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PAPER

CO_2 Activation and Fixation: Highly Efficient Syntheses of Hydroxy Carbamates over Au/Fe_2O_3

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This paper reports an effective route for the syntheses of hydroxy carbamates from the reaction of CO_2, epoxides and amines catalyzed by Au/Fe_2O_3 catalyst. Under the optimized reaction conditions, various hydroxy carbamates were successfully synthesized with 92-98% isolated yields. The catalyst could be reused for several runs without deactivation. A plausible reaction mechanism was proposed that the hydroxy carbamate was formed through ammonium carbamate intermediate and the catalyst mainly promoted the further nucleophilic addition between epoxide and ammonium carbamate.

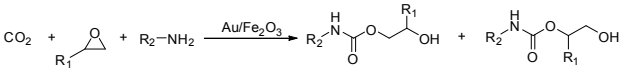
1. Introduction

The reduction, capture, or utilization of CO_2 discharge from industrial processes is one of the greatest scientific and technological challenges of the 21st century. Moreover, CO_2 is a nontoxic, abundant and economical C1 feed stock and transformation of CO_2 to other valuable chemicals has attracted significant interests. [1-13] Among them, catalytic hydrogenation of CO_2 to produce alternate fuels, such as HCOOH, CH_3OH, CH_4, etc, has been extensively studied. [9-13] However, this technique is severely restricted by the current hydrogen supply. In this regard, the direct usage of CO_2 as building block, *i.e.* carbonyl source, in chemical industry should be an ideal choice. [1] Until now, urea production should be the only way for large scale chemical fixation of CO_2. [14-15] Thus, there have been increasing interests in developing new routes for direct use CO_2 as carbonyl source.

Hydroxy carbamate and their derivatives are important industrial intermediates for pharmaceutical, organic synthesis, coatings and so on. [16-18] Generally, the hydroxy carbamates are mainly synthesized by the reaction of cyclic carbonates and amines over organic metal salts such as organic tin, zinc and lead, [19-20] however, the intrinsic problems that the use of poisonous tin or lead salts and the difficult recycle of catalyst limit their practical applications. Recently, the organocatalyst, such as thiourea and TBD, were reported as efficient metal-free catalyst for the reaction of cyclic carbonates and amines. [21-23] Moreover, the reaction of CO_2, epoxides and amines could be a good choice for the developmnt of an environmentally benign method for hydroxyl carbamates synthesis. [24-26] In the previous reports, the amine substrates are mainly focused on secondary aliphatic amines and the corresponding carbamates isolated yields are relative low. Additionally, such reactions are mainly catalyzed by metal complex homogenous catalysts. Thus, it would be highly desirable to explore an efficient heterogenous catalyst for the reaction of CO_2, epoxide and primary aliphatic or aromatic amines.

Since the discovery that highly dispersed Au nanoparticles supported on metal oxides could be highly active catalysts for CO oxidation, [27] Au nanocatalysts have aroused increasing interest in the chemistry community and various Au nanocatalysts have been developed for different chemical reactions including oxidation and hydrogenation, and have shown great promise in catalysis. [28-31] In particular, the supported Au nanoparticles have also been successfully applied in chemical conversion of CO_2. [32-33] The unique nature of Au nanoparticles may render the Au nanocatalysts to find more applications in CO_2 conversion.

As far as we know, there was no report for the reaction of CO_2, epoxides and amines (or the reaction of cyclic carbonates and amines, or the reaction of CO_2 and epoxides) catalyzed by Au/Fe_2O_3. Herein, we report the first work to use Au/Fe_2O_3 as highly effective and recoverable catalyst for hydroxyl carbamates syntheses from the reaction of CO_2, epoxides and amines, Scheme 1. Such a process could fulfill the optimum utilization of CO_2, which is of significance from a standpoint of green chemistry and sustainable development.



