Supplementary Materials

Cyanide-free leaching of gold from used Au/MO_x catalysts assist by oxidative carbonylation

Yanwei Cao, Lin He*

State Key Laboratory of Low Carbon Catalysis and Carbon Dioxide Utilization, State Key Laboratory for Oxo Synthesis and Selective Oxidation, Research Center of Resource Chemistry and Energy Materials, Lanzhou Institute of Chemical Physics (LICP), Chinese Academy of Sciences, Lanzhou 730000, Gansu, China.

***Correspondence to:** Prof. Lin He, State Key Laboratory of Low Carbon Catalysis and Carbon Dioxide Utilization, State Key Laboratory for Oxo Synthesis and Selective Oxidation, Research Center of Resource Chemistry and Energy Materials, Lanzhou Institute of Chemical Physics (LICP), Chinese Academy of Sciences, No.18, Tianshui Middle Road, Lanzhou 730000, Gansu, China. E-mail: helin@licp.cas.cn

EXPERIMENTAL

Materials

Used Au/MO_x catalysts were collected from our laboratory[1]. Morpholine, dibutylamine, butylamine, aniline, cuprous iodide (CuI), potassium iodide (KI), Sodium iodide (NaI), 1-ethyl-3-methylimidazolium iodide (EMMMI), tetrabutylammonium iodide (TBAI), tetramethylammonium iodide (TAAI), toluene, methanol, ethanol, *i*-propanol, *t*-butanol were purchased from SINOPHARM, Adamas, Energy Chemical or Macklin without any pretreatment. Nitrogen (N_2, 99.99%) Carbon monoxide (CO, 99.9%), and synthetic air were provided by Air Liquide Gas Technology Co.

Leaching of gold (0) from used Au/MO_x catalysts

In a typical leaching process, morpholine (1 mmol), 100 mg of used Au/MO_x catalysts, CuI (~ 4 mg, 0.02 mmol), and toluene (5 mL) were loaded in a 10 mL glass tube. At room temperature, the glass tube was placed in a batch reactor, and successively charged with 0.4 MPa of air and 1.6 MPa of CO (caution: the lower and upper explosive limits of CO at RT and atmospheric pressure are, respectively, 12.5 and 74.2 % by volume of air). And then, the reactor was stirred at 60 ^oC for 10 h. Afterward, the pressure was carefully released. The gold concentration both in liquid and solid was analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES, Agilent 720ES). The conversion of morpholine and yield of urea were determined by gas chromatography (Agilent 7890). High-resolution electrospray-ionization mass spectra (ESI-HRMS) were recorded with Agilent 6530 Accurate-Mass Q-TOF in a positive and negative ion mode. Transmission electron microscopy (TEM) was collected by field emission high-resolution transmission electron microscopy (FEI TECNAI G2 F20, Thermo Fisher).

