Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information for:

Multimetallic Catalysts of RuO_2-CuO-Cs_2O-TiO_2/SiO_2 for Direct Gas-Phase Epoxidation of Propylene to Propylene Oxide

T. Chukeaw, A. Seubsai,* P. Phon-in, K. Charoen, T. Witoon, W. Donphai, P. Parpainainar, M. Chareonpanich, D. Noon, B. Zohour and S. Senkan

Table S1 Detailed experiments for the Box–Behnken designs of experiment

Std.	Factor				Response		
	A: Temperature reactions (°C)	B: O_2/C_3H_6 (ratio)	C: $(O_2+C_3H_6)/He$ (ratio)	D: Total flow rate (cc/min)	PO selectivity (%)	C_3H_6 conversion (%)	PO formation rate (g_{PO} h^{-1} kg_{cat}^{-1})
1	190	0.7	0.05	50	31.6	0.2	43
2	310	0.7	0.05	50	8.4	9.0	464
3	190	6.7	0.30	50	35.1	0.7	89
4	310	6.7	0.30	50	10.0	33.5	1876
5	250	11.0	0.14	30	21.5	18.6	1572
6	250	2.2	0.19	30	11.7	29.1	3288
7	250	11.0	0.14	70	15.3	30.8	1753
8	250	2.2	0.19	70	9.4	32.7	2895
9	190	3.7	0.16	30	31.9	0.4	89
10	310	3.7	0.16	30	9.3	40.4	2209
11	190	3.7	0.16	70	35.6	0.2	49
12	310	3.7	0.16	70	7.4	43.8	1862
13	250	2.0	0.03	50	26.9	8.3	817
14	250	20.0	0.27	50	12.3	53.9	3050
15	250	0.4	0.08	50	17.2	5.1	796
16	250	4.0	0.33	50	34.8	7.7	2514
17	190	11.0	0.14	50	34.1	0.7	89
18	310	11.0	0.14	50	14.6	51.2	2190
19	190	2.2	0.19	50	34.5	0.3	128
20	310	2.2	0.19	50	8.4	63.6	1767
21	250	0.7	0.05	30	18.6	7.1	866
22	250	6.7	0.30	30	28.5	13.1	2265
23	250	0.7	0.05	70	18.0	5.9	668
24	250	6.7	0.30	70	20.0	16.9	1908
25	250	3.7	0.16	50	9.4	39.0	2433
26	250	3.7	0.16	50	11.6	32.2	2479
27	250	3.7	0.16	50	9.7	37.9	2435
28	250	3.7	0.16	50	10.8	34.1	2441
29	250	3.7	0.16	50	10.2	35.5	2408

