Journal of Catalysis 377 (2019) 174-182

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

# A switchable-selectivity multiple-interface Ni-WC hybrid catalyst for efficient nitroarene reduction



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#### ARTICLE INFO

Article history: Received 27 April 2019 Revised 10 June 2019 Accepted 11 June 2019

Keywords: Multi-interface Polyoxometalate Synergistic effect Switchable selectivity Nitroarene reduction

# ABSTRACT

Selective reduction of nitroarenes is extremely valuable in industrial chemical production. The main reduced products are usually aniline derivatives obtained using single-component noble- or transition-metal catalysts; however, other important products such as hydrazobenzene derivatives always involve in harsh conditions and multiple reaction steps. Here, we realize an unexpected switchable reduction of nitroarenes into aniline or hydrazobenzene derivatives with high yield and selectivity just by controlling the molar ratio of nitroarenes to  $N_2H_4$ ·H<sub>2</sub>O with a nickel-tungsten carbide composite nanocatalyst loaded on carbon (Ni-WC/C). A series of control experiments and density functional theory (DFT) calculations indicate that the multiple interfaces between Ni and WC can induce a synergistic effect, significantly modulating the electronic structure of the Ni-WC/C catalyst, and endowing the catalyst with switchable selectivity and high activity for the reduction of nitroarenes by hydrogenation. This synergistic multi-interfacial catalyst may offer a new way to design and explore highly efficient and selective catalysts for the controllable reduction of nitroarenes and similar hydrogenation reactions.

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# 1. Introduction

Selective reduction of nitroarenes is of great interest in industrial chemical production [1–3]. Important reduced products such as aniline (AN) and hydrazobenzene (HAB) derivatives, with more than four million metric tons of production per year, represent industrially indispensable intermediates in the manufacture of bulk and fine chemicals such as pharmaceuticals, pesticides, agrochemicals, dyes, and pigments [4–7]. Traditional noncatalytic reduction processes (using Zn/HCl or Fe/HCl, etc.) for the synthesis of AN or HAB derivatives usually generate a large amount of waste, which exacerbates environmental pollution and disposal costs [8– 10]. Thus, the catalytic reduction of nitroarenes has been prompted. The key issue is the rational design and development of efficient and cost-effective heterogeneous catalysts.

To date, a great achievement has been attained in the reduction of nitroarenes to AN derivatives by the use of single-component noble metal (e.g., Au, Pd, Pt, and Ru) and transition metal (e.g., Fe, Ni, and Co) catalysts [11–24]. However, the selective reduction

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of nitroarenes to other important reduced products, such as HAB derivatives, is more difficult, since most single-component catalysts cannot meet the dual requirements of activity and selectivity simultaneously [25-28]. Furthermore, the synthesis of HAB derivatives usually demands partially poisoned noble metals as catalysts and requires more than two reaction steps, resulting in high production cost and low product selectivity [29–33]. Multicomponent catalysts have been regarded as another concept for design and development of catalysts [6,30,34-36]. The interfaces between multicomponent catalysts can induce significant regulation of electronic structure, interfacial stabilization, synergistic effects, and the like, which always play pivotal roles in promoting activity and selectivity of catalysts for hydrogenation reduction of nitroarenes [37,38]. To maximize the interfacial effect, it is necessary to construct as much interfacial contact between different components as possible. However, the synthesis of multicomponent catalysts with nanoscale multi-interfaces is still a big challenge, due to their isolated growth trend and aggregation. Therefore, exploring an effective approach to synthesis of such nanosized multiinterfacial catalysts has been highly desired.

Polyoxometalates (POMs) as a large class of polynuclear oxobridged early transition metal clusters with well-defined structure,





JOURNAL OF CATALYSIS adjustable elemental composition, and uniform nanoscale size have shown potential application prospects in the design of interfacial catalysts [39]. Recently, some nanostructured molybdenum carbide and phosphide/metal hybrid materials have been prepared from POM-based precursors. All of them exhibited remarkable hydrogen evolution reaction (HER) performance due to their specific interfacial effects [40-42]. These concepts for the design of multi-interfacial catalysts via polyoxometalates impel us to explore highly effective catalysts for selective reduction of nitroarenes. Here, we demonstrate that nickel-tungsten carbide composite nanoparticles loaded on carbon (denoted as Ni-WC/C) can act as an efficient catalyst for the selective reduction of nitroarenes by hydrazine hydrate ( $N_2H_4$ · $H_2O$ ) under mild conditions. In a typical experiment with the Ni-WC/C catalyst, nitrobenzene (NB) can be highly selectively reduced to AN or HAB just by adjusting the molar ratio of NB to  $N_2H_4$ ·H<sub>2</sub>O. For example, when the molar ratio of NB to N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O was 1:13. NB was directly reduced to AN with a vield of 98%. This result is comparable to those obtained with commercial 20% Pt/C and 5% Pd/C. When the molar ratio of NB to N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O was modulated to 8:13, HAB became the main product with a yield of 94%. This unexpected switchable catalytic reaction with high activity and selectivity arises from the remarkable synergistic role between Ni and the WC center in the Ni-WC/C catalyst. Density functional theory (DFT) calculation results suggest that the multiple interfacial structure can optimize the electronic structure of the Ni surface, further dominating the final reduced products.