Scheme 1 The hydroxy carbamates syntheses from CO_2, epoxides and amines over Au/Fe_2O_3

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2. Experimental

2.1Hydroxy carbamates synthesis from CO_2, epoxides and amines

All the reactions were conducted in a 90 mL stainless steel autoclave with a glass tube inside equipped with magnetic stirring. In each reaction, CO_2 (1.0-2.0 MPa), epoxide (20-40 mmol), amine (10 mmol) and catalysts (20 mg) were charged successively into the autoclave. After being flushed with CO_2, it was heated up to 80-120^{o}C and reacted for 8 h. Then, the autoclave was cooled to room temperature and opened to air. The catalyst was separated by centrifugation and filtration. The products were qualitatively and quantitatively analyzed with GC-MS (Agilent 6890/5973), GC (Agilent 7890) equipped with a FID detector and ^{1}H NMR (Bruker AMX FT 400-MHz)

2.2 Catalysts preparation and characterization

A series of Au/Fe_2O_3 catalysts with different Au loadings (0.8-7.9 wt%) were prepared by co-precipitation method using $Fe(NO_3)_3{\cdot}9H_2O$ and $HAuCl_4{\cdot}4H_2O$ as starting materials and Na_2CO_3 as precipitant. Dilute aqueous solutions of 0.62-4.25 mL $HAuCl_4{\cdot}4H_2O$ (0.1 g mL^{-1}) and 30 mL $Fe(NO_3)_3{\cdot}9H_2O$ (26 mmol) were mixed uniformly, then added drop-wise into 150 mL aqueous Na_2CO_3 solution (0.47 mol L^{-1}) with vigorous stirring at room temperature, and the pH of the finally resulted solution was controlled to 7-8. After 1 h stirring and 1 h aging, the resulted precipitate was centrifugated (10000 rpm for 15 min), and washed with 2L distilled water under ultrasonic condition. Then, the precursors were calcined at 300 ^{o}C for 5 h in air. The calcined catalysts were denoted as n wt% Au/Fe_2O_3, and the n was the Au loadings. The catalysts Fe_2O_3, Cu/Fe_2O_3, Co/Fe_2O_3, Pd/Fe_2O_3, Pt/Fe_2O_3 and Ru/Fe_2O_3 were prepared with the same procedures.

The BET surface areas, pore volumes and average pore diameters of catalysts were obtained with physisorption of N_2 using a Micromeritics ASAP 2010.

High-resolution transmission electron microscope (HR-TEM) analysis was carried out on a JEM 2010 equipped with an energy dispersive X-ray spectrometer (EDXS) and operating at 200 KeV. The catalysts were suspended in ethanol with an ultrasonic dispersion for 10-15 min and then the resulted solution was dropped on a carbon film of copper grid.

X-ray photoelectron spectroscopy (XPS) analysis were measured using a K-Alpha-surface analysis instrument with Al Kαradiation (1361 eV) and all the binding energies were referenced to the adventitious C 1s at 285 eV.

X-ray diffraction (XRD) measurements were carried out on a Siemens D/max-RB powder X-ray diffractometer. Diffraction patterns were recorded with Cu Kαradiation (40 mA, 40 kV) over the 2θ range 10-80°.

Temperature-programmed reduction (TPR) of H_2 was carried out on TPR/TPD flow system equipped with an MS detector (DM300, AMETEK, USA). TPR analysis was conducted with 10% H_2/Ar (50 mL min^{-1}). In a typical experiment, the solid sample (120 mg with particle size 160-200μm) was pretreated at 300 ^{o}C for 1 h under airflow (50 mL min^{-1}) and cooled to room temperature under argon gas flow (50 mL min^{-1}). The profile was recorded at a heating rate of 10 ^{o}C min^{-1} from room temperature to 300-700 ^{o}C and maintained at this temperature until the MS signal of H_2 returned to the baseline.

Temperature-programmed desorption (TPD) of CO_2 and NH_3 was carried out on a TPD flow system equipped with an MS detector (DM300, AMETEK, USA). In a typical experiment, the solid sample (100 mg with particle size 160-200μm) was pretreated at 300 ^{o}C for 1 h under nitrogen flow (50 mL min^{-1}) and then cooled to room temperature. The sample was subsequently exposed to CO_2 (NH_3) stream (50 mL min^{-1}) at room temperature for 1 h and flushed again with nitrogen for 1 h to remove any physico-adsorbed CO_2 (NH_3). The desorption profile was recorded at a heating rate of 10^{o}C min^{-1} from room temperature to 300 ^{o}C and maintained at this temperature until the MS signal of CO_2 (NH_3) returned to the baseline.

