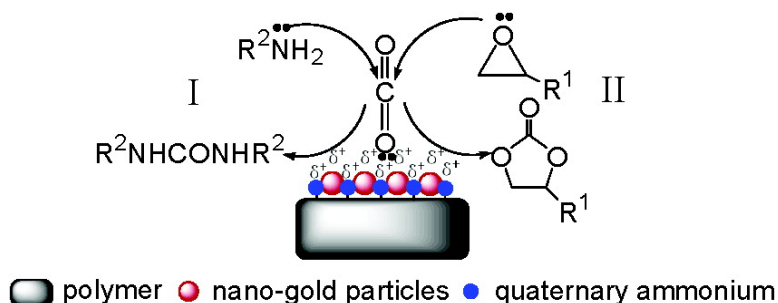## Communication

From CO Oxidation to CO Activation: An Unexpected Catalytic Activity of Polymer-Supported Nanogold

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From CO Oxidation to CO$_2$ Activation: An Unexpected Catalytic Activity of Polymer-Supported Nanogold

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Since the discovery that highly dispersed nanogold particles supported on metal oxides could be highly active catalysts for CO oxidation,[1] there has been an explosion in the interest shown in catalysis by gold;[2] for example, several researchers have made great efforts to expand the application of nanogold catalysts for some reactions, such as hydrogenation of unsaturated substrates,[3] epoxidation of propene using H$_2$ and O$_2$,[4] selective oxidation of alcohol,[5] removal of NO$_X$[6] and methane combustion,[7] etc. Until today, less effort, however, was made to investigate the possibility of nanogold being used as a catalyst for CO$_2$ activation, which would exploit a safe and green carbonyl source, reduce the release of green house gas, and benefit the recycling of carbon when its use is linked with other processes that emit CO$_2$.

With our continuous effort to expand the application of gold catalysis[8] and carbon dioxide activation,[9] we report our new findings that the nanogold could be a highly effective catalyst for cyclization of epoxides (Scheme 1) or carbonylation of aliphatic amines (Scheme 2) with carbon dioxide to yield cyclic carbonate[10] and disubstituted ureas,[9a,11] respectively. Polymer was used as the support to immobilize the nanogold catalysts because the polymer-immobilized catalysts were closer to homogeneous catalysts in chemical character and were attractive for technological applications.[12]

The basic properties of polymer-supported nanogold catalysts are given in Table S1 (Supporting Information). The cyclization reaction of epoxide and carbon dioxide can be conducted with an unprecedented high turn over frequencies (TOF), ca. >50 000 mol/mol/h (Table 1, entry 1), which is significantly superior to those obtained by a classical acid−basic catalyst system (~20−5000 mol/mol/h).[10] All of the selectivities for the desired product nearly reached ~100%, so the yield could be used to indicate the catalytic performances. It is worth noting that catalyst with 0.05 wt % gold loading exhibited the highest yield (71.2%), and lower yields were obtained over catalysts with higher gold loadings due to the formation of larger gold particles (entries 2−5). For 0.05 wt % Au/Poly2, poor results were obtained (entry 6), indicating that the properties of the polymer support had great impact on the catalytic activity of nanogold, and the reason for such tremendous difference in the activities should be attributed to the different functional groups of polymers. The functional group in Poly1 was quaternary ammonium, which may stabilize the nanogold particles, while the functional group in Poly2 was sodium sulfonate, which could not. Poor results were obtained over catalysts Pd/Poly1 and Rh/Poly1 with 3.1 and 1.1% yields, respectively, although palladium and rhodium complexes were usually regarded as more effective catalysts in comparison with gold complexes for carbonylation reactions. Therefore, these gold catalysts had exclusive catalytic activity for carbonylation of epoxides with carbon dioxide, that is, activation of carbon dioxide. To achieve higher yield, longer reaction time (10 h) was adopted over catalyst 0.05 wt % Au/Poly1, and 89.5% yield was obtained (entry 7). The result of catalyst 0.05

Scheme 1. Formation of Carbamate from Amines and Carbon Dioxide

R^1=CH$_3$-, (CH$_3$)$_2$CHOCH$_2$-, PhOCH$_2$- and ClCH$_2$-.
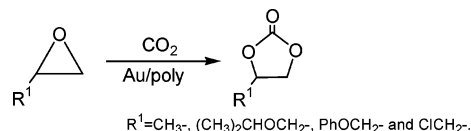
Scheme 2. Cyclization of Epoxides with CO$_2$ over Nanogold Catalysts

$$R^2NH_2 \xrightarrow[\text{Au/poly}]{CO_2} R^2NHCONHR^2$$

R^2=benzyl; cyclohexyl.
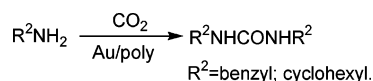
Table 1. Cyclization Reactions of Epoxypropane with CO$_2$ over Au/Poly[a]

entry	catalyst	GC yields (%)	TOF[b]
1	Poly1	trace	
2	0.01 wt % Au/Poly1	53	57900
3	0.05 wt % Au/Poly1	71.2	15400
4	0.1 wt % Au/Poly1	44.2	4800
5	0.5 wt % Au/Poly1	38.3	820
6	0.05 wt % Au/Poly2	12.9	2800
7[c]	0.05 wt % Au/Poly1	89.5	9700
8[d]	0.05 wt % Au/Poly1	66.4	7100

[a] Reaction conditions: 90 mL autoclave, 0.2 g of catalyst, 4 mL of epoxides, 30 atm CO$_2$, 150 °C, 5 h; the yield was obtained with an out-standard method. [b] The mol of epoxides converted per mol gold per hour. [c] Reacted for 10 h. [d] This catalyst was reused at the fifth time.

