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Azo(xy) vs Aniline Selectivity in Catalytic Nitroarene Reduction by Intermetallics: Experiments and Simulations

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ABSTRACT: Intermetallic nanoparticles are promising catalysts in hydrogenation and fuel cell technologies. Much is known about the ability of intermetallic nanoparticles to selectively reduce nitro vs alkene, alcohol, or halide functional groups; less is known about their selectivity toward aniline vs azo or azoxy condensation products that result from the reduction of a nitro group alone. Because azo(xy)arenes bear promise as dyes, chemical stabilizers, and building blocks to functional materials but can be difficult to isolate, developing high surface area nanoparticle catalysts that display azo(xy) selectivity is desirable. To address this question, we studied a family of nanocrystalline group 10 metal (Pd, Pt)- and group 14 metal (Ge, Sn, Pb)-containing intermetallics—Pd₂Ge, Pd₂Sn, Pd₃Sn₂, Pd₃Pb, and PtSn—in the catalytic reduction of nitroarenes. In contrast to



monometallic Au, Pt, and Pd nanoparticles and "random" Pd_xSn_{1-x} nanoalloys, which are selective for aniline, nanoparticles of atomically precise intermetallic Pd_2Ge , Pd_2Sn , Pd_3Sn_2 , and PtSn prefer an indirect condensation pathway and have a high selectivity for the azo(xy) products. The only exception is Pd_3Pb , the most active among the intermetallic nanoparticles studied here, which is instead selective for aniline. Employing a novel application of molecular dynamics—based on machine learned potentials within a DeePMD framework—to heterogeneous catalysis, we are able to identify key reaction species on the different types of catalysts employed, furthering our understanding of the unique selectivity of these materials. By demonstrating how intermetallic nanoparticles can be as active yet more selective than other more traditional catalysts, this work provides new physical insights and opens new opportunities in the use of these materials in other important chemical transformations and applications.

■ INTRODUCTION

Because of their unique catalytic activity, selectivity, and stability compared to their alloyed and monometallic counterparts, 1-6 atomically precise intermetallics are of interest in industrially relevant processes ranging from fuel cell⁷⁻⁹ to hydrogenation technologies. 10 Some of the most promising members of this family are binary 10-14 intermetallic nanoparticles composed of group 10 transition metals such as Pd and Pt and group 14 tetrel elements like Ge, Sn, and Pb. For example, Pd₂Sn nanoparticles are active catalysts in the removal of nitrate from water, 11 ethanol oxidation, 12-14 oxygen reduction, 15 and H₂O₂ generation. 16 Pd₂Sn nanoparticles on Au are active in Sonogashira coupling, as well as in alkene and alkyne hydrogenation.¹⁷ PdSn, Pd₃Sn₂, and Pd₂Sn nanoparticles chemoselectively hydrogenate crotonaldehyde, with PdSn nanoparticles having a high selectivity for the reduction of C=O vs C=C bonds. ¹⁸ Catalytic Pd₃Sn₂ networks have been used in formic acid electrooxidation, ¹⁹ while Pd₂Ge nanoparticles are active in ethanol oxidation²⁰ and the hydrogen evolution reaction (HER).²¹ Pd₃Pb nanoparticles are very active in the electrochemical reduction of oxygen²²⁻²⁴ and of N_2 to NH_3^{25} and in the oxidation of formic acid, 26,27 ethanol, 26,28 and various amines. 29,30 Pd $_2$ Sn, Pd $_2$ Ge, and Pd $_3$ Pb nanoparticles are active in benzylamine oxidation.³⁰ PtSn nanoparticles are active in methanol electrooxidation; 31,32 in

furfural,³³ nitrobenzene,³⁴ styrene,³⁴ 3-nitrostyrene,³⁵ and cinnamaldehyde³⁶ hydrogenation; and in the dehydrogenation of propane,³⁷ cyclohexane,³⁸ and *n*-butane.³⁸

The reduction of nitroarenes—a primary method for synthesizing functionalized anilines that are widely used as pigments, pharmaceuticals, and agrichemicals—is a valuable test bed for intermetallic catalysts.³⁹ To date, a majority of studies in this area focused on a catalyst's ability to chemoselectively reduce the nitro group over other functional groups that may be present in the reactant, such as alkenes, alkynes, alcohols, or halides.^{18,35,40–42} Considerably less attention was paid to the catalyst's ability to chemoselectively reduce the nitro group into an aniline *vs* the much less common azo or azoxy products—together termed "azo(xy)" compounds (Scheme 1). For example, while Au nanoparticles supported on TiO₂ are selective toward anilines, changing the support to CeO₂, ^{42–46} hexagonal BN, ⁴⁷ or polystyrene ⁴⁸ shifts

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Scheme 1. Different Pathways for the Reduction of Nitroarenes

the selectivity toward azo(xy)arenes. ⁴⁹ Other catalysts that favor azo(xy)arenes include Ni/graphene, ⁵⁰ Pd/SiO₂, ⁵¹ Schiff base-modified nano Pt, ⁵² iron-/nitrogen-co-doped mesoporous carbon, ⁵³ "single atom" Co, ^{54,55} and single-site metal oxide catalysts. ⁵⁶ Changing the solvent, reducing agent and temperature, ^{57–60} or employing a photo- $^{61-65}$ or electrocatalyst ⁶⁶ can also affect the selectivity. Because azo(xy) arenes bear promise as dyes, chemical stabilizers, and building blocks to functional materials yet may be difficult to isolate, a better understanding of catalysts that display azo(xy) selectivity is desirable. ^{67–71} Therefore, unveiling the mechanistic factors behind the azo(xy) ν s aniline selectivity is important from both fundamental as well as practical perspectives.