3. Results and discussions

3.1 Hydroxy carbamates syntheses from CO_2, epoxides and amines

A series of catalysts were screened for the Hydroxy isopropyl phenylcarbamates (HPC) synthesis from CO_2, propylene oxide and aniline, Table 1. In the blank test or in the presence of pure Fe_2O_3 (entry 1-2), the conversion of aniline is trace amount, suggested that the efficient catalyst was essential for such a reaction proceeding successfully. A series of M/Fe_2O_3 (M = Cu, Co, Pd, Pt and Ru) catalysts was further tested and showed poor to moderate catalytic activity for such process and 22-52% aniline conversions were achieved, entries 3-7. For the Au/Fe_2O_3, the aniline conversions were greatly improved when the Au component was introduced and increased with increasing the Au loadings, entries 8-10. For example, 98% of aniline conversion and 99% of HPC selectivity could be achieved over 4.9wt% Au/Fe_2O_3.

For the target product HPC, the major one defined as **1** by GC-MS corresponds to the nucleophilic ring opening of the propylene oxide at the less substitute site and was preferentially formed with high selectivity in all cases listed in Table 1.[34] Meanwhile, the product **2** was also observed, which was formed duo to the nucleophilic ring opening of the propylene oxide at methyl substitute site. Additionally, the main byproducts were defined as amino alcohol (such as **3**, **4**, **5** and **6**) by GC-MS, which derived from the ring-opened reaction of epoxides and amines.

Subsequently, the reaction conditions were optimized using 4.9wt% Au/Fe_2O_3 as catalyst. As is easily seen, the conversion of aniline was increased with increasing the reaction temperature and reached 98% at 100 ^{o}C (entries 9, 11-12), however, with further increasing the reaction temperature up to 120 °C resulted in a decrease of the HPC selectivity (entry 13). Additionally, both the aniline conversion and HPC selectivity were increased with increasing CO_2 pressure up to 2 MPa (entries 9, 14-15), but those were more sensitive to pressure up to 1.5 MPa, and the effect of pressure on the conversion and selectivity was much smaller at the higher pressure. This could be due to the fact that CO_2 is a reactant and the concentration and solubility of CO_2 in the reaction phase increased with increasing CO_2 pressure. When the

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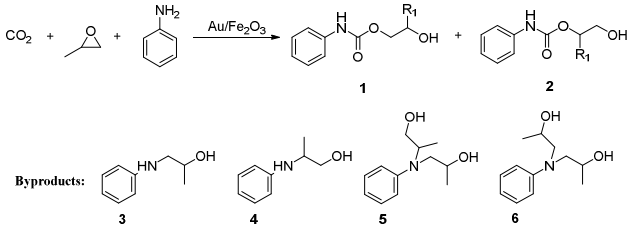
pressure is higher than 1.5 MPa, the concentration of CO_2 in the reaction phase is high enough, and therefore, the effect of pressure on the conversion and selectivity is very limited at the higher pressure.

Moreover, the catalyst was recycled through centrifugation and filtration, and washed with methanol and dried at 100 °C to remove the adsorbed organic materials. The catalyst recycling test showed that the aniline conversion of 96% was obtained even after five runs (entry 16), suggested that the catalyst could be reused without significantly loss in activity after the fifth runs.

Table 1. Hydroxy isopropyl phenylcarbamates (HPC) synthesis under varied catalysts and reaction conditions[a]



Entry	Catalyst	T (°C)	CO_2 pressure (MPa)	Aniline Con. /%	HPC Sel. /% (**1**:**2**)[b]
1	--	100	1.5	--	--
2	Fe_2O_3	100	1.5	<1	--
3	4.9wt%Cu/Fe_2O_3	100	1.5	25	68 (93:7)
4	5.0wt%Co/Fe_2O_3	100	1.5	27	94 (95:5)
5	5.1wt%Pd/Fe_2O_3	100	1.5	22	99 (94:6)
6	5.0wt%Pt/Fe_2O_3	100	1.5	43	88 (94:6)
7	5.1wt%Ru/Fe_2O_3	100	1.5	52	98 (95:5)
8	2.8wt%Au/Fe_2O_3	100	1.5	48	96 (95:5)
9	4.9wt%Au/Fe_2O_3	100	1.5	98	99 (95:5)
10	7.9wt%Au/Fe_2O_3	100	1.5	97	99 (95:5)
11	4.9wt%Au/Fe_2O_3	80	1.5	78	98 (94:6)
12	4.9wt%Au/Fe_2O_3	90	1.5	89	99 (95:5)
13	4.9wt%Au/Fe_2O_3	120	1.5	99	95 (95:5)
14	4.9wt%Au/Fe_2O_3	100	1	85	92 (94:6)
15	4.9wt%Au/Fe_2O_3	100	2	99	99 (95:5)
16[c]	Used 4.9wt%Au/Fe_2O_3	100	1.5	96	99 (95:5)

[a] Reaction conditions: 10 mmol aniline; 20 mmol propylene oxide; 20 mg catalyst; 1.0-2.0 MPa CO_2; 80-100 °C; 8 h. Conversions and selectivities were determined by gas chromatography.

