



 Cite this: *RSC Adv.*, 2022, **12**, 772

 Received 7th July 2021  
 Accepted 5th November 2021

DOI: 10.1039/d1ra05228d

[rsc.li/rsc-advances](http://rsc.li/rsc-advances)

# Carboxylation of sodium arylsulfonates with CO<sub>2</sub> over mesoporous K-Cu-20TiO<sub>2</sub>†

 Yanjiao Chen, Xuan Dai, Wenwei Zhang, Tao Wu, Lei Chen and Xinhua Peng \*

A mesoporous ternary metal oxide (K-Cu-20TiO<sub>2</sub>) from a simple sol–gel method was prepared to catalyze heterogeneously the carboxylation reaction of various sodium arylsulfonates under atmospheric carbon dioxide. The catalyst showed excellent selectivity and good functional group tolerance to carboxylation recycle. The oxidation state of active copper(I) by characterization using FTIR, XRD, TG, XPS and TEM techniques proved to be efficacious to conduct atom economical reactions.

## 1. Introduction

In recent years, the term “green chemistry” is frequently mentioned by researchers.<sup>1</sup> The emissions of carbon dioxide known as the “greenhouse gas” have far exceeded the level of pre-industry concentration.<sup>2,3</sup> Moreover, the utilization of CO<sub>2</sub> is rather attractive because of the abundant C1 source.<sup>4–7</sup> In spite of its high thermodynamic and kinetic stabilities, CO<sub>2</sub> has the characteristics of low electrophilicity.<sup>8–10</sup> Therefore, it is important to activate CO<sub>2</sub> with a Lewis acid to improve the electrophilic ability. For example, Olah *et al.* used the CO<sub>2</sub>–Al<sub>2</sub>Cl<sub>6</sub>/Al system to carboxylate ethylbenzene in 33% yield of *p*-ethyl benzoic acid under 5.7 MPa CO<sub>2</sub> pressure.<sup>11,12</sup>

On the other hand, a strong carbon nucleophile acts on CO<sub>2</sub> to form valuable carboxylic acids and their derivatives.<sup>13,14</sup> The chemical utilization of CO<sub>2</sub> has made considerable progress.<sup>15,16</sup> In particular, some carbon nucleophiles such as Grignard reagents were employed to attack CO<sub>2</sub> in the syntheses of aliphatic carboxylic acids.<sup>17,18</sup> The reaction is usually conducted under strict anhydrous and anaerobic conditions.<sup>19,20</sup>

Some mild reaction conditions are developed towards the CO<sub>2</sub> carboxylation of organo-boron<sup>21,22</sup> and zinc substrates<sup>23,24</sup> in the presence of organometallic complexes. The reaction is accompanied by a cumbersome pre-functionalization process of the substrate and the requirements of sustainable chemistry are different.<sup>25,26</sup> Fujihara *et al.*<sup>27–30</sup> explored the carboxylation of aryl halides, styrene and propylene, *etc.* with CO<sub>2</sub> by synergy between reductants such as Mn or Zn and some organometallic complexes. These typical synthetic methodologies have been summarized in Scheme 1.

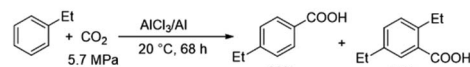
Various transition metal catalysts can catalyze the coupling reaction of sodium sulfonates involving Heck desulfurization

reactions,<sup>31</sup> addition reactions of alkynes<sup>32</sup> and cross-coupling reactions with polyfluoroaromatic hydrocarbons.<sup>33</sup> Performing the carboxylation of sodium arylsulfonates with CO<sub>2</sub> (ref. 34) brings similar advantages, due to the stability and the processability of aromatic sodium sulfonates as aryl sources.<sup>35,36</sup>

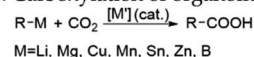
In addition, it has been reported that the homogeneous catalyst CuI was used to catalyze the carbonylation reaction of CO<sub>2</sub> and sodium benzenesulfinate. However, CuI has the disadvantages of non-recoverability and easy loss of active sites. Recycling heterogeneous catalysts remains challenging. Here, the article describes a heterogeneous catalyst to promote the carboxylation of aromatic sodium arylsulfonates with CO<sub>2</sub>.