#### 2. Experimental

#### 2.1. Chemicals and materials

Dicyanamide (DCA), benzene-1,3,5 tricarboxylic acid (H<sub>3</sub>BTC, 98%), nickel chloride hexahydrate (NiCl<sub>2</sub>·6H<sub>2</sub>O), tris(hydroxyme thyl)aminomethane hydrochloride (Tris·HCl), and H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>·nH<sub>2</sub>O were purchased from Aladdin Industrial Company. Commercial 20% Pt/C and 5% Pd/C catalysts were purchased from Alfa Aesar China (Tianjin) Company. All chemicals were used as received without further purification. [Ni(en)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sub>6</sub>{Ni<sub>6</sub>(Tris)(en)<sub>3</sub>(BTC)<sub>1.5</sub>(*B*- $\alpha$ -PW<sub>9</sub>O<sub>34</sub>)]<sub>8</sub>·12en·54H<sub>2</sub>O (abbreviated as **Ni<sub>54</sub>W<sub>72</sub>**) was synthesized according to the method reported by Yang et al. [43].

# 2.2. Synthesis of Ni-WC/C

The synthesis of Ni-WC/C was according to our previous work [39] with slight modifications, as follows: 0.2 g  $Ni_{54}W_{72}$  and 0.1 g DCA were placed in an agate mortar and then absolutely mixed by ball milling. Afterward, the powder was pyrolyzed in a pipe furnace at 500 °C for 30 min under  $N_2$  with a heating rate of 2 °C/min, and then further heated at 650 °C for 6 h with a heating rate of 5 °C/min. The as-obtained sample is denoted as Ni-WC/C.

#### 2.3. The procedure for decomposition of hydrazine hydrate

In a typical case, 2 ml of C<sub>2</sub>H<sub>5</sub>OH and 10 mg of catalyst were added to a hermetic Dewar flask. Under magnetic stirring, 200  $\mu$ l of N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O (80 wt%) was injected into the system and heated at 60 °C for 4 h. An aliquot of gaseous product was periodically removed from the flask. The identity of products and the yield of hydrogen were ascertained by gas chromatography (GC).

# 2.4. The procedure for selective hydrogenation of nitrobenzene

In a typical case, 0.5, 1, 1.5, 2, 2.5, 3, 3.5, or 4 mmol of nitrobenzene (NB), 400  $\mu$ l of N<sub>2</sub>H<sub>4</sub> H<sub>2</sub>O (80 wt%), and 10 mg of catalyst were added to 2 ml of C<sub>2</sub>H<sub>5</sub>OH and stirred at 60 °C. After the reaction, the mixtures were identified by GC–MS and <sup>1</sup>H NMR, and the conversion of nitrobenzene and product yields were analyzed by a gas chromatograph (Ang) equipped with a flame ionization detector (FID) and a capillary column (J & W DB-WAX,  $30 \text{ m} \times 0.32 \text{ mm}$ ) with nonane as an internal standard. The final yield of product is calculated based on the theoretical value of the full conversion.

The recyclability of the Ni-WC/C catalyst was also investigated under the above reaction conditions. Taking the selective hydrogenation of NB to AN as an example, 0.5 mmol of nitrobenzene, 400  $\mu$ l of N<sub>2</sub>H<sub>4</sub> H<sub>2</sub>O (80 wt%), and 10 mg of catalyst were added to 2 ml of C<sub>2</sub>H<sub>5</sub>OH and stirred at 60 °C for 5 min. The reaction time for the recycling experiment that selectively hydrogenates NB to HAB is 1 h. After the reaction, the catalyst was recovered by centrifugation, washed several times with anhydrous ethanol, and then dried for the next cycle.

