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Citation	Chemistry – A European Journal. 2024, 30(13), p. e202303573
Version Type	VoR
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# Nickel Carbide Nanoparticle Catalyst for Selective Hydrogenation of Nitriles to Primary Amines

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Despite its unique physicochemical properties, the catalytic application of nickel carbide (Ni<sub>3</sub>C) in organic synthesis is rare. In this study, we report well-defined nanocrystalline Ni<sub>3</sub>C (nano-Ni<sub>3</sub>C) as a highly active catalyst for the selective hydrogenation of nitriles to primary amines. The activity of the aluminum-oxide-supported nano-Ni<sub>3</sub>C (nano-Ni<sub>3</sub>C/Al<sub>2</sub>O<sub>3</sub>) catalyst surpasses that of Ni nanoparticles. Various aromatic and aliphatic nitriles and dinitriles were successfully converted to the corresponding

primary amines under mild conditions (1 bar H<sub>2</sub> pressure). Furthermore, the nano-Ni<sub>3</sub>C/Al<sub>2</sub>O<sub>3</sub> catalyst was reusable and applicable to gram-scale experiments. Density functional theory calculations suggest the formation of polar hydrogen species on the nano-Ni<sub>3</sub>C surface, which were attributed to the high activity of nano-Ni<sub>3</sub>C towards nitrile hydrogenation. This study demonstrates the utility of metal carbides as a new class of catalysts for liquid-phase organic reactions.

## Introduction

Metal carbides possess several unique properties, including high electrical conductivity, mechanical strength and hardness, and high stability,<sup>[1,2]</sup> which have attracted considerable atten-

tion across various fields, such as superconducting materials<sup>[3]</sup> and solar heat absorbers.<sup>[4]</sup> Recent advancements in nanotechnology have enabled the precise synthesis of metal carbide nanoparticles (NPs), opening avenues for their catalytic functions to be explored.<sup>[5]</sup> In particular, nickel carbide NPs (Ni<sub>3</sub>C NPs) have shown great potential as electrodes in O<sub>2</sub>/H<sub>2</sub> evolution reactions,<sup>[6–9]</sup> photocatalytic applications,<sup>[10]</sup> and dry reforming of methane.<sup>[11]</sup> However, despite their unique catalytic properties, the application of Ni<sub>3</sub>C NPs in liquid-phase molecular transformations is rare.<sup>[12]</sup> Therefore, investigating the potential of Ni<sub>3</sub>C NP catalysts in the liquid-phase is of great interest in organic synthesis.

The hydrogenation of nitriles into primary amines plays a pivotal role in the production of solvents, surfactants, and numerous essential building blocks in fine chemical synthesis. Noble metal catalysts, such as Ru<sup>[13,14]</sup> and Pd,<sup>[15,16]</sup> are among the most effective heterogeneous catalysts for nitrile hydrogenation. Nevertheless, the scarcity and high cost of noble metals impede their widespread industrial use. Alternatively, non-noble metal catalysts are widely used in the industrial hydrogenation of nitriles owing to their earth-abundance and low-cost.<sup>[17]</sup> However, metallic catalysts like Ni,<sup>[18–28]</sup> Co,<sup>[29–32]</sup> and Fe<sup>[33]</sup> typically require harsh reaction conditions, including high temperatures and H<sub>2</sub> pressures. Consequently, developing non-noble-metal catalysts that exhibit high activity under mild conditions is of great importance.<sup>[34–37]</sup>

In this study, we synthesized well-defined nanocrystalline Ni<sub>3</sub>C (nano-Ni<sub>3</sub>C), and its catalytic performance was evaluated. It was found that nano-Ni<sub>3</sub>C supported on aluminum oxide (nano-Ni<sub>3</sub>C/Al<sub>2</sub>O<sub>3</sub>) exhibited high catalytic activity in the hydrogenation of nitriles to primary amines, even under atmospheric H<sub>2</sub> pressure. The catalytic performance of nano-Ni<sub>3</sub>C/Al<sub>2</sub>O<sub>3</sub> significantly differed from that of Ni NPs. nano-Ni<sub>3</sub>C/Al<sub>2</sub>O<sub>3</sub> displayed a broad substrate scope and good reusability. We performed density functional theory (DFT) calculations to explain the high catalytic performance of nano-Ni<sub>3</sub>C.

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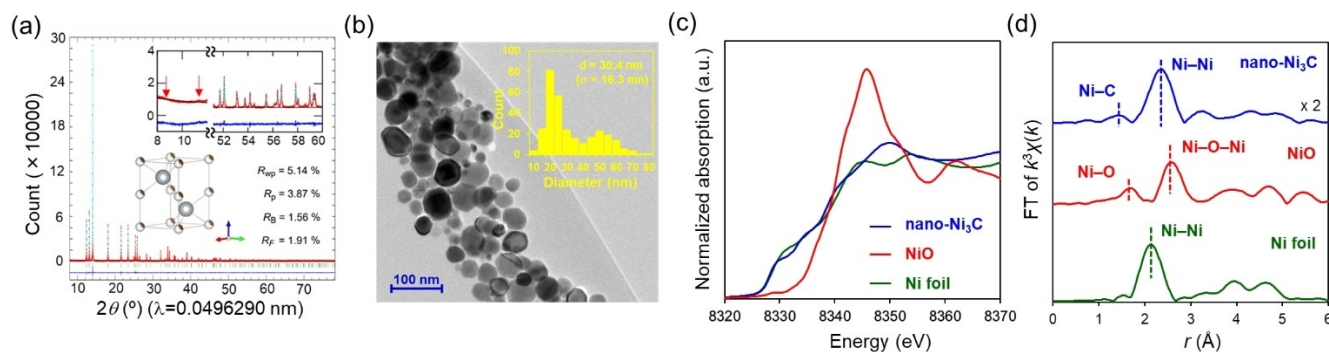
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Supporting information for this article is available on the WWW under <https://doi.org/10.1002/chem.202303573>

