

Supporting Information

Carboxylation of Sodium Arylsulfonates with CO₂ over Mesoporous

K-Cu-20TiO₂

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1. Materials and Methods

All reagents for synthesis and analysis were analytical grade without further purification. Products were purified with TLC process using petroleum ether/ethyl acetate as mobile phase. ^1H and ^{13}C spectra using DMSO- d_6 or CDCl_3 were recorded on Bruker Advance III 500 MHz Digital NMR spectrometer. The yield was determined by Shimadzu GC-2014C gas chromatography based on an internal standard method. XRD was carried out on Bruker D8 Advance diffractometer using a $\text{Cu-K}\alpha$ radiation. FTIR was performed on a Thermo Fisher Nicolet IS-10 spectrometer with KBr pellet. TG was carried out on Discovery TGA 55 thermal analyzer. XPS was carried out on PHI Quantera II using an Al anode radiation. The morphologies of prepared catalysts were obtained over JEOL JEM-1400plus TEM.

1.1 Preparation for catalyst

Mesoporous multi-component metal oxides (MMMO) have attracted much attention in catalytic applications due to their variable oxidation state and tunable pore structure.

AcHE system used a sol-gel method which dissolved cheap polymers and metal alkoxides in the solution composed of glacial acetic acid (HOAc), hydrochloric acid (HCl) and ethanol (Ac, H, E respectively represented HOAc (99.5%), HCl (36% - 38%), ethanol), the use of AcHE method to prepare K-Cu-20TiO₂ catalyst, which was composed of three components. (1) Acetic acid was used as a complexing agent to change the condensation kinetics of $\text{Ti}(\text{OBU})_4$. (2) The controlled additive concentrated hydrochloric acid partially hydrolyzed and charged the modified inorganic precursor to enhance the affinity of F68 (Polyethylene-polypropylene glycol). In addition, concentrated hydrochloric acid may act as charge intermediates between surfactants and inorganic species and inhibit condensation of certain metal ions. (3) Ethanol or acetic acid ensures that all substances have sufficient solubility. For the synthesis of mesoporous $x\text{K-Cu-yTiO}_2$ catalysts (K / Cu / Ti millimolar ratio = $x : 1 : y$), potassium nitrate, copper nitrate together with titanium butoxides were used as inorganic pre-cursors and F68 was used as the soft template.

In a typical synthesis (K-Cu-20TiO₂): The mixture of 10 mmol $\text{Ti}(\text{OBU})_4$, 40 mmol HOAc (99.5%), 12 mmol HCl (36% - 38%), 0.50 mmol $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 0.50 mmol KNO_3 dissolved in 2 mL deionized water and 1.6 g F68 in 30 mL ethanol was stirred vigorously for 1h at room temperature. Then the mixture was further concentrated to form a yellow transparent film by rotary evaporation at 50 °C under reduced pressure. The film was aged for 24 h at 70 °C then calcined for 5 h at 350 °C in nitrogen atmosphere. The film material was ground into a fine powder before use.

1.2 Procedure for carboxylation reaction

To 10 mL sealed Schlenk tube ventilated with CO₂ added substrate (0.10 mmol), K-Cu-20TiO₂ (20.9 mg), ligand (0.03 mmol) + base (0.30 mmol) and DMSO (2.5 mL). The mixture was stirred for 16 h at 120 °C under 0.1 MPa carbon dioxide atmosphere. After the mixture was cooled to room temperature, 1 mol/L HCl (1.5 mL) was added to the mixture. The catalyst was separated by centrifugation and the product was extracted with EtOAc (5ml × 3) and washed with saturated NaCl aqueous solution (5ml × 3). The organic phase was dried by Na₂SO₄, then concentrated by distillation and purified by TLC.

1.3 Regeneration and recycling of the catalyst

The solid catalyst separated from reaction mixture by centrifugation process was stirred for 1 h in 5.0 mL ethanol then in 5.0 mL deionized water. After aged for 24 h at 70 °C then calcined for 5 h at 350 °C in nitrogen atmosphere, the solid was reused in the next run.