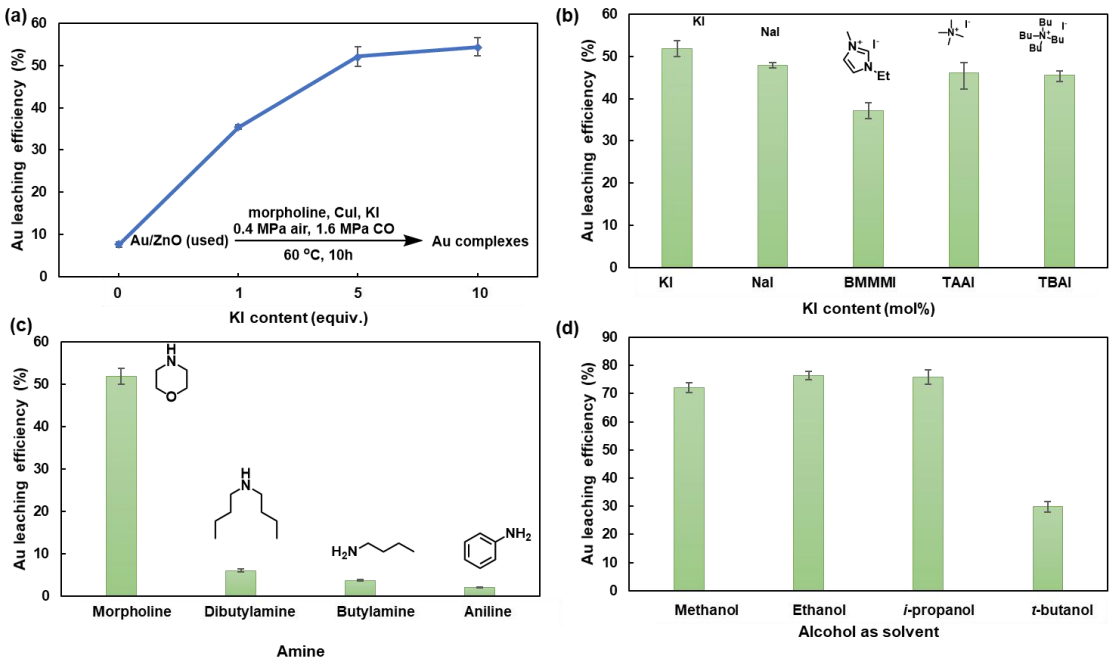
Leaching of gold (0) from used Au/MO_x catalysts in the presence of iodide

In a typical leaching process, morpholine (1 mmol), 100 mg of used Au/MO_x catalysts, CuI (~ 4 mg, 0.02 mmol), iodide (1 ~ 10 equivalents, I^- mol/Au mol), and toluene or other mentioned solvent (5 mL) were loaded in a 10 mL glass tube. At room temperature, the glass tube was placed in a batch reactor, and successively charged with 0.4 MPa of air and 1.6 MPa of CO (caution: the lower and upper explosive limits of CO

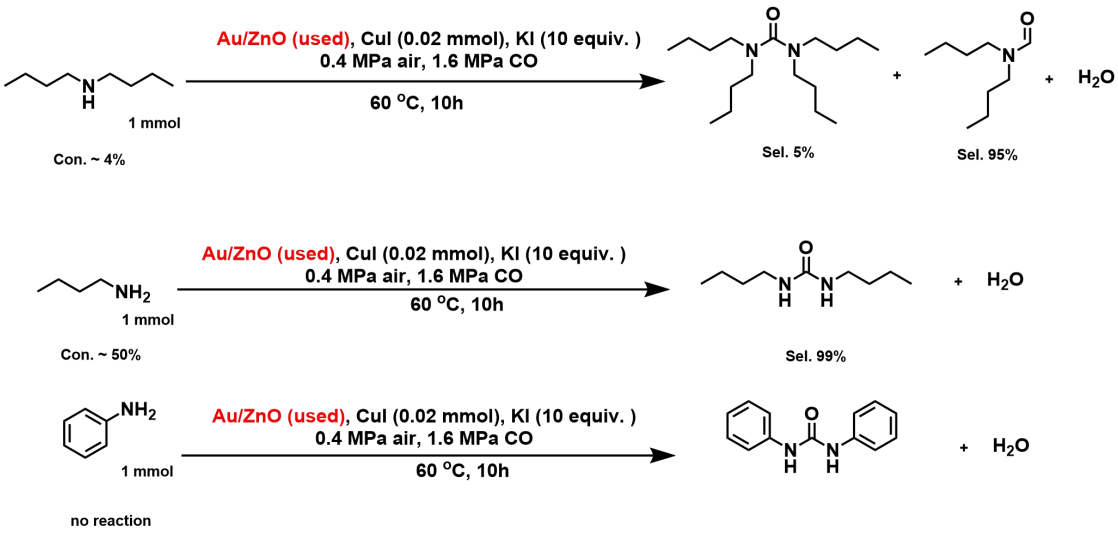
at RT and atmospheric pressure are, respectively, 12.5 and 74.2 % by volume of air). And then, the reactor was stirred at 60 ^{o}C for 10 h. Afterward, the pressure was carefully released. The gold concentration both in liquid and solid was analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES, Agilent 720ES). The conversion of morpholine and yield of urea were determined by gas chromatography (Agilent 7890).

