

**Supporting Information**

for

**A Phenanthroline-Based Porous Organic Polymer for the Iridium-Catalyzed Hydrogenation of Carbon Dioxide to Formate**

Gunniya Hariyanandam Gunasekar, and Sungho Yoon\*

## Contents

Materials and Methods

Characterization Techniques

Synthesis of phen-POP

Synthesis of phen-POP-Ir

Representative procedure for the hydrogenation of CO<sub>2</sub> to formate

## List of Chart

Chart S1. Various modes of metal coordination in reported POPs

## List of Figures

Figure S1. SEM-EDS mapping image of phen-POP

Figure S2. PXRD of phen-POP

Figure S3. TGA of phen-POP

Figure S4. N<sub>2</sub> sorption measurement of phen-POP

Figure S5. SEM-EDS mapping image of phen-POP-Ir

Figure S6. <sup>1</sup>H NMR spectrum of the solution

Figure S7. Gas chromatography results

## List of Tables

Table S1. Catalytic activity of reported heterogeneous catalysts

Table S2. Elemental analysis of phen-POP

Table S3. Atomic composition of catalyst phen-POP-Ir by SEM-EDS

## Materials and Methods

All chemicals purchased were of analytical grade and used without further purification unless otherwise mentioned. Aluminum chloride, anhydrous dichloromethane and methanol, and triethylamine were purchased from Sigma Aldrich. Iridium chloride and 4,7-diphenyl-1,10-phenanthroline were purchased from T.C.I. chemicals and Alfa Aesar, respectively. CO<sub>2</sub> (99.99%) and H<sub>2</sub> (99.99%) were purchased from Sinyang gas industries.

## Characterization Techniques

SEM and EDS measurements were carried out using INSPECT F JEOL LTD (JAPAN) JEM-7610F operated at an accelerating voltage of 20.0 kV. FT-IR measurements were performed on a Nicolet iS 50 (Thermo Fisher Scientific). Elemental analysis was carried out on a vario MICRO Cube instrument. Powder X-ray diffraction (PXRD) was measured on a RIGAKU D/Max 2500V using Cu (40 kV, 30 mA) radiation. Thermogravimetric analysis (TGA) was performed on Q600 analyzer (TA Instrument, US) with a heating rate of 10 °C per minute up to 900 °C under nitrogen atmosphere. N<sub>2</sub> adsorption–desorption measurements were carried out in an automated gas sorption system (Belsorp II mini, BEL Japan, Inc.,) at 77 K; the samples were degassed at 120 °C for 12 h before the measurements. ATR-IR measurements were carried out on a Nicolet iS 50 (Thermo Fisher Scientific) instrument. <sup>13</sup>C cross-polarization magic-angle spinning solid-state nuclear magnetic resonance spectroscopy (<sup>13</sup>C CPMAS ssNMR) data were acquired at ambient temperature on 400 MHz Solid state NMR spectrometer (AVANCE III HD, Bruker, Germany) at KBSI Western Seoul center with an external magnetic field of 9.4 T. The operating frequency was 100.66 MHz for <sup>13</sup>C and the spectra were referenced to TMS. The samples were contained in HX CPMAS probe, with 4 mm

o.d. Zirconia rotor. Iridium content in phen-POP-Ir was analyzed by ICP-OES (iCAP-Q, Thermo fisher scientific) using microwave assisted acid digestion system (MARS6, CEM/U.S.A): phen-POP-Ir (20.0 mg) were digested in a mixture conc.  $\text{HNO}_3$  (5.0 mL) and conc.  $\text{HCl}$  (3.0 mL) solution under microwave rays at 280 °C for 20 min (ramp rate = 25 °C/min). XPS data's were recorded on an ESCA 2000 (VG microtech) at a pressure of  $\sim 3 \times 10^{-9}$  mbar using Al-Ka as the excitation source ( $h\nu=1486.6$  eV) with concentric hemispherical analyzer. High performance liquid chromatography (HPLC) was measured on Waters Alliance 2695 (Waters Corporation) system equipped with an Aminex HPX-87H column and an RI detector at 50 °C using 5.00 mM  $\text{H}_2\text{SO}_4$  solution (0.6 mL/min). Gas chromatography was measured on Younglin instrument, Korea, equipped with a FID-TCD detector and a column of Mol Sieve 13X, using  $\text{N}_2$  as a carrier gas (15 mL/min).