To 10 mL sealed Schlenk tube ventilated with CO₂ added substrate (0.10 mmol), K-Cu-20TiO₂ (20.9 mg), ligand (0.03 mmol) + base (0.30 mmol) and DMSO (2.5 mL). The mixture was stirred for 16 h at 120 °C under 0.1 MPa carbon dioxide atmosphere. After the mixture was cooled to room temperature, 1 mol/L HCl (1.5 mL) was added to the mixture. The catalyst was separated by centrifugation and the product was extracted with EtOAc (5ml × 3) and washed with saturated NaCl aqueous solution (5ml × 3). The organic phase was dried by Na₂SO₄, then concentrated by distillation and purified by TLC.

2. Optimization studies

We have conducted a series of screening and optimization of the experimental conditions such as catalysts, solvent, temperature, ligands, bases, reaction time and dosage.

Table 1 Screening of catalysts^[a]

Entry	Catalyst	Conv. (%) ^[b]	Sel. (%) ^[c]
1	Cu-20TiO ₂	12	> 99.1
2	K-Cu-20TiO ₂	77	> 99.5
3	3K-Cu-20TiO ₂	53	> 99.2
4	K-Cu-10TiO ₂	21	> 99.5
5	K-Cu-30TiO ₂	33	> 99.6
6	K-Cu-50TiO ₂	trace	-

^[a]The mixture of sodium benzenesulfinate (0.10 mmol), CO₂ (0.1 MPa), catalyst (20.9 mg), phen (0.03 mmol) (phen: *o*-phenanthroline, the same as below.), KOtBu (0.30 mmol) and DMSO (2.5 mL) was conducted for 16 h at 120 °C in a sealed Schlenk tube.

^[b]Conversion, determined by product yield and selectivity from GC and GC-MS analyses using 2-methylimidazole as internal standard.

^[c]Selectivity, mass percentage of benzoic acid in the product mixtures from GC and GC-MS analyses using 2-methylimidazole as internal standard.

Table 2 Screening of Solvent^[a]

Entry	Catalyst	Solvent	Conv. (%) ^[a]	Sel. (%) ^[c]
1	K-Cu-20TiO ₂	DMSO	77	> 99.5
2	K-Cu-20TiO ₂	DMF	50	> 99.5
3	K-Cu-20TiO ₂	DMA	35	> 99.3
4	K-Cu-20TiO ₂	dioxane	8.6	> 99.1
5	K-Cu-20TiO ₂	CH ₃ CN	trace	-
6	K-Cu-20TiO ₂	THF	51	> 99.6

^[a]The mixture of sodium benzenesulfinate (0.10 mmol), CO₂ (0.1 MPa), K-Cu-20TiO₂ (20.9 mg), phen (0.03mmol), KOtBu (0.30 mmol) and DMSO (2.5 mL) was conducted for 16 h at 120 °C in a sealed Schlenk tube. ^[b]Conversion, determined by product yield and selectivity from GC and GC-MS analyses using 2-methylimidazole as internal standard. ^[c]Selectivity, mass percentage of benzoic acid in the product mixtures from GC and GC-MS analyses using 2-methylimidazole as internal standard.

Table 3 Screening of temperature^[a]

Entry	Catalyst	Temperature	Conv. (%) ^[b]	Sel. (%) ^[c]
1	K-Cu-20TiO ₂	150	67	> 99.2
2	K-Cu-20TiO ₂	160	70	> 99.3
3	K-Cu-20TiO ₂	140	73	> 99.5
4	K-Cu-20TiO ₂	130	75	> 99.2
5	K-Cu-20TiO ₂	120	77	> 99.5
6	K-Cu-20TiO ₂	110	65	> 99.4
7	K-Cu-20TiO ₂	100	43	> 99.6
8	K-Cu-20TiO ₂	80	8.5	> 99.3
9	K-Cu-20TiO ₂	60	trace	-

^[a]The mixture of sodium benzenesulfinate (0.10 mmol), CO₂ (0.1 MPa), K-Cu-20TiO₂ (20.9 mg), phen (0.03 mmol), KOtBu(0.30 mmol) and

DMSO (2.5 mL) was conducted for 18 h in a sealed Schlenk tube.