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**Figure 1.** Structural and morphological characterization of nano-Ni<sub>3</sub>C. (a) Rietveld refinement profile of synchrotron XRD spectrum and structural position. Observed (red), calculated (sky-blue) patterns, and the difference (blue) between them resulting from Rietveld analysis. Green vertical bars denote positions of Bragg diffraction. Red arrows in the inset indicate the absence of superlattice peaks. (b) TEM image with size distribution histogram (inset). (c) Ni K-edge XANES spectra and (d) Ni K-edge FT-EXAFS spectra of nano-Ni<sub>3</sub>C, NiO, and Ni foil.

## Results and Discussion

### Characterization of nano-Ni<sub>3</sub>C

Figure 1a presents the Rietveld analysis of nano-Ni<sub>3</sub>C (Tables S1 and S2). Ni<sub>3</sub>C is a non-stoichiometric compound that is known to adopt two different hexagonal structures: one with hexagonal parameters of  $a = 2.6449 \text{ \AA}$  and  $c = 4.3296 \text{ \AA}$ <sup>[38]</sup> and the other as a superstructure with the lattice parameters of  $a = 4.555 \text{ \AA}$  and  $c = 12.92 \text{ \AA}$  where the  $a$ - and  $c$ -axis is approximately square root of three times longer and three times longer, respectively.<sup>[39]</sup> The absence of superlattice peaks at lower angles, indicated by red arrows, and the improved fitting factor,  $R_{wpr}$ , transitioning from 5.54% (superstructure) to 5.14% (simple structure) suggest a simple structure, with  $a = 0.264965(1) \text{ nm}$  and  $c = 0.433573(1) \text{ nm}$ . The occupation of the C site converged to 0.309(3); thus, the chemical formula was Ni<sub>3</sub>C<sub>0.927(9)</sub>. Furthermore, a representative transmission electron microscopy (TEM) image of nano-Ni<sub>3</sub>C illustrates the formation of spherical particles with sizes ranging from 10–80 nm (Figure 1b). The electronic states of the Ni species in nano-Ni<sub>3</sub>C were identified using X-ray absorption fine structure (XAFS) spectroscopy. The absorption edge energy in the Ni K-edge X-ray absorption near edge structure (XANES) spectrum of nano-Ni<sub>3</sub>C closely resembled that of Ni foil, indicating that Ni species in nano-Ni<sub>3</sub>C existed in a metallic state (Figure 1c). This result is in good agreement with the X-ray photoelectron spectra, where two peaks at 852.9 and 870.1 eV in the spectrum of nano-Ni<sub>3</sub>C are similar to those of Ni 2<sub>p<sub>3/2</sub></sub> (852.7 eV) and Ni 2<sub>p<sub>1/2</sub></sub> (870.0 eV),<sup>[40]</sup> respectively, in the spectrum of metallic Ni (Figure S1). Figure 1d displays the Fourier transform of the extended XAFS (FT-EXAFS) spectrum of nano-Ni<sub>3</sub>C, with NiO and Ni foils as references. The peaks at 1.50 and 2.42 Å in the spectrum of nano-Ni<sub>3</sub>C were assigned to the Ni–C and Ni–Ni shells, respectively. The curve-fitting analyses of the EXAFS spectra are shown in Figure S2 and the results are summarized in Table S3. The Ni–Ni bond is longer than that in the Ni foil owing to the expansion of the Ni lattice resulting from the insertion of carbon atoms. Moreover, the absence of Ni–O bonds indicates that the nano-Ni<sub>3</sub>C was not oxidized, which is consistent with

the XANES and X-ray photoelectron spectra. These results clearly demonstrate the successful synthesis of spherical, phase-pure nano-Ni<sub>3</sub>C.

