

# Efficient Catalytic System for Chemoselective Hydrogenation of Halonitrobenzene to Haloaniline Using PtZn Intermetallic Compound

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**Supporting Information** 

**ABSTRACT:** Nanoparticulate intermetallic PtZn acts as a highly efficient heterogeneous catalyst for chemoselective hydrogenation of halonitrobenzenes to haloanilines. Chloroanilines, bromoanilines, and iodoanilines, including all regioisomers, were obtained with excellent yields (typically >99%) under 1 atm H<sub>2</sub> at 40 °C. A gram-scale reaction afforded a turnover number (TON) of 8600. PtZn/SiO<sub>2</sub> could be reused at least four times without significant loss of catalytic performance. PtZn/SiO<sub>2</sub> afforded 7-fold higher TOF than Pt/SiO<sub>2</sub>. A combination of kinetic analysis, X-ray photoelectron spectroscopy (XPS) studies, and density functional theory (DFT) calculations revealed that electron-enriched Pt by Zn not only promotes nitro-hydrogenation but also effectively inhibits the carbon–halogen bond scission.



KEYWORDS: halonitrobenzene, chemoselective, hydrogenation, intermetallic, PtZn

Haloanilines (HANs) are valuable intermediates in the synthesis of various chemicals, such as pharmaceuticals, dyes, pigments, and pesticides.<sup>1,2</sup> HANs have been conventionally synthesized from corresponding halonitrobenzenes (HNBs) with stoichiometric reductants such as Fe-HCl (via the Béchamp process),<sup>3</sup> Sn-HCl,<sup>4</sup> or hydride reagents.<sup>5</sup> However, these processes generate stoichiometric amounts of harmful chemical wastes including metal salts. In the principle of high atom efficiency and green chemistry, these stoichiometric systems have been expected to be replaced by heterogeneous catalytic systems, using transition metals and gaseous hydrogen. The heterogeneous hydrogenation of HNBs to HANs involves the intrinsic difficulty of inhibiting the hydrogenolysis of the weak carbon-halogen (C-X) bond, resulting in dehalogenation and loss of the HAN yield.<sup>2,6</sup> This undesired side reaction becomes more prominent and unavoidable as the C-X bond becomes weaker from C-Cl to C-I. The weaker C-X bonds of iodoanilines (IANs) and bromoanilines (BANs), compared with those of chloroanilines (CANs), are greatly valuable in organic synthesis reactions including various coupling reactions.<sup>7,8</sup> Therefore, achieving the selective hydrogenation of iodonitrobenzenes (INBs) and bromonitrobenzenes (BNBs) in the synthesis of the corresponding HANs is not only challenging but also highly demanding. To date, however, attempts to develop a highly selective HNB hydrogenation with heterogeneous catalysts and H<sub>2</sub> have been focused on chloronitrobenzenes (CNBs).<sup>9,10</sup> In this context, devising a highly efficient heterogeneous catalyst for HNB hydrogenation with a wide substrate scope has a great potential for future applications.

Existing strategies for heterogeneous CNB hydrogenation have been based on the use of bimetallic materials, which

typically comprise noble metals (Pt, Ir) and/or base metal oxides (TiO<sub>2</sub>,  $^{f1-13}$  FeO<sub>x</sub>  $^{14-17}$ ). The bimetallic interface appears to provide electronically modified noble metals suitable for selective CNB hydrogenation.<sup>12,15</sup> However, a simple bimetallic composite provides a limited number of interfacial sites and nondrastic electronic modification, which hamper further improvements in the catalytic performance and substrate scope. Ideally, a highly dispersed bimetallic interface at the atomic level should be constructed. Promising candidates for such bimetallic materials are intermetallic compounds, which have specific crystal structures and well-defined atomic arrangements of their metal components. In these structures, all the surface atoms serve as an atomically aligned bimetallic interface. Moreover, a variety of second metal choices enable wide electronic state tuning of the active metal.