Supplementary Table 1. Leaching of gold from used Au/ZnO catalysts assist by oxidative carbonylation of morpholine

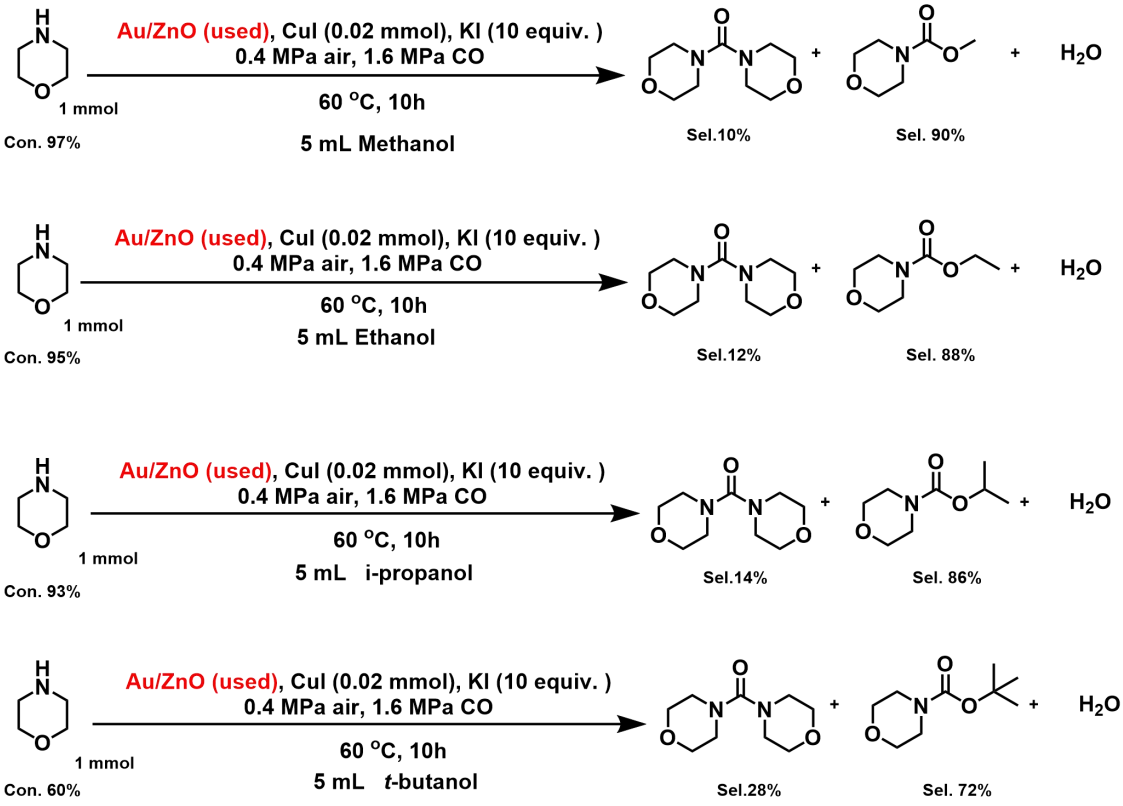
No.	Morpholine	Atmosphere	Con	Sel.	Au (mg/mL)*
1	1 mmol	1.6 Mpa CO/0.4 MPa air	95%	>99%	6.02 mg/mL
2	-	1 MPa N_2	-	-	not detected
3	-	0.4 MPa air	-	-	not detected
4	-	1.6 MPaCO	-	-	not detected
5	-	1.6 MPaCO/0.4 MPa air	-	-	not detected