The heterogeneous catalyst, a mesoporous ternary metal oxide (K-Cu-20TiO<sub>2</sub>) is prepared using a sol–gel method by dissolving cheap polymers and metal alkoxides in a solution composed of glacial acetic acid, hydrochloric acid and ethanol (AcHE) (see ESI for details†).<sup>37–40</sup> K-Cu-20TiO<sub>2</sub> shows stable and

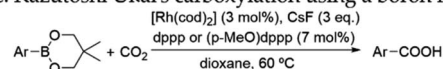
A: Olah's carboxylation with Lewis acid.



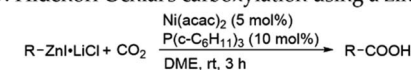
B: Carboxylation of organometallic reagents with CO<sub>2</sub>.



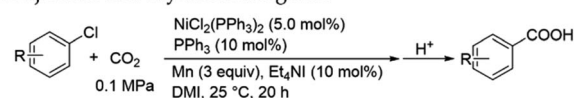
C: Kazutoshi Ukai's carboxylation using a boron reagent.



D: Hidenori Ochiai's carboxylation using a zinc reagent.



E: Fujihara's carboxylation using Mn.



Scheme 1 The utilization of CO<sub>2</sub> in carboxylation reactions.

School of Chemistry and Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094, China. E-mail: xhpeng@njust.edu.cn; xinhpeng@njust.edu.cn

† Electronic supplementary information (ESI) available. See DOI: 10.1039/d1ra05228d



excellent catalytic performances and promotes the high-selective substitution carboxylation of arylsulfonates with CO<sub>2</sub> under mild conditions.

As shown in Fig. 1, 2 and 4, K-Cu-20TiO<sub>2</sub> from a uniform combination of potassium and copper components in *tetra*-butyl titanate stabilizes the oxidation state of active copper(I) based on the characterization of FTIR, XRD and XPS characterizations. In Fig. 3, the TG curve displays its good thermal stability up to 480 °C. In addition, it exhibits a high degree of uniformity with dense accumulation and mesoporous channels in the TEM image (Fig. 5).

## 2. Results and discussion

### 2.1. Characterizations of the catalyst

FTIR spectra of KNO<sub>3</sub>, Cu(NO<sub>3</sub>)<sub>2</sub>, TiO<sub>2</sub> and K-Cu-20TiO<sub>2</sub> are depicted in Fig. 1. K-Cu-20TiO<sub>2</sub> exhibits the characteristic peaks of the stretching vibrations of KNO<sub>3</sub> at 2819–3006 cm<sup>-1</sup> and 2360 cm<sup>-1</sup> in Fig. 1(a). Similarly, the characteristic peak of TiO<sub>2</sub> stretching vibration at 3541–3868 cm<sup>-1</sup> (Fig. 1(b)) exists in the spectrum of catalytic material, which shows the importance of the TiO<sub>2</sub> support.

XRD patterns of Cu-20TiO<sub>2</sub> and K-Cu-20TiO<sub>2</sub> are shown in Fig. 2. There is a strong  $2\theta$  peak at 25.3° corresponding to the (210) plane, which is attributed to TiO<sub>2</sub>. The peaks at 36.2°, 48.0°, 54.3°, 54.5°, 62.0° and 68.9° are in good agreement with (102), (321), (230), (131), (502) and (040) planes of TiO<sub>2</sub> (PDF#72-0100), respectively. Peaks at 42.9° are consistent with the (221) plane of KNO<sub>3</sub> (PDF#81-0070).

The recorded TG curve of K-Cu-20TiO<sub>2</sub> is shown in Fig. 3. When 7.084 mg K-Cu-20TiO<sub>2</sub> is heated to 350 °C and 480 °C, the total mass loss is 0.275 and 0.492 mg, respectively. This shows that the catalyst demonstrates excellent thermal stability under reaction conditions.

XPS is used to characterize the Cu oxidation state. The existence of Cu(I) in fresh K-Cu-20TiO<sub>2</sub> is observed with the major peak at 929.9 eV (Fig. 4), which has no shake-up satellites in the range of 931–933 eV. It is demonstrated that Cu(I) ions are homogeneously incorporated into the TiO<sub>2</sub> matrix in mesoporous K-Cu-20TiO<sub>2</sub> materials.