#### 2.5. Theoretical calculation methods

Periodic DFT calculations were performed using the Vienna ab initio Simulation Package (VASP) with exchange and correlation potential represented by the PBE approximation [44,45]. A suitable *k*-point grid of  $3 \times 3 \times 1$  was generated with the Monkhorst–Pack algorithm [46]. The kinetic energy cutoff was set to 400 eV. Results were obtained until the forces and energy were less than 0.03 eV Å<sup>-1</sup> and 10<sup>-5</sup> eV, respectively.

The parent WC (0 0 1) and Ni (1 1 1) surfaces were simulated by  $4 \times 4$  and  $5 \times 5$  unit cells with three WC and Ni layers, respectively. A vacuum larger than 15 Å perpendicular to the surface avoided interaction between repeated cells. The topmost tungsten–carbon or Ni layer was relaxed, while the remaining layers were frozen. The Ni-WC composite system was constructed with one layer of Ni (1 1 1) atoms adsorbed on top of three WC (0 0 1) layers. During the optimization, the adsorbed species, the Ni layer, and the top WC layer were kept relaxed.

## 3. Results and discussion

## 3.1. Synthesis and characteristics of Ni-WC/C

The nanoscale composite catalyst Ni-WC/C was fabricated via a one-step method according to our previous work [39] with slight modifications by pyrolyzing a mixture of [Ni(en)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sub>6</sub>{Ni<sub>6</sub>(-Tris)(en)<sub>3</sub>(BTC)<sub>1.5</sub>(B- $\alpha$ -PW<sub>9</sub>O<sub>34</sub>)<sub>8</sub>·12en·54H<sub>2</sub>O [43] (denoted as Ni<sub>54</sub>W<sub>72</sub>) and dicyandiamide (DCA) at 650 °C in N<sub>2</sub> (Fig. 1a). TEM and SEM images in Figs. 1 and S1 in the Supporting Information show the morphology and superstructure of as-made Ni-WC/C material composed of Ni-WC hybrid nanoparticles (NPs) with average size ca. 8 nm scattered on porous carbon sheets (Fig. S2). The high-resolution (HR) TEM image in Fig. 1c exhibits intimate contact between Ni and WC, forming unique Ni/WC interfaces. The lattice fringes with interplanar spacings 0.25 and 0.18 nm correspond to the (100) planes of hexagonal WC and the (200) planes of metallic Ni, respectively. The bright-field scanning TEM (BF-STEM) images, high-angle annular dark-filed scanning TEM (HAADF-STEM) images, and corresponding elemental mapping images (Fig. 1e-i) of an individual Ni-WC nanoparticle demonstrate that Ni and W distribute evenly on the surface of Ni-WC nanoparticles, further affirming the presence of Ni/WC interfaces (Fig. S3). EDX results also validate the elemental composition of Ni-WC/C. The content of Ni-WC in Ni-WC/C is almost 58.49 wt% (Tables S1 and S2).

The phase composition of Ni-WC/C was further analyzed by powder X-ray diffraction patterns (PXRD), illustrated in Fig. 2a. The characteristic peaks located at  $31.57^{\circ}$ ,  $35.88^{\circ}$ ,  $48.62^{\circ}$  and  $64.51^{\circ}$  can be indexed to the (001), (100), (101), and (110)



Fig. 1. (a) Illustration of the preparation of nickel-tungsten carbide composite nanoparticles loaded on carbon (Ni-WC/C). (b and c) TEM images of Ni-WC/C. (d) High-resolution TEM image of one Ni-WC nanoparticle. (e-i) Bright-field scanning TEM, high-angle annular dark-filed scanning TEM, and corresponding elemental mapping images of one Ni-WC nanoparticle on carbon.

facets of WC (JCPDS, No. 65-4539), respectively. The diffraction peaks at 44.12° and 51.45° are ascribed to the (1 1 1) and (2 0 0) planes of metallic Ni (JCPDS, No. 65-0380), and the additional weak peak observed at ~25° stems from carbon sheets.

