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Hydrogenation of amides to amines by heterogeneous catalysis: A review

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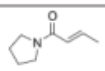
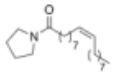
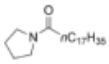
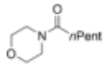
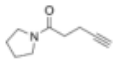
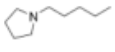
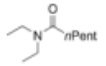
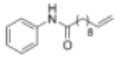
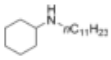
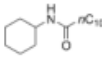
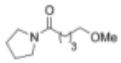
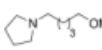
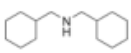
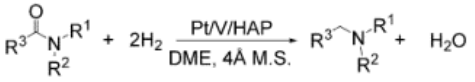
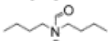
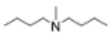
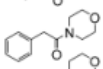
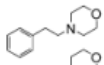
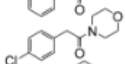
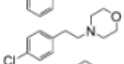
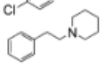
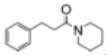
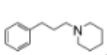
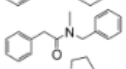
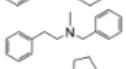
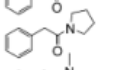
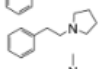
Table S1. Representative examples of the substrate scope in the catalytic hydrogenation with Pd/Re/graphite. Reproduced from Ref. [1] with permission from Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

Entry	Substrate	Conv.[b] [%]	Products	Selectivity [%][b]	Entry	Substrate	Conv.[b] [%]	Products	Selectivity [%][b]
1		>99 (93)[c]		100	12		>99		100
2		>99 (95)[c]		100	13		>99		96
3		72		100					4
4		60		100	14		>99		36
5		10		100					32
6		71		100	15		>99		100
7		89		100	16		>99		100
8		>99		100	17		>99		63[f]
9		>99 (88)[c]		100					29[f]
10		9 (>99)[d]		100 (92)[c]	18		>99		100
11		21 (35)[e]		100					

[a] Reaction conditions: substrate (1.0 mmol, 2% Pd/10% Re/graphite (4 mol% Re), DME (0.2 M), 4 Å MS, H_2 (30 bar), 160 °C, 20 h. [b] Determined by GC, GC/MS, and/or ^{1}H NMR analysis. [c] Values in parentheses are the yield of isolated product after precipitation as a hydrochloride salt. [d] Values in parentheses are for reactions conducted at 200 °C for 72 h. [e] 35% conversion was obtained when montmorillonite K-10 added. [f] Yield of isolated product.

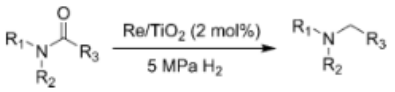
Table S2. Hydrogenation of various amides using Pt-V/HAP as catalyst under mild reaction conditions. Reproduced from Ref. [2] with permission from Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

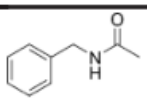
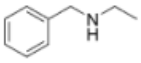
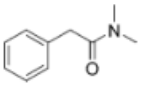
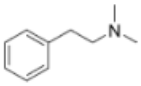
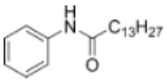
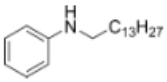
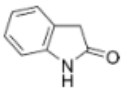
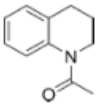
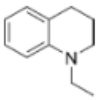
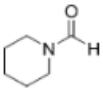
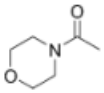
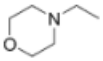
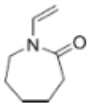
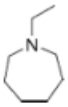


Entry	Substrate	Product	Time [h]	Conv. [%]	Sel. [%]
1			8	99	>99
2[a]			8	99	>99
3[b]			18	99	98
4[b]			36	92	97
5[b]			18	96	96
6[b]			48	92	96
7[b]			18	99	>99
8[b]			36	86	96
9[b]			18	94	96
10			48	97	>99
11[c]			48	99	97
12			48	85	>99
13[b]			24	92	99
14[b]			24	90	>99
15[b]			24	81	>99
16			8	99	98
17[d]			8	96	>99
18			24	90	99
19			24	97	97
20[b]			48	83	93
21[b]			48	92	97
22			24	98	96
23			9	50	89
24			24	0	-

