Advance Publication Cover Page



## Chemoselective hydrogenation of unsaturated nitro compounds to unsaturated amines by Ni-Sn alloy catalysts

Nobutaka Yamanaka, Takayoshi Hara, Nobuyuki Ichikuni, and Shogo Shimazu\*

Advance Publication on the web June 21, 2018 doi:10.1246/cl.180458

© 2018 The Chemical Society of Japan

Advance Publication is a service for online publication of manuscripts prior to releasing fully edited, printed versions. Entire manuscripts and a portion of the graphical abstract can be released on the web as soon as the submission is accepted. Note that the Chemical Society of Japan bears no responsibility for issues resulting from the use of information taken from unedited, Advance Publication manuscripts.

## Chemoselective hydrogenation of unsaturated nitro compounds to unsaturated amines by Ni-Sn alloy catalysts

Nobutaka Yamanaka, Takayoshi Hara, Nobuyuki Ichikuni, and Shogo Shimazu\*

Department of Applied Chemistry and Biotechnology, Graduate School of Engineering, Chiba University,

1-33 Yayoi, Inage, Chiba 263-8522, Japan

E-mail: shimazu@faculty.chiba-u.jp

1 Ni-Sn alloy catalysts were prepared and applied to the 2 hydrogenation of 4-nitrostyrene at 383-423 K using  $H_2$  gas 3 as the hydrogen donor. Ni<sub>3</sub>Sn<sub>2</sub> alloy showed a significantly 4 high conversion and selectivity towards 4-aminostyrene 5 (Conv. 100%, Sel. 99%). Various unsaturated nitro 6 compounds were also successfully converted into their 7 corresponding unsaturated amines.

8	Keywords:	Chemoselective	hydrogenation,
9	Unsaturated ni	tro compounds, Ni-Sn	alloy catalyst

10 The chemoselective hydrogenation from unsaturated nitro compounds to unsaturated amines is an industrially 11 important and valuable process in the production of 12 agrochemicals, pharmaceuticals, dyes, and other high-value 13 14 fine chemicals.<sup>1-3</sup> Typically, the Bechamp process, which uses a zero valent iron and acid, has been employed to 15 reduce nitro group.<sup>4</sup> This process has several drawbacks, 16 17 including a large amount of waste material (e.g., iron oxide sludge and neutralization salts) and poor atom economy as it 18 is a stoichiometric reaction. As a result, it has been regarded 19 as an environmentally harmful process.<sup>3,5-7</sup> Catalytic 20 21 hydrogenation of nitro group overcomes these 22 disadvantages. Recently, novel metals, such as Au and Ag, 23 showed notably high selectivity towards nitro group in the 24 hydrogenation of various substituted nitroarenes. accompanied by low activity because they are intrinsically 25 poor capability for  $H_2$  activation.<sup>1,8-12</sup> On the other hand, a 26 number of transition metals, such as Pt, Pd, Ru, and Ni, 27 have been reported as highly efficient metals for the hydrogenation of nitrobenzene.  $^{1,5,8,13}$  These transition metals, 28 29 however, are well known to have low selectivity towards 30 nitro group when other reducible groups are present in the substrate.<sup>14-18</sup> This low selectivity towards nitro group 31 32 prevents the practical application of these catalysts. Of these 33 metals, Ni is the most inexpensive and would be a good 34 catalytic candidate from an economic and industrial point of 35 view.<sup>15,19</sup> Therefore, the development of an environmentally 36 37 benign, cost-effective, and highly selective Ni-based 38 catalyst for the hydrogenation of various unsaturated nitro 39 compounds is highly desirable.

40 The aid of additives has been reported to enhance the selectivity towards nitro group due to poisoning/blocking the sites for undesired reactions.<sup>9,14</sup> However, the addition of 41 42 soluble metal salts, such as iron salts with Pt-Pb/CaCO3 or 43 vanadium salts with  $Pt/C-H_3PO_4$ , affects the purity of the target products.<sup>20,21</sup> Compared to the above non-bimetallic 44 45 strategy, the modification of the active sites with a metal 46 47 oxide support or a second metal is more environmentally 48 benign and efficient, which is called as strong metal support interaction (SMSI) or alloying, respectively.<sup>9,20,22,23</sup> Both 49