Supplementary Figure 1. Leaching of gold from used Au/MO_x catalysts (a). Au source: used Au/ZnO, effect content of KI equivalent, I^- mol/Au mol, (b). Au source: used Au/ZnO, the effect of cations in iodide, 10 equiv. (c). Au source: used Au/ZnO, the effect of amines, KI, 10 equiv. (d). Au source: used Au/ZnO, effect of alcohol solvents, KI, 10 equiv.. Oxidative carbonylation reaction condition: amine (1 mmol), CuI (0.02 mmol) solvent 5 mL, CO 1.6 MPa, air 0.4 MPa, T = 60 °C, t = 10 h.

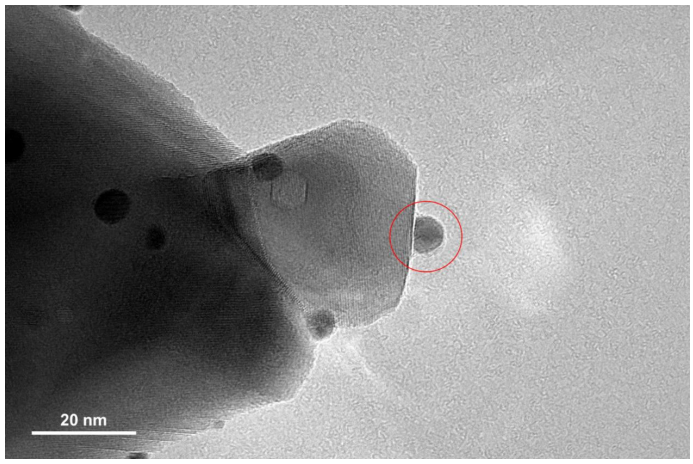


Supplementary Scheme 1. Effect of the amines.

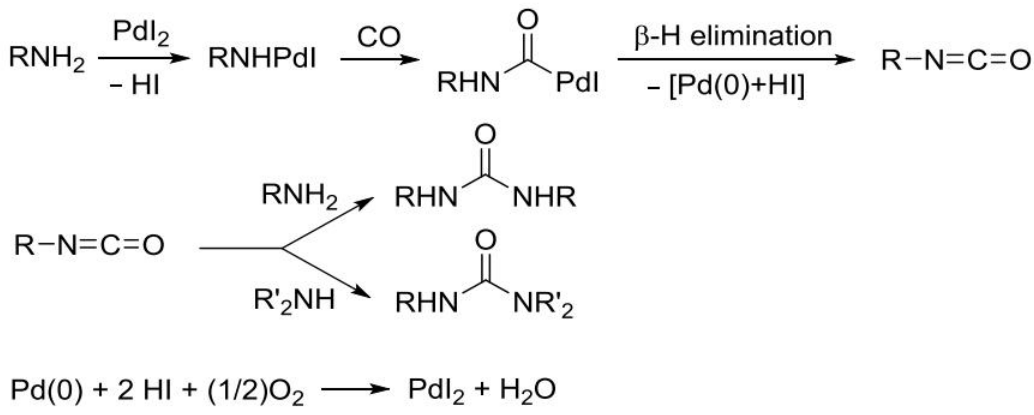


Supplementary Scheme 2. Effect of the solvents.

Based on our current knowledge on SMSI, we hypothesized that some structural features, such as the encapsulation overlayer, provide a potential solution to the problem of unstable of supported catalysts. In this work, however, may inhibit the leaching efficiency of Au. Only weakly bound gold particles on oxides (Au/MO_x catalysis) were leached out even in an alkaline NaCN solutions[2,3]. Figure S2 shows an image of the overlayer structure observed between Au NPs and CeO_2 due to SMSI. So, we proposed the structural features in Au/TiO_2 and Au/CeO_2 may inhibit the leaching efficiency. With the structural features destroyed during the first leaching cycle. Multiple repetitions may improve the leaching efficiency of Au.