### **Synthesis of phen-POP**

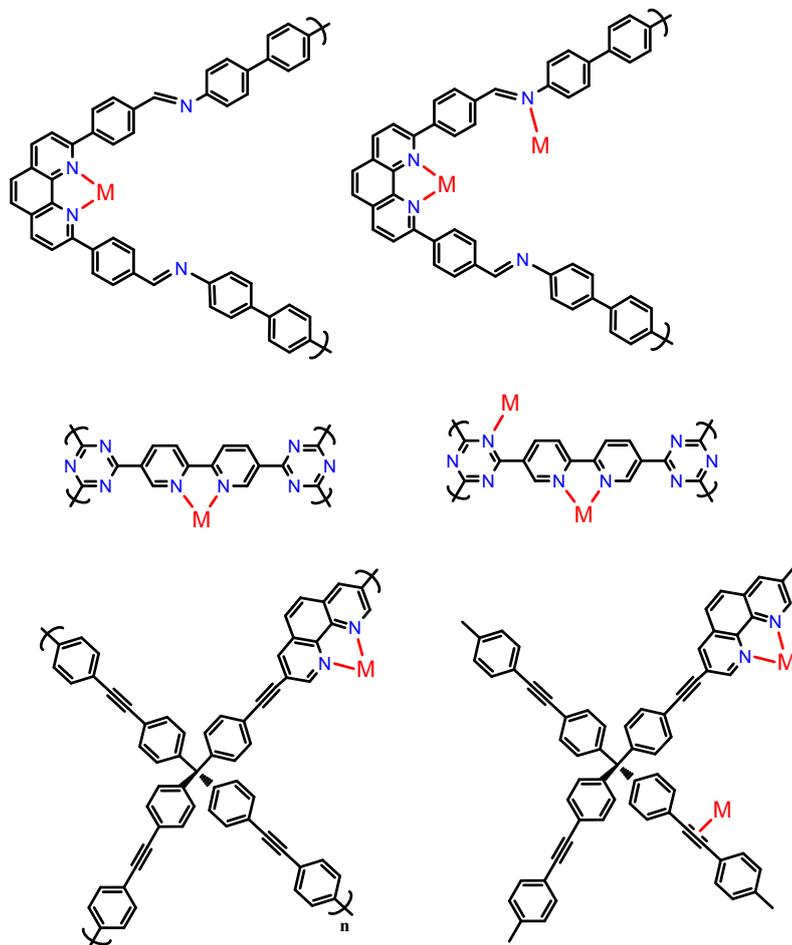
In an oven-dried RBF equipped with a condenser, 4,7-diphenyl-1,10-phenanthroline (500 mg, 1.50 mmol) was added under  $\text{N}_2$  atmosphere. The RBF was cooled to 0 °C and 15.0 mL of dichloromethane was added to obtain light yellow clear solution. After 5 minutes of stirring,  $\text{AlCl}_3$  (3.20 g, 24.06 mmol) was added and stirred at this temperature for 4 h. Heated the mixture and stirred at 30 °C for 8 h, 40 °C for 12 g, 60 °C for 12 h and 80 °C for 24 h. Cooled the dark brown reaction mixture to room temperature and added 2:1 of  $\text{HCl}:\text{H}_2\text{O}$  mixture and stirred for 30 min, and filtered and washed with water (100 mL) and ethanol (100 mL). The solid was then refluxed in 1:2  $\text{HCl}:\text{H}_2\text{O}$  mixture and soxhlet extracted with ethanol for 24 h and dried at 120 °C under vacuum for 24 h to obtain dark brown solid of phen-POP. (Yield, 120 %)