50 bimetallic strategies alter the electronic properties of the 51 active metals, leading to the improvement of the selectivity 52 towards nitro group. Since numerous SMSI effects have 53 been reported for the hydrogenation of nitroarenes, we focus 54 on the application of alloys. To date, Ni-Fe and Ni-B alloy 55 catalysts have been prepared and applied to the transfer hydrogenation of various substituted nitroarenes, using 56 57 sodium borohydride and hydrazine hydrate as the hydrogen donors, respectively.<sup>3,24,25</sup> 58 The reactions gave the corresponding amines with remarkably high yields and 59 60 selectivities. Although these reducing agents are commonly 61 employed in laboratories, H<sub>2</sub> gas is preferred in industry, as it is inexpensive and only produces water as a by-product. 62

Previously, we prepared Ni-Sn alloy catalysts via 63 coprecipitation method and applied them to 64 the hydrogenation of furfural to furfuryl alcohol, using H<sub>2</sub> gas 65 as the hydrogen donor.<sup>27</sup> The synergetic effect between Ni 66 and Sn enhanced the chemoselectivity of the carbonyl group 67 up to 100%. These alloy catalysts had an ordered atom 68 69 arrangement, which could be controlled by varying the 70 molar feed ratios of Ni/Sn. In our ongoing research on this catalyst, we wondered whether Ni-Sn alloy catalysts could 71 72 be applied to the hydrogenation of unsaturated nitro 73 compounds. Herein, the hydrogenation of unsaturated nitro 74 compounds was conducted under H<sub>2</sub> atmosphere over Ni-Sn 75 alloy catalysts. After optimizing the reaction conditions, a 76 wide variety of unsaturated nitro compounds were 77 investigated for the substrate scope.

Ni-Sn(*X*) alloy catalysts (X = Ni/Sn molar ratio) were prepared according to the previously reported procedure and a detailed preparatory procedure is provided in the ESI.<sup>27</sup> After the hydrothermal reaction at 423 K for 24 h, a gray powder was obtained and denoted as Ni-Sn(*X*). The subsequent H<sub>2</sub> treatment at *Y* K for 1 h yielded a black powder, which was denoted as Ni-Sn(*X*)HT-*Y*.

Powder X-ray diffractograms (XRD) were recorded on a MiniFlex 600 Rigaku incident X-ray diffractometer using CuK<sub> $\alpha$ </sub> radiation ( $\lambda = 0.15418$  nm) operated at 40 kV and 15 mA and identified against JCPDS-ICDD. The samples were scanned at a rate of  $0.02^{\circ}$  step<sup>-1</sup> over the range  $20^{\circ} \le 2\theta \le$ 90 80° (scan time = 5 s step<sup>-1</sup>).

91 The catalytic hydrogenation was conducted in a high-92 pressure autoclave with a pressure gauge, a magnetic stirrer, 93 and an oil bath. The mixture of the substrate, catalyst, 94 solvent, and internal standard material was put into a glass 95 reaction tube and stirred at room temperature for a selected 96 time. The tube was placed into the autoclave. Then, pure 97 hydrogen gas was introduced and kept at a desired pressure, 98 and the reaction system was heated to a given temperature. 99 The reaction system was purged with H<sub>2</sub> gas in order to

1 remove the air before heating up the solution. After the 2 reaction, the product was taken out of the reaction system 3 and analyzed by a gas chromatography. The products, 4 expect for nitrobenzene, were analyzed by a gas 5 chromatography (GC-8A, Shimadzu, using a flame 6 ionization detector) equipped with a flexible quartz capillary 7 column coated with Silicon OV-17. On the other hand, 8 nitrobenzene was analyzed by the same gas chromatography with Silicon OV-101. The amount of the products was 9 10 quantified based on the internal standard method using *n*dodecane as an internal standard material. 11

12 We prepared Ni-Sn(1.5) catalysts without H<sub>2</sub> treatment, with H<sub>2</sub> treatment at 623 K, 673 K, and 723 K (denoted as 13 Ni-Sn(1.5), Ni-Sn(1.5)HT623, Ni-Sn(1.5)HT673, and Ni-14 Sn(1.5)HT723, respectively). The XRD pattern of Ni-15 Sn(1.5) catalyst showed broad peaks at  $2\theta = 30.6^{\circ}$ ,  $43.2^{\circ}$ , 16 and 44.2°, which were assigned to the (101), (102), and 17 (110) lattice planes of Ni<sub>3</sub>Sn<sub>2</sub>, respectively (Fig. 1a).<sup>28</sup> After 18 19 H<sub>2</sub> treatment at 673 K, sharp Ni<sub>3</sub>Sn<sub>2</sub> alloy peaks were





21 **Figure 1**. XRD patterns of Ni-Sn(*1.5*) catalysts (a) without 22 H<sub>2</sub> treatment, (b) with H<sub>2</sub> treatment at 723 K, (c) 673 K, and 23 (d) 623 K. ( $\bigtriangledown$ ) Ni<sub>3</sub>Sn<sub>2</sub>.