^[b]Conversion, determined by product yield and selectivity from GC and GC-MS analyses using 2-methylimidazole as internal standard.

^[c]Selectivity, mass percentage of benzoic acid in the product mixtures from GC and GC-MS analyses using 2-methylimidazole as internal standard.

Table 4 Screening of reaction time^[a]

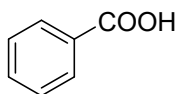
Entry	Catalyst	Time (h)	Conv. (%) ^[b]	Sel. (%) ^[c]
1	K-Cu-20TiO ₂	24	78	> 99.6
2	K-Cu-20TiO ₂	18	80	> 99.6
3	K-Cu-20TiO ₂	16	85	> 99.8
4	K-Cu-20TiO ₂	14	63	> 99.4
5	K-Cu-20TiO ₂	12	35	> 99.2
6	K-Cu-20TiO ₂	6	2.8	> 99.3

^[a]The mixture of sodium benzenesulfinate (0.10 mmol), CO₂ (0.1 MPa), K-Cu-20TiO₂ (20.9 mg), phen (0.03 mmol), Cs₂CO₃ (0.30 mmol) and DMSO (2.5 mL) was conducted at 120 °C in a sealed Schlenk tube.

^[b]Conversion, determined by product yield and selectivity from GC and GC-MS analyses using 2-methylimidazole as internal standard.

^[c]Selectivity, mass percentage of benzoic acid in the product mixtures from GC and GC-MS analyses using 2-methylimidazole as internal standard.

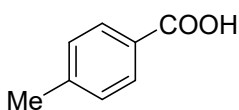
3. ¹H NMR and ¹³C NMR of products



Benzoic acid (entry 1 in Table 3): Purified by TLC (silica gel, EA : PE = 1 : 5). White crystalline powder, m.p. 104 -106 °C.

¹H NMR (500 MHz, CDCl₃) δ 8.14 (m, 2H), 7.61 (m, 1H), 7.45 (t, *J* = 7.7 Hz, 2H).

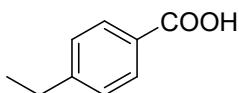
¹³C NMR (126 MHz, CDCl₃) δ 172.57, 133.89, 130.27, 129.35, 128.54.



4-Methylbenzoic acid (entry 2 in Table 3): Purified by TLC (silica gel, EA : PE = 1 : 5). White crystalline powder, m.p. 180 - 181 °C.

¹H NMR (500 MHz, CDCl₃) δ 8.01 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 2.44 (s, 3H).

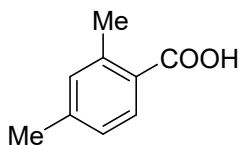
¹³C NMR (126 MHz, CDCl₃) δ 172.54, 144.69, 130.30, 129.24, 126.66, 21.80.



4-Ethylbenzoic acid (entry 3 in Table 3): Purified by TLC (silica gel, EA : PE = 1 : 5). White crystalline powder, m.p. 113 - 114 °C.

¹H NMR (500 MHz, CDCl₃) δ 8.08 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 2.70 (q, *J* = 7.6 Hz, 2H), 1.24 (t, *J* = 7.6 Hz, 3H).

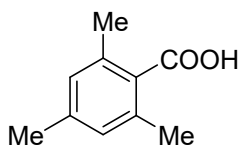
^{13}C NMR (126 MHz, CDCl_3) δ 172.54, 150.86, 130.41, 128.07, 126.83, 29.10, 15.24.



2,4-Dimethylbenzoic acid (entry 4 in Table 3): Purified by TLC (silica gel, EA : PE = 1 : 5). White crystalline powder, m.p. 124 - 125 °C.

^1H NMR (500 MHz, CDCl_3) δ 8.05 (d, J = 8.4 Hz, 1H), 7.50 - 6.97 (m, 2H), 2.69 (s, 3H), 2.43 (s, 3H).

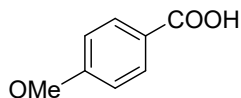
^{13}C NMR (126 MHz, CDCl_3) δ 173.49, 143.70, 141.53, 132.77, 131.87, 126.66, 125.52, 22.19, 21.51.