In this study, we prepared a series of Pt-based intermetallic compounds supported on  $SiO_2$  and investigated their catalytic performance in liquid-phase HNB hydrogenation. Herein, we report excellent catalytic performances of Pt-based intermetallic catalysts for various HNBs and the origin of the chemoselectivity.

Pt-based bimetallic catalysts supported on silica (PtM/SiO<sub>2</sub>, where M = Co, Cu, Fe, Ga, In, Ni, Pb, Sn, and Zn) were prepared by a conventional impregnation method (see Supporting Information for details). The crystal phases of Pt-based catalysts were examined by X-ray diffraction (XRD) measurement. The XRD patterns of the prepared Pt-based

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catalysts are shown in Figure S1 in the Supporting Information. For most catalysts (M = Cu, Ga, Pb, Sn, and Zn), the desired intermetallic or alloy phases were formed in single phases. Ptrich alloy phases were formed for Pt-Co and Pt-Ni catalysts  $(Pt_{0.77}Co_{0.23} \text{ and } Pt_{0.67}Ni_{0.33})$ . Deviations from a 1:1 ratio indicates that a portion of the Co and Ni atoms did not participate in the alloy formation and remained as XRDunobservable (very small or amorphous) species. The crystallite sizes of the intermetallic or alloy particles estimated using Scherrer's equation were typically 4-6 nm. These values were slightly larger than that of the parent Pt crystallite (3 nm), which was the precursor of these bimetallic particles prepared by successive impregnation. This can be attributed to incorporation of the second metal atoms into the Pt lattices. For the Pt-Sn catalyst, coimpregnation and high reduction temperature (800 °C) resulted in a much larger crystallite size (12 nm). Further characterizations were performed to demostrate the formation of intermetallic nanoparticles. Figure 1a shows a TEM image of PtZn/SiO<sub>2</sub>.



**Figure 1.** (a) Wide-range and (b) high-resolution TEM images of  $PtZn/SiO_2$ . (c) Nanobeam diffraction (NBD) patterns focused on the single nanoparticle shown in panel (b). (d) Rhombitruncated cuboctahedron model of PtZn projected along the  $[\overline{1}2\overline{1}]$  direction. Blue lines represent (111) planes.

The particle sizes were typically 2–7 nm (area-weighted mean diameter, 7.4 nm), which is roughly consistent with the XRD results. The high-resolution image focused on a single nanoparticle showed lattice fringes with 2.23 Å spacing (Figure 1b), which agreed well with that of PtZn(111) planes (2.22 Å). The nanobeam diffraction (NBD) pattern of this nanoparticle showed a set of diffraction spots corresponding to an intermetallic PtZn single crystal oriented along the  $[\overline{1}2\overline{1}]$  direction (Figure 1c). These results strongly support the formation of intermetallic nanoparticles on silica. A rhombitruncated cuboctahedron model of PtZn roughly reproduced the shape of the PtZn single nanocrystal (Figure 1d).

The prepared Pt-based catalysts were examined in the hydrogenation of 4-CNB as a test reactant. Figure 2 shows the 4-CNB conversion on each catalyst after 60 min of reaction time (open circles) and the product distribution at ~50% conversion (bars). Monometallic Pt, Pt–Co, Pt–Fe, Pt–Ni, and PtZn exhibited high conversions (>90%), whereas other catalysts gave moderate conversions (PtPb, 70%; PtGa, 40%; PtIn, 25%) or very low conversions (Pt–Cu and PtSn, <1%).



**Figure 2.** Catalytic performances of Pt-M/SiO<sub>2</sub> in 4-CNB hydrogenation: conversion of 4-CNB at 60 min of reaction time and product distribution at ~50% 4-CNB conversion. Reaction conditions: 4-CNB, 0.8 mmol; catalyst, 200 mg (Pt: 3.9 mol %); solvent, 4 mL (methanol); atmosphere, 1 atm H<sub>2</sub>; temperature, 40 °C.

Monometallic Pt and transition-metal-containing catalysts showed low or moderate 4-CAN selectivities (20%-60%). On the other hand, intermetallic PtZn and PtGa exhibited excellent selectivity to 4-CAN (>99%). Figure 3 shows the time course of the product yield for monometallic Pt and PtZn.