TEM images in Fig. 5 are employed to analyze the morphology features of K-Cu-20TiO<sub>2</sub>. From Fig. 5(a) to (e), the morphology of K-Cu-20TiO<sub>2</sub> is a tightly packed cubic structure with sizes in the range 2–50 nm, in which there are some pores on the surface of K-Cu-20TiO<sub>2</sub> as seen in Fig. 5(a). This proves

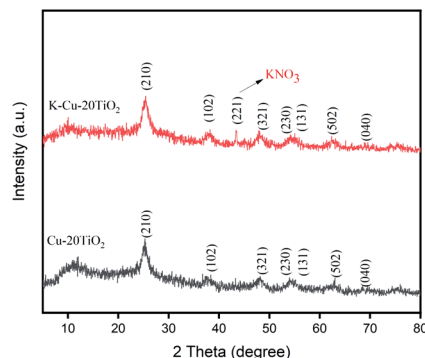


Fig. 2 XRD patterns of Cu-20TiO<sub>2</sub> and K-Cu-20TiO<sub>2</sub>.

that TiO<sub>2</sub> is closely packed as a framework to form the mesoporous structure, while Cu and K are evenly dispersed and embedded in the crystal.

### 2.2. Optimization studies

The reaction of sodium benzenesulfinate with atmospheric CO<sub>2</sub> over the K-Cu-20TiO<sub>2</sub> catalyst turns out to be efficacious for the carboxylation with excellent selectivity. Control experiments were conducted with various bases, ligands and DMSO medium (Table 1). The reaction becomes rather weak in the absence of the catalyst as compared to that without the ligand or base (entries 1–3 in Table 1). Ligands and bases promote the reaction by synergy with the catalyst. Of the tested ligands, *o*-phenanthroline is the most effective as compared with other ligands such as pyridine, 2,2'-bipyridine, 4,4'-bipyridine and 2,2',6',2''-terpyridine in the presence of KO*t*Bu (entries 4–8 in Table 1). Of the tested bases, Cs<sub>2</sub>CO<sub>3</sub> proves to be quite efficient when compared with its counterparts, such as K<sub>2</sub>CO<sub>3</sub>, KOH, NaOC<sub>2</sub>H<sub>5</sub>, LiO*t*Bu and KO*t*Bu, in the presence of *o*-phenanthroline (entries 4, 9–13 in Table 1). An optimum combination of the substrate (0.10 mmol), K-Cu-20TiO<sub>2</sub> (20.9 mg), *o*-phenanthroline (30 mol%) and Cs<sub>2</sub>CO<sub>3</sub> (3.0 equiv.) in DMSO (2.5 mL) produced 85% conversion of sodium benzenesulfinate with 99.8% selectivity of benzoic acid during carboxylation (entry 10 in Table 1).

Moreover, the amounts of catalyst, ligand and base are able to affect the product yield (Table 2). The increase in the amount of the catalyst (entries 1–4 in Table 2), ligands (entries 5–7 in

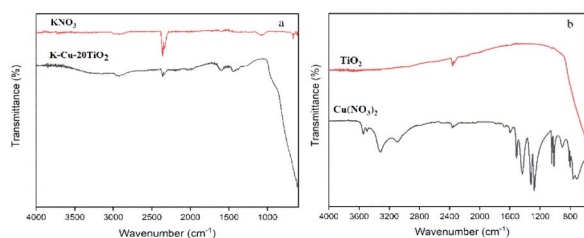


Fig. 1 FTIR spectra of (a) KNO<sub>3</sub> and K-Cu-20TiO<sub>2</sub>, (b) TiO<sub>2</sub> and Cu(NO<sub>3</sub>)<sub>2</sub>.

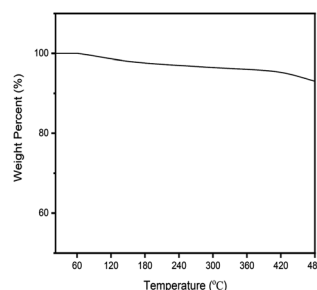


Fig. 3 TG curve of K-Cu-20TiO<sub>2</sub>.



