Chemical Reactions Promoted by BASF Catalysts

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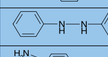
Hydrogenation

	REACTANT	PRODUCT	METAL	Catalyst	T (°C)	P (Atm)	Solvent	Comment
1	—CH=CH—	—CH_2–CH_2—	Pd/Pt	1621, 2621	RT-100	1-5	Various	Pd is used but may cause migration Pt is effective for highly hindered olefins.
2	—CH=CH—CH=CH—	—CH_2–CH_2–CH=CH—	Pd	1391	RT-50	1-5	Various	Inhibited Pd is used. Lindlar catalyst is well known.
3	—C≡C—	—CH=CH—	Pd	1391	RT-50	1-5	Various	Inhibited Pd is used. Lindlar catalyst is well known.
4	—C≡C—	—CH_2–CH_2—	Pd	1421, 1621	RT-50	1-5	Various	Pd catalyst is used.
5			Pd	1391	RT-100	1-5	Various	Modified Pd is used in mild conditions.
6	—CH=CH—X X = OR, OCOR, Cl, Br, NHR	—CH_2–CH_2–X	Pt	2621	RT-100	1-5	Various	Modified Pt carbon catalyst produces high yield.
7	—CH=CH—CH_2–X X = OR, OCOR, Cl, Br, NHR	—CH_2–CH_2–CH_2–X	Pt	2621	RT-100	1-5	Various	Modified Pt carbon catalyst produces high yield.
8	—C≡C—CHOH—	—CH=CH–CHOH—	Pd	1391	RT-50	1-5	Various	Modified Pd carbon catalyst is effective to avoid hydrogenolysis.
9	R–CH=CH–CHO	R–CH_2–CH_2–CHO	Pd	1421, 1621	RT-100	1-10	Various	Pd catalyst is selective.
10			Pd	1421, 1621	RT-150	1-10	Various	Since Pd carbon catalyst has low activity to hydrogenate aliphatic ketones, it is effective.
11			Pd	1391	RT-100	1-5	Various	Modified Pd catalyst is used in mild conditions.
12			Pd	1241	RT-100	1-5	Various	Pd alumina catalyst is effective.
13	Olefinic Polymer	Parafinic Polymer	Pd, Pt	1241, 2941	100- 300	5-50	Various	Pd alumina catalyst is effective.
14			Pt	2421	50-200	10-150	Various	Modified Pt and Re catalysts have low activity for dehalogenation. They are effective for this reaction.
15			Pd/Pt	1421, 2421	RT-100	1-10	Various	Pd may disproportionate at low pressures.
16	RCHO	RCH_2OH	Ru/Pt	4401, 2601	RT-150	3-50	Various	Ru is strongly catalyzed by water. Some base metal act as promoters of Pt catalysts.
17			Ru/Pt	4401, 2601	RT-150	1-50	Various	Ru is strongly catalyzed by water.
18	R–CH=CH–CHO	R–CH=CH–CH_2OH	Pt	2621	RT-100	1-10	Various	Fe and Zn promote the catalyst.
19			Pd/Pt	1421, 2421	RT-150	3-50	Neutral non-polar	Acid may cause hydrogenolysis.
20			Pd/Ru	1421, 4401	RT-100	1-10	Neutral	Acid may avoid hydrogenolysis.
21			Ru/Pd	3401, 1621	50-150	10-50	Various	Hydrogenolysis is avoided by Ru catalyst.
22	R–NO_2	R–NH_2	Pd/Pt	1621, 2621	50-150	1-10	Various	Reaction is slow compared to aromatic nitro groups. Acid may promote or inhibit the reaction.
23	R–CH=CH-NO_2	R–CH_2–CH=NOH	Pd	1421, 1621	RT-100	1-10	Various	Solvent effects are important. Pyridine, dioxane and ethanol/HCl have been used effectively.
24			Pd/Pt	1621, 2931	RT-150	1-10	Neutral	Neutral solvent is used, an acidic solvent may promote the reaction.
25			Pt	2621	RT-50	1-3	Neutral Various	DMSO gives excellent results.
26			Pt	2931	RT-50	<1-3	Dilute H_2SO_4	Conditions adjusted to minimize aniline formation.
27	 X = F, Cl, Br, I		Pt	2931	RT-100	1-10	Various	Stability to hydrogenolysis is in order of F>>Cl>Br>I. Sulfided catalysts may be highly selective.
28			Pt/Pd	2621, 1421	RT-100	1-10	Basic	Organic and inorganic bases are effective.
29			Re	5228	50-150	10-100	Various	Re activity is low but selective. Sulfided Pt catalyst is effective.
30			Pd	1421, 1621	RT-100	1-10	Acidic	Acidic solvent favored to prevent dimerization through the benzyl carbons.
31			Pd	1421, 1621	RT-100	1-10	Basic	Quantitative yields have been obtained in pyridine solvent.
32			Ru	4401	50-150	10-100	Various	Quantitative yields have been obtained in pyridine solvent.
33	NO_3^-	NH_3OH^+	Pd	1621	RT-50	1-5	Acidic	DSM process.
34			Pd	1421, 1621	RT-100	1-10	Various	Pd is effective.
35			Pd	1421	RT-100	1-10	Various	Peroxide compounds are easily hydrogenated.
36			Pd	5225	RT-100	1-10	Various	Hydrogen peroxide process is used for this reaction.
