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RESEARCH NOTE

Polymer-Immobilized Gold Catalysts for the Efficient and Clean Syntheses of Carbamates and Symmetric Ureas by Oxidative Carbonylation of Aniline and Its Derivatives[1]

Feng Shi and Youquan Deng[2]

Centre for Green Chemistry and Catalysis, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, 730000, People's Republic of China

A series of highly efficient polymer-immobilized gold catalysts were prepared for the oxidative carbonylation of aniline and its derivatives to obtain carbamates and symmetric ureas in a clean, simple, solvent-free, and obtainable product-ready way. TEM showed that the average gold particle size of fresh catalyst was less than 10 nm. © 2002 Elsevier Science (USA)

Gold, a less expensive and environmentally benign noble metal in comparison with Pd, Pt, and Rh, has been receiving increased attention as a novel catalyst material. Numerous reactions catalyzed with either supported gold (1–5) or homogeneous gold complexes (6–11) were reported as having excellent performance. Recently, homogeneous Au catalysts used for the syntheses of carbamates and diformamide by carbonylation of amines have also been reported (12, 13). The former are important intermediates for the nonphosgene synthesis of isocyanates and have now been synthesized either by oxidative carbonylation of amines or by reductive carbonylation of nitro compounds (14–17).

With our continuing efforts to apply Au as a novel catalyst material and to search for "greener" or clean technologies for chemical production, polymers (18, 19), as a new kind of catalyst support, were employed to immobilize Au, and oxidative carbonylation of aniline and its derivatives for syntheses of corresponding carbamates and symmetric ureas was performed in this work (Scheme 1).

In comparison with the homogeneous Au catalysts already mentioned, the following advantages were found: (1) catalyst efficiency is greatly enhanced; (2) the catalysts are reusable; the catalysts are easily separable from the resulting product, (4) the system is simple; and (5) there is no need for any organic solvent and a product-ready pure solid is obtained for urea synthesis.

Several polymer-immobilized Au catalysts (or Pd catalysts for the purpose of comparison) were prepared as follows. Au/poly**1** consisted of dried polymer pellets (ca. $\phi = 0.5$ mm, Ionexchanger IV, Merck) without any pretreatment which were impregnated with 0.004 M aqueous solution of $HAuCl_4 \cdot 4H_2O$ and then dried at 60°C for 3 h. Au/poly**2** consisted of dried polymer which was pretreated with NaOH, and then the same preparation procedure as for Au/poly**1** was followed. Au/poly**3** was prepared using the same procedure as for Au/poly**2** except that a 0.004 M solution of $HAuCl_4 \cdot 4H_2O +$ acetone was used. The catalyst pellets could be dried more easily at room temperature using acetone as solvent. Au/poly**4** and **5** were prepared using the same preparation procedure as for Au/poly**3** except that 0.002 M and 0.001 M solutions of $HAuCl_4 \cdot 4H_2O +$ acetone were used respectively. Au-K/poly was prepared using the same procedure as Au/poly**3** but KOH was used instead of NaOH. Pd/poly**1** and **2** were prepared using the same procedure as for Au/poly**2**, but $HAuCl_4 \cdot 4H_2O$ was replaced with H_2PdCl_4 or $Pd(phen)_2Cl_2$ (phen: 1,10-phenanthroline monohydrate), respectively. The basic properties of polymer-immobilized Au catalysts are summarized in Table 1. Only small BET surface areas (Micromeritics ASAP 2010 instrument) for the polymer-immobilized Au catalysts were found. Catalysts with different Au loadings (3520 ICP AES) were obtained, and high Na contents in Au/poly**2**–**5**, were observed. XPS analysis (VG ESCALAB 210) was conducted over the polymer-immobilized Au catalysts. The results showed Au^{+1} in Au/poly**1** but Au^0 in Au/poly**2**–**5** and Au-K/poly. No Au^{+3} species on the polymer could be observed in these catalysts, indicating that redution of Au^{+3} species occurred during catalyst preparation. TEM (JEOL JEM-1200EX) images of Au/poly**3** confirmed that the average size of the Au particles was less than 10 nm (Fig. 1).

As shown in Table 2 (entry 1), almost no conversion could be observed over Au/poly**1**. High conversion with

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[2] To whom correspondence should be addressed. Fax: 86-931-8277088. E-mail: ydeng@ns.lzb.ac.cn.