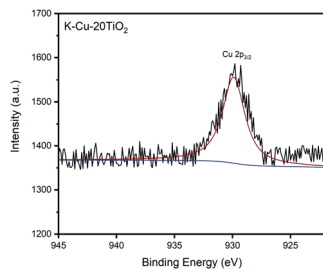


Fig. 4 XPS spectra of mesoporous K-Cu-20TiO<sub>2</sub>.

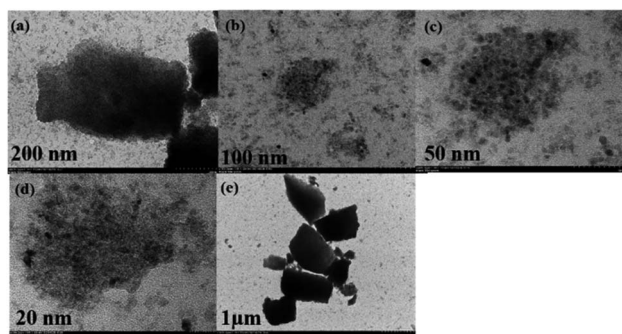


Fig. 5 TEM images of K-Cu-20TiO<sub>2</sub>.

Table 1 Carboxylation of sodium benzenesulfinate with carbon dioxide<sup>a</sup>

Entry	Catalyst	Ligand	Base	Conv. <sup>b</sup> (%)	Sel. <sup>c</sup> (%)
1	K-Cu-20TiO <sub>2</sub>	—	KOtBu	33	>99.2
2	K-Cu-20TiO <sub>2</sub>	Phen	—	15	>99.3
3	—	Phen	KOtBu	Trace	—
4	K-Cu-20TiO <sub>2</sub>	Phen	KOtBu	77	>99.5
5	K-Cu-20TiO <sub>2</sub>	Py	KOtBu	70	>99.5
6	K-Cu-20TiO <sub>2</sub>	Bipy	KOtBu	70	>99.4
7	K-Cu-20TiO <sub>2</sub>	4,4'-Bipy	KOtBu	60	>99.3
8	K-Cu-20TiO <sub>2</sub>	Terpy	KOtBu	50	>99.3
9	K-Cu-20TiO <sub>2</sub>	Phen	K <sub>2</sub> CO <sub>3</sub>	80	>99.5
10	K-Cu-20TiO <sub>2</sub>	Phen	Cs <sub>2</sub> CO <sub>3</sub>	85	>99.8
11	K-Cu-20TiO <sub>2</sub>	Phen	KOH	73	>99.7
12	K-Cu-20TiO <sub>2</sub>	Phen	NaOC <sub>2</sub> H <sub>5</sub>	55	>99.4
13	K-Cu-20TiO <sub>2</sub>	Phen	LiOtBu	50	>99.5

<sup>a</sup> The mixture of sodium benzenesulfinate (0.10 mmol), CO<sub>2</sub> (0.1 MPa), K-Cu-20TiO<sub>2</sub> (20.9 mg), ligand (0.03 mmol, phen: *o*-phenanthroline, py: pyridine, bipy: 2,2'-bipyridine, 4,4'-bipy: 4,4'-bipyridine, terpy: 2,2',6',2''-terpyridine, same as below), base (0.30 mmol) and DMSO (2.5 mL) was reacted at 120 °C for 16 h in a sealed Schlenk tube. <sup>b</sup> Conversion, determined by product yield and selectivity from GC and GC-MS analyses using 2-methylimidazole as internal standard. <sup>c</sup> 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 the amount of catalyst, ligand and base<sup>a</sup>

Entry	K-Cu-20TiO <sub>2</sub> (mg)	Phen (mmol)	Cs <sub>2</sub> CO <sub>3</sub> (mmol)	Conv. <sup>b</sup> (%)
1	62.9	0.03	0.30	87
2	41.8	0.03	0.30	86
3	20.9	0.03	0.30	85
4	10.5	0.03	0.30	41
5	20.9	0.04	0.30	86
6	20.9	0.02	0.30	75
7	20.9	0.01	0.30	35
8	20.9	0.03	0.40	87
9	20.9	0.03	0.20	72
10	20.9	0.03	0.10	55

<sup>a</sup> The mixture of sodium benzenesulfinate (0.10 mmol), CO<sub>2</sub> (0.1 MPa), K-Cu-20TiO<sub>2</sub>, *o*-phenanthroline, Cs<sub>2</sub>CO<sub>3</sub> and DMSO (2.5 mL) was reacted for 16 h at 120 °C in a sealed Schlenk tube. <sup>b</sup> Conversion, determined by product yield and selectivity from GC and GC-MS analyses using 2-methylimidazole as internal standard.