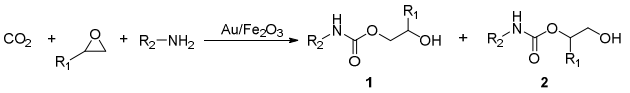
[b] Numbers in the bracket is the molar ratio of product **1** and **2**, and were determined by ^{1}H NMR.

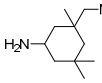
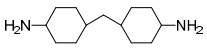
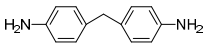
[c] Catalyst reused for five times.

In order to investigate the limitation and scope of the catalysts, reactions of CO_2 with various epoxides and amines for corresponding hydroxy carbamates were further carried out over 4.9wt% Au/Fe_2O_3, the results shown in Table 2.

Firstly, the impact of variation of the epoxides on the reaction to form the corresponding hyroxy carbamates was tested, entries 1-5. Excellent yields of the corresponding hydroxy carbamates were obtained with terminal epoxides (entries 1-4), while the disubstituted epoxide, cyclohexene oxide (entry 5), gave lower activity towards the production of the corresponding hydroxy carbamate, which might be due to the high hindrance of cyclohexene oxide. However, the selectivity of the HPC **1** for the styrene oxide (entry 4) was much lower than that of other epoxides, which might be ascribed to the conjugative effect derived from the benzene ring, which should favourably attack at the carbon atom at which phenyl substitute was connected to afford HPC **2**. [35]

Table 2. Scope an35d limitation of Au/Fe_2O_3 for catalytic syntheses various hydroxy carbamates[a]



Entry	Epoxide	Amine	T (°C)	HPC Yield/% (**1**:**2**)[b]
1			100	97
2			100	97 (94:6)
3			100	96 (62:38)
4			100	96 (28: 72)
5			100	38
6			100	96 (90:10)
7			100	96 (90:10)
8			100	95 (88:12)
9			100	92 (88:12)
10			80	98
11			80	94
12			80	96
13			80	98
14[c]			100	96
15[c]			100	95
16[c]			100	94
17[c]			100	96

[a] Reaction conditions: 10 mmol amine; 20-40 mmol epoxide; 20 mg 4.9wt% Au/Fe_2O_3; 1.5 MPa CO_2; 80-100 °C; 8 h.

[b] Isolated based on the charged amines. Numbers in the bracket is the molar ratio of product **1** and **2**, and were determined by ^{1}H NMR.

[c] molar ratio of propylene oxide and diamines = 4.

Then various monoamines with different structures were further investigated, entries 6-13. The results showed that the

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yields (92-98%) of the corresponding hydroxyl carbamates were achieved both for aliphatic amines and aromatic amines, however, the reaction temperature for the aliphatic amines were lower than the aromatic amines, suggested that the reaction of CO_2 and propylene oxide with aliphatic amines was easier than aromatic amines, which could be ascribed to the nucleophilicity difference in the two types of amines.

Finally, the hydroxyl dicarbamtes were also successfully synthesized in excellent yields (90-96%) from the reaction of CO_2, propylene oxide and diamines, such as 1, 6 - hexamethylenediamine, isophorondiamine, 4, 4 - methylenedicyclohexanamine and 4, 4′ - methylenedianiline, entries 14-17. In one word, the reaction of CO_2, epoxides and amines catalyzed by Au/Fe_2O_3 catalyst could be an efficient process for the syntheses of various hydroxy carbamates.

3.2 Results of catalysts characterization

The physical properties of the Au/Fe_2O_3 catalysts are summarized in Table 3. Clearly, the BET surface area of the Au/Fe_2O_3 gradually decreased when the Au component was introduced into the Fe_2O_3, and continuously decreased with increasing of the Au loadings to 2.8wt%, entries 1-3. However, with further increased the Au loadings, the BET surface area of 4.9wt% Au/Fe_2O_3 sharply increased to 163.6 m^2/g, and then changed slightly for 7.9wt% Au/Fe_2O_3 (entries 4-5). The variation of the BET surface area of those Au/Fe_2O_3 catalysts combined with their catalytic activities for the hydroxy carbamates syntheses from CO_2, propylene oxide and aniline suggested that the higher BET surface area of the catalysts might be more favourable for the CO_2 absorption and activation.