### Catalytic Performance of nano-Ni<sub>3</sub>C in the Hydrogenation of Nitriles

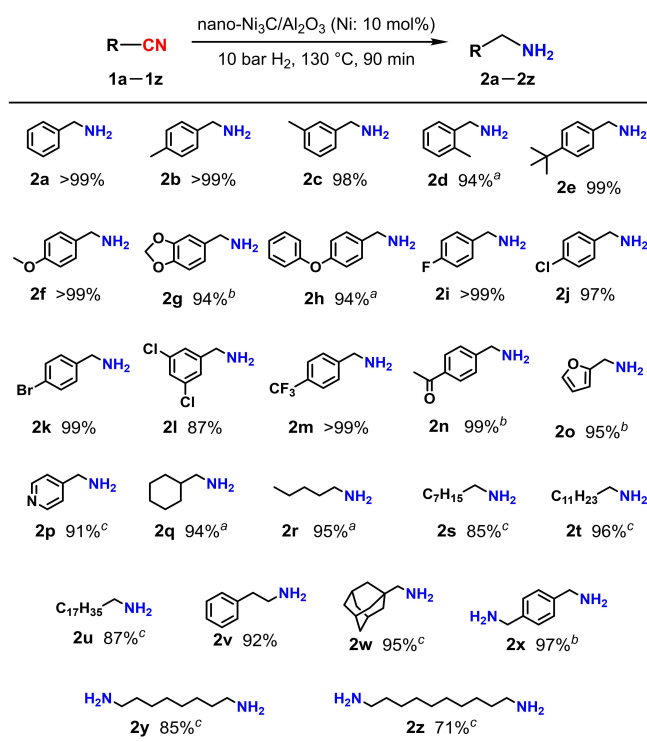
Using ammonia as additives is crucial to promote the selective hydrogenation of **1a** to primary amines (see Scheme S1).<sup>[41]</sup> Thus, the hydrogenation of **1a** using nano-Ni<sub>3</sub>C was performed in the presence of NH<sub>3</sub> aq. at 130 °C under 10 bar H<sub>2</sub> to afford benzylamine (**2a**) and *N*-benzylidenebenzylamine (**3a**) in 31% and 8% yields, respectively (Table 1, Entry 1). nano-Ni<sub>3</sub>C can be easily immobilized on various support materials. nano-Ni<sub>3</sub>C/Al<sub>2</sub>O<sub>3</sub> demonstrated high activity, yielding **2a** in a 68% yield (Table 1, Entry 2). The performance of nano-Ni<sub>3</sub>C/Al<sub>2</sub>O<sub>3</sub> surpassed those of nano-Ni<sub>3</sub>C on other supports of hydrotalcite (HT), TiO<sub>2</sub>, SiO<sub>2</sub>, and activated carbon (see Scheme S2, Figures S3, and Tables S4,5). By increasing the amount of nano-Ni<sub>3</sub>C/Al<sub>2</sub>O<sub>3</sub>, **2a** was obtained in >99% yield (Table 1, Entry 4). These results revealed that the combination of nano-Ni<sub>3</sub>C and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>

**Table 1.** Hydrogenation of benzonitrile (**1a**) to benzylamine (**2a**) using various Ni catalysts.<sup>[a]</sup>

Entry	Catalyst	Conv. of <b>1a</b> [%] <sup>[b]</sup>	Yield of <b>2a</b> [%] <sup>[b]</sup>	Yield of <b>3a</b> [%] <sup>[b]</sup>
1	nano-Ni <sub>3</sub> C	45	31	8
2	nano-Ni <sub>3</sub> C/Al <sub>2</sub> O <sub>3</sub>	78	68	9
3	Ni NPs/Al <sub>2</sub> O <sub>3</sub>	29	16	7
4 <sup>[c]</sup>	nano-Ni <sub>3</sub> C/Al <sub>2</sub> O <sub>3</sub>	> 99	> 99	< 1

[a] Reaction conditions: **1a** (0.5 mmol), 2-propanol (3 mL), and 25% NH<sub>3</sub> aq. (1.2 mL). [b] Conversion and yields were determined by gas chromatography-flame ionization detection (GC-FID) using an internal standard method. [c] Ni 10 mol%.

provided superior catalytic performance for nitrile hydrogenation. The differences in the catalytic activities of the nano-Ni<sub>3</sub>C and Ni NPs were investigated using Ni NPs prepared with a similar shape and size to those of nano-Ni<sub>3</sub>C (Figures S4–S6, see Experimental section for details). In the hydrogenation of **1 a**, Ni NPs/Al<sub>2</sub>O<sub>3</sub> afforded **2 a** in 16% yield (Table 1, Entry 3). The yield of **2 a** obtained using nano-Ni<sub>3</sub>C/Al<sub>2</sub>O<sub>3</sub> was four times higher than that obtained using Ni NPs/Al<sub>2</sub>O<sub>3</sub> (Table 1, Entries 2 and 3), clearly demonstrating the outstanding activity of the nano-Ni<sub>3</sub>C/Al<sub>2</sub>O<sub>3</sub> catalyst.



**Scheme 1.** Hydrogenation of various nitriles using the nano-Ni<sub>3</sub>C/Al<sub>2</sub>O<sub>3</sub> catalyst. Reaction conditions: nano-Ni<sub>3</sub>C/Al<sub>2</sub>O<sub>3</sub> (0.058 g), substrate (0.5 mmol), 2-propanol (3 mL), 25% NH<sub>3</sub> aq. (1.2 mL). Yields were determined by gas chromatography-mass spectrometry (GC-MS) using an internal standard method. [a] 40 bar H<sub>2</sub>, 6 h. [b] 3 h. [c] 150 °C, 40 bar H<sub>2</sub>, 12 h.