The two mechanistic pathways in Scheme 1 were originally proposed by Haber and are widely accepted today. In the direct pathway, the nitroarene is reduced to aniline through subsequent nitrosoarene and hydroxylamine intermediates. Alternatively, two of these intermediates may react together via condensation to form an azoxyarene, which can be further reduced to an azoarene and, in some cases, aniline. In addition to the aforementioned experimental studies, the preference for direct vs indirect pathways over single metals was studied by density functional theory (DFT). 72,73 Based on the calculated reaction and activation energies of each elementary step, the Ni(111)⁷² and Pt(111)⁷³ surfaces were calculated to favor direct reduction under neutral conditions. However, on the Pt(111) surface, a change on the mode of reactant chemisorption from a flat to a tilted configuration rendered the indirect route's N-N coupling steps more favorable under basic conditions.

Previously, we showed that an intermetallic Pd₂Sn nanocatalyst—made from a single source heterobimetallic precursor—is active in nitroarene reduction and has a unique selectivity for azoxyarenes, indicating a preference for the condensation pathway.⁷⁴ Here, we report a full account of the catalytic activity and selectivity of a wider family of 10–14 intermetallic, alloyed, and monometallic nanoparticles. In addition, for the first time, we use density functional theory calculations and machine learning-based *ab initio* molecular dynamic simulations to better understand the nitroarene reduction behavior of these nanomaterials. Our results provide a highly detailed picture of the catalytic activity and azo(xy) vs aniline selectivity of nanoscale binary intermetallics.

■ METHODS

Materials. Sodium borohydride powder (NaBH₄, 98+%), 4-nitrotoluene (99%), and lead(II) bromide (PbBr₂, 98+%) were purchased from Acros Organics; nitrobenzene (99%) was from Oakwood Chemical; palladium (Pd, 99.95%, 15 nm),

platinum (Pt, 99.95%, 15 nm), and tin (Sn, 99.9%, 60–80 nm, metal basis) nanopowders were from US Research Nanomaterials, Inc.; palladium(II) bromide (PdBr₂, 99%), potassium tetrachloropalladate(II) (K₂PdCl₄, 99%), tin(II) chloride dihydrate (SnCl₂·2H₂O, 98%), and gold nanoparticles on titania (1% Au/TiO₂) were from Strem; carbon black (Vulcan XC-72R) was from Fuel Cell Store; nitrosobenzene (>98.0%) was from TCI America; and 1-octadecene (ODE, technical grade, 90%), oleylamine (technical grade, 70%), oleic acid (technical grade, 90%), and ethylene glycol (99.8%, anhydrous) were from Sigma Aldrich. Tax-free ethanol (200 proof) was sourced locally. All chemicals were used as received.

Synthesis of Intermetallic Nanocatalysts. Pd_2Sn , Pd_3Sn_2 , Pd_2Ge , and PtSn nanocrystals were synthesized by the solid-state thermal decomposition of heterobimetallic pyridine-2-thiolate precursors. In short, the relevant precursor was placed in an alumina combustion boat and was heated in a tube furnace under a N_2 atmosphere from 30 to 400 °C (or 600 °C in the case of Pd_3Sn_2) at a rate of 10 °C/min and then allowed to cool to R.T. (25 °C). Pd_3Pb nanocubes were synthesized by the co-reduction of $PdBr_2$ and $PbBr_2$ with oleylamine and oleic acid in ODE at 170 °C for 30 min. TS

Synthesis of Alloyed Pd_xSn_{1-x}/C Nanocatalysts. Alloyed Pd_xSn_{1-x}/C nanocatalysts with two different Pd/Sn ratios (x = 0.95 and 0.87) were prepared using a literature polyol method.⁷⁶ In summary, a stock solution of 12.5 mM Sn colloids was prepared by heating SnCl₂·2H₂O in a 12 mL solution of ethylene glycol and deionized water (11 and 1 mL, respectively) to 180 °C for 1 h. An aliquot of this stock solution (0.02 mmol, 1.6 mL for x = 0.95 or 0.06 mmol, 4.8 mL for x = 0.87) was diluted to 8 mL with ethylene glycol and heated to 130 °C under Ar. Upon reaching 130 °C, a solution of K_2PdCl_4 (0.08 mmol for x = 0.95 or 0.06 mmol for x =0.87) in ethylene glycol was injected and the mixture was stirred at this temperature under Ar flow for 30 min. Upon cooling to R.T., the particles were deposited onto a carbon support by adding 25 mg of Vulcan XC-72R and stirring at a rate of 600 rpm at R.T. for 1 h. The particles were washed with ethanol and acetone, dried under vacuum, and placed under Ar/H₂ flow in a tube furnace for 1 h at 205 °C. The %Sn content was calculated using the (111) reflection shifts relative to the Pd (0% Sn) and Pd₃Sn (25% Sn) fcc standard patterns.

Characterization. Powder XRD was collected on a Rigaku Ultima IV diffractometer with a Cu K α radiation source (40 kV, 44 mA). Two to five milligrams per sample was smeared onto a backgroundless quartz slide. For alloy characterization, 1–10% w/w Si powder was added as an internal standard.

Catalytic Reduction Experiments. Nitroarene (0.1 mmol of nitrobenzene or *p*-nitrotoluene) or nitrosobezene (0.1 mmol), ethanol (2.00 mL), the nanocatalyst (10 mg), and NaBH₄ (0.6 mmol) were placed in a 5 mL vial. The mixture was stirred for 48 h. Small aliquots (0.50 mL) were taken at specific intervals, filtered, and consistently diluted for analysis by gas chromatography—mass spectroscopy (GC–MS) on an Agilent 7250 GC-QTOF.