Figure 3. Time course of product yields in 4-CNB hydrogenation over  $Pt/SiO_2$  and  $PtZn/SiO_2$ . The reaction conditions were identical to those described in Figure 2.

In the case of monometallic Pt, the production of 4-CAN decreased in the high conversion region (>60%) and only aniline (AN) was obtained after 60 min of reaction time. These results indicate that undesired dechlorination of 4-CAN to AN dominated at high conversions. On the other hand, for PtZn, no dechlorination occurred even at complete conversion at 60 min, enabling the quantitative conversion of 4-CNB to 4-CAN (>99% yield). For both Pt/SiO<sub>2</sub> and PtZn/SiO<sub>2</sub> catalysts, no reaction occurred at all when the reaction was performed under an atmosphere of argon in methanol (data not shown). This demonstrates that the methanol solvent does not work as a hydrogen source in this catalytic system. Inductively coupled plasma—atomic emission analysis showed that no Pt or Zn was detected in the filtrate after the reaction.

Next, the substrate scope of the most efficient catalyst (PtZn/SiO<sub>2</sub>) was investigated with various HNBs, as shown in Table 1.

Table 1. C	hemosele	ective	Hydro	gena	tion of
Halonitrob	enzenes	over	PtZn/S	iO2	Catalyst <sup>4</sup>

		NO <sub>2</sub>	catalyst 1 atm H <sub>2</sub>		∕ NH₂
		×	CH <sub>3</sub> OH, 40 <sup>c</sup>	C X	
entry	Х	catalyst	time [h]	conversion [%]	HAN selectivity [%]
1	4-Cl	$PtZn/SiO_2$	1.0	100	>99
2	4-Cl	reuse (1)	1.0	100	>99
3	4-Cl	reuse (4)	1.0	91	>99
4	4-Cl	Pt/SiO <sub>2</sub>	0.8	100	35
5	3-Cl	PtZn/SiO <sub>2</sub>	1.0	100	>99
6	3-Cl	$Pt/SiO_2$	1.0	100	20
7	2-Cl	PtZn/SiO <sub>2</sub>	1.0	100	>99
8	4-Br	PtZn/SiO <sub>2</sub>	1.2	100	>99
9 <sup>b</sup>	4-Br	PtZn/SiO <sub>2</sub>	10	100	>99 (96) <sup>c</sup>
10	4-Br	$Pt/SiO_2$	1.0	100	31
11	3-Br	PtZn/SiO <sub>2</sub>	1.2	100	90
12	3-Br	$Pt/SiO_2$	1.0	100	18
13	2-Br	PtZn/SiO <sub>2</sub>	1.2	100	>99
14 <sup>d</sup>	4-I	$PtZn/SiO_2$	3.0	100	94
15	3-I	PtZn/SiO <sub>2</sub>	2.5	100	>99
16	3-I	Pt/SiO <sub>2</sub>	3.0	100	44
17 <sup>e</sup>	2-I	PtZn/SiO <sub>2</sub>	2.0	95	91

<sup>*a*</sup>Reaction conditions: HNB, 0.8 mmol; catalyst, 200 mg (3.0 wt % Pt); methanol, 4 mL; H<sub>2</sub>, 1 atm; temperature, 40 °C. <sup>*b*</sup>4-BNB, 8.0 mmol. <sup>*c*</sup>Isolated yield. <sup>*d*</sup>Ethyl acetate (4 mL) was used instead of methanol. <sup>*e*</sup>2-INB, 0.4 mmol; catalyst, 400 mg; methanol, 2 mL.