## Applicability and Durability of nano-Ni<sub>3</sub>C in Nitrile Hydrogenation

To demonstrate the broad applicability of nano-Ni<sub>3</sub>C/Al<sub>2</sub>O<sub>3</sub>, the substrate scope was investigated using various (hetero)aromatic and aliphatic nitriles (Scheme 1). Benzonitriles with electron-donating (–Me, –tBu, –OMe, and –OPh) and electron-withdrawing groups (–F, –Cl, –Br, –CF<sub>3</sub> and –acetyl) were efficiently hydrogenated to the corresponding primary amines **2 a–2 n** in high yields. The nano-Ni<sub>3</sub>C/Al<sub>2</sub>O<sub>3</sub> catalyst showed high chemoselectivity toward nitrile group in the intramolecular competitive reaction of halogen substituted benzonitrile; the Cl– and Br– groups of aromatic nitriles (**1 j**, **1 k**) remained intact under the examined reaction conditions, although the supported Ni catalysts are known to promote the hydrodehalogenation of aryl halides.<sup>[42,43]</sup> Indeed, hydrogenation of **1 j** using Ni NPs/Al<sub>2</sub>O<sub>3</sub> catalyst afforded **2 j** with the dehalogenated product **2 b**, clearly demonstrating the advantages of the nano-Ni<sub>3</sub>C/Al<sub>2</sub>O<sub>3</sub> catalyst enabling the chemoselective hydrogenation of halo-benzonitriles (Table S6). 4-Iodobenzonitrile resulted in low selectivity to desired primary amine (Scheme S3a). 4-Aminobenzonitrile was not reacted at all (Scheme S3b). The heteroaromatic nitriles 2-furancarboxitrile (**1 o**) and 4-cyanopyridine (**1 p**) were converted into the desired amines **2 o** and **2 p**, respectively, in excellent yields; however, hydrogenation of 2-thiophenecarbonitrile did not proceed (Scheme S3c). The aliphatic nitriles **1 q–1 v** were also converted to the corresponding amines in high yields, and the sterically hindered nitrile **1 w** smoothly underwent hydrogenation to produce amine **2 w** in 95% yield. Furthermore, the hydrogenation of the aromatic and aliphatic dinitriles **1 x**, **1 y**, and **1 z** afforded the corresponding diamines **2 x**, **2 y**, and **2 z**, which are important precursors in the synthesis of valuable plastics and fibers, in satisfactory yields. These results clearly demonstrate the versatility and substrate scope of nano-Ni<sub>3</sub>C/Al<sub>2</sub>O<sub>3</sub> in the hydrogenation of nitriles to primary amines.

In contrast to most existing non-noble metal catalysts, which require high-pressure H<sub>2</sub>, this nano-Ni<sub>3</sub>C catalyst system operates well under atmospheric H<sub>2</sub> pressure (Tables 2 and S7); nano-Ni<sub>3</sub>C/Al<sub>2</sub>O<sub>3</sub> efficiently hydrogenated a wide range of aromatic and aliphatic nitriles into the corresponding primary

**Table 2.** Comparison of activity between nano-Ni<sub>3</sub>C and reported Ni catalysts for hydrogenation of **1 a**.

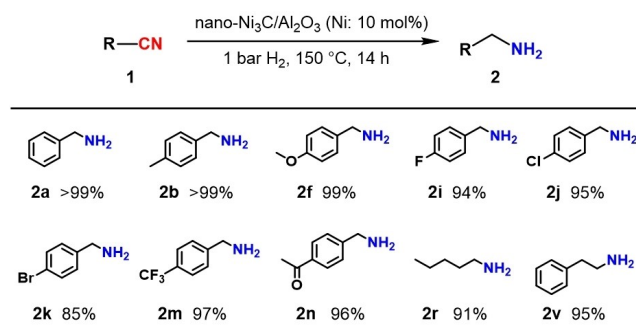
Catalyst	Reaction conditions	Yield of <b>2 a</b> [%]	TON <sup>[a]</sup>	Ref.
nano-Ni <sub>3</sub> C/Al <sub>2</sub> O <sub>3</sub>	10 mol% Ni, 2-propanol, NH <sub>3</sub> aq., 10 bar H <sub>2</sub> , 130 °C, 90 min.	99	10	This work (Table 1 entry 4)
nano-Ni <sub>3</sub> C/Al <sub>2</sub> O <sub>3</sub>	10 mol% Ni, 2-propanol, NH <sub>3</sub> aq., 1 bar H <sub>2</sub> , 150 °C, 14 h.	99	10	This work (Scheme 2)
nano-Ni <sub>3</sub> C/Al <sub>2</sub> O <sub>3</sub>	0.1 mol% Ni, 2-propanol, NH <sub>3</sub> aq., 45 bar H <sub>2</sub> , 150 °C, 40 h.	90	900	This work (Scheme 3)
nano-Ni <sub>2</sub> P	5 mol% Ni, NH <sub>3</sub> aq., 40 bar H <sub>2</sub> , 130 °C, 3 h.	95	19	35
nano-Ni <sub>2</sub> P	5 mol% Ni, NH <sub>3</sub> aq., 1 bar H <sub>2</sub> , 150 °C, 12 h.	85	17	35
Ni NPs <sup>[b]</sup>	0.7 mol% Ni, [BMIM]NTf <sub>2</sub> , 25 bar H <sub>2</sub> , 90 °C, 22 h.	80	114	21
Ni-phen@SiO <sub>2</sub>	4.5 mol% Ni, 7 M NH <sub>3</sub> /MeOH, 50 bar H <sub>2</sub> , 100 °C, 20 h.	91	20	23
MC/Ni	13 mol% Ni, MeOH, NH <sub>3</sub> aq. (36 wt. %), 2.5 bar H <sub>2</sub> , 80 °C, 6 h.	> 99	8	25
NiMg <sub>0.75</sub> Al <sub>0.25</sub> O-op	12 mol% Ni, MeOH, 40 bar H <sub>2</sub> , 100 °C, 2 h.	91	8	26
Ni/Al <sub>2</sub> O <sub>3</sub> -600	12 mol% Ni, EtOH, NH <sub>3</sub> ·H <sub>2</sub> O (36.5 wt%), 2.5 bar H <sub>2</sub> , 60 °C, 6 h.	95	8	27

[a] Based on total active metal atoms. [b] Embedded in imidazolium based ionic liquids.