Ab Initio Molecular Dynamic Simulations/DFT Calculations. To gain insights into the mechanism of nitrobenzene hydrogenation, we performed *ab initio* molecular dynamic (MD) simulations with DFT. The main features of the simulations are as follows: (1) There are 4 nitrobenzene, 4 ethanol, and 48 hydrogen molecules in a simulation box with periodic boundary conditions. (2) Catalysts are simulated by a

nanocluster of 10 or 20 atoms for Au and Pt, and 12 or 24 atoms for Pd₂Sn NC. (3) MD simulations were performed using the NVT ensemble. To obtain reactions in a feasible time scale, simulations were performed at elevated temperature and pressure, typically from 1000 to 2000 K and between 10 to 50 kbar, and for 10 ps. Simulation results are then analyzed by a homemade Python software with extensive use of the Atomic Simulation Environment (ASE) package. Specifically, we used ASE to construct an adjacency matrix and then used the breadth-first search algorithm to find individual molecules. For systems with catalysts, we removed the catalyst from the system first. At this stage, we only identified the resulting molecules using the molecular formula and manually examined and identified selected examples. We note that a similar and somewhat more sophisticated code tailored for MD simulations using ReaxFF has been developed.⁷⁷ simulations using machine learned potentials were also performed. Machine learning enabled MD simulations with larger systems and for longer times at near DFT level of accuracy. While some details of the methodology are described below, a more comprehensive description is forthcoming.

RESULTS AND DISCUSSION

Intermetallic Nanocatalysts and Benchmarks. To better understand the unique catalytic behavior of intermetallic nanocatalysts, a family of binary 10–14 intermetallic nanocrystals—Pd₂Ge, Pd₂Sn, Pd₃Sn₂, Pd₃Pb, and PtSn (Figures 1 and 2)—was synthesized and tested for the catalytic reduction of nitroarenes (see the Supporting Information (SI) and

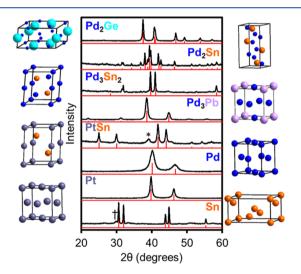


Figure 1. Powder XRD and corresponding unit cells of 10-14 intermetallic nanoparticles and monometallic nanocatalysts tested against nitroarene reduction. Standard patterns are shown in red: Pd₂Sn, orthorhombic, Pnma, ref. 158364; Pd₃Sn₂, hexagonal, P6₃/ mmc, ref. 197134; Pd₂Ge, hexagonal, P-62m, ref. 76140; Pd₃Pb, cubic, Pm-3m, ref. 42600; PtSn (* = Pt₃Sn, 1%), hexagonal, P6₃/mmc, ref. 42593; Pd, cubic, Fm-3m, ref. 52251; Pt, cubic, Fm-3m, ref. 243678; β -Sn († = SnO, 8%), tetragonal, I4₁/amd, ref. 252800.⁷⁸ XRD data for Pd₂Ge, Pd₂Sn, Pd₃Sn₂, and PtSn nanoparticles were adapted with permission from Daniels, C.L.; Knobeloch, M.; Yox, P.; Adamson, M.A.S.; Chen, Y.; Dorn, R.W.; Wu, H.; Zhou, G.; Fan, H.; Rossini, A.J.; Vela, J. Intermetallic Nanocatalysts from Heterobimetallic Group 10-14 Pyridine-2-Thiolate Precursors. Organometallics 2020, 39, 1092–1104. Copyright 2020 American Chemical Society. 4 Of these, only Pd₂Sn was previously employed in a preliminary study of nitrobenzene hydrogenation.

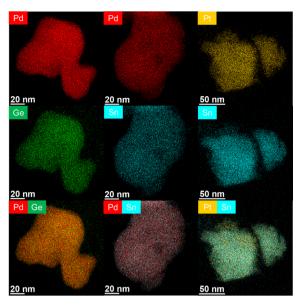


Figure 2. EDX elemental mapping of the intermetallic Pd₂Ge, Pd₂Sn, and PtSn nanoparticles (additional TEM data are available in the Supporting Information).

Methods). All intermetallic nanophases were characterized by powder X-ray diffraction (Figure 1). Average single crystalline domain (Scherrer) sizes remained 12-51 nm in all cases. While this family encompasses a variety of structure types, it provides a diverse platform to compare how each nanocatalyst behaves based on the presence of differing transition metals (Pd, Pt), group 14 elements or "tetrels" (Ge, Sn, Pb), and metal-to-tetrel ratios (Pd₂Sn, Pd₃Sn₂). For comparison, monometallic nanoparticles of Pd, Pt, and Sn available commercially were also tested as catalysts for the same transformation. Powder X-ray diffraction of these samples showed relatively phase pure Pd and Pt nanoparticles with Scherrer sizes ranging from 5 to 16 nm, while Sn nanoparticles had a Scherrer size of about 55 nm and a small amount (~8%) of SnO impurity. As an additional benchmark and to address the possible effect(s) of the structure as well as composition on catalysis, we also tested Pd_xSn_{1-x}/C alloyed nanoparticles made through a modified polyol approach (see SI).⁷⁶ Analyses of referenced peak shifts and peak widths show compositions of Pd_{0.95}Sn_{0.05}/C and Pd_{0.87}Sn_{0.13}/C and Scherrer sizes of 8-10 nm (Figure 3).

Nitrobenzene Reduction. An ethanol solution of nitrobenzene and NaBH₄—a conveniently safer surrogate for H₂⁷⁹—undergoes no appreciable change at room temperature (R.T., 25 °C) for at least 48 h (Scheme 2). In contrast, nitrobenzene is reduced to aniline in as little as 4 h in the presence of a suitable nanocatalyst such as titania-supported nano gold (Au/TiO₂, Figure 4).^{74,79} Under identical conditions—ethanol, R.T.—Pd2Ge nanoparticles are less active but have different selectivity, with azoxybenzene being the main observed product after 48 h (Table 1). When Pd₂Sn nanoparticles are used, nitrobenzene is reduced in 8 h, at which time the major product is also azoxybenzene;⁷⁴ interestingly, longer reaction times lead to a decrease in the concentration of azoxybenzene and a concomitant increase in the concentration of azobenzene, with the latter becoming the sole product after 48 h. A similar behavior is observed with Pd₃Sn₂ nanoparticles; however, in this case, both azobenzene and aniline begin to appear after 24 and 48 h, respectively—see SI. In comparison,

