Supporting Information

CO2 Activation and Fixation: Highly Efficient Synthesis of Hydroxy Functionalized Carbamates over Au/Fe2O3

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**General procedures for the preparation of Fe$_2$O$_3$**

An aqueous solutions (30 mL) of Fe(NO$_3$)$_3$·9H$_2$O (26 mmol) was drop-wise added into 150 mL aqueous Na$_2$CO$_3$ 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 ºC for 5 h in air. The calcined catalysts were denoted as Fe$_2$O$_3$.

**General procedures for the preparation of Cu/Fe$_2$O$_3$**

The 4.9wt% Cu/Fe$_2$O$_3$ catalysts was prepared by co-precipitation method using Fe(NO$_3$)$_3$·9H$_2$O and Cu(NO$_3$)$_2$·3H$_2$O as starting materials and Na$_2$CO$_3$ as precipitant. Dilute aqueous solutions (30 mL) of Fe(NO$_3$)$_3$·9H$_2$O (26 mmol) and Cu(NO$_3$)$_2$·3H$_2$O (1.7 mmol) were mixed uniformly, then added drop-wise into 150 mL aqueous Na$_2$CO$_3$ 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 ºC for 5 h in air. The calcined catalysts were denoted as 4.9wt% Cu/Fe$_2$O$_3$.

**General procedures for the preparation of Co/Fe$_2$O$_3$**

The 5.0wt% Co/Fe$_2$O$_3$ catalysts was prepared by co-precipitation method using Fe(NO$_3$)$_3$·9H$_2$O and Co(NO$_3$)$_2$·6H$_2$O as starting materials and Na$_2$CO$_3$ as precipitant. Dilute aqueous solutions (30 mL) of Fe(NO$_3$)$_3$·9H$_2$O (26 mmol) and Co(NO$_3$)$_2$·6H$_2$O (1.9 mmol) were mixed uniformly, then added drop-wise into 150 mL aqueous Na$_2$CO$_3$ 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 ºC for 5 h in air. The calcined catalysts were denoted as 5.0wt% Co/Fe$_2$O$_3$.

**General procedures for the preparation of Pd/Fe$_2$O$_3$**

The 5.1wt% Pd/Fe$_2$O$_3$ catalysts was prepared by co-precipitation method using Fe(NO$_3$)$_3$·9H$_2$O and PdCl$_2$·2H$_2$O as starting materials and Na$_2$CO$_3$ as precipitant. Dilute aqueous solutions (30 mL) of Fe(NO$_3$)$_3$·9H$_2$O (26 mmol) and PdCl$_2$·2H$_2$O (1.05 mmol) were mixed uniformly, then added drop-wise into 150 mL aqueous Na$_2$CO$_3$ 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 °C for 5 h in air. The calcined catalysts were denoted as 5.1wt% Pd/Fe₂O₃.

**General procedures for the preparation of Pt/Fe₂O₃**

The 5.1wt% Pt/Fe₂O₃ catalysts was prepared by co-precipitation method using Fe(NO₃)₃·9H₂O and H₂PtCl₆·6H₂O as starting materials and Na₂CO₃ as precipitant. Dilute aqueous solutions (30 mL) of Fe(NO₃)₃·9H₂O (26 mmol) and H₂PtCl₆·6H₂O (0.56 mmol) were mixed uniformly, then added drop-wise into 150 mL aqueous Na₂CO₃ 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 °C for 5 h in air. The calcined catalysts were denoted as 5.0wt% Pt/Fe₂O₃.

