A smart heterogeneous catalyst for efficient, chemo- and stereoselective hydrogenation of 3-hexyn-1-ol

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Detailed results obtained during the course of this study.

Table 1. Hydrogenation of (**I**) catalysed by Cat 1. Preliminary investigation.

Run {t (min)}	(**I**) Conv. (%)[a]	(*Z*)-(**II**) (%)[a]	(*E*)-(**II**) (%)[a]	(**III**) (%)[a]	{(Z)-(**II**)/ [(Z)-(**II**) + (E)-(**II**)]} (%)
1 {10}	6	6	-	-	>99
1 {30}	29	27	1	1	96.4
1 {60}	64	59	3	2	95.2
1 {90}	>99	64	19.4	15.6	76.7

Substrate (**I**) = 138.4 mg (1.41 mmol); (**I**)/Pd (mol) = 500; pH_2 = 0.1 MPa; Solvent = i-propanol (10 mL); T = 25°C. [a]Area% determined by gc analysis.

Table 2. Hydrogenation of (**I**) catalysed by a commercial catalyst.[a]

Run {t (min)}	(**I**) Conv. (%)[b]	(*Z*)-(**II**) (%)[b]	(*E*)-(**II**) (%)[b]	(**III**) (%)[b]	{(Z)-(**II**)/ [(Z)-(**II**) + (E)-(**II**)]} (%)
1 {120}	5.4	5.4	-	-	>99
1 {150}	11.3	11.3	-	-	>99
1 {180}	15.1	15.1	-	-	>99
1 {210}	20.7	19.5	0.8	0.4	96.1
1[c]	>99	-	-	>99	-

Substrate (**I**) = 138.4 mg (1.41 mmol); (**I**)/Pd (mol) = 500; pH_2 = 0.1 MPa; Solvent = i-propanol (10 mL); T = 25°C. [a] BASF (catalyst code 543136) 0.6% Pd/C; [b] Area% determined by gc analysis. [c] Control after 24h

Table 3. Hydrogenation of (**I**) catalysed by Cat 1, in presence of additives.

Run {t (min)}	Additive	(**I**)Conv. (%)[a]	(Z)-(**II**) (%)[a]	(E)-(**II**) (%)[a]	(**III**) (%)[a]	{(Z)-(**II**)/ [(Z)-(**II**) + (E)-(**II**)]} (%)
1 {120}	$NH_4Cl/CH_3COONa·3H_2O$[b]	6.6	6.6	-	-	>99
1 {150}	$NH_4Cl/CH_3COONa·3H_2O$[b]	38.1	36.9	1.2	-	96.9
1 {180}	$NH_4Cl/CH_3COONa·3H_2O$[b]	89.3	86.5	2.6	-	97.1
1 {210}	$NH_4Cl/CH_3COONa·3H_2O$[b]	>99	93.1	5.2	1.7	94.7
2 {90}	NH_4Cl[c]	45.5	40.3	3	2.2	93.1
2 {120}	NH_4Cl[c]	67.9	60	4.3	3.6	93.3
2 {150}	NH_4Cl[c]	88.7	76.3	7.1	5.3	91.5
2 {180}	NH_4Cl[c]	>99	78.2	12.6	9.2	86.1
3 {30}	$CH_3COONa·3H_2O$[d]	13.6	13.6	-	-	>99
3 {60}	$CH_3COONa·3H_2O$[d]	60.1	60.1	-	-	>99
3 {90}	$CH_3COONa·3H_2O$[d]	>99	86.8	9.7	3.5	89.9
3 {120}	$CH_3COONa·3H_2O$[d]	>99	66.4	19.7	13.9	77.1

Substrate (**I**) = 138.4 mg (1.41 mmol); (**I**)/Pd (mol) = 500; pH_2 = 0.1 MPa; Solvent =i-propanol (10 mL); T = 25°C. [a]Area% determined by gc analysis. [b] 75 mg of NH_4Cl and 192 mg of $CH_3COONa·3H_2O$; [c] 75 mg of NH_4Cl; [d] 192 mg of $CH_3COONa·3H_2O$

Table 4. Hydrogenation of (**I**) catalysed by Cat 1 in CPME and in i-propanol

Run {t (min)}	Solvent	T	(**I**) Conv. (%)^a	(*Z*)-(**II**) (%)^a	(*E*)-(**II**) (%)^a	(**III**) (%)^a	{(Z)-(**II**)/ [(Z)-(**II**) + (E)-(**II**)]} (%)
1 {210}	CPME	25°C	>99	85.4	13.6	1	86.3
2 {150}	i-PrOH	60°C	94.3	89.9	3.4	1	96.4
2 {180}	i-PrOH	60°C	>99	76	18.5	5.5	80.4

Substrate (**I**) = 138.4 mg (1.41 mmol); (**I**)/Pd (mol) = 2000; pH_2 = 0.1 MPa; Solvent = 10 mL. ^{a}Area% determined by gc analysis.

