3391.
27 C. Copéret, A. Comas-Vives, M. P. Conley, D. P. Estes, A. Fedorov, V. Mougel, H. Nagae, F. Núñez-Zarur and P. A. Zhizhko, *Chem. Rev.*, 2016, **116**, 323–421.
28 A. Fedorov, H.-J. Liu, H.-K. Lo and C. Copéret, *J. Am. Chem. Soc.*, 2016, **138**, 16502–16507.
29 K. Searles, K. W. Chan, J. A. Mendes Burak, D. Zemlyanov, O. Safonova and C. Copéret, *J. Am. Chem. Soc.*, 2018, **140**, 11674–11679.
30 N. Kaeffer, K. Larmier, A. Fedorov and C. Copéret, *J. Catal.*, 2018, **364**, 437–445.
31 A. M. Raspolli Galletti, C. Antonetti, M. Bertoldo and F. Piccinelli, *Appl. Catal., A*, 2013, **468**, 95–101.
32 S.-D. Yang, C.-L. Sun, Z. Fang, B.-J. Li, Y.-Z. Li and Z.-J. Shi, *Angew. Chem., Int. Ed.*, 2008, **47**, 1473–1476.
33 A. C. Brown and J. Gibson, *J. Chem. Soc., Trans.*, 1892, **61**, 367–369.
34 M. Mascal, S. Dutta and I. Gandarias, *Angew. Chem., Int. Ed.*, 2014, **53**, 1854–1857.