Besides, X-ray photon spectroscopy (XPS) was conducted to determine the elemental compositions and valence states of Ni-WC/C (Figs. S4 and 2b–d). As depicted in Fig. S4, the elements of Ni, W, C, and N can be obviously identified. The high-resolution XPS spectrum of Ni2*p* in Fig. 2c exhibits two distinct peaks at around 852.7 and 870.1 eV with two obvious 2*p* satellite peaks (858.6 and 876.0 eV), which could be assigned to metallic Ni2*p*<sub>3/2</sub> and 2*p*<sub>1/2</sub>, respectively. The W4*f* peaks of Ni-WC/C at around 32.2 and 34.4 eV could be ascribed to 4*f*<sub>7/2</sub> and 4*f*<sub>5/2</sub> of WC (Fig. 2d). The peaks at higher binding energy 35.0 and 37.2 eV are caused by unavoidable surface oxidation [47]. In addition, the N<sub>2</sub> adsorption/desorption isotherm of Ni-WC/C displays a mesoporous structure with a Brunauer–Emmett–Teller (BET) surface area of 61 m<sup>2</sup> g<sup>-1</sup>, which conduces to the diffusion and adsorption of organic substrate to catalytic sites (Fig. S5).

# 3.2. Catalytic performance of Ni-WC/C in N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O decomposition

The catalytic activity of Ni-WC/C in the dissociation of N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>-O to generate hydrogen was first investigated. In addition, 5% Pd/C, 20% Pt/C, Ni/C, WC/C, a physical mixture of Ni/C and WC/C, and Ndoped carbon (NC) were checked in this reaction system as control catalysts. Fig. 3a shows that the hydrogen yield is 54.92 µmol in 4 h for Ni-WC/C. In comparison, the reactions with commercial 5% Pd/C and 20% Pt/C exhibit higher reaction rates and the hydrogen yields are 198.73 and 138.24 µmol in 4 h, respectively (Fig. S6a). Ni/C can produce 13.86 µmol H<sub>2</sub> in 4 h (Figs. S6 and S7 and Tables S3 and S4), while the hydrogen yields with WC/C and NC (Figs. S6 and S7 and Tables S5 and S6) can be almost negligible (less than 5 µmol) within the same duration. The physical mixture of Ni/C and WC/C contributes 7.36 µmol H<sub>2</sub> in 4 h (Fig. S6). These results reveal that WC and NC almost have no catalytic activity, while the Ni species shows considerable catalytic activity in the decomposition of N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O for H<sub>2</sub>, which is in accord with previous reports [48]. Thus, the main active center for N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O decomposition is the Ni center in the Ni-WC/C composite catalyst.

## 3.3. Catalytic performance of Ni-WC/C in nitroarene reduction

The catalytic activity of Ni-WC/C was further investigated by reducing NB to AN at a NB/N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O molar ratio of 1:13. Fig. 3b shows that Ni-WC/C could achieve full conversion of NB within 20 min and the yield of AN was 98%, which is nearly comparable those for to 20% Pt/C and 5% Pd/C (Fig. S8 and Table S8, entries 1 and 2). For comparison, the Ni/C catalyst also exhibits almost complete conversion of NB in 30 min with an 88% yield of AN as well as a small amount of azobenzene (AB) and HAB (Fig. S9 and Table S8, entry 3). The reaction with WC/C requires 2 h to achieve a 97% yield of AN (Fig. S9 and Table S8, entry 4), which might be ascribed to the weak catalytic ability of WC for the decomposition of N<sub>2</sub>H<sub>4</sub>-·H<sub>2</sub>O into active hydrogen. The NC catalyst shows only 25% conversion of NB into AN when the reaction time is prolonged to 2 h (Fig. S9c and Table S8, entry 5). We also verified that a physical mixture of Ni/C and WC/C has low catalytic activity in comparison



Fig. 2. (a) The powder X-ray diffraction patterns (PXRD) of Ni-WC/C. (b-d) High-resolution XPS spectra of Ni-WC/C: (b) C, (c) Ni, and (d) W.

with Ni-WC/C (Fig. S9d and Table S8, entry 6), implying that the interfacial structure in Ni-WC/C can induce significant synergistic enhancement of catalytic performance for NB reduction. To gain further insight into the catalytic activity of Ni-WC/C, we explored the reaction kinetics of the reduction of NB to AN. The results demonstrate that NB reduction follows pseudo-first-order kinetics in NB concentration, and the slope is equal to the rate constant *k* (0.26 min<sup>-1</sup>), implying high catalytic activity of Ni-WC/C (Fig. S10) [49–52]. In addition, the apparent activation energy ( $E_a$ ) of this catalytic reaction (Fig. 3c) was calculated to be 52.1 ± 2.8 kJ mol<sup>-1</sup> and is comparable to those for active noblemetal catalysts [52–54], further confirming the good catalytic performance of Ni-WC/C (Fig. S11 and Table S9).

