Coprecipitated Gold–Tricobalt Tetraoxide Catalyst for Heterogeneous Hydroformylation of Olefins

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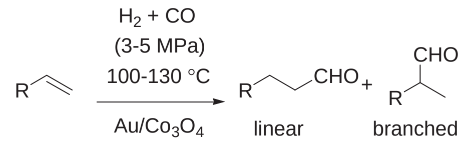
The combination of gold (Au^0) and tricobalt tetraoxide (Co_3O_4) prepared by coprecipitation gives high-performance heterogeneous catalysts for hydroformylation reaction with selectivity above 85% in desired aldehydes, although neither Au^0 nor Co_3O_4 have been demonstrated in this reaction and show poor activities. The Au/Co_3O_4 catalysts can be recycled by simple decantation with slight decrease in catalytic activity along with recycle times. The role of Au may mainly promote in situ reduction of Co_3O_4 to Co^0 catalyzing the hydroformylation reaction.

Hydroformylation, also known as "oxo synthesis," is an important homogeneous industrial process for the production of aldehydes from alkenes.[1] This process has witnessed continuous growth since its invention in the 1930s. Notwithstanding a number of advantages over their heterogeneous counterparts such as high accessibility of all catalytic sites and possibility of tuning selectivity, homogeneous systems have problems inevitably associated with separating the catalyst from the products and its recycling use.[2] In addition, the cost of dominantly used rhodium catalysts are about 4000 times as that of cobalt.

Thus, possible solutions to the problems are to heterogenize Co^0 metal or Co^0 complex catalysts by anchoring the catalyst on a support such as polymer,[3] silica,[4] and active carbon.[5] Active sites can be fixed on the support through strong bonding or physical interaction to form heterogeneous catalysts to develop economically and environmentally friendly green processes.

Recently, gold has been proven to be an effective catalytic component for many reactions.[6] The most important key is to support nanoparticles of gold on select metal oxides or to design bimetallic structures. The fact that gold nanoparticles exhibit markedly high catalytic activity and selectivity by the synergy with the metal oxide supports have motivated us to prepare a heterogeneous hydroformylation catalyst based on Co_3O_4. Gold nanoparticles deposited on base metal oxides can adsorb CO[7] moderately and are active for CO oxidation, water gas shift reaction, olefin hydrogenation, and methanol synthesis.

In a similar manner to these reactions, for the seventy-year-old hydroformylation reaction (Scheme 1), various supported gold-containing catalysts were prepared for reaction test. The 5 atom % Au/Fe_2O_3 and Au/Co_3O_4 were prepared by coprecipitation. The 3 wt % Au/TiO_2 and 1.5 wt % Au/AC (activated carbon) were prepared by deposition–precipitation. The 1 wt % Au/Al_2O_3 was prepared by directly grinding dimethylgold(III) acetylacetonate with Al_2O_3. In details, the preparation of Au/Co_3O_4 catalyst was performed by introducing an aqueous solution of cobalt(II) nitrate hexahydrate and $HAuCl_4$ into a sodium carbonate solution at room temperature. The coprecipitates were washed, dried overnight at 100 °C, and calcined at 400 °C for 4 h. The Co_3O_4 was prepared in the same way.



Scheme 1. Au/Co_3O_4-catalyzed hydroformylation of 1-olefins.

As shown in Table 1, Au/AC (activated carbon), Au/Al_2O_3, Au/TiO_2, and Au/Fe_2O_3 showed only little or no hydroformylation activities (Table 1, Entries 1–4). The reactant 1-olefin introduced mainly remained unchanged and the major products were isomerized olefins or hydrogenated paraffin depending on the catalyst component and the reaction conditions. The Co_3O_4 did not exhibit any activity for 1-hexene conversion (Table 1, Entry 5). In contrast, very interestingly, supported nanoparticulate gold catalysts 5 or 10 atom % Au/Co_3O_4 exhibit noticeably high hydroformylation activity (Table 1, Entries 6–9) and the selectivity to aldehydes was in the range of 85–90%. The catalytic activity is appreciably increased with increasing gold loading (Table 1, Entries 6 and 8). A chemical yield >80% (Table 1, Entry 9) of desired aldehydes was obtained with 10 atom % Au/Co_3O_4 catalyst.