Supplementary Figure 2. The TEM pattern of the Au/CeO_2 catalysts.



Supplementary Scheme 3. The possible mechanism of PdI_2-catalyzing oxidative carbonylation of amine.

PdI_2 can easily react with amino groups to form carbamoylpalladiumiodide intermediates. This reactivity can be conveniently exploited for the synthesis of ureas, when applied to simple primary amines. In fact, in this case, the initially formed RNH(CO)PdI intermediate may undergo β-H elimination from the HN-CO-Pd moiety, with the formation of an isocyanate and palladium (0). While the latter is readily reoxidized to PdI_2 in the presence of oxygen, the isocyanate may be attacked by a second molecule of amine (either the same primary amine or a secondary amine, used as additional substrate) to yield a symmetrical 1,3-disubstituted or a trisubstituted urea, respectively[4].

$$I_{2(aq)} + I^- = I_3 \quad (1)$$

$$2Au + I_3^- + I^- = 2AuI_2 \quad (2)$$

$$AuI_2^- + I_3^- = AuI_4^- + I \quad (3)$$

$$AuI_4^- = AuI_{(s)} + Au + I_3 \quad (4)$$

$$AuI_{(s)} + I^- = AuI_2 \quad (5)$$

$$AuI_{(s)} + I_3^- = AuI_4 \quad (6)$$

$$2AuI_{(s)} + I^- = 2Au_{(s)} + I_3 \quad (7)$$

Supplementary Scheme 4. Recovery of gold in iodine-iodide system.

The main components of the iodide system are iodine (I_2) and iodide (I^-). Therefore, iodide system is actually the iodine-iodide system. In this system, I_3^- (generated by I^- and I_2) serves as oxidant. It's the oxidant I_3^- that plays an important role, which can dissolve gold metal as the aurous or the auric complex (Scheme R2). There are two kinds of soluble gold-iodide complexes: AuI_2^- and AuI_4^-. The latter is with high potential, and hardly to be formed. Also, AuI_4^- is easily disproportionate into AuI(s) (7). Solid aurous iodide (AuI(s)) exists in aqueous solution merely as an intermediate or a bridging species. According to reaction (5) it will form AuI_2^- with excess I^- in iodide solution or regenerate AuI_4^- with surplus I_3^- (reaction 6), so AuI_2^- is still the predominant specie in aqueous solution[5].

REFERENCES

1. Cao, Y.; Peng, Y.; Cheng, D.; Chen, L.; Wang, M.; Shang, C.; Zheng, L.; Ma, D.; Liu, Z.-P.; He, L. Room-Temperature CO Oxidative Coupling for Oxamide Production over Interfacial Au/ZnO Catalysts. *ACS Catal.* **2023**, *13*, 735-743, doi:10.1021/acscatal.2c05358.
2. Wang, C.; Yang, M.; Flytzani-Stephanopoulos, M. Single gold atoms stabilized on nanoscale metal oxide supports are catalytic active centers for various reactions. *AIChE J.* **2015**, *62*, 429-439, doi:10.1002/aic.15134.
3. Liu, M.-H.; Chen, Y.-W.; Liu, X.; Kuo, J.-L.; Chu, M.-W.; Mou, C.-Y. Defect-Mediated Gold Substitution Doping in ZnO Mesocrystals and Catalysis in CO Oxidation. *ACS Catal.* **2015**, *6*, 115-122, doi:10.1021/acscatal.5b02093.
4. Mancuso, R.; Della Ca', N.; Veltri, L.; Ziccarelli, I.; Gabriele, B. PdI2-Based Catalysis for Carbonylation Reactions: A Personal Account. *Catalysts* **2019**, *9*, 610, doi:10.3390/catal9070610.
5. Liang, C.J.; Li, J.Y. Recovery of gold in iodine-iodide system – a review. *Sep. Sci. Technol.* **2019**, *54*, 1055-1066, doi:10.1080/01496395.2018.1523931.