### **Synthesis of IrCl<sub>3</sub>-phen-POP**

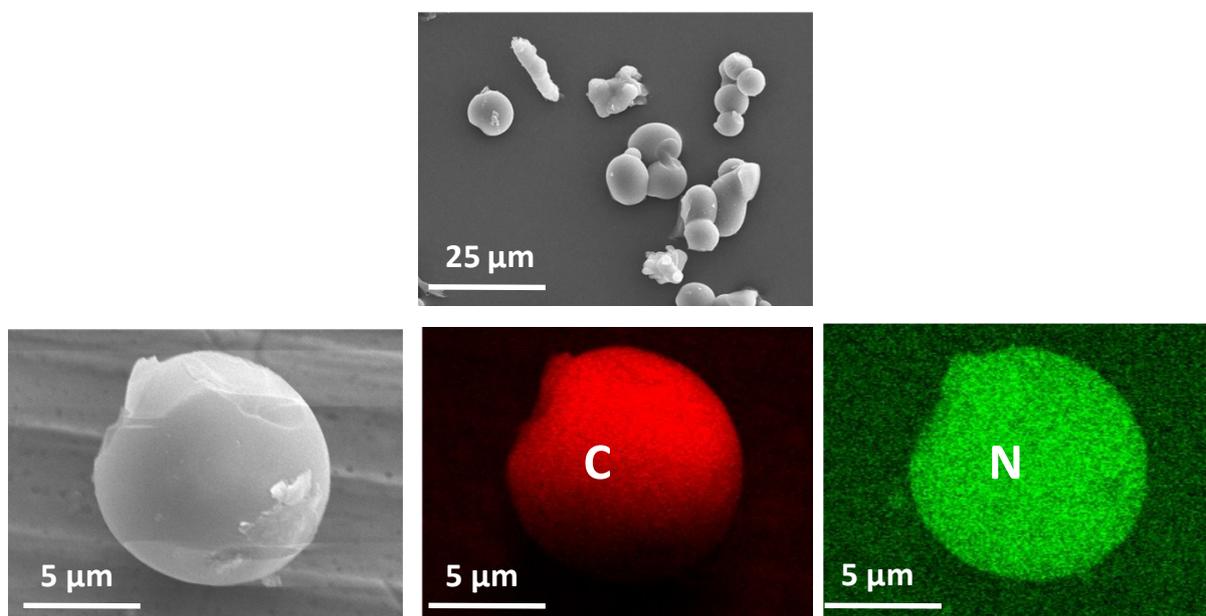
To a suspension of phen-POP (500.0 mg) in methanol (100 mL, anhydrous), iridium (III) chloride (23.0 mg) dissolved in methanol (50 mL) was added and gently heated at 60 °C under N<sub>2</sub> atmosphere for 12 h. The dark solid was filtered at room temperature, washed with methanol (3 x 200 mL), water (3 x 100 mL) and acetone (3 x 100 mL). Finally, the powder was dried at 80 °C under vacuum for 18 h.

### **Representative procedure for the hydrogenation of CO<sub>2</sub> to formate**

The hydrogenation was performed in a stainless steel reactor (Volume = 100 mL, homemade). In a typical run, the phen-POP-Ir ([Ir] = 0.054 mM) was dispersed in an aqueous solution with Et<sub>3</sub>N (1 M) in the reactor vessel. The reactor was tightly closed without any leak and purged with CO<sub>2</sub> for 5-10 min. Then, the reactor was initially pressurized with CO<sub>2</sub> and then with H<sub>2</sub> (1:1) to the desired pressure at room temperature and heated at 80-140 °C. The reaction was cooled to room temperature after appropriate time and slowly released the pressure. The concentration of formate was analyzed by HPLC. In the recycling experiments, the catalyst was recovered after each cycle by filtration, washed with water and acetone, and dried under vacuum before next run. By following the similar procedure, the solid was then used for the successive runs.