37	R—C≡N	R—CH_2–NH_2	Pd/Rh	1621, 3401	RT-100	5-50	Acid or ammonia addition	Coupling is increased by increased temperature and decreased by increased pressure.
38	R—C≡N		Rh	3401	RT-100	1-50	Neutral	Rh carbon produces high yield with low aliphatic nitriles.
39	R—C≡N		Pd/Pt	1621, 2621	50-150	1-50	Various	Pd and Pt carbon produce high yield with low aliphatic nitriles.
40			Pd	1421, 1621	RT-100	1-10	Acidic	Prolonged hydrogenation may cause hydrogenolysis.
41			Pt/Rh	2421, 2621	RT-100	1-10	Neutral non-polar	Pt catalyst is effective.
42			Pd	1421, 1621	RT-100	1-3	Alcohol with water and acid	Hydrolysis of intermediate imine is faster than reduction to the amine.
43	$RCN + R'NH_2$	RCH_2-$NHR' + NH_3$	Rh	3401	RT-100	1-10	Neutral	Rh catalysts provide an excellent route to mixed secondary amines.
44	$RCN + 2\ R'NH_2$	RCH_2-$NR'R' + 2\ NH_3$	Pd	1421, 1621	50-150	1-10	Various	Coupling is increased by higher temperature and low pressures. The highest yield is obtained by using excess amine
45			Pd	1421, 1621	50-150	1-10	Acidic	N-substitution improves the yield. Thus, order is tertiary > secondary > primary.
46			Ru/Rh/ Pt	4401, 3401	50-150	5-50	No solvent	Ru catalyst is used in mild conditions.
47			Pd/Rh	1421, 3401	RT-250	1-10	Various Vapor phase	Basic promoters enhance the activity. Rh is the best for partial hydrogenation of resorcinols to dihydroresorcinols.
48			Pt	2421, 2621	RT-150	1-10	Acidic	Pt catalyst is effective.
49			Ru/Rh	4401, 3401	RT-150	10-50	Neutral non polar	Hydrogenolysis is minimized by low temperature and high pressure.
50			Pd/Ru	1421, 4401	RT-150	1-50	Various	Pd catalyst is used.
51			Ru/Rh	4401, 3401	RT-150	1-50	Non polar	Ru catalysts are normally used at high temperature and pressure and may require pre-reduction.
52			Ru/Pd	4401, 1421	RT-150	1-50	Various	Neutral conditions and moderate temperatures minimize hydrogenolysis.
53			Ru/Rh	4401, 3401	RT-150	1-50	No water	Water may cause formation of carbonyl or alcohol. Secondary amine formation minimized by ammonia addition
54			Pt/Rh	2421, 3401	RT-150	1-50	Acidic	Acidic solvents may minimize deactivation.
55			Pd, Pt	1241	RT-150	1-50	Various	Platinum Group metal catalysts are effective.
56			Pd	1241	RT-150	1-50	Various	Much work was done by P.P. Fu, H.M. Lee, R.G. Harvey, J. Org. Chem., 45 (1980) 2797.
57			Pt	2621	RT-150	1-50	Various	Much work was done by P.P. Fu, H.M. Lee, R.G. Harvey, J. Org. Chem., 45 (1980) 2797.
58			Pd	1391	RT-150	1-50	Various	Modified Pd catalyst is effective.
59			Pd	1421, 1621	RT-150	1-50	Various	Hydrogenation of either ring or both rings depend on pH of solvent.
60			Pd	1241	RT-150	1-50	Various	Pd on alumina produces high yield at high temperature.
61			Ru/Pd	4401, 1421	RT-150	1-50	Various often acidic	Ruthenium requires higher pressure and avoids N-alkylation by alcoholic solvents.
62			Pd	1421, 1621	RT-100	1-10	Various, water is effective	Exposure to air deactivates the catalyst. Various additives may minimize hydrogenolysis.
63			Pd/Pt	1421, 2421	RT-100	1-10	Neutral	Neutral solvent is used, an acidic solvent may promote this reaction.
64			Pd	1421, 1621	RT-100	1-10	Acidic or basic	Acidic or ammoniacal solvents are often used to prevent coupling reactions.
65			Pd/Pt	1421, 2421	RT-100	1-10	Neutral	Acid conditions should be avoided. Water-free systems will avoid formation of alcohols.
66			Pt	2421, 2621	RT-100	1-10	Acidic	Acetic acid/H_2SO_4 and methanol/HCl have been proven effective.
67	R—COOH	R—CH_2OH	Ru	4401	200-300	50-150	Various	Addition of base prevents hydrogenolysis.
68	R—COCl	R—CHO	Pd	1431	RT-50	1-5	Various	Toluene, benzene and xylene are used under reflux conditions. HCl is removed from the system.
69	R—COCl	R—CH_2OH	Pd	1431	RT-100	1-10	Various	For high yields, a two-stage procedure is necessary. The alcohol formed will react with RCOCl.