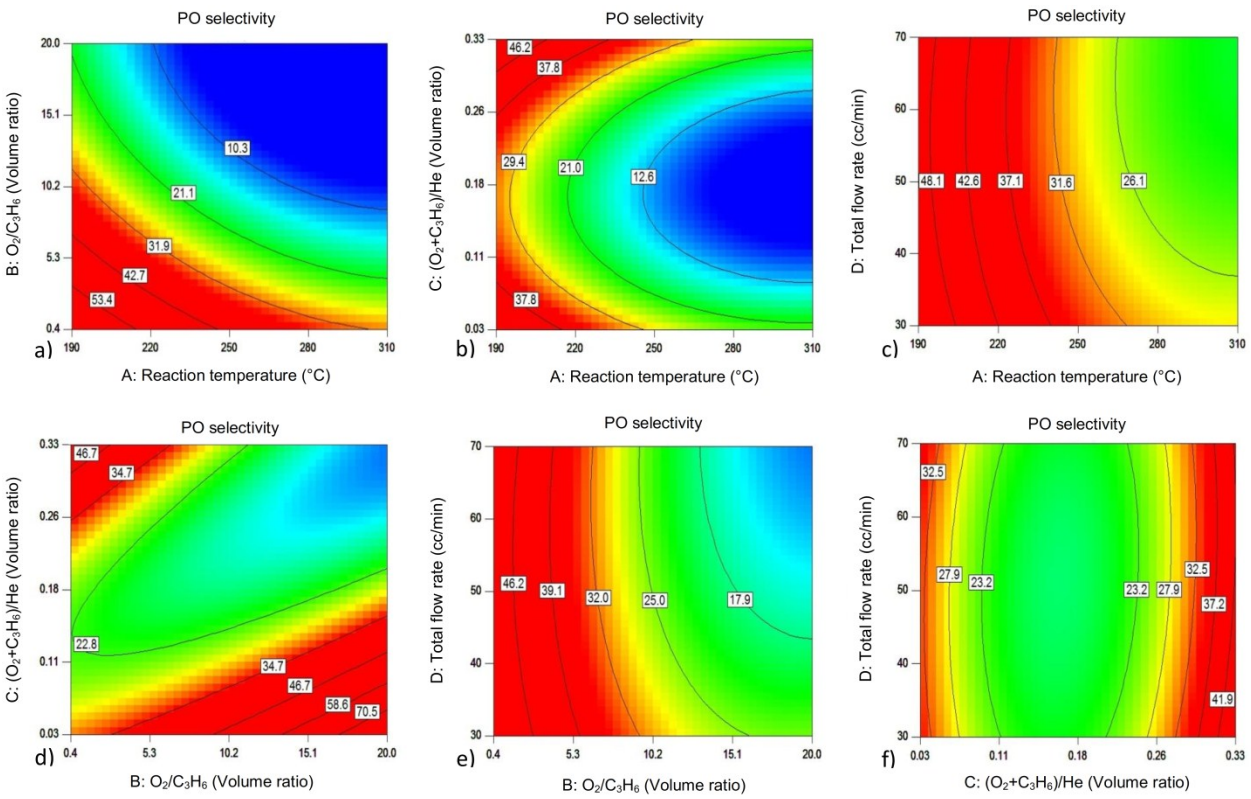


Fig. S1 a) – f) Contour plots showing % PO selectivity from all combinations of 4 parameters; a) A *vs* B, b) A *vs* C, c) A *vs* D, d) B *vs* C, e) B *vs* D, f) C *vs* D; where A = Reaction temperature (190–310 °C), B = O_2/C_3H_6 ratio (0.4–20), C = $(O_2+C_3H_6)$/He ratio (0.03–0.33), and D = total feed gas flow rate (30–70 cc/min by using He as balance gas)]. When two parameters were studied, A, B, C and/or D were fixed at 219 °C, 4.1, 0.32, and/or 70 cc/min, respectively.