Table 2) and base (entries 8–10 in Table 2) can improve substrate conversion and carboxylation yield.

The carboxylation performance of various aromatic sodium arylsulfonates is inspected in optimum reaction conditions. As shown in Table 3, the reactions of arylsulfonates with CO<sub>2</sub> form corresponding carboxylated products smoothly with moderate substrate conversion and high product selectivity. These substrates with functional groups involving methyl, ethyl, methoxy, chloro, iodo and phenyl have no intimate relevance to the electron and conjugate effects by the electron-donating and electron-withdrawing groups on the aromatic ring.

The reusability of K-Cu-20TiO<sub>2</sub> for the carboxylation of sodium benzenesulfinate was investigated. The results under optimal conditions are shown in Fig. 6. It is clear that there are only insignificant decreases in conversion and selectivity after five cycles; the conversion and selectivity were about 83% and 99.8%, respectively. The catalyst is regenerated by the usual process involving centrifugation separation, washing with ethanol and deionized water, followed by drying at 70 °C prior to reuse.

The catalytic properties are implied by the mechanism presented in Scheme 2. Sodium benzenesulfinate in stronger alkaline conditions can favor metathesis from active Cu(I) of K-Cu-20TiO<sub>2</sub> based on the XPS analysis. The Cu(I) complex on solid surface is further coordinated with ligands to form an intermediate Ar-CuL (aromatic copper complex), accompanied by the release of molecular sulfur dioxide from the substrate. Subsequently, CO<sub>2</sub> is inserted into Ar-CuL to form a carbon-carbon coupling product of benzoate by the electrophilic substitution effect. This method based on the catalytic cycle can readily synthesize aromatic carboxylic acid by mild desulfination.

## 3. Experimental

### 3.1. Preparation and regeneration for catalyst

A mixture of 10 mmol Ti(OBu)<sub>4</sub>, 40 mmol HOAc (99.5%), 12 mmol HCl (36–38%), 0.50 mmol Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O and 0.50 mmol KNO<sub>3</sub> was dissolved in 2 mL deionized water, and



Table 3 Extension of the substrate scope<sup>a</sup>

Entry	Substrate	Product	Conv. <sup>b</sup> (%)	Sel. <sup>c</sup> (%)
1			85	>99.8
2			80	>99.6
3			75	>99.3
4			78	>99.6
5			70	>99.3
6			23	>99.1
7			83	>99.3
8			77	>99.3
9			45	>99.4
10			66	>99.5

<sup>a</sup> The mixture of substrate (0.10 mmol), CO<sub>2</sub> (0.1 MPa), K-Cu-20TiO<sub>2</sub> (20.9 mg), phen (0.03 mmol), Cs<sub>2</sub>CO<sub>3</sub> (0.30 mmol) and DMSO (2.5 mL) was reacted for 16 h at 120 °C in a sealed Schlenk tube. <sup>b</sup> Conversion, determined by product yield and selectivity from GC and GC-MS analyses using 2-methylimidazole as internal standard. <sup>c</sup> Selectivity, mass percentage of benzoic acid in the product mixtures from GC and GC-MS analyses using 2-methylimidazole as internal standard.