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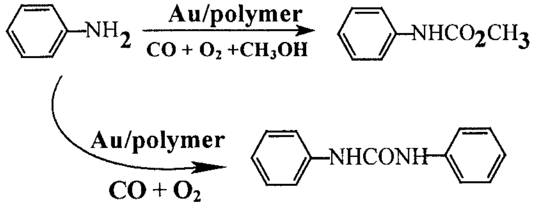


SCHEME 1

excellent selectivity for desired carbamate, however, was obtained over Au/poly**2**, and the best catalytic performance was achieved over Au/poly**3**, where the corresponding TOF number reached 530, which is much higher than that of either homogeneous organometallic gold catalyst (13) or the palladium catalyst system reported in previous papers (8, 11). In comparision with Au/poly**2**, better catalyst activity was unexpectedly obtained over Au/poly**3** when acetone as a solvent was used during preparation, indicating that these catalysts are very sensitive to the preparation procedure, although the detailed reason is not clear at this stage. Au-K/poly catalyst (entry 4), in which potassium hydroxide instead of sodium hydroxide was used in the catalyst preparation, was tested in the synthesis of carbamate, and it can be seen that poor catalyst activity was observed. These results suggest that sodium in or on the polymer played an important role in keeping the Au species in a highly active state and that the catalyst acitivity is very sensitive to modification of the polymer since almost no or lower activities can be observed over Au/poly**1** without sodium and Au-K/poly containing potassium. In addition to ease of separation, it is noteworthy that the catalyst activity and selectivity were nearly stable after the catalyst was repeatedly used five times (entry 5), and 77% of conversion and 98% of selectivity were maintained even after it was repeatedly used 12 times (entry 6), showing that recycling of the catalyst is possible. Although not shown here, XRD (Siemens D/max-RB) analysis of a Au/poly**3** sample that was reused several times indicated the appearance of metal Au peaks not present in fresh Au/poly**3** and that the calculated sizes of Au crystallite in the used Au/poly**3** were ca. 12 nm. This may imply that the particle dimension of Au was not very stable but grows slightly, and also, this may be the main reason for the partial deactivation of the catalyst.

TABLE 1

The Basic Properties of Polymer Immobilized Au Catalysts

Catalyst	BET (m^2/g)	Au (wt%)	Na (K) (wt%)	Au4$f_{7/2}$ (eV)
Pure Polymer	2.82	—	—	—
Au/poly**1**	1.50	0.9	0	85.6
Au/poly**2**	1.46	1.0	7.5	84.4
Au/poly**3**	1.69	1.0	7.4	84.2
Au/poly**3**[a]	1.43	1.0	7.6	83.9
Au-K/poly	1.71	1.02	11.8	83.9
Au/poly**4**	1.48	0.51	7.2	84.1
Au/poly**5**	1.51	0.19	7.6	84.3

[a] Au/poly**3** used for synthesis of carbamate 12 times.

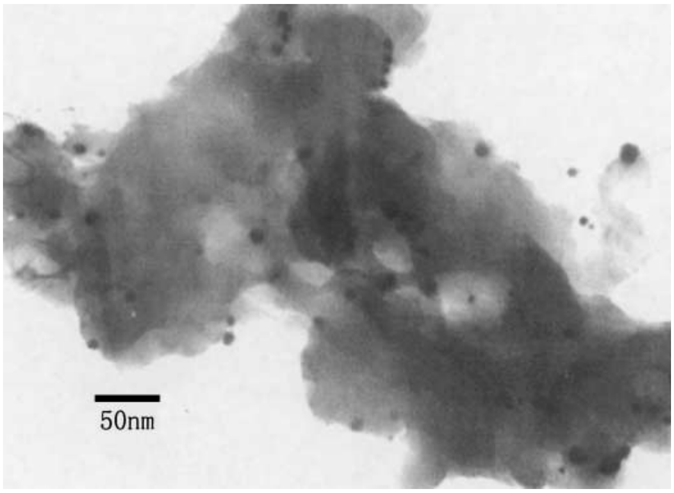


FIG. 1. TEM picture of Au/poly**3** catalyst.

The oxidative carbonylation of aniline over the polymer-immobilized Au catalysts with even lower Au loading (ca. 0.5 wt% for Au/poly**4** and 0.2 wt% for Au/poly**5**) was also tested. Althogh the conversions were reduced to 71 and 63% (entries 7 and 8), excellent selectivities were maintained and higher TOF numbers were achieved for Au/poly**4** (513) and Au/poly**5** (553).

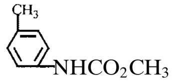
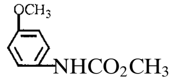
For the purpose of comparison, Pd catalysts (i.e., Pd/poly**1** and Pd/poly**2** in this work), the most efficient catalysts for carbonylation reactions, were also examined (entries 9 and 10), but only 1.8–2% conversions were obtained, although Pd/poly**1** and Pd/poly**2** were also treated with sodium hydroxide during preparation as was Au/poly**2** or **3**.

When *p*-amino toluene, 4-methoxybenzamine, and *m*-nitroaniline over the Au/poly**3** catalyst were subjected to carbonylation (entries 11–13) the catalytic activities decreased in turn. The big difference in the conversions is mainly attributed to the big difference in the electronic properties of the aniline substituents.