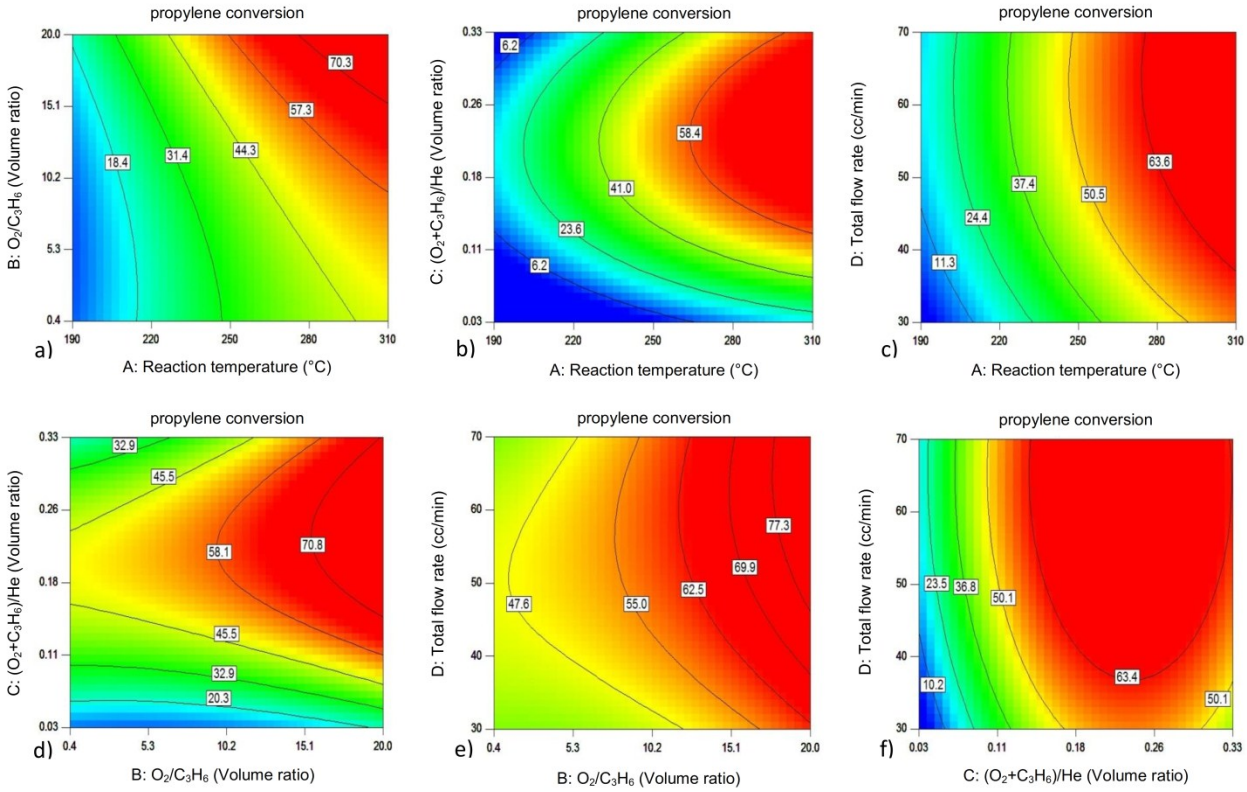


Fig. S2 Contour plots showing % propylene conversion from all combinations of 4 parameters; a) A *vs* B, b) A *vs* C, c) A *vs* D, d) B *vs* C, e) B *vs* D, f) C *vs* D; where A = Reaction temperature (190–310 °C), B = O_2/C_3H_6 ratio (0.4–20), C = $(O_2+C_3H_6)/He$ ratio (0.03–0.33), and D = total feed gas flow rate (30–70 cc/min by using He as balance gas)]. When two parameters were studied, A, B, C and/or D were fixed at 310 °C, 17.4, 0.23, and/or 57 cc/min, respectively.

Table S2 Predicted and experimental values of optimal PO selectivity and PO formation rate obtained from the Box–Behnken designs of experiment.

Optimization	Temperature (°C)	O_2/C_3H_6 (ratio)	$(O_2+C_3H_6)/He$ (ratio)	Total flow rate (cc/min)	PO selectivity (%)		C_3H_6 conversion (%)		PO formation rate ($g_{PO}\ h^{-1}\ kg_{cat}^{-1}$)	
					Predict	Test	Predict	Test	Predict	Test
PO Selectivity	219	4.1	0.32	70	37.3	38.4	-	1.3	-	573
PO formation rate	272	3.1	0.26	34	-	7.1	-	40.1	2973	3015