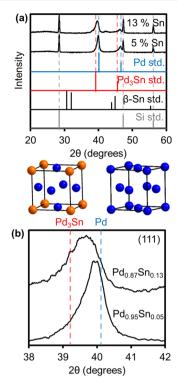


Figure 3. (a) Powder XRD patterns of alloyed Pd_xSn_{1-x}/C nanoparticles. Reflections shift to lower 2θ values upon Sn incorporation. Because β-Sn's tetragonal structure ($I4_1/amd$) is different from that of fcc Pd (Fm-3m), the pattern for the binary intermetallic nanophase Pd_3Sn —which does adopt a topologically similar structure to Pd—was used as a surrogate for a hypothetical nanoalloy with a reference Sn content of 25% (*i.e.*, $Pd_{0.75}Sn_{0.25}$). A small amount (1-10% w/w) of powdered crystalline silicon was used as an internal standard. (b) (111) reflection.

Scheme 2. Catalytic Reduction of Nitrobenzene and Nitrosobenzene

 Pd_3Pb nanoparticles are very active, with nitrobenzene being reduced almost completely in just 1 h (Figure 4); in this case, neither azoxybenzene nor azobenzene is observed, with the sole product being aniline. PtSn nanoparticles behave similarly to Pd_2Sn nanoparticles but achieve lower nitrobenzene conversion; in this case, azoxybenzene and azobenzene start to appear at 4 h, with azobenzene becoming the major product at 48 h.

Effect of Intermetallic Nanoparticle Composition. In the nitrobenzene reduction experiments with intermetallic nanoparticle catalysts, the observed turnover numbers (TONs) of 725–45.6 are all significantly larger than one (\gg 1), which attest to the true catalytic nature of these nanomaterials (Table 1). The intermetallic nanocatalysts show maximum turnover frequencies (TOF_{max}) of 194–11.4 h⁻¹ (Table 1 and Figure 5); these are not far behind that observed for nano Au/TiO₂ of $302~h^{-1}$, the most active among the literature benchmarks used here. The intermetallic nanoparticle TOF_{max} values are 1–2 orders of magnitude larger than those observed for unsupported monometallic nanocatalysts, $26.1-8.09~h^{-1}$;

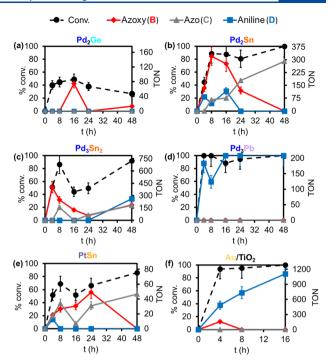


Figure 4. Representative examples of nitrobenzene reduction over intermetallic 10-14 nanoparticle catalysts (a) Pd_2Ge , (b) Pd_2Sn , (c) Pd_3Sn_2 , (d) Pd_3Pb , and (e) PtSn vs the monometallic nanoparticle catalyst (f) Au/TiO_2 (0.1 mmol nitrobenzene, 0.6 mmol $NaBH_4$, 10 mg catalyst, 2 mL ethanol, 25 °C; see Methods). The standard deviation of conversion measurements obtained from multiple runs across all catalyst types averaged 11%.

they are also 3 orders of magnitude larger than those observed for alloyed Pd_xSn_{1-x}/C nanocatalysts, 0.400-0.320 h⁻¹ (see below). Among intermetallic nanocatalysts, Pd₂Ge nanoparticles display modest activity, with a TOF_{max} of 17.6 h⁻¹ and 27% conversion after 48 h; at this time, azoxybenzene is the only product detected, indicating that the reduction reaction over Pd₂Ge nanoparticles follows the condensation pathway (Scheme 1). Pd₂Sn and Pd₃Sn₂ nanoparticles are both more active than Pd₂Ge nanoparticles, with TOF_{max} values of 42.7 and 101 h⁻¹, respectively, and >99–92% conversion after 48 h (Figure 5). These suggest that, for a given transition metal, Sn is a more active tetrel than Ge. Interestingly, while the reactions with both Pd₂Sn and Pd₃Sn₂ nanoparticles also follow the condensation pathway, each nanocatalyst exhibits a different selectivity. At 48 h, Pd₂Sn nanoparticles are selective for azobenzene, while Pd₃Sn₂ nanoparticles give a mixture of all possible products, with aniline being the most abundant (Figures 4 and 5 and Table 1). This suggests that the reduction of azobenzene to aniline is more favorable for Pd₃Sn₂ than Pd₂Sn nanoparticles and that this step is faster than the reduction of azoxybenzene to azobenzene with Pd₂Sn nanoparticles. When the reaction is carried out with pnitrotoluene instead of nitrobenzene, the same patterns are observed, except that the reaction proceeds beyond the azo reduction step (see SI). This suggests that the more electronrich reactant 4,4'-azotoluene is more easily reduced than azobenzene. The reduction of nitrobenzene over PtSn nanoparticles is similar to that over Pd₂Sn than Pd₃Sn₂ nanoparticles, where the only product observed at 48 h is azobenzene. Therefore, the PtSn nanoparticles also prefer the condensation pathway; however, PtSn nanoparticles are less