Reductive Alkylation

	REACTANT	PRODUCT	METAL	Catalyst	T °C	P (Atm)	Solvent	Comment
70			Pt/Pd	7079, C3699	RT-100	1-50	Various	Sulfided Pt catalyst is recommended to avoid formation of alcohols.
71			Pt/Pd	7079, C3699	100-200	1-50	Various	Sulfided Pt catalyst is recommended to avoid formation of alcohols.
72			Pt/Pd	2421, 1421	100-200	1-50	Various	Temperature and pressure may have to be raised after reduction of the nitro groups.

Reductive Amination

73			Pd	1421, 1621	50-300	5-50	Various	Cyclohexanone acts as an intermediate.
74			Pd	1421, 1621	50-300	5-50	Various	Pd catalyst is effective.
75	R—OH + NH_3	R—NH_2	Pd	1421, 1621	50-300	5-50	Various	Pd catalyst is effective.
76			Pd	1421, 1621	50-300	5-50	Various	Pd catalyst is effective.

Hydrogenolysis

77	—CH=CHX X = -OR, -OCOR, -NHR	—CH_2–CH_3 + HX	Pd/Pt	1471, 2621	50-150	1-10	Acidic	Hydrogenolysis is favored at low pressures and high temperatures.
78	—CH=CH—CH_2X X = -OR, -OCOR, -NHR	—CH_2–CH_2–CH_3 + HX	Pd	1931, 1951	50-150	1-10	Various	Acid promotes hydrogenolysis.
79			Pd	1931, 1951	50-150	1-10	Various	Acid promotes hydrogenolysis.
80			Pd	1931, 1951	50-150	1-10	Various	Acid promotes hydrogenolysis.
81	 X = -NH2, -NHR, -OR, -OCOR		Pd	1931, 1951	50-150	1-10	Various	Acid promotes hydrogenolysis.
82		RCHOH$(CH_2)_2R'$	Pd	1471	RT-100	1-50	Various	Acid solvent may minimize deactivation.
83			Pd	1471	RT-100	1-50	Various	Regiospecificity and stereospecificity are influenced by presence or absence of alkali.
84			Re		150-250	100-200	Various	Re produces high yields.

Dehalogenation

85	—HC=CHX X = Cl, Br, I	—CH_2–CH_3 + HX	Pd/Pt	1421, 1621	50-150	1-10	Basic	Hydrogenolysis is favored at low pressures and high temperatures.
86	—HC=CH—CH_2X X = Cl, Br, I	—CH_2–CH_2–CH_3 + HX	Pd	1421, 1621	50-150	1-10	Various	Hydrogenolysis is favored at low pressures and high temperatures.
87	—R—X X = Cl, Br, I	—RH + HX	Pd	1421, 1621	50-200	1-10	Basic polar	Hydrogenolysis is favored at low pressures and high temperatures.
88	 X = Cl, Br, I	+ HX	Pd	1421, 1621	50-150	1-10	Basic polar	Hydrogenolysis is favored at low pressures and high temperatures.

Isomerization / Disproportionation / Migration

89			Pt		350-500	10-50	Vapor phase	Xylene isomerization, Octafining process.
90			Pd	1421, 1621	50-150	1-50	No solvent	Pd catalyst is effective.
91	—CH_2–CH_2–CH=CH_2	—CH_2–CH=CH–CH_3	Pd	1421, 1621	50-150	1-50	Various	Pd catalyst is used.