2,4,6-Trimethylbenzoic acid (entry 5 in Table 3): Purified by TLC (silica gel, EA : PE = 1 : 5). White crystalline powder, m.p. 155 - 156 °C.

^1H NMR (500 MHz, CDCl_3) δ 6.95 (s, 2H), 2.49 (s, 6H), 2.36 (s, 3H).

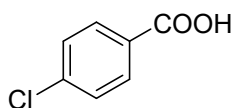
^{13}C NMR (126 MHz, CDCl_3) δ 175.88, 140.15, 136.23, 129.31, 128.85, 21.20, 20.40.



4-Anisic acid (entry 6 in Table 3): purified by TLC (silica gel, EA : PE = 1 : 5). White crystalline powder, m.p. 182 - 185 °C.

^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ 12.63 (s, 1H), 7.95 - 7.85 (m, 2H), 7.06 - 6.95 (m, 2H), 3.82 (s, 3H).

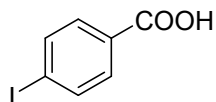
^{13}C NMR (126 MHz, $\text{DMSO}-d_6$) δ 167.47, 163.28, 131.80, 123.40, 114.24, 55.85.



4-Chlorobenzoic acid (entry 7 in Table 3): purified by TLC (silica gel, EA : PE = 1 : 5). White crystalline powder, m.p. 242 - 243 °C

^1H NMR (500 MHz, DMSO) δ 13.10 (br, 1H), 7.90 (d, J = 8.1 Hz, 2H), 7.60 (d, J = 8.1 Hz, 2H).

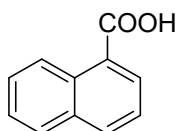
^{13}C NMR (126 MHz, DMSO) δ 166.92, 138.25, 131.59, 130.07, 129.18.



4-Iodobenzoic acid (entry 8 in Table 3): purified by TLC (silica gel, EA : PE = 1 : 5). White crystalline powder, m.p. 270 - 271 °C.

^1H NMR (500 MHz, DMSO) δ 13.14 (br, 1H), 7.89 (m, J = 8.5 Hz 2H), 7.69 (m, J = 8.5 Hz, 2H).

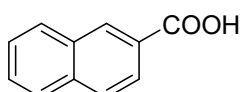
^{13}C NMR (126 MHz, DMSO) δ 167.36, 138.03, 131.51, 130.73, 101.62.



1-Naphthoic acid (entry 9 in Table 3): purified by TLC (silica gel, EA : PE = 1 : 5). White crystalline powder, m.p. 157 - 160 °C.

^1H NMR (500 MHz, CDCl_3) δ 9.13 (d, J = 8.7 Hz, 1H), 8.45 (dd, J = 7.3, 1.3 Hz, 1H), 8.12 (d, J = 8.2 Hz, 1H), 7.94 (dd, J = 8.2, 1.3 Hz, 1H), 7.69 (ddd, J = 8.5, 6.8, 1.4 Hz, 1H), 7.58 (q, J = 7.3 Hz, 2H).

^{13}C NMR (126 MHz, CDCl_3) δ 173.41, 134.72, 133.98, 131.94, 131.69, 128.77, 128.17, 126.38, 125.97, 125.63, 124.59.



2-Naphthoic acid (entry 10 in Table 3): purified by TLC (silica gel, EA : PE = 1 : 5). White crystalline powder, m.p. 183 - 185 °C.

^1H NMR (500 MHz, CDCl_3) δ 8.74 (d, J = 1.6 Hz, 1H), 8.14 (dd, J = 8.5, 1.7 Hz, 1H), 8.00 (d, J = 8.1 Hz, 1H), 7.92 (t, J = 8.7 Hz, 2H), 7.63 (ddd, J = 8.2, 6.8, 1.3 Hz, 1H), 7.58 (ddd, J = 8.1, 6.8, 1.2 Hz, 1H).

^{13}C NMR (126 MHz, CDCl_3) δ 171.93, 135.70, 132.18, 131.90, 129.29, 128.40, 128.07, 127.56, 126.51, 126.27, 125.13.