24

25 observed (Fig. 1c). Notably, no peaks from the original Ni 26 and Sn metals could be assigned, even without H<sub>2</sub> treatment. 27 Using the Scherrer's equation on the Ni<sub>3</sub>Sn<sub>2</sub>(101) peak at  $2\theta$ = 30.6°, the Ni<sub>3</sub>Sn<sub>2</sub> particle sizes of both Ni-Sn(1.5) and Ni-28 29 Sn(1.5)HT673 catalysts were calculated to be 10.0 and 27.3 30 nm, respectively (Table S1, ESI). Then, several Ni-Sn(1.5)31 catalysts were prepared by varying the H<sub>2</sub> treatment 32 temperatures. The XRD results exhibited sharp Ni<sub>3</sub>Sn<sub>2</sub> alloy 33 peaks for all prepared catalysts (Fig. 1). The Ni<sub>3</sub>Sn<sub>2</sub> particle 34 sizes increased from 18.9 nm to 39.8 nm when the  $H_2$ 35 treatment temperature was increased from 623 K to 723 K (Table S1, ESI), which was consistent with a previous report 36 that Pt nanoparticle size in Pt/ZnO catalyst increased with 37

an increased reductive pretreatment temperature.<sup>20</sup> Finally, 38 Ni-Sn alloy catalysts with various Ni/Sn molar ratios were 39 40 prepared and treated under H<sub>2</sub> atmosphere at 673 K. 41 According to the XRD results, the observed Ni/Sn molar ratios in the Ni-Sn alloy catalysts matched the feed ratios of 42 43 the precursors; Ni-Sn(3.0)HT673 and Ni-Sn(0.75)HT673 44 catalysts exhibited Ni<sub>3</sub>Sn and Ni<sub>3</sub>Sn<sub>4</sub> alloy patterns, respectively.<sup>28</sup> The Ni-Sn particle sizes did not correlate 45 with the Ni/Sn molar ratios (Table S1, ESI). 46

47 The hydrogenation of 4-nitrostyrene was used as a 48 model reaction in order to evaluate the catalytic 49 performance as the selective hydrogenation of nitro group is 50



51 **Scheme 1** Hydrogenation pathway of 4-nitrostyrene 52

53 a challenging task when one or more reducible group is present in the same molecule (Scheme 1).<sup>1,8,29</sup> The results 54 55 are summarized in Table 1. The metallic Ni catalyst showed 56 excellent activity but poor selectivity towards 4-57 aminostyrene, which was attributed to the intrinsic property of metallic Ni (Table 1, entry 1). The conversion and 58 59 selectivity reached 79% and 60%, respectively, after 0.75 h. 60 The addition of electropositive Sn to Ni produced a significant improvement in the chemoselectivity of nitro 61 62 group, which may be attributed to the synergistic effect 63 between the two metals. Ni-Sn(1.5) and Ni-Sn(1.5)HT673 catalysts gave 4-aminostyrene selectivity of 95% and 87%, 64 65 respectively, with full conversion of 4-nitrostyrene (Table 1, 66 entries 2 and 4). Although Ni gave 4-ethylnitrobenzene and 67

68 **Table 1**. Hydrogenation of 4-nitrostyrene with the 69 prepared catalysts

En tran	Catalant	Time	Conv. <sup>a</sup>	Sel. <sup>b</sup>
Entry	Catalyst	(h)	(%)	(%)
1	Ni	0.75	79	60
2	Ni-Sn(1.5)	41	100	95
3 <sup><i>c</i></sup>		165	90	100
4	Ni-Sn(1.5)HT673	11	100	87
$5^{c}$		26	100	99
$6^d$		16	93	91
$7^e$		30	92	93
8	Ni-Sn(1.5)HT723	11	100	80
9	Ni-Sn(1.5)HT623	2	100	28
10	Ni-Sn(3.0)HT673	14	87	90
11	Ni-Sn(0.75)HT673	22	19	60

70 *Reaction conditions*: 4-nitrostyrene, 0.50 mmol; 4-71 nitrostyrene/Ni molar ratio = 10; 1,4-dioxane, 5 mL; *n*-

72 dodecane, 0.30 mmol; H<sub>2</sub>, 3.0 MPa; 423 K. <sup>a</sup>The conversion

73 was determined by GC using an internal standard technique.