**General procedures for the preparation of Ru/Fe₂O₃**

The 5.1wt% Pt/Fe₂O₃ catalysts was prepared by co-precipitation method using Fe(NO₃)₃·9H₂O and RuCl₃·3H₂O as starting materials and Na₂CO₃ as precipitant. Dilute aqueous solutions (30 mL) of Fe(NO₃)₃·9H₂O (26 mmol) and RuCl₃·3H₂O (1.1 mmol) were mixed uniformly, then added drop-wise into 150 mL aqueous Na₂CO₃ 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 °C for 5 h in air. The calcined catalysts were denoted as 5.1wt% Ru/Fe₂O₃.
After reaction and it was cooled to room temperature, the crude mixture was filtrated by methanol to recover catalyst, and then distilled at 50 °C for 5 h. Following the procedure above, 2-hydroxyethyl phenylcarbamate was obtained as a white liquid. \(^1\)H NMR (400MHz, CDCl\(_3\), ppm): \(\delta\) 7.09-7.14 (m, 2H), \(\delta\) 6.60-6.67 (m, 2H), \(\delta\) 6.54-6.57 (t, 1H), \(\delta\) 4.92 (s, 1H), \(\delta\) 4.54-4.57 (t, 2H), \(\delta\) 4.11-4.16 (t, 2H), \(\delta\) 2.47-2.49 (t, 1H).

![1](image1)

After reaction and it was cooled to room temperature, the crude mixture was filtrated by methanol to recover catalyst, and then distilled at 50 °C for 5 h. Following the procedure above, two isomer of hydroxypropyl phenylcarbamate were obtained as a pale yellow and viscid liquid. \(^1\)H NMR (400MHz, CDCl\(_3\), ppm): \(\delta\) 7.08-7.14 (m, 4H) (1, 2), \(\delta\) 6.61-6.67 (m, 4H) (1, 2), \(\delta\) 6.51-6.56 (m, 2H) (1, 2), \(\delta\) 5.12 (s, 1H) (2), \(\delta\) 4.92 (s, 1H) (1), \(\delta\) 3.65-4.10 (m, 6H) (1, 2), \(\delta\) 2.48-2.49 (t, 2H) (1, 2), \(\delta\) 1.24-1.25 (d, 3H) (1), \(\delta\) 1.16-1.17 (d, 3H) (2).

![2](image2)

After reaction and it was cooled to room temperature, the crude mixture was filtrated by methanol to recover catalyst, and then distilled at 50 °C for 5 h. Following the procedure above, two isomer of hydroxypropyl phenylcarbamate were obtained as a pale yellow and viscid liquid. \(^1\)H NMR (400MHz, CDCl\(_3\), ppm): \(\delta\) 7.08-7.14 (m, 4H) (1, 2), \(\delta\) 6.60-6.67 (m, 4H) (1, 2), \(\delta\) 6.51-6.56 (m, 2H) (1, 2), \(\delta\) 5.12 (s, 1H) (2), \(\delta\) 4.92 (s, 1H) (1), \(\delta\) 3.65-4.10 (m, 6H) (1, 2), \(\delta\) 2.23-2.25 (t, 1H) (1, 2).

![3](image3)

After reaction and it was cooled to room temperature, it was filtrated by methanol and then distilled. The crude mixture was purified by
column chromatograph (ethyl acetate / triethylamine / dichloromethane = 25/1/75, v/v/v; Silica Gel: 200-300 mesh; Rf = 0.207). Following the procedure above, two isomer of hydroxyphenylethyl phenylcarbamate were obtained as a white and viscid liquid. \(^1\)H NMR (400MHz, CDCl\(_3\), ppm): \(\delta\) 7.08-7.14 (m, 4H) (1, 2), \(\delta\) 6.60-6.66 (m, 14H) (1, 2), \(\delta\) 6.51-6.56 (s, 2H) (1, 2), \(\delta\) 5.92 (s, 1H) (2), \(\delta\) 5.71 (s, 1H) (1), \(\delta\) 5.33-5.38 (t, 1H) (2), \(\delta\) 4.92-5.03 (t, 1H) (1), \(\delta\) 4.64-4.73 (m, 1H) (1), \(\delta\) 4.41-4.49 (m, 1H) (1), \(\delta\) 4.11-4.20 (m, 1H) (2), \(\delta\) 3.94-4.08 (m, 1H) (2), \(\delta\) 2.24-2.25 (t, 2H) (1, 2).