In addition to 4-CNB, 2- and 3-CNBs were selectively converted to the corresponding CANs (>99%, entries 5 and 7). The PtZn/SiO<sub>2</sub> catalyst also afforded excellent HAN yields (typically >99%) for the hydrogenation of a series of BNB (entries 8, 11, and 13) and INB (entries 14, 15, and 17) regioisomers. The spatial adjacence of two reducible functional groups in the 1,2- or 1,3-regioisomer might cause overhydrogenation (here, dehalogenation), compared with the 1,4regioisomer. Nevertheless, PtZn/SiO2 effectively inhibited the undesired dechlorination for all regioisomers. Note that the selective hydrogenation of BNBs and INBs into the corresponding HANs successfully proceeded without C-X bond scissions. To the best of our knowledge, this is the first report of a selective heterogeneous catalytic system for hydrogenation of various HNBs including iodosubstrates and bromosubstrates with all regioisomers. Conversely, the use of monometallic Pt/SiO<sub>2</sub> in the hydrogenation of several HNBs resulted in poor HAN yields (18%-44%, entries 4, 6, 10, 12, and 16). The PtZn/SiO<sub>2</sub> catalyst could be separated from the reaction medium by simple decantation and reused at least four times without a major loss of catalytic activity (entries 2 and 3). We also performed a gram-scale reaction with 4-BNB (8.0 mmol, 1.6 g), affording a stoichiometric conversion into 4-BAN in 10 h with an isolated yield of 96% (entry 9). This catalytic run recorded a high turnover number (TON = 8600, based on

the exposed Pt). Our catalytic system can work well under atmospheric H<sub>2</sub> pressure at near room temperature (40 °C), which is very rare in the reported systems and is valuable for laboratory-scale applications. Thus, PtZn/SiO<sub>2</sub> provided a highly efficient catalytic system for HNB hydrogenation, showing not only high catalytic activity and chemoselectivity but also wide substrate scope and applicability.

We now discuss the origin of the excellent chemoselectivity of PtZn in HNB hydrogenation. For a possible factor governing chemoselectivity, we focused on the electronic state of Pt-based intermetallic compounds. As a scale of the electronic state, the binding energy of the Pt 4f core electron was measured for each Pt-based catalyst (Figure S2 in the Supporting Information). Monometallic Pt exhibited a 4f7/2 emission peak at 71.5 eV, consistent with the reported value of metallic Pt supported on SiO<sub>2</sub>.<sup>18,19</sup> The binding energies for the bimetallic catalysts ranged from 70.8 eV (PtZn) to 71.7 eV (Pt-Cu), representing widely modified Pt electronic states. Bimetallic catalysts, except PtCu, showed lower Pt  $4f_{7/2}$  binding energies than monometallic Pt, indicating that Pt atoms are typically electronenriched by the second metals. The most electron-rich Pt was obtained with PtZn. The electron-enriched Pt in PtZn was consistent with the results of density functional theory (DFT) calculations in the literature.<sup>20</sup> Figure 4 shows the relationship between the product selectivities in 4-CNB hydrogenation over the Pt-based catalysts and their Pt 4f<sub>7/2</sub> binding energies.



Figure 4. Relationship between product selectivities in 4-CNB hydrogenation (at ~50% conversions) over Pt-based catalysts and their Pt  $4f_{7/2}$  binding energies.

A positive dependence of 4-CAN selectivity on the electronrich nature of Pt was observed, whereas a negative dependence of AN selectivity was observed. This strongly suggests that dechlorination was increasingly inhibited as the electron density on Pt sites increased.

The observed tendency can be rationalized by considering the electron density at the C–Cl moiety, which is expected to be high due to the electron-withdrawing chloro group. This should be prominent for 4-CAN because of the presence of a strong electron-donating amino group. Our DFT calculation clearly demonstrated these features (see Figure S3 in the Supporting Information). As dechlorination proceeds on Pt sites via dissociative adsorption of the C–Cl bond, an electrostatic repulsion between the C–Cl moiety and the electron-enriched Pt sites and/or destabilization of the transition state might inhibit dechlorination. Thus, the enhanced chemoselectivity of PtZn can be explained by the unfavored adsorption (or activation) of the C-Cl moiety.

To demonstrate this feature, periodic DFT calculations were performed using Pt(111) and PtZn(111) slab models (see Figure 5).