Table 5. Hydrogenation of (**I**) catalysed by Cat 1*.

Run {t (min)}	(I)/Pd (mol)	(**I**) Conv. (%)^a	(*Z*)-(**II**) (%)^a	(*E*)-(**II**) (%)^a	(**III**) (%)^a	{(Z)-(**II**)/ [(Z)-(**II**) + (E)-(**II**)]} (%)
1 {60}	2000	>99	86.3	13.7	-	86.3
2 {120}	6000	73.2	71.3	1.9	-	97.4
2 {150}	6000	>99	92.4	7.6	-	92.4
3 {120}	6000	77.2	74.8	2.4	-	96.9
4 {120}	6000^b	56.4	56.4	-	-	>99
5 {120}	6000^b	46.1	44.7	1.4	-	97.0
6 {210}	10000	79.1	79.1	-	-	>99

Substrate (**I**) = 332.1 mg (3.38 mmol); pH_2 = 0.1 MPa; Solvent = i-propanol (10 mL); T = 60°C. ^{a}Area% determined by gc analysis. ^{b}Recycling the catalyst of the previous run

Table 6. Hydrogenation of (**I**) catalysed by Cat 2.

Run {t (min)}	(**I**) Conv. (%)^a	(*Z*)-(**II**) (%)^a	(*E*)-(**II**) (%)^a	(**III**) (%)^a	{(Z)-(**II**)/ [(Z)-(**II**) + (E)-(**II**)]} (%)
1 {120}	37.9	37.9	-	-	>99
1 {150}	40.8	40.8	-	-	>99
1 {180}	57.0	57.0	-	-	>99
1 {210}	66.9	65.0	1.9	-	97.2

Substrate (**I**) = 172.7mg (1.76 mmol); (**I**)/ Cu,Pd (mol) = 500; pH_2 = 0.1 MPa; Solvent = i-propanol (10 mL); T = 40°C. ^{a}Area% determined by gc analysis.

SEM images of 0.25% Pd/Al_2O_3 (Cat 1 and Cat*1) prepared during the course of this study.

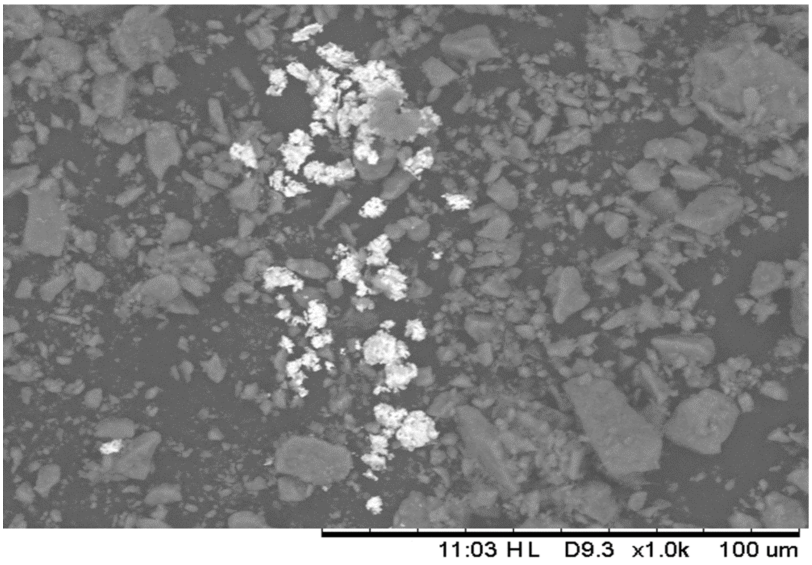

Figure 1. SEM of Cat1 0.25%Pd/Al_2O_3 (1000 magnifications)