74 <sup>b</sup>The selectivity of 4-aminostyrene. <sup>c</sup>383 K. <sup>d</sup>H<sub>2</sub>, 2.0 MPa.

75 <sup>*e*</sup>H<sub>2</sub>, 1.0 MPa.

4-ethylaniline as byproducts, Ni-Sn(1.5) catalysts clearly 1 2 suppressed the formation of 4-ethylnitrobenzene. This 3 suggests that nitro group is preferentially hydrogenated over 4 olefin group. This high chemoselectivity towards nitro 5 group may be caused by an interaction between the electron 6 lone pair of nitro group and the partially electropositive Sn. 7 In other words,  $\sigma$ -interaction between electron lone pair on 8 oxygen of nitro group and the Sn surface of the catalyst 9 plays an important role in the chemoselectivity.<sup>30</sup> Here, we can safely conclude that Ni<sub>3</sub>Sn<sub>2</sub> alloy observed in the XRD 10 measurements contributed the high chemoselectivity in 11 hydrogenation of 4-nitrostyrene. In addition, H<sub>2</sub> treatment is 12 crucial in order to obtain higher activity towards nitro group, 13 14 when compared to the hydrogenation results of Ni-Sn(1.5)15 and Ni-Sn(1.5)HT673 catalysts.

16 To optimize the reaction conditions, at first, the 17 hydrogenation was conducted under different reaction 18 temperatures (Table 1, entries 2-5). By lowering the reaction 19 temperature from 423 K to 383 K, the selectivity was somewhat enhanced for both Ni-Sn(1.5) and Ni-20 Sn(1.5)HT673 catalysts, consistent with the report.<sup>31</sup> Since 21 22 the reaction intermediates were slowly transformed to final product at lower temperatures, the product concentration 23 24 became higher. This similar tendency was observed in the previous report.31 At 383 K, Ni-Sn(1.5)HT673 catalyst 25 showed a selectivity of 99% towards 4-aminostyrene with 26 27 full conversion of 4-nitrostyrene after 26 h (Fig. 2). 28 However, the best catalytic activity was achieved at 423 K. 29



Figure 2. Time profile of the hydrogenation of 4nitrostyrene with Ni-Sn(1.5)HT673 catalyst at 383 K. *Reaction conditions*: 4-nitrostyrene, 0.50 mmol; 4nitrostyrene/Ni molar ratio = 10; 1,4-dioxane, 5 mL; *n*dodecane, 0.30 mmol; H<sub>2</sub>, 3.0 MPa; 383 K.

Then, we investigated the effect of  $H_2$  pressure on the catalytic performance (Table 1, entries 4, 6, and 7). As seen in the results, as hydrogen pressure increased, the reaction time became shorter, and the selectivity decreased. The dependence of the reaction time on the  $H_2$  pressure suggests 41 that the activation of  $H_2$  is the rate-limiting step. Ni-42 Sn(1.5)HT673 catalyst showed the highest activity when the 43 hydrogenation was conducted at a pressure of 3.0 MPa.

44 To determine the optimal  $H_2$  treatment temperature and 45 Ni/Sn molar ratio, several Ni-Sn alloy catalysts were 46 prepared and applied to the reaction (Table 1, entries 4 and 47 8-11), and Ni-Sn(*1.5*)HT673 catalyst showed the best 48 catalytic performance.

49 After optimizing the reaction conditions for the 50 hydrogenation of 4-nitrostyrene, the substrate scope of this 51 catalytic system was investigated. The catalyst with the best 52 performance, Ni-Sn(1.5)HT673 catalyst, was applied for the 53 hydrogenation of a variety of unsaturated nitro compounds. 54 The results are summarized in Table 2. From Table 2, Ni-55 Sn(1.5)HT673 efficiently yielded the corresponding 56 unsaturated amines. The position of olefin group had little 57

58 **Table 2.** Hydrogenation of various unsaturated nitro 59 compounds



60 *Reaction conditions*: Substrate/Ni molar ratio = 10; 1,4-61 dioxane, 5 mL; *n*-dodecane, 0.30 mmol;  $H_2$ , 3.0 MPa; 423 K. 62 <sup>*a*</sup>The conversion was determined by GC using an internal 63 standard technique. <sup>*b*</sup>The selectivity of unsaturated amines. 64