Table 3. Physicochemical properties of the catalysts

Entry	Catalyst	S_{BET} (m^2/g)	dp[a] (nm)	Vp[b] (cm^3/g)	Total basic Sites (μmol/g)
1	Fe_2O_3	135.2	11.0	0.40	49
2	0.8wt%Au/Fe_2O_3	131.6	12	0.38	44
3	2.8wt%Au/Fe_2O_3	126.5	12.2	0.35	36
4	4.9wt%Au/Fe_2O_3	163.6	12.4	0.51	29
5	7.9wt%Au/Fe_2O_3	162.7	12.6	0.53	26

[a] average pore size

[b] average pore volume

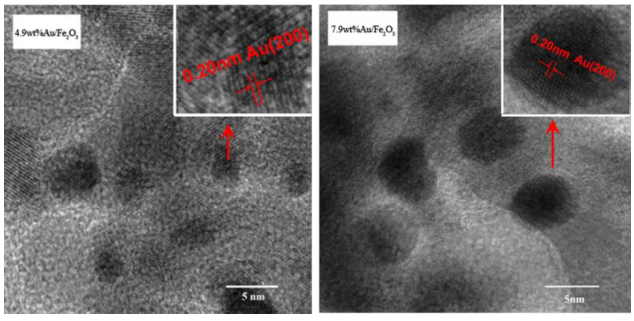

Fig. 1. HR-TEM images of 4.9wt% and 7.9wt% Au/Fe_2O_3, and local lattice of Au (200) plane.

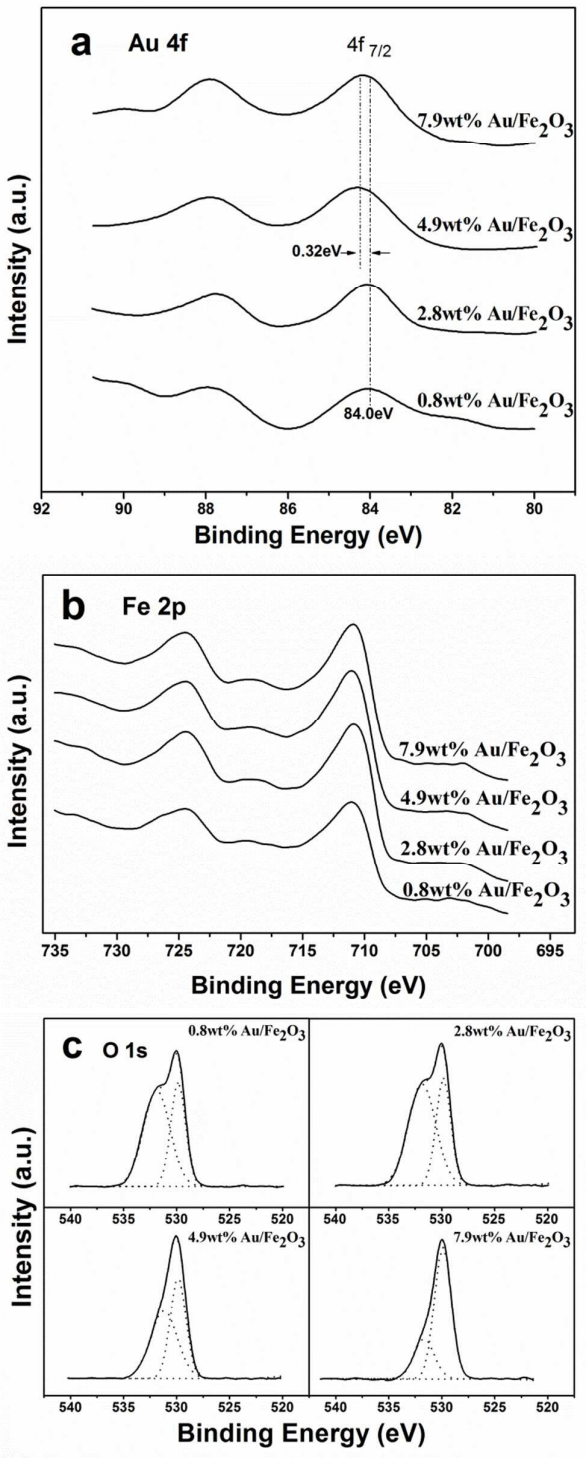

Fig. 2. XPS spectra of (a) Au 4f, (b) Fe 2p and (c) O 1s spectra of Au/Fe_2O_3 with different Au loadings.