After reaction and it was cooled to room temperature, the crude mixture was filtrated by methanol to recover catalyst, and then distilled at 50 °C for 5 h. Following the procedure above, two isomer of hydroxypropyl p-tolylcarbamate were obtained as a pale yellow and viscid liquid. \(^1\)H NMR (400MHz, CDCl\(_3\), ppm): \(\delta\) 7.09-7.14 (m, 4H) (1, 2), \(\delta\) 6.60-6.66 (m, 4H) (1, 2), \(\delta\) 5.92 (s, 1H) (2), \(\delta\) 5.71 (s, 1H) (1), \(\delta\) 5.33-5.38 (t, 1H) (2), \(\delta\) 4.92-5.03 (t, 1H) (1), \(\delta\) 3.64-4.01 (m, 6H) (1, 2), \(\delta\) 2.59 (s, 6H) (1, 2), \(\delta\) 2.23-2.25 (d, 2H) (1, 2), \(\delta\) 1.44-1.46 (d, 3H) (2), \(\delta\) 1.35-1.37 (d, 3H) (1).

After reaction and it was cooled to room temperature, the crude mixture was filtrated by methanol to recover catalyst, and then distilled at 50 °C for 5 h. Following the procedure above, two isomer of hydroxypropyl o-tolylcarbamate were obtained as a pale yellow and viscid liquid. \(^1\)H NMR (400MHz, CDCl\(_3\), ppm): \(\delta\) 7.09-7.10 (d, 2H) (1, 2), \(\delta\) 6.60-6.67 (m, 4H) (1, 2), \(\delta\) 6.34-6.36 (m, 2H) (1, 2), \(\delta\) 5.02 (s, 1H) (2), \(\delta\) 4.82 (s, 1H) (1), \(\delta\) 3.64-4.01 (m, 6H) (1, 2), \(\delta\) 2.55 (s, 6H) (1, 2), \(\delta\) 2.23-2.25 (d, 2H) (1, 2), \(\delta\) 1.44-1.45 (d, 3H) (2), \(\delta\) 1.36-1.37 (d, 3H) (1).
distilled at 50 °C for 5 h. Following the procedure above, two isomer of hydroxypropyl benzylcarbamate were obtained as a white and viscid liquid. \(^1\)H NMR (400MHz, CDCl\(_3\), ppm): \(\delta\) 7.09-7.14 (m, 4H) (1, 2), \(\delta\) 6.60-6.67 (m, 4H) (1, 2), \(\delta\) 6.51-6.56 (m, 2H) (1, 2), \(\delta\) 5.02 (s, 1H) (2), \(\delta\) 4.83 (s, 1H) (1), \(\delta\) 3.65-4.14 (m, 10H) (1, 2), \(\delta\) 2.23-2.25 (d, 2H) (1, 2), \(\delta\) 1.44-1.45 (d, 3H) (2), \(\delta\) 1.36-1.37 (d, 3H) (1).

After reaction and it was cooled to room temperature, the crude mixture was filtrated by methanol to recover catalyst, and then distilled at 50 °C for 5 h. Following the procedure above, two isomer of hydroxypropyl \(p\)-chlorophenylcarbamate were obtained as a pale yellow and viscid liquid. \(^1\)H NMR (400MHz, CDCl\(_3\), ppm): \(\delta\) 7.49-7.54 (m, 4H) (1, 2), \(\delta\) 6.77-6.85 (m, 4H) (1, 2), \(\delta\) 5.02 (s, 1H) (2), \(\delta\) 4.82 (s, 1H) (1), \(\delta\) 3.65-4.01 (m, 6H) (1, 2), \(\delta\) 2.23-2.25 (s, 2H) (1, 2), \(\delta\) 1.45-1.46 (d, 3H) (2), \(\delta\) 1.36-1.37 (d, 3H) (1).

After reaction and it was cooled to room temperature, the crude mixture was filtrated by methanol to recover catalyst, and then distilled at 50 °C for 5 h. Following the procedure above, hydroxypropyl cyclohexylcarbamate was obtained as a pale and yellow viscid liquid. \(^1\)H NMR (400MHz, CDCl\(_3\), ppm): \(\delta\) 4.73-4.87 (m, 1H), \(\delta\) 3.55-4.08 (m, 3H), \(\delta\) 2.67-2.74 (d, 2H), \(\delta\) 1.51-1.95 (m, 6H), \(\delta\) 1.12-1.39 (m, 7H).