**Chart 1.** Various modes of Metal coordination in reported POPs

**Figure S1.** SEM-EDS mapping image of phen-POP



**Figure S2.** PXRD of phen-POP

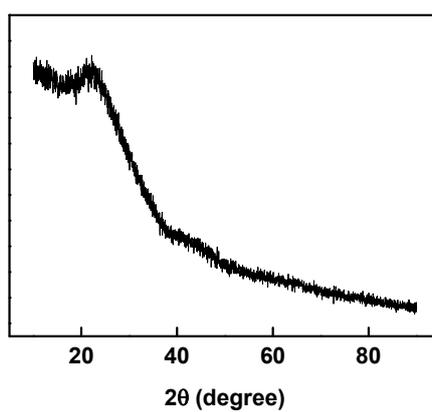
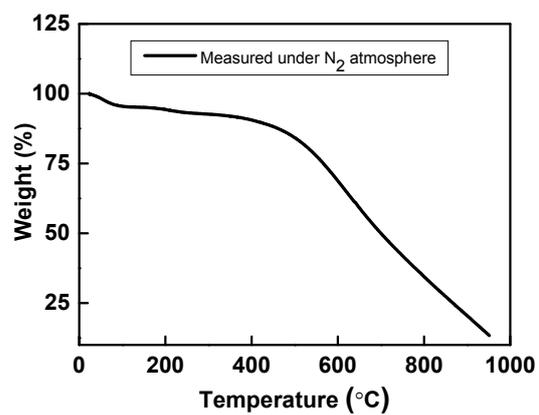
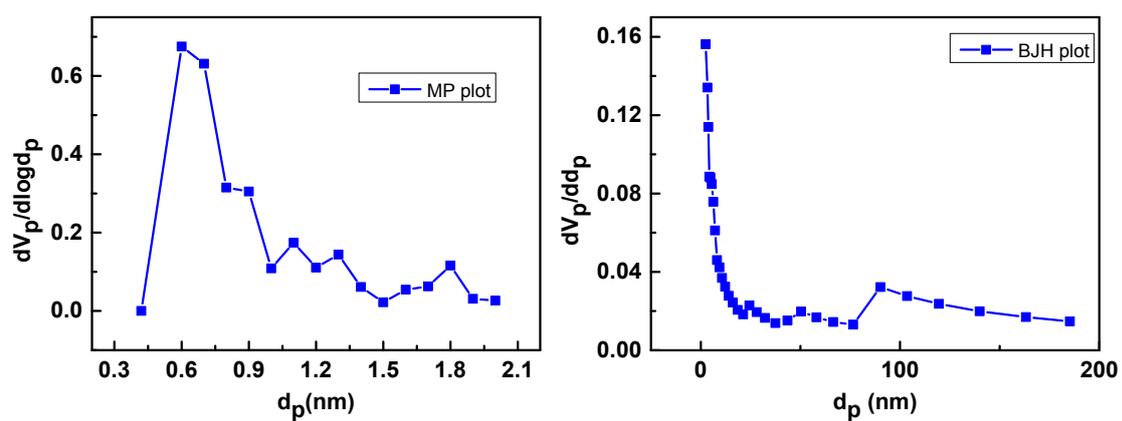
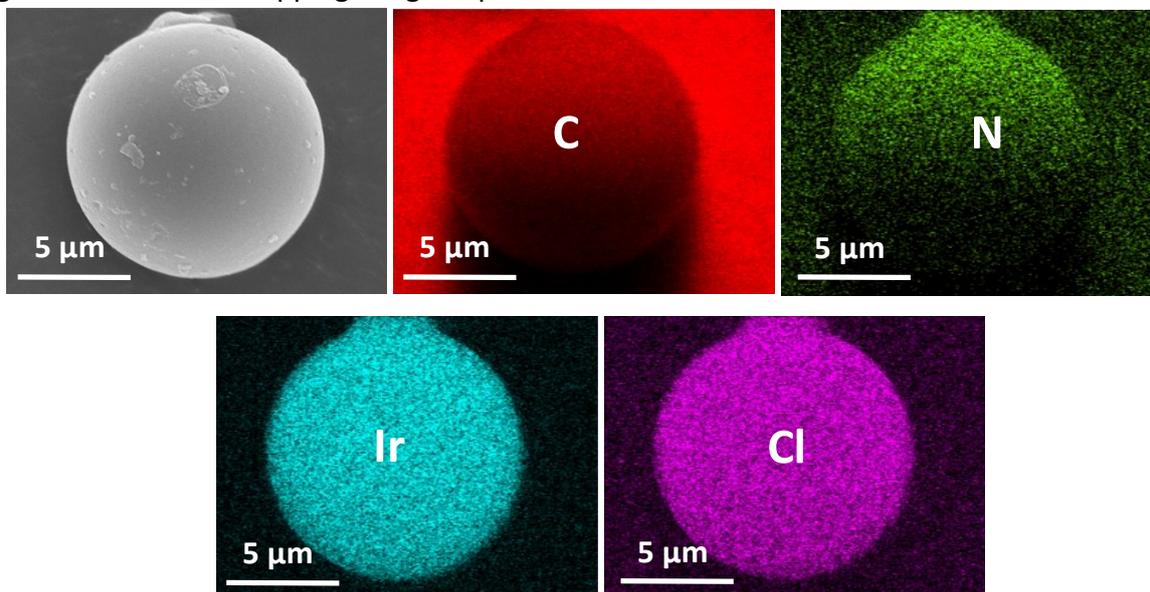
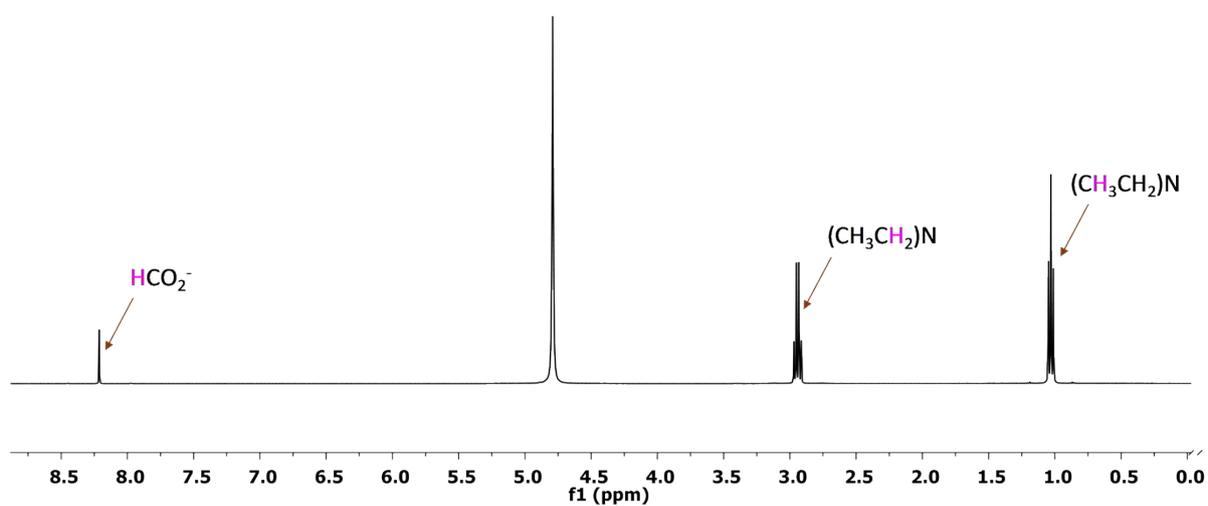
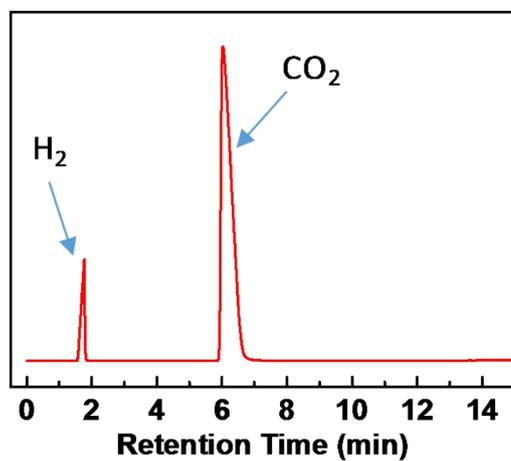