Table 1. Representative Nitro- (PhNO₂, A) and Nitroso-benzene (PhNO, I) Reduction Data Using Binary 10–14 Intermetallic Nanoparticles vs Monometallic and Alloyed Pd_xSn_{1-x}/C Nanocatalysts^a

nanocatalyst (size nm ^b)	reactant	time (h)	conv. ^c (%)	$TON^d (TOF^e / h)$	selectivity ^f (%)		
					azoxy (B)	azo (C)	aniline (D)
none (control)	$PhNO_2(A)$	48	0	0 (0)	0	0	0
	PhNO (I)	4	>99	N/A	>99	0	0
		48	>99	N/A	80	20	0
$\mathrm{Au}/\mathrm{TiO}_2{}^{\mathcal{G}}$ (1 wt % Au, 4.4)	$PhNO_2(A)$	4	94	1210 (302)	25	0	75
		16	>99	1287 (80.4)	0	0	>99
	PhNO (I)	1	>99	1287 (1287)	10	41	48
		48	>99	1287 (26.8)	0	30	70
$Pd_2Ge^h (28 \pm 7)$	$PhNO_2(A)$	4	40	70.5 (17.6)	0	0	0
		48	27	47.7 (0.994)	>99	0	0
$Pd_2Sn^h \ (49 \pm 11)$	$PhNO_2(A)$	4	45	171 (42.7)	62	0	38
		48	>99	378 (7.88)	0	>99	0
	PhNO (I)	1	>99	378 (378)	54	46	0
		48	>99	378 (7.88)	0	>99	0
$Pd_3Sn_2^h (51 \pm 7)$	$PhNO_2(A)$	4	51	402 (101)	>99	0	0
		48	92	725 (15.1)	30	29	42
$Pd_3Pb^{75} (12 \pm 1)$	$PhNO_2(A)$	1	93	194 (194)	0	0	>99
		2	>99	208 (104)	0	0	>99
$PtSn^{h} (24 \pm 4)$	$PhNO_2(A)$	4	52	45.6 (11.4)	38	36	26
		48	86	75.4 (1.57)	0	>99	0
$Pd^g (5 \pm 1)$	$PhNO_2(A)$	1	89	8.09 (8.09)	0	0	>99
		4	>99	9.09 (2.27)	0	0	>99
$Pt^g (16 \pm 1)$	$PhNO_2(A)$	1	49	26.1 (26.1)	78	0	22
		48	95	50.5 (12.6)	2.5	6.9	91
$\beta-\mathrm{Sn}^g\ (55\pm 6)$	$PhNO_2(A)$	4	82	61.2 (15.3)	>99	0	0
		48	95	70.9 (1.48)	0	33	67
$Pd_{0.95}Sn_{0.05}/C^{76} (10 \pm 2)$	$PhNO_2(A)$	48	>99	19.3 (0.400)	0	0	>99
$Pd_{0.87}Sn_{0.13}/C^{76}$ (8 ± 1)	$PhNO_2(A)$	48	91	15.4 (0.320)	0	0	>99

^aTen milligrams of the nanocatalyst, 0.1 mmol reactant, 0.6 mmol NaBH₄, 2 mL of ethanol, and 25 °C (see Methods). ^bSingle crystalline domain (Scherrer) size in nm. ^cThe standard deviation of conversion measurements obtained from multiple runs across all catalyst types averaged 11%. ^dTON = moles of converted reactant/moles of individual (per atom) surface active nanocatalyst sites. ^eTOF = TON/time. ^fDetermined by GC–MS. ^gCommercial. ^hThis work and ref 74.

active, with a TOF_{max} of 11.4 h^{-1} and 86% conversion after 48 h (Table 1 and Figure 5).

In contrast to the other intermetallic nanoparticle catalysts studied here, we note that Pd_3Pb nanoparticles show a preference for the direct—rather than the condensation—pathway (Scheme 1). In fact, azoxy or azo intermediates remain undetected during the progress of the reaction when this nanocatalyst is used. The activity of Pd_3Pb nanoparticles is significantly higher compared to that of Ge- and Sn-based intermetallic nanoparticles; their TOF_{max} is $194 \, h^{-1}$, with 1 and 2 h conversions of 93 and >99%, respectively (Table 1). Overall, moving down group 14—as the tetrel gets heavier—generally increases the catalytic activity, 1,10,28,29 with noticeable effects also on each of the nanocatalysts' selectivity.

Comparison to Single Metal Nanoparticles and Nanoalloys. In addition to the literature catalyst nano Au/ ${\rm TiO_2}^{76}$ —see above—we also studied nitrobenzene reduction catalyzed by monometallic Pd, Pt, and Sn nanoparticles obtained commercially. Among these unsupported catalysts, Pt nanoparticles are the most active with a ${\rm TOF_{max}}$ of 26.1 and >99% conversion within 4 h (Table 1). The reduction of nitrobenzene over Pt and Sn nanoparticles may proceed through both the direct and condensation pathways, as indicated by the presence of azoxy and azo intermediates at early reaction times (Table 1). In both Pt and Sn nanoparticle cases, aniline is the major product after 48 h, showing that both

metals are able to reduce azobenzene to aniline. Pt nanoparticles are slightly better at this step than Sn nanoparticles, with an aniline selectivity at 48 h of 91 and 67%, respectively (Figure 5). In contrast to monometallic Pt or Sn nanoparticles, no intermediates are observed during nitrobenzene reduction over Pd nanoparticles, indicating that the latter prefer the direct pathway. This strongly indicates that the presence of the group 14 (tetrel) element—Ge, Sn, Pb—in the intermetallic nanoparticles affects the activity and—in the case of Ge and Sn but not Pb nanoparticles—the preferred pathway and selectivity of the reaction.

To probe the effect of nanoparticle atomic structuring on catalytic behavior, we tested disordered—also called "random"— Pd_xSn_{1-x} nanoalloys as catalysts for nitrobenzene reduction. While these only reach limited TOF_{max} values of 0.400-0.320, they otherwise behave similarly to monometallic Pd nanoparticles, with 48 h conversions of >99 and 91% for $Pd_{0.95}Sn_{0.05}$ and $Pd_{0.87}Sn_{0.13}$ nanoalloys, respectively (Figure 5). Both nanoalloy catalysts are selective for aniline, with no azo(xy) intermediates observed throughout the reaction. This indicates that the reaction over these catalysts follows the direct pathway, as it does with Pd nanoparticles. Further, as observed for Pd-Sn nanoparticle intermetallics, the specific Sn content affects the catalytic activity because both nanoalloys and intermetallic nanoparticles with a lower Sn content show a higher conversion. However, unlike Pd-Sn intermetallic