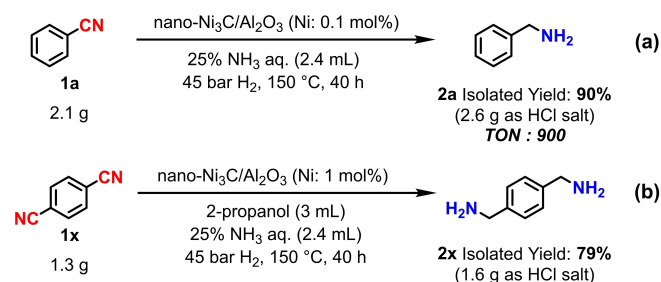


amines (**2a**, **2b**, **2f**, **2i–2k**, **2m**, **2n**, **2r** and **2v**, Scheme 2). The nano-Ni<sub>3</sub>C/Al<sub>2</sub>O<sub>3</sub> catalyst also enabled gram-scale hydrogenation. Under organic solvent-free conditions, 2.1 g of **1a** was efficiently converted to **2a**, which was obtained as the hydrochloride salt in 90% isolated yield with a turnover number of 900. This turnover number is among the highest reported in nitrile hydrogenation (Scheme 3a and Tables 2 and S7). Hydrogenation of the dinitrile 1,4-dicyanobenzene (**1x**) afforded the diamine product in 79% isolated yield (Scheme 3b).

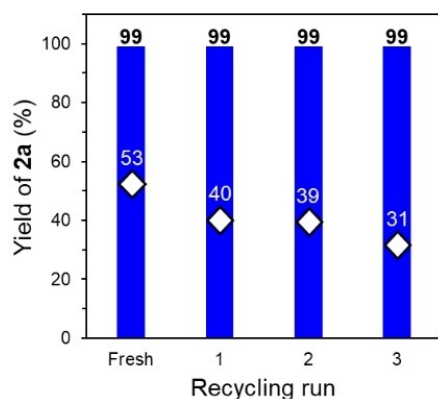
A hot filtration experiment was performed to confirm that the hydrogenation of nitriles proceeded on the nano-Ni<sub>3</sub>C/Al<sub>2</sub>O<sub>3</sub>



**Scheme 2.** Hydrogenation of various nitriles using the nano-Ni<sub>3</sub>C/Al<sub>2</sub>O<sub>3</sub> catalyst under 1 bar H<sub>2</sub>. Reaction conditions: nano-Ni<sub>3</sub>C/Al<sub>2</sub>O<sub>3</sub> (0.058 g), substrate (0.5 mmol), 2-propanol (1.5 mL), 25% NH<sub>3</sub> aq. (0.6 mL).



**Scheme 3.** Gram-scale hydrogenation of (a) **1a** and (b) **1x** with nano-Ni<sub>3</sub>C/Al<sub>2</sub>O<sub>3</sub>.

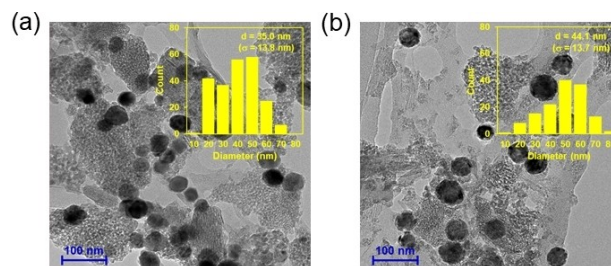


**Figure 2.** Evaluation of the nano-Ni<sub>3</sub>C/Al<sub>2</sub>O<sub>3</sub>-catalyzed hydrogenation of **1a** over 4 catalytic cycles. Reaction conditions: **1a** (0.5 mmol), nano-Ni<sub>3</sub>C/Al<sub>2</sub>O<sub>3</sub> (0.058 g, 10 mol% Ni), 2-propanol (3 mL), 25% NH<sub>3</sub> aq. (1.2 mL), H<sub>2</sub> (10 bar), 130 °C, blue bars and white diamonds represent reaction times of 90 min and 40 min, respectively.