It is noteworthy that the molar ratio of NB to  $N_2H_4$ · $H_2O$  has a great influence on the selectivity of final product in the NB reduction. When the molar ratio changed from 1:13 to 8:13, the yield of AN gradually decreased (Fig. 3d, black line), while that of HAB increased obviously. The formation and disappearance of the intermediate AB can be also detected. When the molar ratio was enhanced to 8:13, the yield of HAB soared to 94% in 2.5 h (Fig. S12 and Table S10). With 5% Pd/C and 20% Pt/C as catalysts, NB can only transform into AN, and no HAB is detected (Fig. 4 and Table S11, entries 1 and 2), in accordance with the relevant reports [16-19]. Under the same reaction conditions, Ni/C can provide a 48% yield of HAB, and the conversion of NB just reaches 67% after 2.5 h, lower than that for Ni-WC/C (Fig. 4 and Table S11, entry 3). WC/C shows low NB conversion, independent of the molar ratio (Fig. 4 and Table S11, entry 4). In general, the Ni-WC/C catalyst shows a perfect product switch between AN and HAB just from adjusting the NB/N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O molar ratio.

A broad range of functionalized nitroarenes were further examined to understand the effect of various substituents on the catalytic activity of Ni-WC/C. As shown in Tables 1 and S12, electron-donating substrates exemplified bv methyl-. ethyl-, isopropyl-, and methoxysubstituted NBs are smoothly and selectively converted into corresponding ANs or HABs with good vields by simply adjusting the molar ratio of NBs and hydrazine (Table 1, entries 1–6). Likewise, electron-withdrawing substrates, including fluoro-, chloro-, bromo-, and iodosubstituted NBs, can also be selectively reduced to the desired ANs or HABs with considerable yields by tuning the molar ratio of NBs and N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O (Table 1, entries 7-12). A Hammett plot for reduction of p-substituted nitroarenes (Fig. S13) was also made to explore the mechanism of reduction of NBs, which displays a positive slope (+1.39), indicating that reduction of NB processes via cationic intermediate and electron-donating groups may enhance the rate of reduction of NB (Table S13) [55–57]. Therefore, the reason for the higher reaction rates of *p*-methylnitrobenzene and *p*-methoxynitrobenzene than of *p*-chloronitrobenzene may be due mainly to the electronic effect. The steric effects of the substituent also have an obvious effect on the reduction of NBs. First, for the disubstituted NBs, 1,3-dimethy-5nitrobenzene required longer reaction times to achieve full conversion and gave good yields of the corresponding ANs and HABs (Table S12, entry 1). 2,3-Dichloro-, 2,4-dichloro-, and 2,5dichloronitrobenzenes could only afford the corresponding ANs products, and no hydrazo product was detected (Table S12, entries 2–4). These results may arise from the steric hindrance effect, which impedes the coupling of two adjacent reduction intermediates. resulting in AN-derived products. Second, the yields of psubstituted HABs were somewhat higher than those for the



**Fig. 3.** (a) The yield of hydrogen from  $N_2H_4$ · $H_2O$  decomposition with Ni-WC/C as a function of reaction time. Insert: comparison of hydrogen evolution rates between Ni-WC/C and control catalysts. Reaction conditions: 2 ml C<sub>2</sub>H<sub>5</sub>OH, 10 mg catalyst, 200  $\mu$ l  $N_2H_4$ · $H_2O$  (80 wt%); 60 °C. (b) The yield of AN in the NB reduction with Ni-WC/C as a function of reaction time. Insert: the comparison of reaction rates between Ni-WC/C and various catalysts. Reaction conditions: 1 equiv. NB, 13 equiv. 80%  $N_2H_4$ · $H_2O$ , 10 mg catalyst, 2 ml C<sub>2</sub>H<sub>5</sub>OH at 60 °C. (c) Arrhenius plots of reactions with Ni-WC/C in the temperature range 313–343 K. Insert: the rate curves for the hydrogenation of NB at different reaction temperatures; (d) The functional curves between NB/ $N_2H_4$  molar ratio and the product distribution with Ni-WC/C.