The HR-TEM images of the Au/Fe_2O_3 are shown in Fig. 1. From the TEM images, it can be seen that the average size of Au nanoparticles was 3-5nm and the average particle sizes of the Au nanoparticles for 7.9wt% Au/Fe_2O_3 were larger than that for 4.9wt% Au/Fe_2O_3, indicated that the Au nanoparticles

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were agglomerated with increasing the Au loadings. Moreover, the Au nanoparticles were spherical and the Au (200) plane was observed in HR-TEM images.

The XPS spectra of Au/Fe_2O_3 with different Au loadings showed that the binding energies of Au $4f_{7/2}$ and Fe $2p_{3/2}$ were in the range of 84.0 and 710.7 eV, respectively, suggested that chemical states of Au and Fe species on the catalyst surface were mainly Au^0 and Fe^{3+}, Fig. 2 a and b. Moreover, a positive shift of 0.32eV for the binding energies of Au $4f_{7/2}$ was observed when the Au loadings reached to 4.9 wt% or higher, indicated that some extent of partially oxidized state $Au^{\delta+}$ species could be existed, which might be attributed to the interaction between the Au nanoparticles and the Fe_2O_3 support. [36-37] As shown in Fig. 1c, two O 1s peaks could be well resolved with their binding energy at 529.8 and 531.7 eV, which should be assigned to oxygen of oxide and hydroxyl groups, respectively. [38] Meanwhile, the relative ratio of oxygen of hydroxyl and oxide groups decreased gradually with increasing of Au loadings, suggested that the Au component was favorable for the transformation of $Fe(OH)_3$ to Fe_2O_3. Furthermore, the surface atom ratio of Au/Fe over 4.9 wt % Au/Fe_2O_3 was 0.011, which was much lower than that of the corresponding bulk composition (0.073), suggested that the Au species might be encapsulated with Fe_2O_3 and acted as a metal substrate to support Fe_2O_3, which leads to an increase of the BET surface area of 4.9wt% Au/Fe_2O_3.

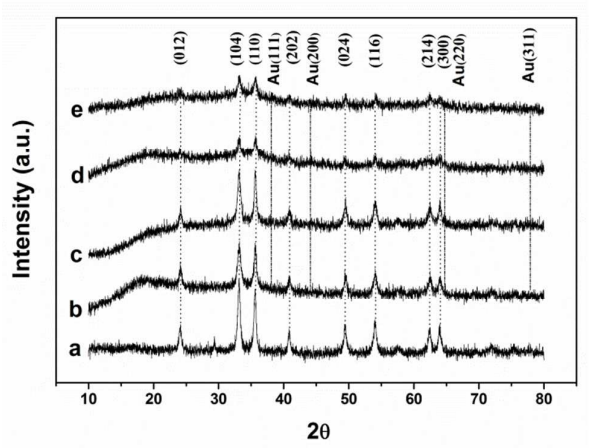

Fig. 3. XRD patterns of (a) Fe_2O_3, (b) 0.8wt% Au/Fe_2O_3, (c) 2.8wt% Au/Fe_2O_3, (d) 4.9wt% Au/Fe_2O_3 and (e) 7.9wt% Au/Fe_2O_3.

XRD patterns of pure Fe_2O_3 and Au/Fe_2O_3 catalysts with different Au loadings are shown in Fig. 3. The results showed that the characteristic diffraction peaks of Fe_2O_3 (2θ=33.2°, 35.7°, 54.1°) were observed for all samples and confirmed Fe_2O_3 formation. For 0.9-4.9wt% Au/Fe_2O_3 samples, the XRD results indicated that the Au species were highly dispersed on the Fe_2O_3 as the characteristic diffraction peaks of Au (2θ = 38.2°, 44.4°, 77.5°) cannot be discerned (Fig.3 b, c and d), however, the characteristic diffraction peaks of Au species were weakly exhibited for 7.9wt% Au/Fe_2O_3 (Fig.2 e), suggested that Au nanoparticles might be agglomerated with higher Au loadings, which is consistent with the results of HR-TEM. Moreover, the intensity of the Fe_2O_3 diffraction peaks were decreased with increasing of the Au loadings, especially for 4.9wt% and 7.9wt% Au/Fe_2O_3, probably duo to the strong interaction of Au nanoparticles and Fe_2O_3.