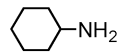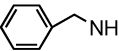**Table 2.** Cyclization Reactions of Epoxides with CO$_2$ over 0.05 wt % Au/Poly1[a]

Entry	Epoxides	GC Yields (%)	TOF
1		90	11600
2		93.2	10400
3[b]		93.7	6300

[a] Same reaction conditions as Table 1. [b] Reacted for 15 h.

wt % Au/Poly1, reused at the fifth time, indicated that the reusability of the catalyst system was possible, although relatively lower yield (66.4%) was given (entry 8), which should be attributed to the loss of gold species during reaction (only 0.03 wt % gold loading maintained after reused five times). 2,3-Epoxypropyl phenyl ether, 2,3-epoxypropyl isopropyl ether, and epichlorohydrin were further tested, and satisfactory results could also be achieved with relatively longer reaction time for epichlorohydrin, which may be attributed to the presence of electro attractive chloride methyl (Table 2, 1−3).

The polymer-immobilized nanogold could also be an effective catalyst for carbonylation of amines with carbon dioxide to yield

Table 3. Carbonylation of Amines with CO_2 over 0.05 wt % Au/Poly1[a]

Entry	Amines	Yields (isolated,%)	TOFP[b]
1	⟨cyclohexyl⟩—NH₂	85	2900
2	⟨benzyl⟩—NH₂	83	3000

[a] Reaction conditions: 90 mL autoclave, 0.2 g of catalyst (0.05 wt % Au/Poly1), 4 mL of amines, 1 mL of water, 50 atm CO_2, 180 °C, 20 h. [b] Turn over frequencies for products, mol product per mol gold per hour.

Scheme 3. Carbonylation of Amines with CO_2 over Nanogold Catalysts

$$2R^2NH_2 + CO_2 \xrightarrow{\text{Fast}} [R^2N(H)CO_2][R^2NH_3]$$
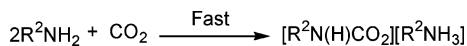
corresponding disubstituted ureas (Table 3). It can be seen that the isolated yields of dicyclohexyl urea and dibenzyl urea were 85 and 83%. Here, we use TOFP (turn over frequency for product) in instead of the TOF concept because the alkylamines could react with carbon dioxide to yield the corresponding carbamate under any conditions (Scheme 3), and TOF, therefore, could not denote the difference of catalytic activity of different catalysts. The TOFP numbers of 0.05 wt % Au/Poly1 catalyst in the carbonylation of amines, therefore, were 2900 and 3000 mol/mol/h, respectively, which were much better than that of previously reported homogeneous catalysts (10−20 mol/mol/h).[9a] These results suggested that the activation of carbon dioxide over polymer-supported nanogold catalysts could be universal.

For 0.05 wt % Au/Poly1, XPS analysis showed that the gold content on the surface of the polymer was 8.7 wt % and the chemical state of gold species was partially cationic (BE = 84.3 eV) (Figures S1,2). These results indicated that the nanogold particles were assembled on the surface of the polymer support, which ensured the high catalytic activity with lower gold content, and some interactions occurred between the nanogold particles and the cationic terminal group of the polymer. Further TEM characterization (Figure 1) indicated the formation of nanogold particles, and the average particle sizes of the nanogold were ∼3, ∼6, ∼10, and ∼12 nm (Figures S3−5) for 0.01 wt % Au/Poly1, 0.05 wt % Au/Poly1, 0.1 wt % Au/Poly1, and 0.5 wt % Au/Poly1. Therefore, the catalytic activity of the polymer-supported nanogold catalysts was regulated by the particle size of nanogold particle, that is, higher catalytic activity exhibited over a smaller nanogold particle. XRD characterization confirmed the formation of crystal gold species when the gold loadings were high enough (Figure S6).

As to the reaction mechanism, it is still not clear at this stage, but the activation of carbon dioxide at the nanogold particle should be the key step, and the synergism between nanogold species and the peculiar microenvironment of the polymer surface should be indispensable (Figure 2), which may be completely different from previous reported processes for carbon dioxide activation with the acid−base catalysts.[9a,10]

In conclusion, we have shown that polymer-immobilized nanogold catalysts had unprecedented catalytic activity for activation of carbon dioxide, with TOF > 50 000 mol/mol/h for the synthesis of cyclic carbonate and TOFP ≈ 3000 mol/mol/h for the synthesis of disubstituted ureas. The synergism between the nanogold species and the peculiar microenvironment of the polymer surface resulted in the exclusive catalytic activity for these two kinds of reactions. The particle size of the nanogold, other than gold loading, had much stronger impact on the catalytic performance. Further investigation is now underway.
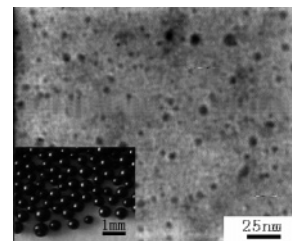
Figure 1. Picture and HRTEM image of 0.05 wt % Au/Poly1.

□ polymer ○ nano-gold particles ● quaternary ammonium
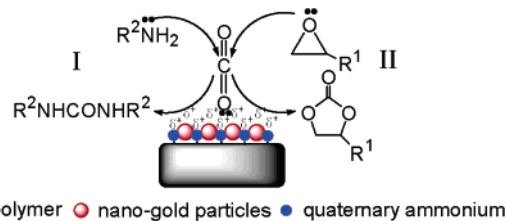
Figure 2. Possible mechanisms for (I) disubstituted urea synthesis and (II) cyclization reactions of epoxides.

Supporting Information Available: Details for the preparation of polymer-supported nanogold catalysts, XPS, TEM, and XRD characterizations of polymer-supported nanogold catalysts, and complete ref 2b. This material is available free of charge via the Internet at http://pubs.acs.org.

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