Figure S3. TGA of phen-POP

Figure S4. N<sub>2</sub> sorption measurement of phen-POP

**Figure S5.** SEM-EDS mapping image of phen-POP-Ir**Figure S6.**  $^1\text{H}$  NMR spectrum of the solution

**Figure S7.** Gas chromatography results

Gas	Retention Time (min)
H <sub>2</sub>	1.58
CH <sub>4</sub>	3.83
CO	4.44
CO <sub>2</sub>	6.44

**Table S1.** Catalytic activity of most important reported heterogeneous catalysts

Catalyst	T (°C)	P (MPa)	TON	TOF (h <sup>-1</sup> )	Ref.
<b>Au-based catalysts</b>					
AUROLite®	40	18	855	16.4	1
Au NP/Al <sub>2</sub> O <sub>3</sub>	70	40	215	11	2
Au NP/TiO <sub>2</sub>	70	40	111	5.5	2
Au NP/ZnO	70	40	2	<1	2
Au NP/CeO <sub>2</sub>	70	40	8	<1	2
Au NP/MgAl-HT	70	40	91	4.5	2
Au NP/MgCr-HT	70	40	52	2.6	2
Au NP/CuCr <sub>2</sub> O <sub>4</sub>	70	40	6	<1	2
Au@schiff base	90	8	14470	352	3
<b>Pd-based catalysts</b>					
Pd black	25	0.1	2.1	<1	4
Pd/BaSO <sub>4</sub>	25	0.1	19	<1	4
Pd/γ-Al <sub>2</sub> O <sub>3</sub>	25	0.1	50	<1	4
Pd/AC	20	2.75	1769	118	5
Pd/AC	20	5.52	1672	836	5
Pd/Al <sub>2</sub> O <sub>3</sub>	20	2.75	278	278	5
Pd/CaCO <sub>3</sub>	20	2.75	20	20	5
Pd/BaSO <sub>4</sub>	20	2.75	212	212	5
Pd/AC	20	2.75	845	105	6
Pd/r-GO (1 wt%)	100	4	7088	221	7
PdNi/CNT-GR	40	5	6.4	<1	8
Pd-NP/g-C <sub>3</sub> N <sub>4</sub>	150	4	106	4.4	9
Pd/C	40	8	594	25	10

Catalyst	T (°C)	P (MPa)	TON	TOF (h <sup>-1</sup> )	Ref.
<b>Ru-based Catalysts</b>					
Ru/MgO	80	13.5	0	-	11
Ru/AC	80	13.5	10	10	11
Ru/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	80	13.5	91	91	11
Ru/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> (n)	80	13.5	731	731	12
Silica-supported Ru-phosphine complex	80	16	1384	1384	13
[bpy-CTF-Ru(acac) <sub>2</sub> ] <sup>+</sup>	120	8	21200	22700	14
[bpy-CTF-RuCl <sub>3</sub> ]	120	8	20000	38800	15
Ru/LDH	100	2	698	-	16
Ru NP/TiO <sub>2</sub>	80	4	23500	4690	17
Metallic Ru	150	13	6351	635	18
Ru/hydrotalcite	80	30	1886	317	19
Ru-CNC-SBA	85	40	18000	750	20
Ru@CTF-b	120	100	~700	175	21
Ru@pDPPE	120	100	13170	3292	21
Ru-PPh <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub>	80	18	591	591	22
Ru-NHC-MOF	120	8	3803	1900	23
RuCl <sub>3</sub> /Troger's base	60	12	2254	94	24
<b>Bimetallic catalysts</b>					
Pd-Au/AC	60	5	5820	5820	25
PdAg	100	2	2496	104	26
PdAu/PDA-rGO	80	5	52	2	27
PdAg/amine-MSC	100	2	859	36	28
RuFe	60	3	400	23.5	29
PdAg/SBA-15	100	2	874	36	30

**Table S2.** Elemental analysis of phen-POP

Sample	C	H	N	C/N
phen- monomer	86.15	4.89	8.54	10.08
phen-POP	70.32	3.57	6.00	11.72

**Table S3.** Atomic composition of phen-POP-Ir by SEM-EDS analysis

C	N	Cl	Ir
74.96	14.12	4.23	1.31

## References

- 1 D. Preti, C. Resta, S. Squarzialupi and G. Fachinetti, *Angew. Chem. Int. Ed.*, 2011, **50**, 12551-12554.
- 2 G. A. Filonenko, W. L. Vrijburg, E. J. M. Hensen and E. A. Pidko, *J. Catal.*, 2016, **343**, 97-105.
- 3 Q. Liu, X. Yang, L. Li, S. Miao, Y. Li, Y. Li, X. Wang, Y. Huang and T. Zhang, *Nat. Commun.*, 2017, **8**, 1407.
- 4 C. J. Stalder, S. Chao, D. P. Summers and M. S. Wrighton, *J. Am. Chem. Soc.*, 1983, **105**, 6318-6320.
- 5 J. Su, L. Yang, M. Lu and H. Lin, *ChemSusChem*, 2015, **8**, 813-816.
- 6 J. Su, M. Lu and H. Lin, *Green Chem.*, 2015, **17**, 2769-2773.
- 7 Q.-Y. Bi, J.-D. Lin, Y.-M. Liu, D.-L. Du, J.-Q. Wang, H.-Y. He and Y. Cao, *Angew. Chem. Int. Ed.*, 2014, **53**, 13583-13587.

