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Cu/SiO$_2$: an Improved Catalyst for the Chemoselective Hydrogenation of α,β-unsaturated Ketones

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Abstract: Cu/SiO$_2$ can be conveniently used for the quantitative hydrogenation of conjugated enones to saturated ketones, also when another olefinic bond is present in the molecule, under very mild conditions. Molecular H$_2$ or 2-propanol can be used as hydrogen source.

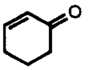
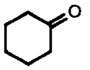
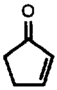
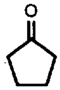
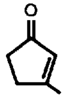
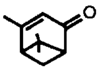
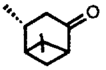
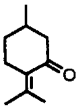
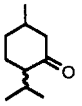
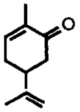
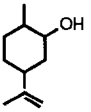
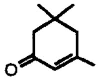
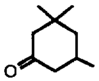
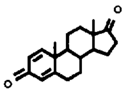
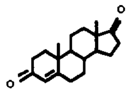
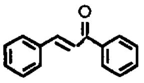
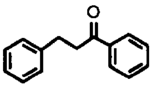
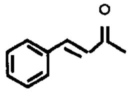
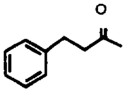
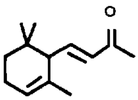
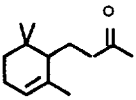
We recently reported that Cu/Al$_2$O$_3$ is an effective catalyst for the selective reduction of α,β-unsaturated carbonyl compounds of the steroid family[1] and of other molecules where an isolated olefinic bond is also present[2]. However, in the case of α- and β-ionone, the yields did not exceed 80% due to side reactions.

Here we wish to report that when using silica (Degussa Aerosil^R 380) as the support, quantitative yields in the saturated ketones could be obtained also for α- and β-ionone. According to the mechanism already proposed for 1,4 H$_2$ addition in the presence of supported copper catalysts, these results can be ascribed to enhanced stability of copper hydride on the surface of pyrogenic silica[3] resulting in higher activity and selectivity. Results obtained for a series of unsaturated ketones are reported in Table 1.

Contrary to hexenones, whose selective reduction was fast and complete, unsubstituted and 3-substituted cyclopentenones were hydrogenated only sluggishly (entries 2 and 3) and 2-substituted ones did not react at all. Hydrogenation of the tetrasubstituted double bond in pulegone (entry 5) required superatmospheric pressure to go to completion. Reduction to the saturated alcohol takes place in a well separated step for cyclic compounds, except for 2-alkyl substituted ketones (e.g. carvone, entry 6) as already observed with Cu/Al$_2$O$_3$[2]. However, in all the reactions tested, the isolated olefinic bond was never affected, the same chemo- and regio-selectivity being obstructed only in the hydrogenation of 1,4-androstadien-3,17-dione (entry 8). Even better results were obtained in the hydrogenation of open chain carbonyl compounds, particularly ionones. In this case, neither alcohols nor other byproducts were detected even for prolonged reaction times. As the selectivity obtained by us in the hydrogenation of β-ionone is among the best ones reported in the literature, and moreover unique for a heterogeneous catalyst, results obtained in the hydrogenation of this molecule by using different experimental conditions are summed up in Table 2. Re-use of the catalyst was found to be possible without significant loss of activity or selectivity (entries 4 [1-4]).

Catalyst preparation: to a solution of Cu(NO$_3$)$_2$·3H$_2$O (25 mL, 160 g/L), concentrated NH$_4$OH was added till pH=9, then the support (10 g) was added and the mixture slowly diluted to 3 L in order to allow hydrolysis of

Table 1. Hydrogenation of unsaturated ketones in the presence of 8% copper on silica, 1 atm H_2, T=90°C, toluene as solvent.

Entry	Substrate	Product	t (h)	conv.(%)	select.(%)
1			2	100	100
2			24	95	100
3			80	80	91
4			16	95	94
5[a]			4	96	93 (57%cis)
6			9	100	94 (40% eq,ax)
7			1.5	69	76
8[b]			5	93	68
9			3	100	100
10			6	100	96
11[c]			5	97	98
12[c,d]	"	"	24	89	100

[a] = at 140 °C under 10 atm H_2; [b] = at 60°C; [c] = substrate/Cu = 2; [d] = N_2, 2-propanol as hydrogen donor.

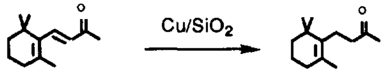
the $Cu[NH_3]_4^{++}$ complex and deposition of the finely dispersed product to occur. The solid was separated by filtration, washed with water, dried overnight at 120°C and calcined in air at 350°C for 3 hours. In this way 8% Cu samples, 308 m^2/g BET surface area, were obtained. The catalyst was reduced at 270°C with H_2 at atmospheric pressure, removing the water formed under reduced pressure, before the hydrogenation reaction.

Experimental conditions: The substrates (2 mmoles) were dissolved in toluene (12 ml) and the solution transferred under H_2 into a glass reaction vessel where the catalyst (0.3 g) had been previously reduced. Reactions were carried out at 90°C and atmospheric pressure with magnetic stirring, the final charge of hydrogen being adjusted to 1 atm with a mercury leveling bulb, and monitored by withdrawing 20 µL samples through a viton septum and analyzing them by capillary GLC. After completion the catalyst was filtered off, the solvent removed and the reaction mixture analyzed by NMR. Superatmospheric pressure (1,5-5 atm) could be conveniently used to speed up the reaction without loss in selectivity when higher substrate/Cu ratios were used. For the recycle tests (entries 4 (1-4) in Table 2) the catalyst was washed with diethylether, dried and reactivated at 270°C.

It is worth noting that the reaction can be carried out also using 2-propanol as a hydrogen donor, thus limiting the use of molecular H_2 to the catalyst pretreatment.

The very high yields obtained, excellent chemoselectivity and absence of work up procedures, support this catalyst as an effective alternative to homogeneous copper hydrides or complex transition metal hydrides[4,5].

Table 2. Hydrogenation of β-ionone at different experimental conditions



Entry	Substr./Cu (mol/mol)	P_{H_2} (atm)	T (°C)	time (h)	Conv. (%)	Select. (%)
1	20	3	110	48	87	95
2	10	1.5	110	6	94	97
3	5	1	90	30	96	96
4(1)	2	1	90	2.5	98	100
4(2)	"	"	"	"	83	98
4(3)	"	"	"	"	89	97
				3.5	99	98
4(4)	"	"	"	"	90	98
5	2[a]	1	90	5	99	100
6	2	[b]	90	8.5	97	96

[a]= catalyst reduced at 180°C; [b]= N_2, 2-propanol as hydrogen donor.

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