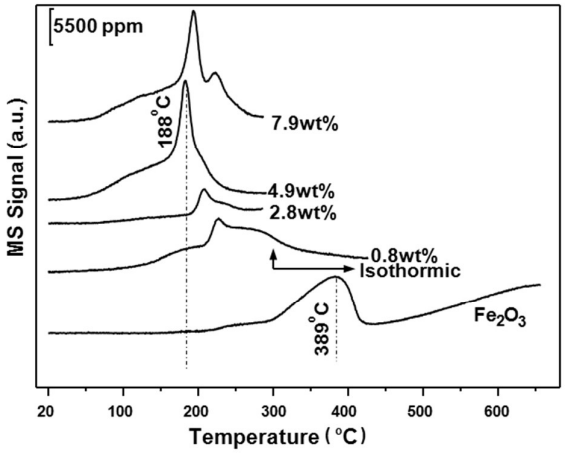

Fig. 4. TPR-H_2 profiles of (a) Fe_2O_3, (b) 0.8wt% Au/Fe_2O_3, (c) 2.8wt% Au/Fe_2O_3, (d) 4.9wt% Au/Fe_2O_3 and (e) 7.9wt% Au/Fe_2O_3.

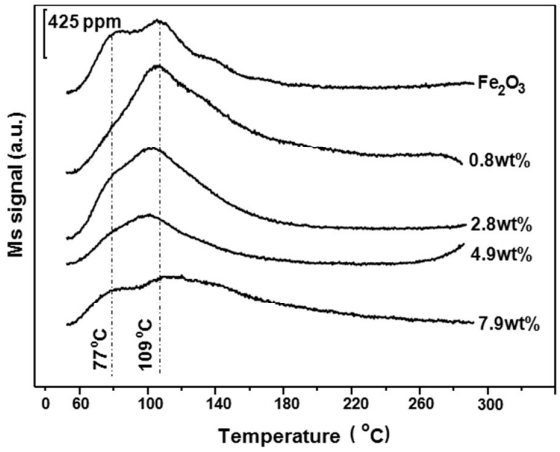

Fig. 5. TPD-CO_2 profiles of (a) Fe_2O_3, (b) 0.8 wt% Au/Fe_2O_3, (c) 2.8 wt% Au/Fe_2O_3, (d) 4.9 wt% Au/Fe_2O_3 and (e) 7.9 wt% Au/Fe_2O_3.

TPR-H_2 results of Fe_2O_3 and Au/Fe_2O_3 with different Au loadings are shown in Fig. 4. For Fe_2O_3, the reduction peak centered at 389 °C was observed, which could be assigned to the reduction of Fe_2O_3 to Fe_3O_4. [39] For Au/Fe_2O_3, the reduction peak of Fe_2O_3 to Fe_3O_4 sharply decreased when the Au component was introduced into the Fe_2O_3, and continuously decreased to 188 °C when the Au loadings reached to 4.9wt%. However, the reduction peak of Fe_2O_3 to Fe_3O_4 slightly increased when the Au loadings further increased to 7.9wt%, which might be duo to the agglomeration of Au nanoparticles resulted in the weakness of the interaction between Au nanoparticles and Fe_2O_3. The shift in the reduction temperature from 389 to 188 °C suggested that there existed a strong interaction between Au species and Fe_2O_3 support and

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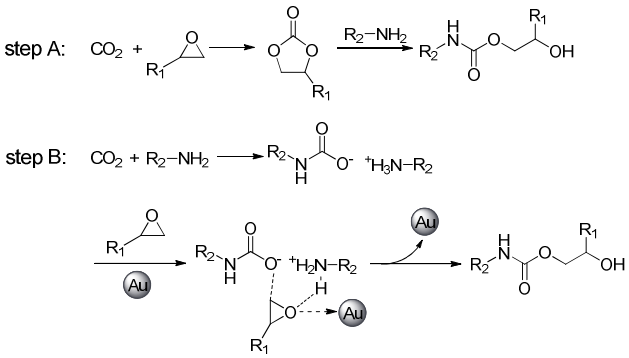
addition of Au component favoured the reduction of the iron oxide, which is consistent with the results of XPS and XRD.

