Coprecipitated Gold-Tricobalt Tetraoxide Catalyst for Heterogeneous Hydroformylation of Olefins

Xiaohao Liu, ^{1,3} Masatake Haruta, ^{2,3} and Makoto Tokunaga*^{1,3}

¹Department of Chemistry, Graduate School of Science, Kyushu University,
6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581

²Materials Chemistry Course, Faculty of Urban Environmental Sciences, Tokyo Metropolitan University,
1-1 Minami-osawa, Hachioji, Tokyo 192-0397

³JST (Japan Science and Technology Cooperation) CREST

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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. 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. 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 Co⁰ metal or Co⁰ 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. 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/Fe₂O₃ and Au/Co₃O₄ were prepared by coprecipitation. The 3 wt % Au/TiO₂ and 1.5 wt % Au/AC (activated carbon) were prepared by deposition–precipitation. The 1 wt % Au/Al₂O₃ was prepared by directly grinding dimethylgold(III) acetylacetonate with Al₂O₃. In details, the preparation of Au/Co₃O₄

Scheme 1. Au/Co₃O₄-catalyzed hydroformylation of 1-olefins.

catalyst was performed by introducing an aqueous solution of cobalt(II) nitrate hexahydrate and HAuCl₄ into a sodium carbonate solution at room temperature. The coprecipitates were washed, dried overnight at $100\,^{\circ}$ C, and calcined at $400\,^{\circ}$ C for 4 h. The Co_3O_4 was prepared in the same way.

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/Co₃O₄ compared to Co₃O₄ or other supported Au nanoparticles (Au on AC, Al₂O₃, TiO₂, and Fe₂O₃) may be ascribed to active Co⁰ metal generated on the surface⁸ by spillover hydrogen from gold nanoparticles, or to other synergistic effects between gold and cobalt.

As evidenced with XRD data (Figure S1), the fresh 10 atom % Au/Co₃O₄ catalyst gives only Co₃O₄ 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 H₂ (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 Co⁰ peaks at $2\theta=44.1,\ 47.6,\ and\ 75.9,\ but not of Co₃O₄ peaks. This reduction behavior is consistent with a temperature-programmed reduction (TPR) experiment that the reduction of Co₃O₄ in Au/Co₃O₄ to elemental cobalt took place at a temperature about 200 °C lower than the reduction temperature for pure$

T/P $n/\overline{i^{\mathrm{b}}}$ Entry Au/(Au+Co) Co/Substrate Conversion/% Selectivity/% Catalyst (mg) Hexane Internal olefins Aldehydes Alcohols Heavy end /atom % /atom % (°C/MPa) 1.5 175/3.8 1 Au/AC (35) 2.6 0.3 96.7 3.1 0 1^c 2 Au/Al_2O_3 (200) 175/3.8 32.7 20.6 76.2 0.4 1.7 0.8 1.1 30 3 Au/TiO₂ (40) 160/12.1 10.9 66.2 30.6 0 32 0 1 1 5° 0 4 Au/Fe_2O_3 (50) 195/3.8 22.2 8.3 82.8 8.8 0.1 3 1 Co_3O_4 (50) 0 7.8 $100^{d}/4$ 0 5 0 Au/Co₃O₄ (20) 5 3.0 100/4 19.6 6.5 88.3 1.7 3.6 2.2 6 Au/Co₃O₄ (50) 5 7.5 100/4 81.8 0 5.8 87.5 3.1 3.6 2.1 Au/Co₃O₄ (20) 10 2.9 100/4 60.3 0 3.3 91.2 2.6 3.0 2.3 Au/Co₃O₄ (20) 10 2.9 130/4 99.5 0.3 5.4 83.9 5.9 1.2 4.4

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

^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.

 ${\rm Co_3O_4~(350\text{--}370\,^\circ C).^8}$ 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 ${\rm Co^0}$ metal plays a role in catalyzing the hydroformylation reaction. On the other hand, the prereduced ${\rm Co_3O_4}$ 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 ${\rm Co^0}$ 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.

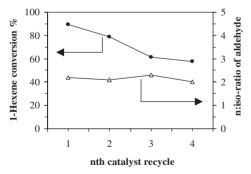


Figure 1. Recycle use of the Au/Co_3O_4 catalyst for the hydroformylation of 1-hexene. Reaction conditions: same to Table 1, Entry 6, the catalyst pretreated with hydrogen (2 MPa, 100 °C, 3 h) before the first run.

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