After reaction and it was cooled to room temperature, the crude mixture was filtrated by methanol to recover catalyst, and then distilled at 50 °C for 5 h. Following the procedure above, hydroxypropyl butylcarbamate was obtained as a white and viscid liquid. \(^1\)H NMR (400MHz, CDCl\(_3\), ppm): \(\delta\) 4.86-4.89 (m, 1H), \(\delta\) 3.90-4.12 (m, 2H), \(\delta\) 3.56-3.69 (m, 1H), \(\delta\) 3.17-3.18 (m, 2H), \(\delta\) 2.59 (d, 1H), \(\delta\) 1.39-1.52 (m, 2H), \(\delta\) 1.25-1.38 (m, 2H), \(\delta\) 1.20-1.23 (m, 3H), \(\delta\) 0.91-0.95 (t, 3H).
mixture was filtrated by methanol to recover catalyst, and then distilled at 50 °C for 5 h. Following the procedure above, hydroxypropyl heptylcarbamate was obtained as a white and viscous liquid.

$^1$H NMR (400MHz, CDCl$_3$, ppm): δ 4.81-4.90 (m, 1H), δ 3.89-4.12 (m, 2H), δ 3.56-3.69 (m, 1H), δ 3.15-3.20 (m, 2H), δ 2.63 (d, 1H), δ 1.18-1.51 (m, 13H), δ 0.86-0.90 (t, 3H).

After reaction and it was cooled to room temperature, the crude mixture was filtrated by methanol to recover catalyst, and then distilled at 50 °C for 5 h. Following the procedure above, hydroxypropyl docanancarbamate was obtained as a white and viscous liquid.

$^1$H NMR (400MHz, CDCl$_3$, ppm): δ 4.78-4.91 (m, 1H), δ 3.91-4.14 (m, 2H), δ 3.59-3.72 (m, 1H), δ 3.18-3.20 (m, 2H), δ 2.56-2.60 (d, 1H), δ 1.14-1.53 (m, 23H), δ 0.88-0.92 (t, 3H).

After reaction and it was cooled to room temperature, the crude mixture was filtrated by methanol to recover catalyst, and then distilled at 50 °C for 5 h. Following the procedure above, dihydroxypropyl-1,6-hexamethylenedicarbamate were obtained as a pale yellow solid. $^1$H NMR (400MHz, CDCl$_3$, ppm): δ 4.83-5.04 (m, 2H), δ 3.49-4.07 (m, 6H), δ 3.12-3.16 (m, 4H), δ 2.92 (s, 2H), δ 1.45-1.48 (m, 4H), δ 1.30-1.32 (m, 4H), δ 1.14-1.18 (m, 6H).

After reaction and it was cooled to room temperature, the crude mixture was filtrated by methanol to recover catalyst, and then distilled at 50 °C for 5 h. Following the procedure above, dihydroxypropyl isophoronedicarbamate were obtained as a yellow and viscous liquid. $^1$H NMR (400MHz, CDCl$_3$, ppm): δ 4.70-4.92 (m, 2H), δ 3.50-4.01 (m, 6H), δ 2.65-3.15 (m, 3H), δ 1.64-1.85 (s, 2H), δ 0.81-1.48 (m, 21H).

After reaction and it was cooled to room temperature, the crude mixture was filtrated by methanol to recover catalyst, and then distilled at 50 °C for 5 h. Following the procedure above, dihydroxypropyl-4, 4'-dicyclohexylmethylene dicarbamate were obtained as a white solid. $^1$H NMR (400MHz, CDCl$_3$, ppm):
ppm): δ 4.56-4.90 (m, 2H), δ 3.40-4.10 (m, 6H), δ 2.63-2.70 (d, 2H), δ 1.98-2.00 (m, 2H), δ 0.94-1.81 (m, 26H).

After reaction and it was cooled to room temperature, the crude mixture was filtrated by methanol to recover catalyst, and then distilled at 50 °C for 5 h. Following the procedure above, dihydroxpropyl-4, 4'-diphenylmethylenedicarbamate were obtained as a yellow solid. 1H NMR (400MHz, CDCl3, ppm): δ 6.56-7.25 (m, 8H), δ 3.96-4.00 (s, 2H), δ 2.92-3.84 (m, 8H), δ 2.16-2.17 (s, 2H), δ 1.15-1.28 (m, 6H).