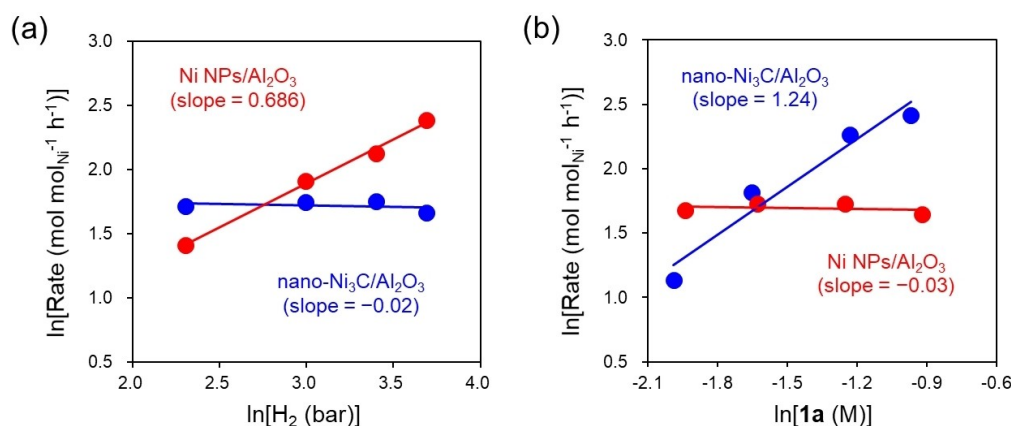
surface (Figure S7). After the removal of the nano-Ni<sub>3</sub>C/Al<sub>2</sub>O<sub>3</sub> catalyst from a reaction mixture that provided a 53% yield of **2a**, the filtrate was treated under the optimized reaction conditions (Table 1); consequently, no additional **2a** was detected in the filtrate. Moreover, the nano-Ni<sub>3</sub>C/Al<sub>2</sub>O<sub>3</sub> catalyst was easily separated from the reaction mixture and reused without pre-treatment. After four reactions, there was no reduction in the yield of **2a** (Figure 2). To obtain more detailed information regarding the catalyst reusability, the initial rate was further investigated during the recycling experiments at an incomplete reaction time (40 min). A reduction in the yield of **2a** was observed (diamonds in Figure 2). The powder X-ray diffraction (XRD) patterns (Figure S8) of nano-Ni<sub>3</sub>C/Al<sub>2</sub>O<sub>3</sub> obtained before and after the reaction were identical. The Ni K-edge XANES spectrum and the result of the curve-fitting analysis of the EXAFS of the spent nano-Ni<sub>3</sub>C/Al<sub>2</sub>O<sub>3</sub> are very similar to those of the fresh nano-Ni<sub>3</sub>C/Al<sub>2</sub>O<sub>3</sub> (Figures S2,S9 and Table S3), indicating that the electronic state and the local structure of nano-Ni<sub>3</sub>C/Al<sub>2</sub>O<sub>3</sub> do not significantly change after the reaction. However, inductively coupled plasma atomic emission spectroscopy analyses showed that the amount of Ni in the spent catalyst was 0.7 wt% lower than that of the fresh sample (Table S8). The TEM image of the spent nano-Ni<sub>3</sub>C/Al<sub>2</sub>O<sub>3</sub> catalyst revealed that the average size of the Ni carbide NPs was slightly larger than those in the fresh catalyst (Figure 3), which would explain a slight reduction in the yield of **2a** during the reuse experiments.

### Elucidation of the High Catalytic Performance of nano-Ni<sub>3</sub>C/Al<sub>2</sub>O<sub>3</sub>

To elucidate the origin of the high catalytic activity of nano-Ni<sub>3</sub>C/Al<sub>2</sub>O<sub>3</sub>, the influence of H<sub>2</sub> pressure and concentration of **1a** on the conversion rate was examined using nano-Ni<sub>3</sub>C/Al<sub>2</sub>O<sub>3</sub> and Ni NPs/Al<sub>2</sub>O<sub>3</sub> catalysts (Figure 4). In these experiments, the ranges of H<sub>2</sub> pressure and **1a** amount are 10–40 bars and 0.4–1.2 mmol, respectively (Figure S10). The initial rates using nano-Ni<sub>3</sub>C/Al<sub>2</sub>O<sub>3</sub> showed no correlation with H<sub>2</sub> pressure, but were positively correlated with the concentration of **1a**. Conversely, the initial reaction rates using Ni NPs/Al<sub>2</sub>O<sub>3</sub> were dependent on the H<sub>2</sub> pressure and were independent of the concentration of **1a**. Previous reports on the nitrile hydrogenation using Ni NPs revealed that the initial rates were more strongly dependent on the H<sub>2</sub> pressure than on the substrate concentration, which are