65 effect on the hydrogenation (Table 2, entry 1). The 66 selectivity of 3-aminostyrene reached 86% with full 67 conversion of 3-nitrostyrene after 10 h, which was similar to 68 the hydrogenation of 4-nitrostyrene. The hydrogenation of 69 4-nitrostilbene resulted in remarkably high selectivity, 70 which may be attributed to the steric hindrance from the two 71 benzene rings of 4-nitrostilbene (Table 2, entry 2). 72 Nitrobenzene, 1-nitronaphthalene, and 5-nitroindol were 73 also successfully hydrogenated with excellent conversion 74 and selectivity, as it was difficult to hydrogenate the olefin 75 group inside five- or six-membered rings due to the 76 aromatic property (Table 2, entries 3-5). No side products 77 were detected by GC. Although halogen-substituted 78 nitrobenzene tends to dehalogenate, in this study, 4-79 chloronitrobenzene was completely hydrogenated into the

corresponding chloroaniline without any hydrogenolysis of 1 the C-X bond (Table 2, entry 6).<sup>32-34</sup> Hydrogenation of 4-2 nitrophenol proceeded almost quantitatively (Table 2. entry 3 4 7). Finally, -COOCH<sub>3</sub> and -COCH<sub>3</sub> groups showed high 5 tolerance and their corresponding unsaturated amines were 6 obtained with significantly high selectively (Table 2, entries 7 8 and 9). The catalytic system developed here is an 8 attractive approach for the catalytic hydrogenation of 9 unsaturated nitro compounds, even if they contain other 10 reducible functional groups.

Ni-Sn alloy catalysts were prepared with various Ni/Sn 11 12 molar ratios by simply varying the feed ratio of the Ni and Sn precursors. These catalysts were applied to the 13 14 hydrogenation of 4-nitrostyrene, which was used as a model reaction to evaluate and optimize their performances. Ni-15 Sn(1.5)HT673 catalyst gave the best catalytic performance 16 with full conversion of 4-nitrostyrene and a significantly 17 18 high selectivity towards 4-aminostyrene under the optimized 19 reaction conditions (Conv. 100%, Sel. 87%). This result 20 may be attributed to an electrostatic interaction between the 21 polar nitro group and the electropositive Sn. By lowering 22 the reaction temperature to 383 K, the selectivity was enhanced to 99%. Furthermore, a wide variety of 23 24 unsaturated nitro compounds were almost quantitatively 25 transformed into their corresponding unsaturated amines, demonstrating the overall potential for this efficient catalyst 26 27 in the chemoselective hydrogenation of substituted nitro 28 compounds. 29

30 This work was financially supported in part by JSPS 31 KAKESHI Grant Number 15K06565 and JSPS Bilateral 32 Joint Research Project (2014-2017).

34 If your manuscript has Electronic Supporting Information, a 35 statement of the availability should be placed in this section 36 as follows:

38 Supporting Information is available on http://dx.doi.org/10.1246/cl.\*\*\*\*\*. 39

## 40 **References and Notes**

33

37

- 41 K. Xu, Y. Zhang, X. Chen, L. Huang, R. Zhang, J. Huang, Adv. 1. 42 Synth. Catal. 2011, 353, 1260.
- 43 2. A. M. Tafesh, J. Weiguny, Chem. Rev. 1996, 96, 2035.
- 44 D. R. Petkar, B. S. Kadu, R. C. Chikate, RSC Adv. 2014, 4, 8004. 3.
- 45 V. Popat, N. Padhiyar, Int. J. Chem. Eng. Appl. 2013, 4, 401. 4.
- N. Mei, B. Liu, Int. J. Hydrogen Energy 2016, 41, 17960. 46 5
- 47 48 6. P. Luo, K. Xu, R. Zhang, L. Huang, J. Wang, W. Xing, J. Huang, Catal. Sci. Technol. 2012, 2, 301.
- 49 50 51 52 53 54 55 56 57 7. P. Zhou, D. Li, S. Jin, S. Chen, Z. Zhang, Int. J. Hydrogen Energy 2016, 41, 15218.
- 8. H. Wei, X. Wei, X. Yang, G. Yin, A. Wang, X. Liu, Y. Huang, T. Zhang, Chin. J. Catal. 2015, 36, 160.
- 9 A. Corma, P. Serna, P. Concepción, J. J. Calvino, J. Am. Chem. Soc. 2008, 130, 8748.
- 10. M. Boronat, P. Concepción, A. Corma, S. González, F. Illas, P. Serna, J. Am. Chem. Soc. 2007, 129, 16230.
- 11. A. Corma, P. Serna, Science 2006, 313, 332.
- 58 S. Zhang, C.-R. Chang, Z.-Q. Huang, J. Li, Z. Wu, Y. Ma, Z. 12. 59 Zhang, Y. Wang, Y. Qu, J. Am. Chem. Soc. 2016, 138, 2629.
- 60 13. F. Leng, I. C. Gerber, P. Lecante, S. Moldovan, M. Girleanu, M. 61 R. Axet, P. Serp, ACS Catal. 2016, 6, 6018.