Dehydrogenation

92	—CH_2–CH_2–CH_2–CH_3	—CH_2–CH_2–CH=CH_2	Pt		350-450	1-5	Vapor phase	Alkaline metal prevents carbon deposit.
93			Pt/Pd	1421, 2621	300-400	1-5	Various	Acidic support should be avoided.
94			Ru	4401	300-400	1-5	Various	Acidic support should be avoided.
95			Pt	2621	300-400	1-5	Various	Acidic support should be avoided.
96			Pd	1421, 2421	300-400	1-5	High boiling solvent	Hydrogen acceptor is useful. Liquid phase reaction.
97			Pd	1421	150-250	1-5	Various	Hydrogen acceptor is useful. Liquid phase reaction.
98			Pd/Pt	1421	150-250	1-5	Vapor phase or high boiling solvent	Pd on carbon is effective in liquid phase reaction. Pt catalysts are used in gas phase reaction.

Decomposition

99	N_2H_2	$N_2 + H_2$	Ir		RT-800	1-5	Vapor phase	Ir catalyst is used.
100	H_2O_2	$1/2\ O_2 + H_2O$	Ru/Pt	4401, 2421	RT-200	1-5	Water	Ru catalyst is effective.
101	O_3	$3/2\ O_2$	Pt/Pd	2941, 1241	RT-150	1-5	Vapor phase	Pt catalyst is used for decomposition of ozone in air planes.
102	H_3C-OH	$CO + 2H_2$	Ru	4401	150-350	1-5	Various	Pd catalyst is effective.
103	NH_3	$1/2\ N_2 + 3/2H_2$	Rh	3401	500-800	1-5	Various	Rh catalyst is used to produce pure hydrogen.

Carbonylation / Decarbonylation

104	R—OH + CO $\xrightarrow{O_2}$		Pd	1421	RT-150	10-100	Various	Pd catalyst is effective.
105	$H_2C=CH_2$ + CO $\xrightarrow{O_2}$	H_3C-CHO	Pd	1421	RT-150	10-100	Various	Pd catalyst is effective.
106	H_3C-OH + CO	$H_3C-COOH$	Rh		100-200	10-50	No solvent	Monsanto process.
107	CH_2=CH–CH_2 + CO + H_2	CH_3–CH_2–CH_2–CHO	Rh		50-150	5-30	Various	Hydroformylation, Octanol process.
108		+ CO	Pd	1421	100-200	1-5	Various	Pd catalyst is effective under reflux conditions.

Catalyst Description

Strem product code	Escat number	Description
46-1951	1241	5%Pd/AP dry
46-2090	1351	5%Pd/SiO_2 reduced, dry
46-2022	1371	5%Pd/$CaCO_3$ unreduced, dry
46-2021	1391	5% Pd - 2.7% Pb/ $CaCO_3$ reduced, dry (Lindlar's catalyst)
46-1903	1421	5%Pd/CP (wood) edge, reduced
46-1902	1431	5%Pd/CP (wood) edge, reduced, dry
46-1904	1471	5%Pd/CP (wood) edge, unreduced
46-1901	1621	5%Pd/CP (peat) edge, reduced
46-1907	1911	3%Pd/CP (wood) reduced
46-1906	1921	10%Pd/CP (wood) unreduced
46-1905	1931	10%Pd/CP (wood) reduced
46-1908	1941	5%Pd/CP (wood) reduced
46-1707	1951	20%Pd/CP (peat) (Pearlman's catalyst)
46-1909	1961	5%Pd/CP (peat) reduced
46-1911	1971	5%Pd/CP (wood) reduced
78-1675	2351	5%Pt/SiO_2 reduced, dry
78-1665	2371	5%Pt/$CaCO_3$ unreduced, dry
78-1612	2421	5%Pt/CP (wood) mixed, reduced
78-1611	2431	5%Pt/CP (wood) mixed, reduced, dry
78-1613	2441	5%Pt/CP (wood) mixed, unreduced
78-1615	2621	5%Pt/CP (peat) mixed, reduced
78-1614	2931	3%Pt/CP (wood) edge, reduced
78-1661	2941	5%Pt/AP reduced, dry
44-4065	4401	5%Ru/CP (wood) reduced
45-1875	3401	5%Rh/CP (wood) reduced

Order samples at www.strem.com/basf with the indicated Strem product code