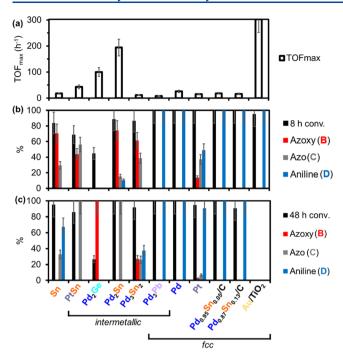


Figure 5. Representative activity and selectivity data for the catalytic reduction of nitrobenzene over binary 10-14 intermetallic nanoparticles, monometallic nanoparticles, and Pd_xSn_{1-x}/C nanoalloys (0.1 mmol nitrobenzene, 0.6 mmol NaBH₄, 10 mg of the nanocatalyst, 2 mL of ethanol, 25 °C; see Methods). (a) TOF_{max} (4 h data for Pd_2Ge , Pd_2Sn , Pd_3Sn_2 , PtSn, Sn, and Au/TiO_2 and 1 h data for Pd_3Pb , Pd, Pt, $Pd_{0.95}Sn_{0.05}/C$, and $Pd_{0.87}Sn_{0.13}/C$), % conversion, and product selectivities at (b) 8 h and (c) 48 h. The standard deviation of conversion measurements obtained from multiple runs across all catalyst types averaged 11%.

nanoparticles, the Sn content does not appear to impact the selectivity of the Pd_xSn_{1-x} nanoalloys. Together, these observations strongly indicate that atomic ordering has a significant impact in catalysis by intermetallic nanoparticles.

Nitrosobenzene Reduction. To gain a deeper insight into the mechanism of the catalytic reaction, we replaced the reactant with nitrosobenzene, a possible intermediate of nitrobenzene reduction (I in Scheme 1). In this case, even in the absence of a catalyst, nitrosobenzene is rapidly reduced by NaBH₄ to azoxybenzene (Scheme 2 and Figure 6). However, after this initial reduction, only a small amount of azoxybenzene is converted to azobenzene, and the azoxybenzene to azobenzene ratio levels off at ca. 4:1 after 48 h (Figure 6). In contrast, in the presence of Pd₂Sn, the azoxybenzene is fully converted to azobenzene after 8 h (Figure 6b), demonstrating once more the impact of the Pd₂Sn intermetallic nanoparticle on the chemoselectivity of the reaction. This experiment supports the observation that nitrobenzene reduction over Pd₂Sn nanoparticles almost exclusively follows the condensation pathway, with Pd₂Sn nanoparticles being very active for the conversion of azoxybenzene to azobenzene but not as active for the sequential reduction of azobenzene to aniline. When Au/ TiO₂ is used as the catalyst, nitrosobenzene reduction results in ~50% aniline, ~40% azobenzene, and very minimal ~10% azoxybenzene in 1 h. After 48 h, azoxybenzene disappears and the aniline to azobenzene ratio levels off at ca. 7:3 (Figure 6c). This reveals that, while Au/TiO₂ normally follows the direct

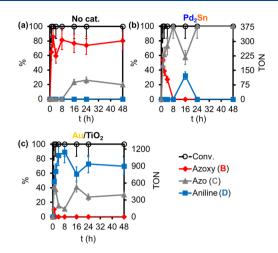


Figure 6. Reduction of nitrosobenzene (a) without a catalyst, (b) over Pd₂Sn nanoparticles, and (c) over Au/TiO₂. TON was not calculated for (a) because no catalyst was used. The standard deviation of conversion measurements obtained from multiple runs across all catalyst types averaged 11%.

pathway to aniline, it is also able to reduce azoxybenzene to azobenzene.

Nanoreactor Simulations. We first attempted to elucidate the selectivity for nitroarene reduction on intermetallic nanoparticle catalysts using standard "static" DFT analysis of reactant configuration energetics on perfect low-index single-crystal surfaces. However, these surfaces do not necessarily reflect relevant catalyst configurations. Furthermore, this is not a viable way to successfully probe the large configurational phase space to extract relevant catalytic pathways and energetics.

Instead, molecular dynamic (MD) simulations with reliable interactions, e.g., obtained from the density functional theory (DFT), provide a way to address this challenge. Indeed, our ab initio MD simulations have allowed us to identify a phenylamino radical $(C_6H_5N\bullet)$ as an important reaction intermediate on the Pd2Sn nanocatalyst (see details in Methods). In all circumstances where the phenylamino intermediate is stable for an extended amount of time, its N atom is bonded to two Sn atoms; in addition, this pair of Sn atoms is bonded together, which differs from the intermetallic bulk catalyst structure. Ab initio MD simulations show that at 1200 K, an arbitrary temperature set artificially high enough to speed up the simulations in silico, using Pd₂Sn catalysts leads to nitrosobenzene and its hydrogenation products, with the chemical formula C_6H_nNO (n = 5-10). The mechanism of this reaction involves the hydrogenation of one of the two oxygen atoms in nitrobenzene with subsequent removal of the newly formed OH group. Increasing the temperature to 1500 K results in the removal of the second oxygen atom; in this case, most of the product is aniline (C_6H_7N) , but there is still a significant amount of phenylamino radical present. Simulations with Au clusters as catalysts show a much smaller amount of phenylamino intermediate, which was observed in only one simulation at 2000 K. Simulations with Pt clusters as catalysts show that the hydrogenation process is much quicker than that over Au or Pd₂Sn catalysts. Most notably, various aniline hydrogenation products, with the chemical formula C_6H_nN (n = 9, 11, etc.), dominate over Pt catalysts, with a minimal amount of phenylamino present.

The aforementioned *ab initio* MD simulations are computationally expensive and limited to very small systems and short time scales. Recently, potentials that can be trained by machine learning were developed that can speed up the MD simulations by several orders of magnitude. The MD simulations by several orders of magnitude. DeePMD framework, which has been used for various applications in physical and materials science. Here, we employ the DeePMD framework for what we believe is the first such analysis of a heterogeneous catalytic system.