- 62 14. L. Wang, J. Zhang, H. Wang, Y. Shao, X. Liu, Y.-Q. Wang, J. P. 63 Lewis, F.-S. Xiao, ACS Catal. 2016, 6, 4110.
- 64 15. C. Jiang, Z. Shang, X. Liang, ACS Catal. 2015, 5, 4814.
- 65 16 H. Wei, Y. Ren, A. Wang, X. Liu, X.Liu, L. Zhang, S. Miao, L. 66 Li, J. Liu, J. Wang, G. Wang, D. Su, T. Zhang, Chem. Sci. 2017, 8, 67 5126
- 68 69 17. H. Wei, X. Liu, A. Wang, L. Zhang, B. Qiao, X. Yang, Y. Huang, S. Miao, J. Liu, T. Zhang, Nat. Commun. 2014, 5, 5634.
  - 18 L. Wang, E. Guan, J. Zhang, J. Yang, Y. Zhu, Y. Han, M. Yang, C. Cen, G. Fu, B. C. Gates, F.-S. Xiao, Nat. Commun. 2018, 9, 1362
- 70 71 72 73 74 75 76 77 78 79 80 19. Y. Ren, H. Wei, G. Yin, L. Zhang, A. Wang, T. Zhang, Chem. Commun. 2017, 53, 1969.
  - C. Berguerand, A. Yarulin, F. Cárdenas-Lizana, J. Wärna, E. 20. Sulman, D. Y. Murzin, L. Kiwi-Minsker, Ind. Eng. Chem. Res. 2015. 54. 8659-8669.
  - 21 A. Corma, P. Concepción, P. Serna, Angew. Chem. Int. Ed. 2007, 46, 7266.
  - 22. A. Vicente, G. Lafaye, C. Especel, P. Marécot, C. T. Williams, J. Catal. 2011, 283, 133-142.
- 81 82 23. A. Yarulin, C. Berguerand, A. O. Alonso, I. Yuranov, L. Kiwi-Minsker, Catal. Today 2015, 256, 241.
- 84 24 H. Wen, K. Yao, Y. Zhang, Z. Zhou, A. Kirschning, Catal. Commun. 2009, 10, 1207.
  - 25. L.-F. Chen, Y.-W. Chen, Ind. Eng. Chem. Res. 2006, 45, 8866.
- 87 P. Serna, A. Corma, ACS Catal. 2015, 5, 7114. 26

83

85

86

91

- 88 27. Rodiansono, S. Khairi, T. Hara, N. Ichikuni, S. Shogo, Catal. Sci. 89 Technol. 2012, 2, 2139.
- **9**0 28. Powder diffraction files, JCPDS-International center for diffraction data (ICDD) 1997.
- 92 29. Y. Tan, X. Y. Liu, L. Zhang, A. Wang, L. Li, X. Pan, S. Miao, M. <u>9</u>3 Haruta, H. Wei, H. Wang, F. Wang, X. Wang, T. Zhang, Angew. 94 Chem. Int. Ed. 2017, 56, 2709.
- 95 F. Delbecq, P. Sautet, J. Catal. 2003, 220, 115. 30
- 96 M. Turáková, T. Salmi, K. Eränen, J. Wärnå, D. Y. Murzin, M. 31. 97 Králik, Appl. Catal., A 2015, 499, 66.
- 98 32. I. Tamiolakis, S. Fountoulaki, N. Vordos, I. N. Lykakis, G. S. 99 Armatas, J. Mater. Chem. A. 2013, 1, 14311.
- 100 33. B. Tang, W.-C. Song, E.-C. Yang, X.-J. Zhao, RSC Adv. 2017, 7, 101 1531.
- 102 34. X. Sun, A. I. Olivos-Suarez, D. Osadchii, M. J. V. Romero, F. 103 Kapteijin, J. Gascon, J. Catal. 2018, 357, 20.