Taking into account the catalytic activity order in hydroformylation widely accepted (Rh, Co, Ir, Ru, Os, Pt, Pd, Fe, Ni, etc.), we may assume that the remarkably enhanced catalytic activity of Au/Co_3O_4 compared to Co_3O_4 or other supported Au nanoparticles (Au on AC, Al_2O_3, TiO_2, and Fe_2O_3) may be ascribed to active Co^0 metal generated on the surface[8] by spillover hydrogen from gold nanoparticles, or to other synergistic effects between gold and cobalt.

As evidenced with XRD data (Figure S1),[9] the fresh 10 atom % Au/Co_3O_4 catalyst gives only Co_3O_4 peaks at $2\theta = 19.0$, 31.4, 36.9, 44.7, 55.7, 59.3, 65.2, and 77.5 and gold peaks at $2\theta = 38.2$, 44.4, 64.7, and 77.6. When the catalyst is reduced with H_2 (100 °C, 2.0 MPa, 3 h) in 2.0 mL of heptane, its XRD patterns are composed of a CoO peak at $2\theta = 42.4$ and strong Co^0 peaks at $2\theta = 44.1$, 47.6, and 75.9, but not of Co_3O_4 peaks. This reduction behavior is consistent with a temperature-programmed reduction (TPR) experiment that the reduction of Co_3O_4 in Au/Co_3O_4 to elemental cobalt took place at a temperature about 200 °C lower than the reduction temperature for pure

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/% Hexane	Internal olefins	Aldehydes	Alcohols	Heavy end	n/i[b]
1	Au/AC (35)	1.5[c]		175/3.8	2.6	0.3	96.7	3.1	0	0	—
2	Au/Al_2O_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_2O_3 (50)	5[c]		195/3.8	22.2	8.3	82.8	0	8.8	0.1	3.1
5	Co_3O_4 (50)	0	7.8	100[d]/4	0	—	—	—	—	—	—
6	Au/Co_3O_4 (20)	5	3.0	100/4	19.6	0	6.5	88.3	1.7	3.6	2.2
7	Au/Co_3O_4 (50)	5	7.5	100/4	81.8	0	5.8	87.5	3.1	3.6	2.1
8	Au/Co_3O_4 (20)	10	2.9	100/4	60.3	0	3.3	91.2	2.6	3.0	2.3
9[e]	Au/Co_3O_4 (20)	10	2.9	130/4	99.5	0.3	5.4	83.9	4.4	5.9	1.2

[a] Reaction 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). [b] n/i = linear-to-branched ratio of aldehydes (Entries 1 and 6–9), linear-to-branched ratio of corresponding alcohols (Entries 2, 3, and 4). [c] Gold loading by weight% ($= 100 \times Au/(Au + M_xO_y)$). [d] At 140 °C, 0.5% conversion and trace amount of aldehydes were observed. [e] Reaction time = 5.5 h.

Co_3O_4 (350–370 °C).[8] The Au/Co_3O_4 catalyst pretreated with hydrogen (H_2 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 Co^0 metal plays a role in catalyzing the hydroformylation reaction. On the other hand, the prereduced Co_3O_4 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 indispensible to generate the effectively active Co^0 species or to catalyze the reaction.

Figure 1 shows the recycle use of 5 atom % Au/Co_3O_4 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 Co^0 metal formed by the reducing treatment. The active species Co^0 metal is mainly fixed on catalyst surface, not leached into liquid phase for homogeneous catalysis.

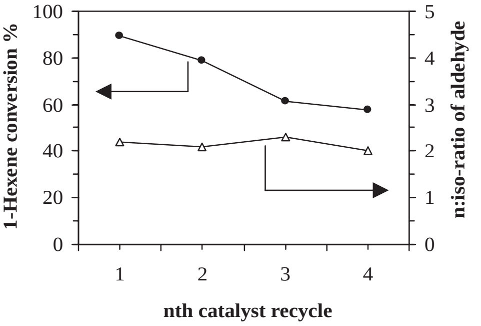


Figure 1. Recycle use of the Au/Co_3O_4 catalyst for the hydroformylation of 1-hexene. Reaction conditions: same to Table 1, Entry 6, the catalyst pretreated with hydrogen (2 MPa, 100 °C, 3 h) before the first run.

In summary, we have demonstrated the heterogeneous hydroformylation of olefins with Au/Co_3O_4 catalyst under mild conditions (100–130 °C, 3–5 MPa). Neither Au^0 nor Co_3O_4 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/Co_3O_4 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 Co_3O_4 to Co metal under reaction conditions.

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

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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.

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