**Figure 5.** Energy diagram of 4-CAN dechlorination over PtZn(111) and Pt(111) slabs. The sum of 4-CAN and bare slab energies was set to zero for each plane. Side and top views for the transition state (TS) and the final state are shown. [Legend: Pt, black; Zn, pink; C, gray; Cl, light green; N, blue; H, white.]

Geometry optimization revealed that the dissociated aryl ring displayed an interfacial angle of ~45° toward each slab surface. On Pt(111), the dissociation formed aryl C–Pt and Cl–Pt bonds at a hexagonal closely packed (hcp) hollow and top sites, respectively, with an adsorption energy ( $\Delta E_{ad}$ ) of -18.6 kJ mol<sup>-1</sup>. A similar DFT result has also been reported for the Pd(111) plane.<sup>21</sup> Conversely, on PtZn(111), the corresponding bond formations occurred at a Pt top and a Pt<sub>1</sub>Zn<sub>2</sub> hollow sites, respectively, with  $\Delta E_{ad} = +27.8$  kJ mol<sup>-1</sup>. The dechlorination activation energy for PtZn(111) (134 kJ mol<sup>-1</sup>) was much higher than that for Pt(111) (78.2 kJ mol<sup>-1</sup>). Thus, the calculation demonstrates that the C–Cl bond activation on PtZn(111) is unfavorable kinetically and thermodynamically, compared with that on Pt(111).

A kinetic study was also performed for Pt/SiO<sub>2</sub> and Pt-M/ SiO<sub>2</sub>, revealing that a first-order dependence of the 4-CNB conversion rate on hydrogen pressure was observed. This indicates that nitro-hydrogenation is much faster than the ratelimiting H<sub>2</sub> adsorption. We confirmed that hydrogen diffusion is not rate-limiting by control experiments with different stirring rates (125 and 375 rpm), which showed the same reaction rate. On the other hand, a kinetic study using 4-CAN as a reactant exhibited that dechlorination showed a first-order dependence on the 4-CAN concentration for each catalyst, suggesting that dissociative adsorption of 4-CAN is the ratedetermining step of dechlorination. Note that the ratedetermining step differs between nitro-hydrogenation and dechlorination. The reaction rate order is as follows: nitrohydrogenation > H<sub>2</sub> adsorption > dechlorination, consistent with the observation that 4-CAN was obtained as a main product over most catalysts.

We also investigated the effect of the electron-rich nature of Pt on the nitro-hydrogenation of 4-CNB to 4-CAN. A strong positive correlation between the turnover frequency (TOF) of the nitro-hydrogenation of 4-CNB and the electron-rich nature of Pt (Pt  $4f_{7/2}$  binding energy) was observed (see Figure S4 in the Supporting Information). Note that PtZn afforded a TOF 7-fold higher than that of Pt. This trend suggests that the rate-

limiting  $H_2$  adsorption (activation) is accelerated on electronenriched Pt catalysts. A possible interpretation is that the enhanced  $\sigma$  back-donation from Pt to the H–H antibonding orbital reduced the activation energy of  $H_2$  adsorption. Alternatively, the electron-enriched Pt might have weakened the adsorption of the nitro group that was competitive to  $H_2$ adsorption. Thus, the electron-enriched Pt not only inhibited undesired dechlorination but also promoted the desired nitrohydrogenation, each of which concertedly improved the chemoselectivity.

In conclusion, intermetallic PtZn exhibited high catalytic activity, high chemoselectivity, and a wide substrate scope in HNB hydrogenation to HAN. This highly efficient heterogeneous catalyst worked well under the atmospheric pressure of  $H_2$  at near room temperature. The excellent chemoselectivity of PtZn was attributed to unfavored C–Cl dissociation and the promotion of nitro-hydrogenation on electron-enriched Pt sites.

## ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.5b02464.

Experimental details, XRD patterns, and TOF data (PDF)

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# Notes

The authors declare no competing financial interest.

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### REFERENCES

(1) Ono, N. In The Nitro Group in Organic Synthesis, Vol. 9; John Wiley & Sons: New York, 2003; pp 170–175.