**Figure 3.** TEM images of (a) fresh and (b) spent nano-Ni<sub>3</sub>C/Al<sub>2</sub>O<sub>3</sub>.



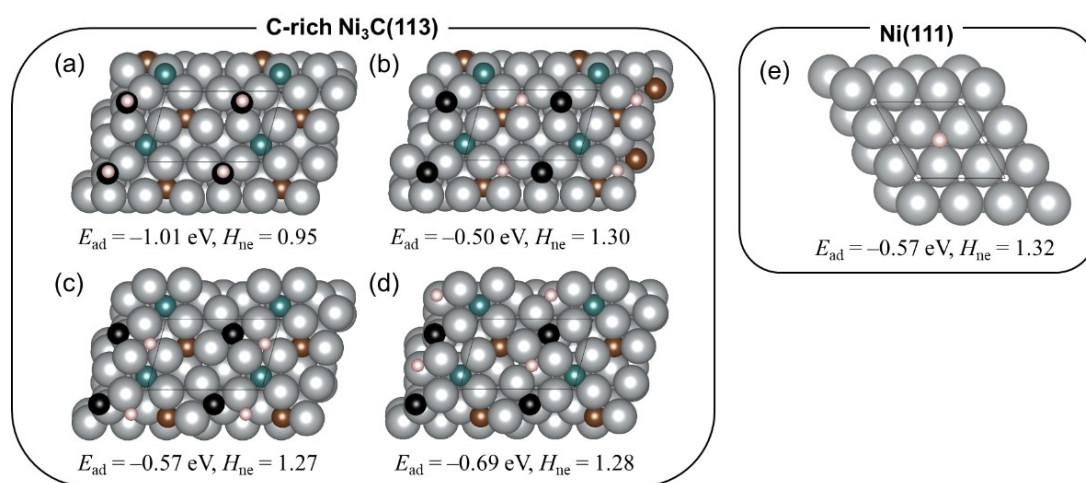
**Figure 4.** Dependence of the initial reaction rate on (a)  $H_2$  pressure and (b) concentration of **1a**. Reaction conditions: **1a** (0.4–1.2 mmol), nano- $Ni_3C/Al_2O_3$  (4.0–12.5 mol%), 2-propanol (3 mL), 25%  $NH_3$  aq. (1.2 mL),  $H_2$  (10–40 bar), 130 °C, 10–35 min.

consistent with the above results.<sup>[44–46]</sup> These results indicate that  $H_2$  strongly interacts with nano- $Ni_3C/Al_2O_3$  under the examined nitrile hydrogenation conditions.

DFT calculations were performed to gain additional insight into the interaction between  $H_2$  and the nano- $Ni_3C$  surface (**Supporting Information**). Based on previous reports,<sup>[47,48]</sup> the present study adopted a C-terminated (C-rich  $Ni_3C(113)$ ) model surface (Figure S12). The adsorption of H by C-rich  $Ni_3C(113)$  occurs at tri-coordinate C exposed on the model surface; adsorption onto the on-top site is the most stable, with an adsorption energy ( $E_{ad}$ ) of  $-1.01$  eV (Figure 5a). Figures 5b–5d show the adsorption of H on the hexagonal close-packed (hcp), face-centered cubic (fcc), and body-centered cubic (bcc) hollow sites of Ni, respectively. The  $E_{ad}$  values of the hollow sites range from 0.5–0.7 eV, and these adsorptions were 0.3–0.5 eV less stable than the most stable adsorption ( $E_{ad} = -1.01$  eV). Conversely, the  $E_{ad}$  of H adsorption on the fcc hollow site of the Ni(111) surface was  $-0.57$  eV (Figure 5e). H adsorption readily occurs on tri-coordinate C and at hollow Ni sites of the C-rich

$Ni_3C(113)$  surface, indicating that the dissociated hydrogen species interact more strongly with nano- $Ni_3C$  than with Ni NPs.

The properties of hydrogen species adsorbed on nano- $Ni_3C$  surface were further discussed. The number of valence electrons of H ( $H_{ne}$ ) adsorbed on the Ni hollow sites of  $Ni_3C(113)$  is greater than 1, that is they are hydridic, whereas the H adsorbed on the tri-coordinate C is slightly protonic (Figure 5). This suggests that  $H_2$  strongly adsorbed on nano- $Ni_3C$  surface is dissociated in a heterolytic manner. In contrast,  $H_2$  is typically homolytically dissociated on the Ni NP surface.<sup>[49,50]</sup> In addition, hydrogen species formed through the heterolytic dissociation of  $H_2$  are known to be more effective for nitrile hydrogenation than those formed through homolytic dissociation.<sup>[50–54]</sup> Hence, the high catalytic activity of nano- $Ni_3C$  can be explained as follows: the hydridic H adsorbed on the Ni sites of nano- $Ni_3C$  reacts with nitriles, whereupon the H adsorbed on the carbon atom is efficiently supplied to the substrate, thereby facilitating the hydrogenation of nitriles.



**Figure 5.** Top views of typical adsorption structures of H/ $Ni_3C(113)$  and H/Ni(111) with their  $E_{ad}$  and  $H_{ne}$  values estimated by DFT calculations. (a–d) C-rich  $Ni_3C(113)$  and (e) Ni(111). All initial and optimized structures are summarized in the **Supporting Information**. Black, green, and brown spheres represent tri-, penta-, and hexacoordinate C atoms before H adsorption, respectively. Gray and pale pink spheres represent Ni and H atoms, respectively.

## Conclusions

We have synthesized phase-pure Ni<sub>3</sub>C NPs (nano-Ni<sub>3</sub>C) and demonstrated that the nano-Ni<sub>3</sub>C catalyzes selective hydrogenation of nitrile to primary amine. The catalytic activity of nano-Ni<sub>3</sub>C/Al<sub>2</sub>O<sub>3</sub> is superior to that of Ni NPs/Al<sub>2</sub>O<sub>3</sub>. Furthermore, nano-Ni<sub>3</sub>C/Al<sub>2</sub>O<sub>3</sub> shows broad substrate scope, allowing the conversion of various (hetero)aromatic and aliphatic nitriles into the corresponding primary amines, even under 1 bar of H<sub>2</sub>. nano-Ni<sub>3</sub>C/Al<sub>2</sub>O<sub>3</sub> can also be easily recovered and successfully reused for three times. DFT calculations suggest that polar H species were formed on the nano-Ni<sub>3</sub>C surface through the heterolytic dissociation of H<sub>2</sub>. Hydridic H adsorbed on Ni reacts with nitriles, whereupon the H adsorbed on carbidic carbon combines with the resulting substrate, which could be attributed to the excellent catalytic activity of nano-Ni<sub>3</sub>C. We envisage that the attractive catalytic properties of nickel carbide can be applied to various liquid-phase hydrogenation reactions.