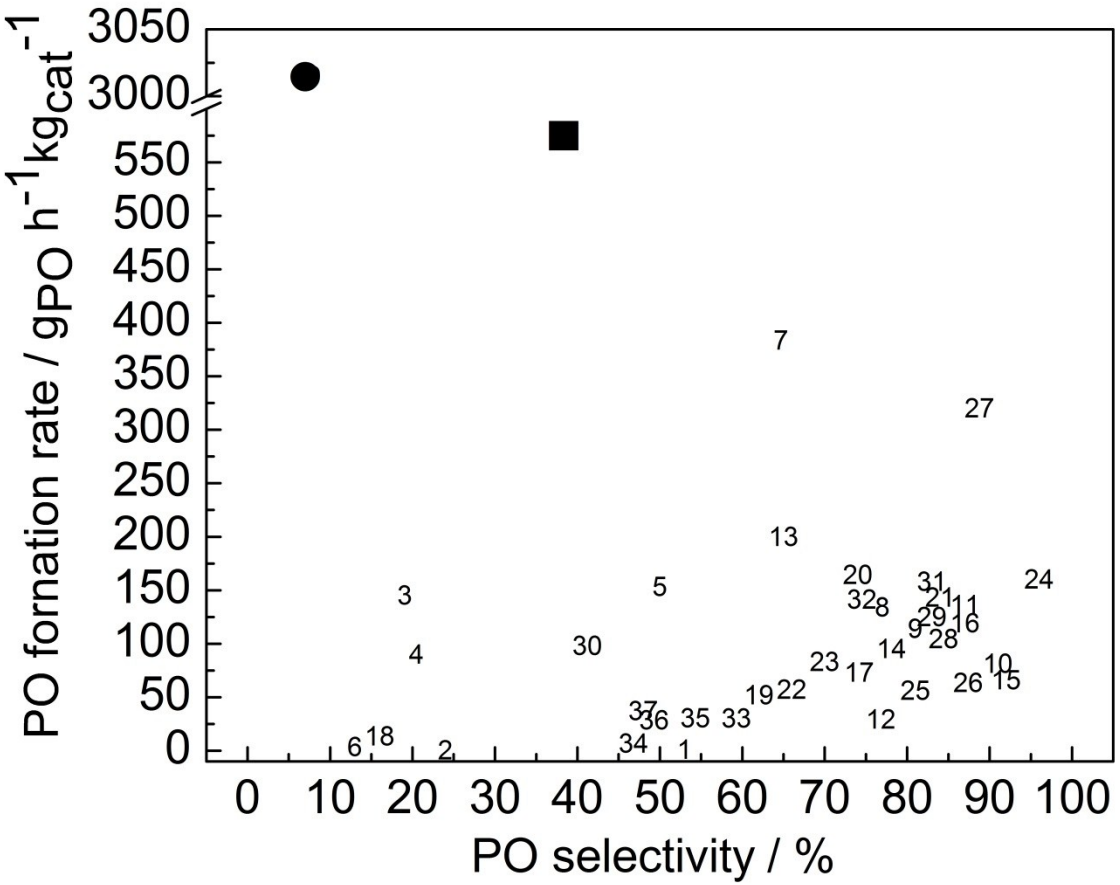


Fig. S3 PO formation *vs* PO selectivity of various catalysts for the direct gas-phase epoxidation of propylene to PO reported in literature from 2005 – present.

Table S3 Catalysts reported in literature for catalysts the direct gas-phase epoxidation of propylene to PO reported in literature from 2005 – present.

No.	Catalyst	Reactions	Temperature (°C)	Pressure (atm)	C_3H_6 conversion (%)	PO selectivity (%)	PO formation rate (g_{PO} h^{-1} kg_{cat}^{-1})	Ref.
1	Cu/SiO_2	Epoxidation	225	1	0.3	53.0	1	[1]
2	K^+–Cu/SBA–15	Epoxidation	350	1	2.2	24.0	1	[2]
3	(KAc)–Cu/SiO_2	Epoxidation	325	1	0.3	19.1	145	[3]
4	K–Cu/m–SiO_2	Epoxidation	350	1	2.9	20.5	90	[4]
5	RuO_2–CuO–$NaCl/SiO_2$	Epoxidation	270	1	20.0	50.0	153	[5]
6	d–Cu_2O	Epoxidation	250	1	0.8	13.0	3	[6]
7	Ti–MoO_3–Bi_2SiO_5/SiO_2	Epoxidation	400	1.4	20.5	64.7	383	[7]
8	Au/TS–1	Hydroperoxide	200	1	10.0	76.0	134	[8]
9	Au/TS–1(36)	Hydroperoxide	200	n/a	8.8	81.0	116	[9]
10	Au-–$Ba(NO_2)_3/Ti–SiO_2$	Hydroperoxide	150	1	8.5	91.0	81	[10]
11	0.33Au/PCTS–1(28)	Hydroperoxide	200	n/a	9.7	87.0	132	[11]
12	Au–Ba/Ti–TUD	Hydroperoxide	150	1	2.1	76.8	29	[12]
13	Au/TS–1	Hydroperoxide	212	n/a	16.0	65.0	200	[13]
14	0.09Au/TS–1(170)	Hydroperoxide	200	1	6.7	78.1	95	[14]
15	0.14Au/0.04Ge–TS–1(100)	Hydroperoxide	170	1	4.0	91.0	66	[15]
16	Au/TS–1(48) –Na1	Hydroperoxide	200	n/a	7.4	85.0	119	[16]
17	$Ba(NO_2)_3$–Au/Ti–MCM–41	Hydroperoxide	150	n/a	5.4	74.2	73	[17]
18	VO_x–Cu	Hydroperoxide	230	1	2.7	16.0	13	[18]