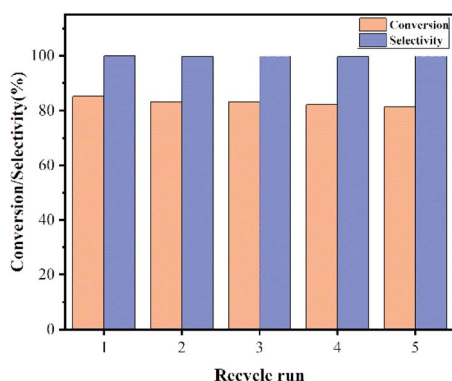
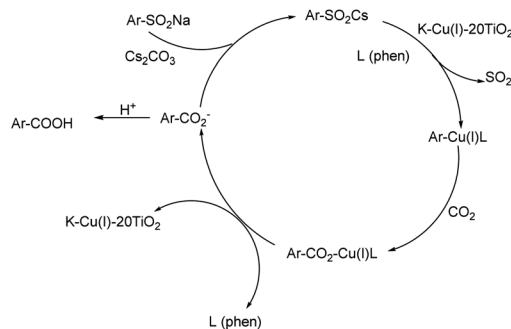


Fig. 6 Recycling of the catalyst.

1.6 g F68 (polyethylene-polypropylene glycol) in 30 mL ethanol was stirred vigorously for 1 h at room temperature. Then the mixture was further concentrated to form a yellow transparent



Scheme 2 The proposed electrophilic mechanism.

film by rotary evaporation at 50 °C under reduced pressure. The film was aged for 24 h at 70 °C and then calcined for 5 h at 350 °C in nitrogen atmosphere. The film material was ground into a fine powder before use.

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

### 3.2. Procedure for carboxylation reaction

A 10 mL sealed Schlenk tube was ventilated with CO<sub>2</sub> added substrate (0.10 mmol), K-Cu-20TiO<sub>2</sub> (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<sup>-1</sup> HCl (1.5 mL) was added to the mixture. The catalyst was separated by centrifugation, and the product was extracted with EtOAc (5 mL × 3) and washed with saturated NaCl aqueous solution (5 mL × 3). The organic phase was dried by Na<sub>2</sub>SO<sub>4</sub>, and then concentrated by distillation and purified by TLC.

## 4. Conclusions

In summary, an excellent K-Cu-20TiO<sub>2</sub> catalyst is used to promote the atom economic carboxylation of CO<sub>2</sub> as the C1 source. Carboxylation of arylsulfonates does not need the usual pre-activation on the substrate in the presence of the solid catalyst. In addition, the reaction is heterogeneously performed in mild conditions on the solid surface with high product selectivity. Therefore, this methodology expands CO<sub>2</sub> fixation utilization.

## Conflicts of interest

There are no conflicts to declare.

## References

- 1 S. Fenner and L. Ackermann, *Green Chem.*, 2016, **18**, 3804–3807.