Reaction conditions: Pt/V/HAP 0.1 g (Pt: 6 mol% and V: 7 mol%), substrate (0.5 mmol), DME (5 mL), 4 Å M.S. (0.1 g) in H_2 (30 bar) at 70 °C. Conversion and selectivity were determined by GC using an internal standard. [a] The 10th reuse of Pt/V/HAP. [b] Mass of Pt/V/HAP 0.3 g. [c] In H_2 (1 bar) at 100 °C. [d] At RT. M.S. = molecular sieves.

Table S3. Catalytic hydrogenation of various amides to amines using Re/TiO_2 as catalyst. Reproduced from Ref. [3] with permission from 2017 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.



Entry	Substrate	Product	T [°C]	t [h]	Yield [%]
1			180	24	86 (78)
2			200	24	83
3			200	20	91
4			180	24	54
5			180	24	85
6			180	24	99
7			180	24	99
8			180	24	94
9			180	24	94
10			200	36	56
11			200	24	87
12			180	36	70

[a] Reaction conditions: Re (2 mol%), amide (1 mmol), octane (3 mL), $p^{H_2} = 5$ MPa. Yields were determined by GC analysis by using *n*-dodecane as the internal standard. Yields of isolated products are given in parenthesis.

Table S4. Catalytic hydrogenation of tertiary, secondary and primary amides over Rh-V/Al_2O_3 catalyst and dimethoxyethane as solvent. Reproduced from Ref. [4] with permission from Elsevier.

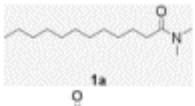
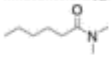
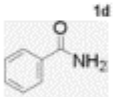
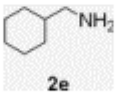
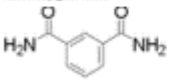
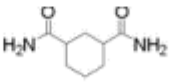
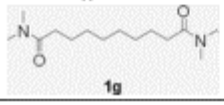
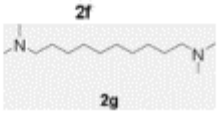
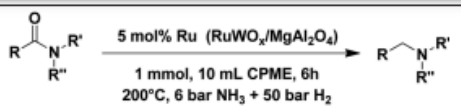
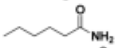
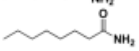
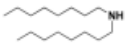
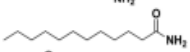
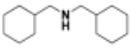
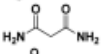
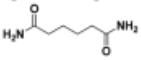
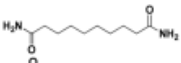
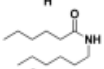
Entry	Amine	Amide	Yield, %	TOF, s^{-1}
1	 1a	2a	99	1.18×10^{-1}
2	 1b	2b	99	1.18×10^{-1}
3	1c	2c	95	1.14×10^{-1}
4	1d	2d	40	4.79×10^{-2}
5	 1e	 2e	70	8.37×10^{-2}
6	 1f	 2f	<5	–
7	 1g	 2g	10	1.20×10^{-2}

Table S5. Substrate scope investigation for amide hydrogenation using RuWOx/$MgAl_2O_4$ as catalyst. Reproduced from Ref. [5] with permission from The Royal Society of Chemistry.



	Substrate	X^a [%]	Major product	S^b [%]	Minor product	S^b [%]
1		96		84		15
2		>99		83		17
3		99		81		17
4		97		82		14
5		>99		80		18
6		>99		30		23[c]
7		>99		85		8
8		>99		85		6
9		>90[d]	Main product[d]:			>50%
10		93[e]		87		13
11		6		>99	—	—
12		57[e]		88		9
13		>99		45		17

[a] Conversion. [b] Selectivity. [c] Very volatile compound; therefore, yields are underestimated by analysing the liquid phase. [d] 1,10-Decanediamine partially precipitates out of CPME resulting in an less precise product yield calculation. [e] Mixture of original amide and propionamide.

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