Specifically, we use clusters with total number of atoms N=192—in the case of Pd_2Sn , this corresponds to 128 Pd's and 64 Sn's—and 32 molecules of nitrobenzene, 32 of ethanol, and 384 of H_2 in a periodic cube of side length 3 nm to analyze nitroarene reduction with 10 ps simulations. We can discern several trends not evident in our *ab initio* MD simulations. First, the ability to dissociate H_2 into chemisorbed H is very strong on pure Pd but intermediate on Pd_2Sn and very weak on pure Sn catalysts. Second, at the temperature where around half of the nitrobenzene reactants are converted, the most populous N containing species is nitrosobenzene (C_6H_5NO) on Pd_2Sn (2000 K), N-oxido-N-phenylhydroxylamine ($C_6H_6NO_2$) on Pd (2000 K), and phenylamino radical ($C_6H_5N\bullet$) on Sn catalysts (1400 K) (Figure 7). Further,

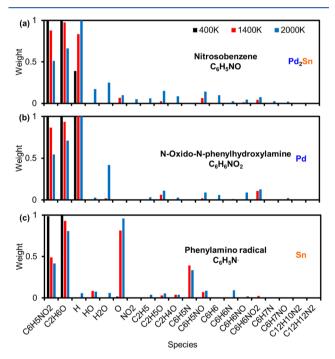


Figure 7. Selected results of simulations with (a) Pd_2Sn , (b) Pd, and (c) Sn nanocatalysts at various temperatures (see details in Methods). The major products at 50% nitrobenzene conversion are displayed in bold in each case.

while the initial conversion of nitrobenzene is very fast on Sn catalysts, the hydrogenation of O adatoms is slower on Sn compared to that on Pd and Pd₂Sn catalysts. This impedes further conversion of nitrobenzene after the catalyst is covered by O adatoms or partially oxidized. At these temperatures, however, the final products may not be indicative of real experimental data near room temperature.

Longer simulations (up to 100 ps) lead to similar observations. At temperatures with 50% conversion, the most populous nitrogen species is nitrosobenzene (C_6H_5NO) on

Pd₂Sn (1200 K), *N*-oxido-*N*-phenylhydroxylamine ($C_6H_6NO_2$) on Pd (1400 K), and phenylamino radical ($C_6H_5N\bullet$) on Sn nanocatalysts (800 K) (Figure 8). While

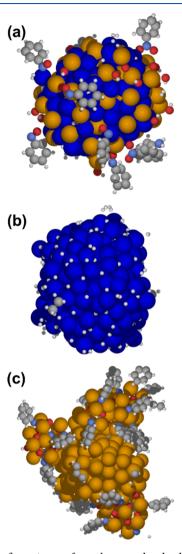


Figure 8. Configurations of catalysts and adsorbed molecules obtained from 100 ps simulations at 50% conversion temperatures: (a) 1200 K Pd₂Sn, (b) 1400 K Pd, and (c) 800 K Sn catalysts (initially with 32 molecules of nitrobenzene, 32 of ethanol, and 384 of $\rm H_2$) (see SI as well as Methods).

these temperatures are still much higher than R.T., the results are consistent with simulations run for 1/10 shorter time. Further examination of the simulation results shows that ethanol does not directly participate in the reaction. Because it also does not adsorb to the catalyst significantly, we ignored ethanol in further analyses.

DeePMD Reaction Pathway Analysis. Even with machine learned potentials, long enough simulations at realistic temperatures are nearly impossible. Therefore, we tailored the simulations to gain more insight into the intermediate steps of the reactions. Using Pd_2Sn as a catalyst, our initial simulations for nitrobenzene reduction show that nitrosobenzene is the most populous product between t=10 and 100 ps at T<1200 K. Simulations starting with nitrosobenzene and H_2 molecules as reactants initially yield only phenylamino radical $(C_6H_5N\bullet)$ along with nitrosobenzene dimers $(C_{12}H_{10}N_2O_2)$. Azoxyben-

zene $(C_{12}H_{10}N_2O)$ starts to appear at around T=1200 K, while aniline (C_6H_7N) formation remains minimal. This shows that Pd_2Sn catalysts have a clear selectivity toward azoxybenzene $(C_{12}H_{10}N_2O)$ when the initial reactant is nitrosobenzene (C_6H_5NO) . In other words, simulations show that the reaction from C_6H_5NO to $C_6H_5N\bullet$ and O on Pd_2Sn catalysts is very facile and that this is followed by the reaction of $C_6H_5N\bullet$ and C_6H_5NO to produce $C_{12}H_{10}N_2O$. Notably, azobenzene $(C_{12}H_{10}N_2)$ is not observed, demonstrating that azoxybenzene $(C_{12}H_{10}N_2O)$ is a necessary intermediate for the formation of any final azobenzene.

With azoxybenzene ($C_{12}H_{10}N_2O$) and H_2 as reactants, we start to observe azobenzene ($C_{12}H_{10}N_2$) at $T=1200~\rm K$. However, the conversion rate is surprisingly low, much less than the rates for oxygen detachment from nitrobenzene and nitrosobenzene. Further analysis of these data shows that the conversion rate of azoxybenzene can be fitted to an Arrhenius equation with a barrier of 0.94 eV and a prefactor of $6.4\times10^{13}~\rm s^{-1}$, which can be extrapolated to 0.01 s⁻¹ at 300 K, in reasonable agreement with experiments.