19	Au–Ti(0.05) –M	Hydroperoxide	150	1	2.2	62.0	52	[19]
20	Au/TS–1(35)	Hydroperoxide	300	1	14.6	74.0	164	[20]
21	0.2Au/TS–1–Na	Hydroperoxide	200	n/a	8.3	84.0	127	[21]
22	Au–00	Hydroperoxide	200	1	4.8	66.0	57	[22]
23	Au/TS–1_{35}/Si/1.0%	Hydroperoxide	300	1	12.6	70.0	83	[23]
24	0.081Au/TS–1(127)	Hydroperoxide	200	1	5.1	96.0	160	[24]
25	0.57Au/0.4In–TS–1	Hydroperoxide	170	1	3.8	81.0	56	[25]
26	0.05–Au/Ti–SiO_2–1L	Hydroperoxide	200	1	2.7	89.4	63	[26]
27	0.16Au/TS–1(121)Cs	Hydroperoxide	200	1	11.4	88.8	320	[27]
28	0.08Au/NTS–1–10	Hydroperoxide	150	1	6.8	84.4	105	[28]
29	Au/TS–1	Hydroperoxide	200	1	n/a	83.0	125	[29]
30	0.04Au/U–TS–1(119)	Hydroperoxide	200	1	3.2	41.2	98	[30]
31	0.13 wt% Au/TS–1–B(40)	Hydroperoxide	200	1	n/a	83.0	158	[31]
32	0.5Au/TS–1–15 g/L	Hydroperoxide	300	1	11.5	74.5	141	[32]
33	4.5Au/A–TiYNU–1	Hydroperoxide	225	1	3.3	59.3	30	[33]
34	V–Ti/MCM–41	Photo reaction	50	1	24.4	46.8	7	[34]
35	Au/TS–1	Photo reaction	50	1	56.1	54.3	30	[35]
36	V–Ti/MCM–41	Photo reaction	50	1	n/a	49.3	29	[36]
37	$V_{0.2}Ti_{0.3}$/MCM–41	Photo reaction	50	1	0.2	48.0	37	[37]
■	RuO_2-CuO-Cs_2O-TiO_2/SiO_2	Epoxidation	219	1	1.3	38.4	573	This work
●	RuO_2-CuO-Cs_2O-TiO_2/SiO_2	Epoxidation	273	1	40.1	7.1	3015	This work

* n/a = not available

Table S4 Multiple test runs of the optimal RuO_2-CuO-Cs_2O-TiO_2/SiO_2 catalyst with (w/) and without (w/o) treating with fumed HCl under the optimal operating condition for PO formation rate.

Run no.	PO selectivity (%)		AC selectivity (%)		C_3H_6 conversion (%)		PO formation rate (g_{PO} h^{-1} kg_{cat}^{-1})	
	W/O	W/	W/O	W/	W/O	W/	W/O	W/
1	7.1	-	0.5	-	40.1	-	3015	-
2	10.5	7.6	0.8	0.7	18.8	34.9	2202	3010
3	15.0	7.7	1.2	0.5	6.9	34.1	1156	2997
4	12.5	7.7	1.2	0.7	6.7	34.0	935	2984
5	11.7	7.5	1.4	0.3	5.6	34.7	732	2965
6	10.8	8.0	1.4	0.3	5.8	32.5	696	2971