The TPD-CO_2 profiles of Fe_2O_3 and Au/Fe_2O_3 with different Au loadings are shown in Fig. 5. Generally, broadened CO_2 desorption peaks in the temperature region of 60-160 ^oC were observed over all the tested samples, which were derived from the weak strength basic sites. From the quantitative results of TPD-CO_2, it can be seen that the total basic sites ranged from 48 to 29 μmol/g for pure Fe_2O_3 and 4.9wt% Au/Fe_2O_3, respectively, when Au component was added and Au content was increased. Though not shown here, similar TPD-NH_3 characterization was also carried out over the Au/Fe_2O_3 catalysts. Almost no NH_3 desorption peak on the TPD-NH_3 curves could be observed. These TPD-CO_2 (or NH_3) results showed that these catalysts have weak or almost no acidities, but possessed weak basicities.

3.3 Possible reaction mechanism

There may be two possible reaction pathways for the formation of hydroxy carbamates from CO_2, epoxides and amines. One is the hydroxy carbamates formed by the reaction of amines with cyclic carbonate, which could be produced from CO_2 and epoxides (Scheme 2, step A) and another is through the formation of ammonium carbamate intermediate and the hydroxy carbamate was obtained through nucleophilic addition between epoxide and ammonium carbamate (Scheme 2, step B).



Scheme 2 Possible reaction mechanism for the hydroxy carbamates syntheses from CO_2, epoxides and amines over Au/Fe_2O_3

Since the cyclic carbonate was not detected in the reaction mixture of amines, epoxides and CO_2, the formation of hydroxy carbamate by the reaction of amines with cyclic carbonate might be excluded. Therefore, the nucleophilic addition reaction between epoxide and ammonium carbamate is considered as reasonable reaction pathway. Moreover, the ammonium carbamate was readily obtained by the reaction of amines and CO_2, [7, 40] so the catalysts mainly catalyzed the nucleophilic addition process between epoxide and ammonium carbamate.

According to the results of the characterization and catalytic performance of 4.9wt% Au/Fe_2O_3 catalysts, the formed Au nanoparticles, especially the $Au^{\delta+}$ species, would induce activation of the epoxide ring through coordination with the oxygen atom in epoxides, illustrated in scheme 2 step B. Additionally, the relative larger BET surface area and weak basic site favoured the CO_2 absorption and conversion to the ammonium carbamate, which would be easily nucleophilic attacked on the neighbouring activated epoxides to produce the hydroxy carbamates.

Conclusions

In conclusion, an effective route for the syntheses of hydroxy carbamates from the reaction of CO_2, epoxides and amines over Au/Fe_2O_3 catalyst was developed. Under the optimized reaction conditions, several important hydorxy carbamates were successfully synthesized with 92-98% isolated yields. The Au/Fe_2O_3 catalyst could be reused for several runs without deactivation. The characterization results of the catalysts suggested that the formed Au nanoparticles, larger BET surface area and weak basic sites all favoured the CO_2 absorption and epoxides activation, and resulted in the highly catalytic activity of 4.9wt% Au/Fe_2O_3. A plausible reaction mechanism was also proposed that the hydroxy carbamate was formed through ammonium carbamate intermediate and the catalyst mainly promoted the further nucleophilic addition between epoxide and ammonium carbamate.

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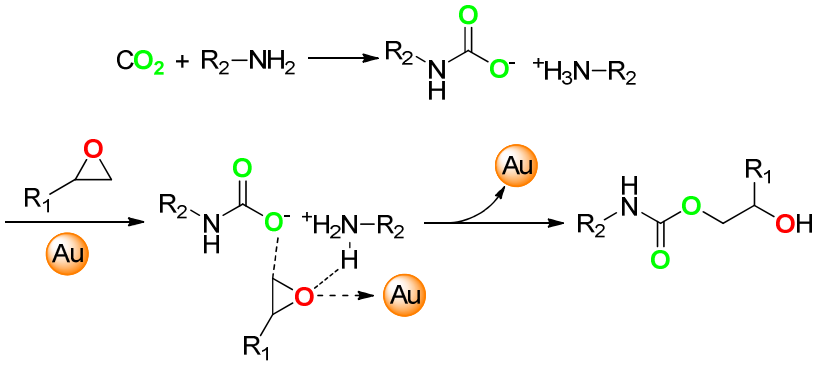
An effective route for hydroxyl carbamates syntheses from CO_2, epoxides and amines over Au/Fe_2O_3 was developed. Such a process could fulfill the optimum utilization of CO_2, which is of significance from a standpoint of green chemistry and sustainable development.



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