## Experimental Section

### Synthesis of nano-Ni<sub>3</sub>C

All reactions were conducted in an Ar atmosphere using standard Schlenk line techniques. In a typical reaction, a mixture of Ni(acac)<sub>2</sub> (1.0 mmol) and oleylamine (30 mmol) was stirred at 120 °C for 1 h *in vacuo* in a Schlenk flask.<sup>[55]</sup> The reaction temperature was then increased to 320 °C and maintained constant for 3 h with continuous stirring, resulting in the formation of a black colloidal solution. After cooling the mixture to 25 °C, a black precipitate was collected by adding *n*-hexane to the solution. The obtained product was washed through repeated redispersion and precipitation cycles using a mixed solvent containing ethanol and *n*-hexane (ethanol:*n*-hexane = 1:1). Subsequently, the resulting powder was dried overnight at 120 °C *in vacuo* and stored in air.

### Preparation of the Al<sub>2</sub>O<sub>3</sub>-supported nano-Ni<sub>3</sub>C and Ni NPs

nano-Ni<sub>3</sub>C (0.04 g) was dispersed in *n*-hexane (30 mL) and stirred with γ-Al<sub>2</sub>O<sub>3</sub> (0.7 g) for 5 h at 25 °C. The resulting powder was then dried *in vacuo* overnight at 25 °C to yield nano-Ni<sub>3</sub>C/Al<sub>2</sub>O<sub>3</sub> as a gray powder. This product was stored in air at 25 °C and used for characterization and reaction experiments without any pretreatment. nano-Ni<sub>3</sub>C/Al<sub>2</sub>O<sub>3</sub> was treated with flowing H<sub>2</sub> at 350 °C for 3 h to produce Ni NPs/Al<sub>2</sub>O<sub>3</sub>. Figures S4–S6 show the TEM image, XRD pattern, and Ni *K*-edge XANES spectrum of Ni NPs/Al<sub>2</sub>O<sub>3</sub>, respectively. The Ni NPs in Ni NPs/Al<sub>2</sub>O<sub>3</sub> exhibited an average particle size of 39.0 nm, which is similar to that of nano-Ni<sub>3</sub>C/Al<sub>2</sub>O<sub>3</sub>. Ni NPs/Al<sub>2</sub>O<sub>3</sub> was used as a catalyst without exposure to air.

### General Procedure for Nitrile Hydrogenation

In a typical procedure, **1a** (0.5 mmol), 2-propanol (3 mL), and NH<sub>3</sub> aq. (25%, 1.2 mL) were added to nano-Ni<sub>3</sub>C/Al<sub>2</sub>O<sub>3</sub> (0.029 g, Ni: 5 mol%) in a 50 mL stainless-steel autoclave equipped with a Teflon inner cylinder. The reaction mixture was vigorously stirred at 130 °C under 10 bar H<sub>2</sub>. The conversion and yield of the reaction were determined by GC-FID, using diethylene glycol dimethyl ether as an internal standard. Primary amines were subsequently isolated in the form of hydrochloride salts. The crude reaction mixture was filtered to remove the solid catalyst, and NH<sub>3</sub> was removed under vacuum.

The mixture was then added to a solution of hydrogen chloride (1.25 M in 1,4-dioxane, 0.5 mL total volume). Analytically pure hydrochloride salts of the primary amines were obtained as solids (further details are provided in the **Supporting Information**).

## Acknowledgements

We thank Dr. Tetsuo Honma and Dr. Toshiaki Ina (SPRING-8) for conducting XAFS measurements (2022B1585, 2022B1699, and 2023A1896). The computational work in this study was conducted at the Research Institute for Information Technology, Kyushu University (ITO). This work was supported by JSPS KAKENHI (G. Nos. 20H02523, 20K15177 and 21K04776), and JST PRESTO (G. No. JPMJPR21Q9). This study was partially supported by JST-CREST (G. No. JPMJCR21L5), and the Cooperative Research Program of the Institute for Catalysis, Hokkaido University (G. No. 22AY0097). A part of experimental analysis was supported by the "Advanced Research Infrastructure for Materials and Nanotechnology in Japan (ARIM)" (JPMXP1222HK0062) of the Ministry of Education, Culture, Sports, Science and Technology (MEXT). This work was the result of using the research equipment shared in the MEXT Project for promoting public utilization of advanced research infrastructure (Program for supporting the construction of core facilities) (G. Nos. JPMXS0441200022 and JPMXS0441200023).

## Conflict of Interests

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available on request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions.

**Keywords:** nickel carbide · hydrogenation · nitrile · amine · heterogeneous catalyst

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Manuscript received: October 28, 2023

Accepted manuscript online: January 5, 2024

Version of record online: January 16, 2024