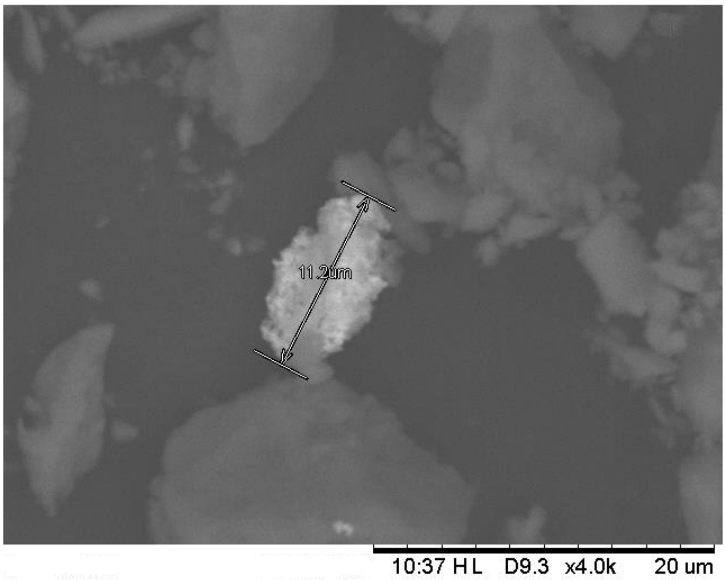

Figure 2. SEM of Cat1 0.25%Pd/Al_2O_3 (1000 magnifications)

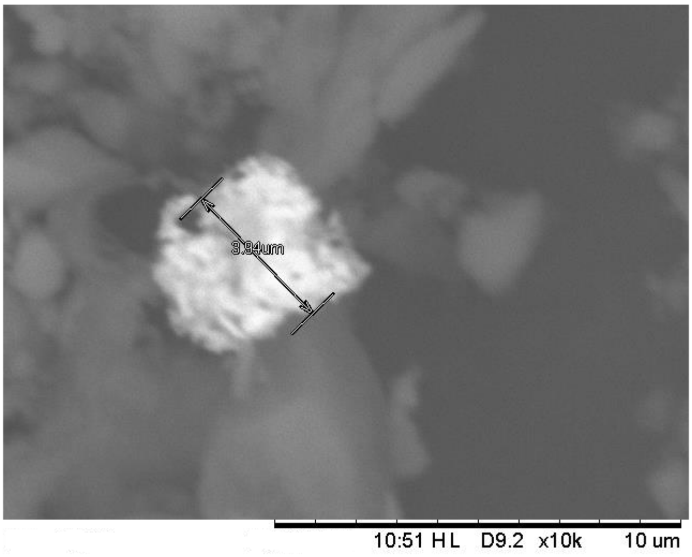

Figure 3. SEM of Cat1 0.25%Pd/Al_2O_3 (1000 magnifications)

Figure 4. SEM of Cat1* 0.25%Pd/Al_2O_3 (100000 magnifications)

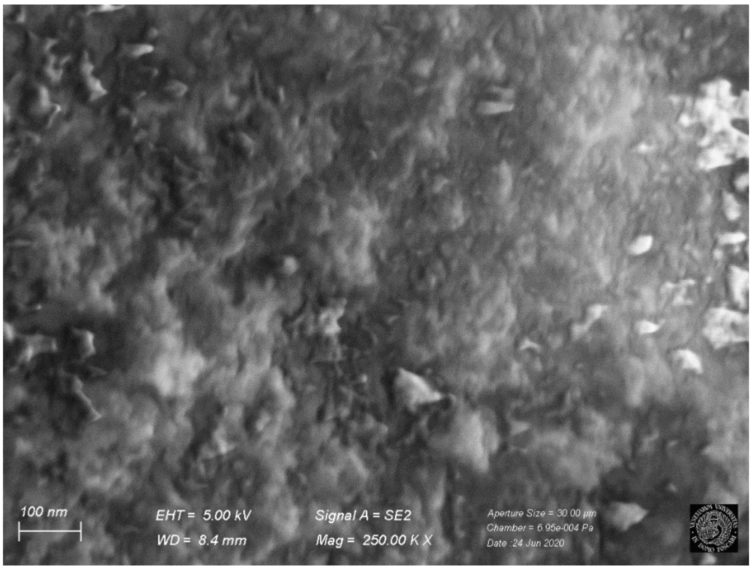

Figure 5. SEM of Cat1* 0.25%Pd/Al_2O_3 (250000 magnifications)

The preparation of these two catalysts differs only in the order of addition of alumina: in the case of Cat 1, it was introduced as a solid into the reaction mixture containing the colloidal reduced metal in cyclopentyl methyl ether (CPME) while, for Cat 1*, the reaction mixture containing the colloidal reduced metal was added to a suspension of alumina in CPME. As it is possible to see, in the Cat 1* sample the average metal particle sizes are significantly smaller (<<100 nm) if compared with those of Cat 1 (where bigger metal particles up to 200nm are present) and a better distribution occurs.