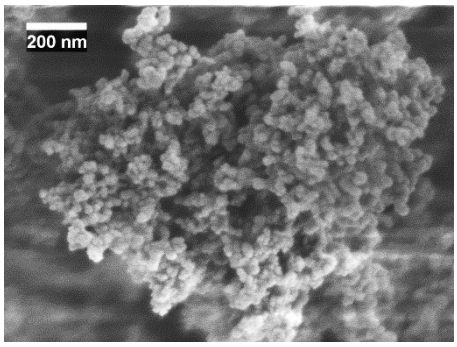
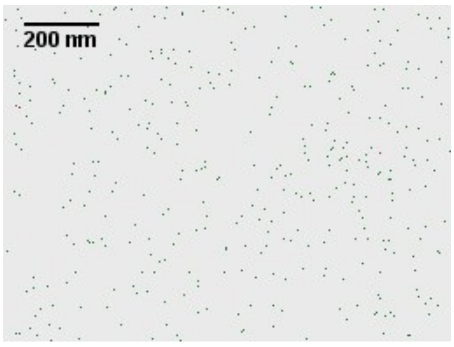
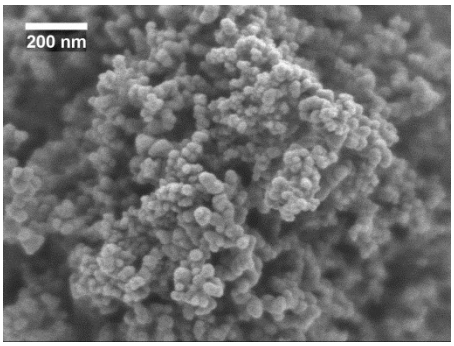
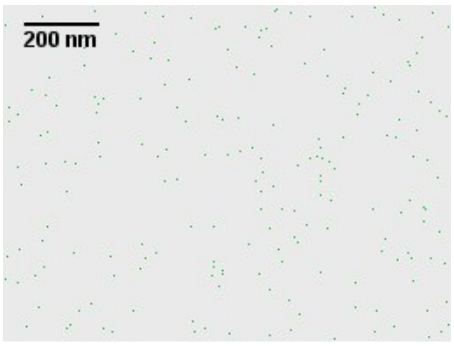
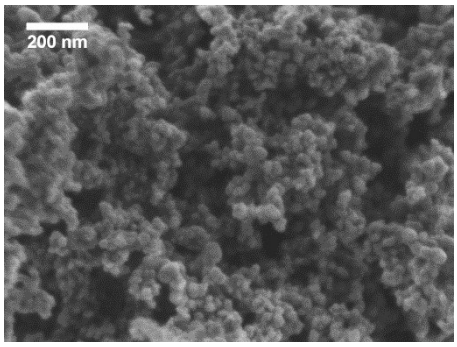
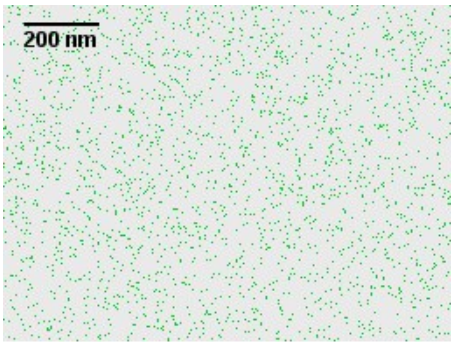
Catalyst	SEM	Cl
Fresh		
After 6 runs		
Treated by fumed HCl		

Fig. S4 SEM-EDS showing Cl of the optimal RuO_2-CuO-Cs_2O-TiO_2/SiO_2 catalyst; fresh catalyst, after 6 runs of testing, and after treated by fumed HCl.

References:

1 O. P. H. Vaughan, G. Kyriakou, N. Macleod, M. Tikhov and R. M. Lambert, *Journal of Catalysis*, 2005, **236**, 401-404.
2 H. Chu, L. Yang, Q. H. Zhang and Y. Wang, *Journal of Catalysis*, 2006, **241**, 225-228.
3 W. G. Su, S. G. Wang, P. L. Ying, Z. C. Feng and C. Li, *Journal of Catalysis*, 2009, **268**, 165-174.
4 D. Duzenli, E. Seker, S. Senkan and I. Onal, *Catalysis Letters*, 2012, **142**, 1234-1243.
5 A. Seubsai, B. Zohour, D. Noon and S. Senkan, *ChemCatChem*, 2014, **6**, 1215-1219.
6 Q. Hua, T. Cao, X. K. Gu, J. Lu, Z. Jiang, X. Pan, L. Luo, W.-X. Li and W. Huang, *Angewandte Chemie International Edition*, 2014, **53**, 4856-4861.
7 Y. Lei, X. Chen, C. Xu, Z. Dai and K. Wei, *Journal of Catalysis*, 2015, **321**, 100-112.
8 L. Cumaranatunge and W. N. Delgass, *Journal of Catalysis*, 2005, **232**, 38-42.
9 B. Taylor, J. Lauterbach and W. N. Delgass, *Applied Catalysis A: General*, 2005, **291**, 188-198.
10 B. Chowdhitry, J. J. Bravo-Suarez, M. Date, S. Tsubota and M. Haruta, *Angewandte Chemie-International Edition*, 2006, **45**, 412-415.
11 B. Taylor, J. Lauterbach and W. N. Delgass, *Catalysis Toda*y, 2007, **123**, 50-58.
12 J. Lu, X. Zhang, J. J. Bravo-Suárez, K. K. Bando, T. Fujitani and S. T. Oyama, *Journal of Catalysis*, 2007, **250**, 350-359.
13 S. T. Oyama, X. Zhang, J. Lu, Y. Gu and T. Fujitani, *Journal of Catalysis*, 2008, **257**, 1-4.
14 J. Q. Lu, X. M. Zhang, J. J. Bravo-Suarez, T. Fujitani and S. T. Oyama, *Catalysis Today*, 2009, **147**, 186-195.
15 T. Liu, P. Hacarlioglu, S. T. Oyama, M. F. Luo, X. R. Pan and J. Q. Lu, *Journal of Catalysis*, 2009, **267**, 202-206.
16 J. H. Huang, T. Takei, T. Akita, H. Ohashi and M. Haruta, *Applied Catalysis B: Environmental*, 2010, **95**, 430-438.
17 L. Y. Wu, Y. Huan, Z. X. Ming and S. J. Shuan, *Acta Physico-Chimica Sinica*, 2010, **26**, 1585-1592.
18 L. J. Yang, J. L. He, Q. H. Zhang and Y. Wang, *Journal of Catalysis*, 2010, **276**, 76-84.
19 C. H. Liu, Y. Guan, E. J. M. Hensen, J. F. Lee and C. M. Yang, *Journal of Catalysis*, 2011, **282**, 94-102.
20 M. Du, G. Zhan, X. Yang, H. Wang, W. Lin, Y. Zhou, J. Zhu, L. Lin, J. Huang, D. Sun, L. Jia and Q. Li, *Journal of Catalysis*, 2011, **283**, 192-201.
21 J. Huang, E. Lima, T. Akita, A. Guzma¡n, C. Qi, T. Takei and M. Haruta, *Journal of Catalysis*, 2011, **278**, 8-15.
22 J. Gaudet, K. K. Bando, Z. Song, T. Fujitani, W. Zhang, D. S. Su and S. T. Oyama, *Journal of Catalysis*, 2011, **280**, 40-49.
23 G. Zhan, M. Du, J. Huang and Q. Li, *Catalysis Communications*, 2011, **12**, 830-833.
24 W. S. Lee, M. C. Akatay, E. A. Stach, F. H. Ribeiro and W. Nicholas Delgass, *Journal of Catalysis*, 2012, **287**, 178-189.
25 J. Q. Lu, N. Li, X. R. Pan, C. Zhang and M. F. Luo, *Catalysis Communications*, 2012, **28**, 179-182.
26 J. Chen, S. J. A. Halin, E. A. Pidko, M. W. G. M. Verhoeven, D. M. P. Ferrandez, E. J. M. Hensen, J. C. Schouten and T. A. Nijhuis, *ChemCatChem*, 2013, **5**, 467-478.
27 W. S. Lee, M. Cem Akatay, E. A. Stach, F. H. Ribeiro and W. Nicholas Delgass, *Journal of Catalysis*, 2013, **308**, 98-113.
28 Y. Liu, X. Zhang and J. Suo, *Chinese Journal of Catalysis*, 2013, **34**, 336-340.
29 X. Feng, X. Duan, G. Qian, X. Zhou, D. Chen and W. Yuan, *Applied Catalysis B: Environmental*, 2014, **150–151**, 396-401.
30 W. S. Lee, M. C. Akatay, E. A. Stach, F. H. Ribeiro and W. N. Delgass, *Journal of Catalysis*, 2014, **313**, 104-112.

31 X. Feng, X. Duan, J. Yang, G. Qian, X. Zhou, D. Chen and W. Yuan, *Chemical Engineering Journal*, 2015, **278**, 234-239.
32 M. Du, J. Huang, D. Sun and Q. Li, *Applied Surface Science*, 2016, **366**, 292-298.
33 F. Jin, Y. Wu, S. Liu, T. H. Lin, J. F. Lee and S. Cheng, *Catalysis Today*, 2016, **264**, 98-108.
34 V. H. Nguyen, H. Y. Chan, J. C. S. Wu and H. Bai, *Chemical Engineering Journal*, 2012, **179**, 285-294.
35 V. H. Nguyen, H. Y. Chan and J. C. S. Wu, *Journal of Chemical Sciences*, 2013, **125**, 859-867.
36 V. H. Nguyen, S. D. Lin, J. C. S. Wu and H. Bai, *Catalysis Today*, 2015, **245**, 186-191.
37 V. H. Nguyen, S. D. Lin and J. C. S. Wu, *Journal of Catalysis*, 2015, **331**, 217-227.