- 8 L. T. M. Nguyen, H. Park, M. Banu, J. Y. Kim, D. H. Youn, G. Magesh, W. Y. Kim and J. S. Lee, *RSC Adv.*, 2015, **5**, 105560-105566.
- 9 J. H. Lee, J. Ryu, J. Y. Kim, S. W. Nam, J. H. Han, T. H. Lim, S. Gautam, K. H. C. Chae and W. Yoon, *J. Mater. Chem. A*, 2014, **2**, 9490-9495.
- 10 Y. Wu, Y. Zhao, H. Wang, B. Yu, X. Yu, H. Zhang and Z. Liu, *Ind. Eng. Chem. Res.*, 2019, **58**, 6333-6339.
- 11 C. Y. Hao, S. P. Wang, M. S. Li, L. Q. Kang and X. Ma, *Catal. Today*, 2011, **160**, 184-190.
- 12 N. Liu, R. Du and W. Li, *Adv. Mater. Res.*, 2013, **821-822**, 1330-1335.
- 13 Y. Zhang, J. Fei, Y. Yu and X. Zheng, *Catal. Commun.*, 2004, **5**, 643-646.
- 14 G. H. Gunasekar, J. Shin, K.-D. Jung, K. Park and S. Yoon, *ACS Catal.*, 2018, **8**, 4346-4353.
- 15 G. H. Gunasekar, K.-D. Jung and S. Yoon, *Inorg. Chem.*, 2019, **58**, 3717-3723.
- 16 K. Mori, T. Taga and H. Yamashita, *ACS Catal.*, 2017, **7**, 3147-3151.
- 17 P. R. Upadhyay and V. Srivastava, *RSC Adv.*, 2016, **6**, 42297-42306.
- 18 T. Umegaki, Y. Enomoto and Y. Kojima, *Catal. Sci. Technol.*, 2016, **6**, 409-412.
- 19 T. Srivastava, *Open Chem.*, 2018, **16**, 853-863.
- 20 H.-K. Lo and C. Coperet, *ChemCatChem*, **11**, 430-434.
- 21 A. Kann, H. Hartmann, A. Besmehn, P. J. C. Hausoul and R. Palkovits, *ChemSusChem*, 2018, **11**, 1857-1865.
- 22 W. Zhang, S. Wang, Y. Zhao and X. Ma, *Fuel Processing Technology*, 2018, **178**, 98-103.
- 23 C. Wu, F. Irshad, M. Luo, Y. Zhao, X. Ma and S. Wang, *ChemCatChem*, **11**, 1256-1263.
- 24 Z.-Z. Yang, H. Zhang, B. Yu, Y. Zhao, G. Ji and Z. Liu, *Chem. Commun.*, 2015, **51**, 1271-1274.
- 25 K. Nakajima, M. Tominaga, M. Waseda, H. Miura and T. Shishido, *ACS Sustainable Chem. Eng.*, 2019, **7**, 6522-6530.
- 26 K. Mori, T. Sano, H. Kobayashi and H. Yamashita, *J. Am. Chem. Soc.*, 2018, **140**, 8902-8909.
- 27 H. Zhong, M. Iguchi, M. Chatterjee, T. Ishizaka, M. Kitta, Q. Xu and H. Kawanami, *ACS Catal.*, 2018, **8**, 6, 5355-5362.
- 28 S. Masuda, K. Mori, Y. Futamura and H. Kawanami, *ACS Catal.*, 2018, **8**, 2277-2285.
- 29 M. I. Qadir, A. Weilhard, J. A. Fernandes, I. Pedro, B. J. C. Vieira, Josa. C. Warenborgh and J. Dupont, *ACS Catal.*, 2018, **8**, 1621-1627.
- 30 K. Mori, S. Masuda, H. Tanaka, K. Yoshizawa, M. Che and H. Kawanami, *Chem. Commun.*, 2017, **53**, 4677-4680.