(2) Tafesh, A. M.; Weiguny, J. Chem. Rev. 1996, 96, 2035-2052.

(3) Sidgwick, N. V.; Rubie, H. E. J. Chem. Soc., Trans. 1921, 119, 1013-1024.

- (4) Hodgson, H. H. J. Soc. Dyers Colour. 1926, 42, 76-80.
- (5) Tumma, M.; Srivastava, R. Catal. Commun. 2013, 37, 64-68.

(6) Wang, X. D.; Liang, M. H.; Zhang, J. L.; Wang, Y. Curr. Org. Chem. 2007, 11, 299-314.

(7) Yamada, Y. M. A.; Sarkar, S. M.; Uozumi, Y. J. Am. Chem. Soc. **2012**, 134, 3190–3198.

(8) Jia, Z. J.; Wu, Y.; Huang, W.; Goldman, E.; Zhang, P.; Woolfrey, J.; Wong, P.; Huang, B.; Sinha, U.; Park, G.; Reed, A.; Scarborough, R. M.; Zhu, B.-Y. *Bioorg. Med. Chem. Lett.* **2002**, *12*, 1651–1655.

(9) Cardenas-Lizana, F.; Hao, Y. F.; Crespo-Quesada, M.; Yuranov, I.; Wang, X. D.; Keane, M. A.; Kiwi-Minsker, L. ACS Catal. 2013, 3, 1386–1396.

(10) Wang, X.; Perret, N.; Delgado, J. J.; Blanco, G.; Chen, X.; Olmos, C. M.; Bernal, S.; Keane, M. A. J. Phys. Chem. C 2013, 117, 994–1005.

(11) Lin, W. W.; Zhao, J.; Cheng, H. Y.; Li, X. R.; Li, X. N.; Zhao, F. Y. J. Colloid Interface Sci. **2014**, 432, 200–206.

(12) Corma, A.; Serna, P.; Concepcion, P.; Calvino, J. J. J. Am. Chem. Soc. 2008, 130, 8748-8753.

(13) Han, X. X.; Zhou, R. X.; Lai, G. H.; Yue, B. H.; Zheng, X. M. J. Mol. Catal. A: Chem. 2004, 209, 83–87.

(14) Evangelisti, C.; Aronica, L. A.; Botavina, M.; Martra, G.; Battocchio, C.; Polzonetti, G. J. Mol. Catal. A: Chem. 2013, 366, 288–293.

(15) Liang, M. H.; Wang, X. D.; Liu, H. Q.; Liu, H. C.; Wang, Y. J. Catal. 2008, 255, 335–342.

(16) Jagadeesh, R. V.; Surkus, A. E.; Junge, H.; Pohl, M. M.; Radnik, J.; Rabeah, J.; Huan, H. M.; Schunemann, V.; Bruckner, A.; Beller, M. *Science* **2013**, *342*, 1073–1076.

(17) Wei, H. S.; Liu, X. Y.; Wang, A. Q.; Zhang, L. L.; Qiao, B. T.; Yang, X. F.; Huang, Y. Q.; Miao, S.; Liu, J. Y.; Zhang, T. *Nat. Commun.* **2014**, *5*, 5634–5641.

(18) Llorca, J.; Delapiscina, P. R.; Fierro, J. L. G.; Sales, J.; Homs, N. J. Catal. **1995**, 156, 139–146.

(19) Ramallo-Lopez, J. M.; Santori, G. F.; Giovanetti, L.; Casella, M. L.; Ferretti, O. A.; Requejo, F. G. *J. Phys. Chem. B* **2003**, *107*, 11441–11451.

(20) Rodriguez, J. A.; Kuhn, M. J. Chem. Phys. 1995, 102, 4279-4289.

(21) Lyu, J. H.; Wang, J. G.; Lu, C. S.; Ma, L.; Zhang, Q. F.; He, X. B.; Li, X. N. J. Phys. Chem. C 2014, 118, 2594–2601.