- 2 R. Zevenhoven, S. Eloneva and S. Teir, *Catal. Today*, 2006, **115**, 73–79.
- 3 S. N. Riduan and Y. Zhang, *Dalton Trans.*, 2010, **39**, 3347–3357.
- 4 T. Sakakura, J. C. Choi and H. Yasuda, *Chem. Rev.*, 2007, **107**, 2365–2387.
- 5 X. Gao, Z. Zhang, X. Wang, J. Tian, S. Xie, F. Zhou and J. Zhou, *Chem. Sci.*, 2020, **11**, 10414–10420.
- 6 A. Tortajada, F. Juliá-Hernández, M. Börjesson, T. Moragas and R. Martin, *Angew. Chem., Int. Ed.*, 2018, **130**, 16178–16214.
- 7 J. Louie, *Curr. Org. Chem.*, 2005, **9**, 605–623.
- 8 T. Ohishi, M. Nishiura and Z. Hou, *Angew. Chem., Int. Ed.*, 2008, **47**, 5792–5795.
- 9 J. Luo and I. Larrosa, *ChemSusChem*, 2017, **10**, 3317–3332.
- 10 M. Aresta, *Focus on Catalysts*, 2010, **4**, 1351–4180.
- 11 G. A. Olah, B. Torok, J. P. Joschek, I. Bucsí, P. M. Esteves, G. Rasul and G. K. Surya Prakash, *J. Am. Chem. Soc.*, 2002, **124**, 11379–11391.
- 12 Y. Suzuki, T. Hattori, T. Okuzawa and S. Miyano, *Chem. Lett.*, 2002, **31**, 102–103.
- 13 Q. Liu, L. Wu, R. Jackstell and M. Beller, *Nat. Commun.*, 2015, **6**, 5933.
- 14 T. E. Muller and W. Leitner, *Beilstein J. Org. Chem.*, 2015, **11**, 675–677.
- 15 Y. Kuwahara and H. Yamashita, *J. CO<sub>2</sub> Util.*, 2013, **1**, 50–59.
- 16 J. Rintjema, L. P. Carrodegua, V. Laserna, S. Sopena and A. W. Kleij, *Top. Organomet. Chem.*, 2016, **53**, 39–71.
- 17 A. Correa and R. Martin, *Angew. Chem., Int. Ed.*, 2009, **48**, 6201–6204.
- 18 O. Vechorkin, N. Hirt and X. Hu, *Org. Lett.*, 2010, **12**, 3567–3569.
- 19 A. Nagaki, Y. Takahashi and J. Yoshida, *Chem.–Eur. J.*, 2014, **20**, 7931–7934.
- 20 A. Polyzos, M. O'Brien, T. P. Petersen, I. R. Baxendale and S. V. Ley, *Angew. Chem., Int. Ed.*, 2011, **123**, 1222–1225.
- 21 J. Takaya, S. Tadami, K. Ukai and N. Iwasawa, *Org. Lett.*, 2008, **10**, 2697–2700.
- 22 K. Ukai, M. Aoki, J. Takaya and N. Iwasawa, *J. Am. Chem. Soc.*, 2006, **128**, 8706–8707.
- 23 C. S. Yeung and V. M. Dong, *J. Am. Chem. Soc.*, 2008, **130**, 7826–7827.
- 24 H. Ochiai, M. Jang, K. Hirano, H. Yorimitsu and K. Oshima, *Org. Lett.*, 2008, **10**, 2681–2683.
- 25 K. Shimomaki, K. Murata, R. Martin and N. Iwasawa, *J. Am. Chem. Soc.*, 2017, **139**, 9467–9470.
- 26 X. Zhang, W. Z. Zhang, L. L. Shi, C. X. Guo, L. L. Zhang and X. B. Lu, *Chem. Commun.*, 2012, **48**, 6292–6294.
- 27 Y. Sato, M. Mori, M. Takimoto and M. Kawamura, *Synlett*, 2005, **134**, 2019–2022.
- 28 J. Takaya and N. Iwasawa, *J. Am. Chem. Soc.*, 2008, **130**, 15254–15255.
- 29 T. Fujihara, K. Nogi, T. Xu, J. Terao and Y. Tsuji, *J. Am. Chem. Soc.*, 2012, **134**, 9106–9109.
- 30 T. Moragas, M. Gaydou and R. Martin, *Angew. Chem., Int. Ed.*, 2016, **55**, 5053–5057.
- 31 G. W. Wang and T. Miao, *Chemistry*, 2011, **17**, 5787–5790.
- 32 S. Liu, Y. Bai, X. Cao, F. Xiao and G. Deng, *Chem. Commun.*, 2013, **49**, 7501–7503.
- 33 T. Miao and L. Wang, *Adv. Synth. Catal.*, 2014, **356**, 429–436.
- 34 S. Sun, J. Yu, Y. Jiang and J. Cheng, *Adv. Synth. Catal.*, 2015, **357**, 2022–2026.
- 35 W. Chen, P. Li, T. Miao, L. G. Meng and L. Wang, *Org. Biomol. Chem.*, 2013, **11**, 420–424.
- 36 M. Wang, D. Li, W. Zhou and L. Wang, *Tetrahedron*, 2012, **68**, 1926–1930.
- 37 J. Fan, S. W. Boettcher and G. D. Stucky, *Chem. Mater.*, 2006, **18**, 6391–6396.
- 38 P. Yang, D. Zhao, D. I. Margolese, B. F. Chmelka and G. D. Stucky, *Chem. Mater.*, 1999, **11**, 2813–2826.
- 39 D. Grosso, F. Cagnol, G. J. d. A. A. Soler-Illia, E. L. Crepaldi, H. Amenitsch, A. Brunet-Bruneau, A. Bourgeois and C. Sanchez, *Adv. Funct. Mater.*, 2004, **14**, 309–322.
- 40 J. Fan, Y. Dai, Y. Li, N. Zheng, J. Guo, X. Yan and G. D. Stucky, *J. Am. Chem. Soc.*, 2009, **131**, 15568–15569.