Above, we concluded that when a Pd catalyst is used, the first reaction product is N-oxido-N-phenylhydroxylamine ($C_6H_6NO_2$). Simulations starting from N-oxido-N-phenylhydroxylamine and H_2 show that nitrosobenzene (C_6H_5NO) is the main product below 1000 K, aside from that converted back to nitrobenzene ($C_6H_5NO_2$). Some N,N-dihydroxyaniline ($C_6H_7NO_2$) can also be found at low T. When starting from nitrosobenzene and H_2 for a Pd catalyst, the main product below 1000 K is N-oxidoaniline (C_6H_6NO), with some nitrosobenzene dimers ($C_{12}H_{10}N_2O_2$) also present. Starting with N-oxidonaniline (C_6H_6NO) and H_2 , the first product is phenylhydroxylamine (C_6H_7NO). Starting from phenylhydroxylamine, the phenylamino radical ($C_6H_5N\bullet$) quickly forms by detaching one $HO\bullet$ radical. Subsequently, this can be easily hydrogenated to aniline (C_6H_7N).

As also mentioned above, in the presence of the O-covered Sn catalyst, nitrobenzene $(C_6H_5NO_2)$ is very quickly converted to phenylamino radical $(C_6H_5N\bullet)$ and nitrosobenzene (C_6H_5NO) . Further reaction is inhibited by the oxygen because Sn catalysts can neither accept more oxygen from nitrobenzene nor dissociate any H unless the surface oxygen is hydrogenated. Direct simulation on a Sn cluster with O_2 and O_2 and O_3 molecules yields a barrier for oxygen hydrogenation of 0.91 eV and a prefactor of O_3 note oxygen is removed, hydrogenation proceeds similarly to that over O_3 no catalysts.

With insight from DeePMD simulations, it is clear that nitrosobenzene (C₆H₅NO) forms easily from nitrobenzene and thus is not a limiting step with any of the nanocatalysts tested. Further, nitrosobenzene is reduced to phenylamino radical (C₆H₅N•) over Pd₂Sn, whereas it is hydrogenated to N-oxidoaniline (C_6H_6NO) over Pd catalysts. Starting with nitrobenzene (C₆H₅NO₂) over either Pd or Pd₂Sn catalysts, there is also a reaction pathway going through N-oxido-Nphenylhydroxylamine (C₆H₆O₂), N,N-dihydroxyaniline $(C_6H_7NO_2)$, and N-oxidoaniline (C_6H_6NO) . N-Oxidoaniline is then converted to aniline (C₆H₇N) through the aforementioned pathway with Pd nanocatalysts, allowing some aniline production on Pd₂Sn catalysts starting from nitrobenzene. However, starting with nitrosobenzene, this pathway is blocked, and thus, aniline production is blocked at low temperatures, in agreement with our experimental observations. In summary, there are two pathways for the hydrogenation of nitrobenzene with Pd catalysts, both leading to aniline. The first is through nitrosobenzene, and the other is through *N*,*N*-dihydroxyaniline. On Pd₂Sn nanocatalysts, the pathway through nitrosobenzene leads to azoxybenzene and azobenzene, while the pathway through *N*,*N*-dihydroxyaniline may lead to aniline at sufficiently high temperatures.

CONCLUSIONS

In summary, we find that a majority of the intermetallic nanoparticle catalysts tested—namely, Pd₂Ge, Pd₂Sn, Pd₃Sn₂, and PtSn nanoparticles—favor the indirect condensation pathway and are selective for azoxybenzene. The only exceptions are Pd₃Pb nanoparticles, which prefer the direct pathway and are selective for aniline. Interestingly, Pd₃Pb nanoparticles are also unique among these nanocatalysts in adopting a face centered cubic (fcc) structure, a feature shared with monometallic Au, Pd, and Pt nanoparticles and Pd_xSn_{1-x} nanoalloys, all of which are also selective for aniline. In all cases studied, the observed turnover numbers are significantly higher than 1, which attest to the catalytic nature of the intermetallic nanoparticles. Maximum turnover frequencies are 1 to 3 orders of magnitude faster than those of other unsupported monometallic and alloyed nanocatalysts and comparable to those of nano Au on TiO₂. Among the different intermetallic nanocatalyst compositions, the observed order of activity is Pd_3Pb (highest) > Pd_3Sn_2 > Pd_2Sn > Pd_2Ge > PtSn. In other words, for a given set of group 10 metal-based intermetallic nanoparticles, moving down group 14—using a heavier tetrel—increases the catalytic activity.

While standard DFT analysis of the reaction on low-index single-crystal surfaces fails to explain the selectivity of intermetallic nanocatalysts, ab initio molecular dynamic (MD) simulations allow us to observe critical intermediates and discern significant differences among various nanocatalysts. Machine learned potentials using a deep neural network (DeePMD), which speed up the simulations by several orders of magnitude, show that (1) the ability to chemisorb H₂ is very strong on Pd, intermediate on Pd₂Sn, and very weak on pure Sn nanoparticles; (2) at 50% conversion temperatures, the most populous N containing species are nitrosobenzene on Pd₂Sn, N-oxido-N-phenylhydroxylamine on Pd, and the phenylamino radical on Sn nanoparticles; and (3) while the initial conversion is very fast on Sn nanoparticles, the hydrogenation of O adatoms is slow, impeding further conversion. DeePMD simulations tailored to gain more insight into the intermediate steps of the reactions show that (4) the nitrosobenzene formation from nitrobenzene is easy and not a limiting step with any of the nanocatalysts tested; (5) the reaction from nitrosobenzene to the phenylamine radical and O on Pd₂Sn nanoparticles is facile, and this is followed by the reaction with nitrosobenzene to produce azoxybenzene; and (6) nitrosobenzene is further reduced to the phenylamino radical or N-oxidoaniline over Pd nanoparticles, both of which can be further reduced to aniline. We hope that this contribution will continue to motivate additional studies and catalytic applications of highly selective binary and other more complex intermetallic nanomaterials.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.1c08569.

Additional synthesis and catalysis schemes, catalyst stability and recycling data for Pd₂Sn, a comparison of the activity and selectivity for nitrobenzene and *p*-nitrotoluene reduction with different nanoparticle catalysts and reaction times, UV–vis absorption data of different catalysis products, additional computational data, and mechanistic pathways (PDF)

Partial simulation movie (AVI)

Partial simulation movie (MP4)

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

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