It is worth noting that a new, clean, and highly efficient method for the synthesis of symmetric diphenyl ureas can be established when methanol is removed from this carbonylation reaction, forming a crystalline product. The results are listed in Table 3 (entry 1). The corresponding TOF could reach 1475, which is much higher than that reported previously (20). The reason that Au/poly**4** was chosen for the synthesis of ureas is that Au/poly**4** may be a more promising catalyst for industrial application because of its lower Au loading in comparison with Au/poly**3** and its high enough activity in comparison with Au/poly **5**. In addition to ease of prduct recovery, high catalytic performance was

TABLE 2

The Results of Oxidative Carbonylation of Amines to Cabamater

Entry	Substrate	Catalyst	Con. (%)	Sel. (%)	TOF	Product
1	aniline	Au/poly**1**	<1	>99	~5	
2	aniline	Au/poly**2**	83	>99	459	
3	aniline	Au/poly**3**	95	>99	530	
4	aniline	Au-K/poly	18.3	>98	102	
5[a]	aniline	Au/poly**3**	90	>99	510	
6[b]	aniline	Au/poly**3**	77	>98	510	
7[c]	aniline	Au/poly**4**	71	>98	513	
8[d]	aniline	Au/poly**5**	63	>99	553	
9	aniline	Pd/poly**1**	1.8	>99	3.1	
10	aniline	Pd/poly**2**	2	>99	22.6	
11	*p*-amino toluene	Au/poly**3**	73	>99	330	
12	*p*-methoxybenzen-amine	Au/poly**3**	60	>99	110	
13	*m*-nitroaniline	Au/poly**3**	25	>99	40	

[a] Used 5 times.
[b] Used 12 times.
[c] Reacted for 1.5 h.
[d] Reacted for 3 h.

still maintained after the catalyst was repeatdly used three times (entry 2), indicating that recycling of the catalyst for urea formation is also possible. With the same reaction conditions and catalyst, aniline derivatives as substrates were also tested (entries 3–5) and high selectivity and TOF numbers were still maintained.

Almost the same reaction tendencies as aniline carbonylation to carbamate were observed when the contributions

TABLE 3

Results of the Oxidative Carbonylation of Amines to Synthesize Ureas

Entry	Subs.	Catalyst	Con. (%)	Sel. (%)	TOF	Products
1	aniline	Au/poly**4**	70	99	1475	
2[a]	aniline	Au/poly**4**	71	99	1493	
3	*p*-amino toluene	Au/poly**4**	43	99	780	
4	4-methoxybenzamine	Au/poly**4**	13	99	640	
5	*m*-nitroanilne	Au/poly**4**	<1	—	—	
6	aniline	poly[b]	–0	—	—	
7	aniline	Au/poly**1**	<1	—	—	
8	aniline	Pd/poly**2**	<1	—	—	

[a] Catalyst Au/poly**4** used for the third time.
[b] Polymer treated with aqueous sodium hydroxide only.

of polymer, polymer-immobilized Au (entries 6 and 7), and the polymer-immobilized Pd (entry 8) to aniline transformation to urea were examined.

Several other polymers, though not shown here, were also tested to immobilize the Au. Lower or even no catalytic activity for the carbonylation was observed, indicating that the polymer itself has a strong impact on the catalytic activity.

Based on the analysis of the results summarized in Tables 1–3, it can be conjectured that (1) the carbonylation of aniline and its derivatives to carbamates or ureas followed similar reaction mechanisms; (2) some kind of synergism among the sodium, gold, and polymer is the key factor for such high activity toward the carbonylation of aniline to synthesize the carbamate or ureas; and (3) the reason for the partial deactivation of catalyst after repeated operation was related to the size of the gold particles because no loss of gold was detected after it was repeatedly used for synthesis of carbamate 12 times.

In conclusion, reusable polymer-immobilized Au catalysts for the syntheses of carbamates and symmetric ureas by oxidative carbonylation of aniline and its derivatives have been developed for the first time with a clean, simple, solvent-free, and obtainable product-ready way. The synergism, established among Au, Na, and polymer, is the key factor for such high activity and selectivity, although their detailed relationship is not clear at this stage, and the catalyst preparation can be further optimized. Also, it has been shown for the first time that the performance of a properly prepared Au catalyst could be better than that of Pd catalysts, which have long been believed to be the best catalysts for carbonylation reactions.

Experimental

The oxidative carbonylation of amines was performed in a 90 cm^3 autoclave with a glass tube and magnetic stirring inside. Catalyst (0.2 g), 0.5 g (0.5 ml) amine, 5 ml methanol (for carbamate synthesis), 3.0 g (3.0 ml) amine only (for urea synthesis), and 5.0 MPa mixed gases (CO of 99.99% purity at 4.0 MPa and O_2 of 99.99% purity at 1.0 MPa) were successively introduced into the reactor. The reaction was normally proceeded at 175°C for 1–3 h. Qualitative and quantitative analyses were conducted with a HP 6890/5793 GC-MS. When conversion and selectivity were high enough, nearly dry solid product mixed with the catalyst pellets could be obtained after reaction. The desired pure product and catalyst pellets could be easily separated by sieving with a 30 mesh sieve because the size of the catalyst pellets is much larger than that of the solid product.

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