

Table 1. Hydroformylation of 1-hexene over gold catalysts with several different supports^a

Entry	Catalyst (mg)	Au/(Au+Co) /atom %	Co/Substrate /atom %	T/P (°C/MPa)	Conversion/%	Selectivity/%					n/i ^b
						Hexane	Internal olefins	Aldehydes	Alcohols	Heavy end	
1	Au/AC (35)	1.5 ^c		175/3.8	2.6	0.3	96.7	3.1	0	0	—
2	Au/Al ₂ O ₃ (200)	1 ^c		175/3.8	32.7	20.6	76.2	0.4	1.7	0.8	1.1
3	Au/TiO ₂ (40)	3 ^c		160/12.1	10.9	66.2	30.6	0	3.2	0	1.1
4	Au/Fe ₂ O ₃ (50)	5 ^c		195/3.8	22.2	8.3	82.8	0	8.8	0.1	3.1
5	Co ₃ O ₄ (50)	0	7.8	100 ^d /4	0	—	—	—	—	—	—
6	Au/Co ₃ O ₄ (20)	5	3.0	100/4	19.6	0	6.5	88.3	1.7	3.6	2.2
7	Au/Co ₃ O ₄ (50)	5	7.5	100/4	81.8	0	5.8	87.5	3.1	3.6	2.1
8	Au/Co ₃ O ₄ (20)	10	2.9	100/4	60.3	0	3.3	91.2	2.6	3.0	2.3
9 ^e	Au/Co ₃ O ₄ (20)	10	2.9	130/4	99.5	0.3	5.4	83.9	4.4	5.9	1.2

^aReaction conditions: reaction time = 20 h; 1-hexene 5.6 mmol, pentane 12.1 mmol (Entries 1, 2, and 4); 1-hexene 3.2 mmol, pentane 6.9 mmol (Entry 3); 1-hexene 8 mmol, heptane 14 mmol, (Entries 5–9). ^bn/i = linear-to-branched ratio of aldehydes (Entries 1 and 6–9), linear-to-branched ratio of corresponding alcohols (Entries 2, 3, and 4). ^cGold loading by weight% (=100 × Au/(Au + M_xO_y)). ^dAt 140 °C, 0.5% conversion and trace amount of aldehydes were observed. ^eReaction time = 5.5 h.

Co₃O₄ (350–370 °C).⁸ The Au/Co₃O₄ catalyst pretreated with hydrogen (H₂ 2.0 MPa, 100 °C, 3 h) provided appreciable improvement in 1-hexene conversion from 19.6% (Table 1, Entry 6) to 89.1% (first run in Figure 1) under the same reaction conditions, which indicates that the Co⁰ metal plays a role in catalyzing the hydroformylation reaction. On the other hand, the pre-reduced Co₃O₄ with flowing hydrogen of 40 mL/min in atmospheric pressure at 400 °C for 3 h or with 2.0 MPa hydrogen at 100 °C for 3 h in solvent heptane exhibits no catalytic activity. This result suggests Au is indispensable to generate the effectively active Co⁰ species or to catalyze the reaction.

Figure 1 shows the recycle use of 5 atom % Au/Co₃O₄ catalyst. It can be seen that catalyst separation and recycle use (4 times) by simple decantation were successfully carried out, while the liquid phase was vigorously stirred during the reaction. It should be noted that the activity in the fourth cycle (59% convn. in Figure 1) is still much higher than a fresh catalyst without hydrogen pretreatment (19.6%, Table 1, Entry 6), which suggests that the active species in recycle experiments are derived from the heterogeneous solid Co⁰ metal formed by the reducing treatment. The active species Co⁰ metal is mainly fixed on catalyst surface, not leached into liquid phase for homogeneous catalysis.

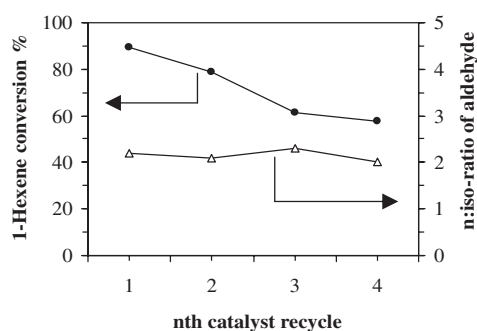


Figure 1. Recycle use of the Au/Co₃O₄ catalyst for the hydroformylation of 1-hexene. Reaction conditions: same to Table 1, Entry 6, the catalyst pretreated with hydrogen (2 MPa, 100 °C, 3 h) before the first run.

In summary, we have demonstrated the heterogeneous hydroformylation of olefins with Au/Co₃O₄ catalyst under mild conditions (100–130 °C, 3–5 MPa). Neither Au⁰ nor Co₃O₄ have been known as hydroformylation catalysts and show poor activities. The combination leads to high performance catalysts with selectivity above 85% in desired aldehydes. The Au/Co₃O₄ catalysts can be recycled by simple decantation, which is a great advantage over homogeneous catalysts. The role of promoter gold nanoparticles may mainly provide spillover H to in situ reduction of Co₃O₄ to Co metal under reaction conditions.

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Dedicated to Professor Ryoji Noyori on the occasion of his 70th birthday.

References and Notes

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- 9 Supporting Information (XRD pattern) is available electronically on the CSJ-Journal Web site, <http://www.csj.jp/journals/chem-lett/index.html>.