**Fig. 4.** The yields of three main products (AN, HAB, and AB) in the reduction of NB with various catalysts and different amounts of NB in the reaction system. Reaction conditions: 1–4 mmol (2–8 equiv.) NB, 400 µl (13 equiv.) 80 wt% N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O, 10 mg catalyst, 2 ml C<sub>2</sub>H<sub>5</sub>OH, 60 °C, reaction time 2.5 h.

corresponding *o*- or *m*-substituted HABs (Table 1, entries 2, 6, 8, and 9), which may also be caused by the combination of steric effects and electronic effects. The above experimental results demonstrate that the Ni-WC/C catalyst exhibits relatively rich compatibility with the electron-donating and withdrawing substituent groups, but the steric effects have an obvious influence on the catalytic selectivity of Ni-WC/C. Furthermore, Ni-WC/C can easily be recycled by simple filtration or a magnet (Fig. S14). No significant decay in the catalytic activity or selectivity for Ni-WC/C was found even after the catalyst

was recycled from 10 runs (Fig. S15). The PXRD pattern and TEM image after 10 runs reveal that the catalyst retains structural integrity, indicating the high stability of Ni-WC/C (Fig. S16).

## 3.4. Theoretical investigation

To gain further understanding into the remarkable switchable selectivity and activity of Ni-WC/C catalyst for nitrobenzene reduction, we obtained a series of computational results

#### Table 1

Selective hydrogenation of various nitroarenes to primary amines or hydrazobenzenes:



| Entry | Low molar ratio <sup>a</sup>      |              |                        | High molar ratio <sup>b</sup>          |              |                        |
|-------|-----------------------------------|--------------|------------------------|--|--------------|------------------------|
|       | Product                           | <i>t</i> (h) | Yield <sup>c</sup> (%) | Product                                | <i>t</i> (h) | Yield <sup>c</sup> (%) |
| 1     |                                   | 0.5          | 99                     |  | 2.5          | 95 ± 2                 |
| 2     |                                   | 0.5          | 99                     | H <sub>3</sub> C-                      | 3.0          | 94 ± 3                 |
| 3     |                                   | 0.6          | 99                     |  | 3.5          | 92 ± 3                 |
| 4     |                                   | 1.5          | 96 ± 1                 |  | 5.0          | 94 ± 2                 |
| 5     | H <sub>3</sub> CO-NH <sub>2</sub> | 0.7          | 97 ± 2                 | H <sub>3</sub> CO- N, N-OCH3           | 3.5          | 95 ± 1                 |
| 6     | H <sub>3</sub> C NH <sub>2</sub>  | 1.0          | 99                     |  | 8.0          | 80 ± 2                 |
| 7     |                                   | 1.0          | 98 ± 1                 | F-€−−H <sub>N</sub> −F                 | 3.5          | 92 ± 2                 |
| 8     |                                   | 1.0          | 99                     |  | 4.0          | 93 ± 3                 |
| 9     |                                   | 1.5          | 96 ± 2                 |  | 8.0          | 40 ± 2                 |
| 10    |                                   | 1.0          | 96 ± 2                 | Br──────────────────────────────────── | 4.0          | 90 ± 4                 |
| 11    |                                   | 1.5          | 95 ± 2                 |  | 4.5          | 88 ± 5                 |
| 12    | F <sub>3</sub> C-NH <sub>2</sub>  | 1.0          | 94 ± 2                 |  | 4.5          | 85 ± 4                 |

<sup>a</sup> Standard low-molar-ratio reaction conditions: 0.5 mmol (1 equiv.) nitroarene, 10 mg Ni-WC/C catalyst, 2 ml C<sub>2</sub>H<sub>5</sub>OH, 13 equiv. (400 µl) 80% N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O at 60 °C.

 $^{
m b}$  High-molar-ratio conditions: 4.0 mmol (8 equiv.) nitroarene, 10 mg Ni-WC/C catalyst, 2 ml C<sub>2</sub>H<sub>5</sub>OH, 13 equiv. (400  $\mu$ l) 80% N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O at 60 °C.

<sup>c</sup> Conversion and yield measured by GC analysis.

using DFT. The corresponding computational details are supplied in the Supporting Information. Our previous work has demonstrated that the interfacial structure of the Ni monolayer and the WC (001) substrate can optimize the electronic interaction for enhanced HER activity [39]. Here, a similar calculation model has been constructed (Fig. 5). In the first step, we modeled the adsorption and dissociation of  $N_2H_4$  on the

Ni-WC surface to evaluate the active sites for the hydrogen source. It was found that the adsorption and dissociation energy  $(N_2H_4^* = N_2H_3^* + H^*)$  for  $N_2H_4$  on Ni and WC are -1.19 and -0.55 eV, respectively. Obviously both steps are exothermic enough, indicating a thermodynamically feasible process to provide active in situ hydrogen atoms and support to interact with nitrobenzene.



Fig. 5. Side views of different reaction species with the most stable configurations on the Ni-WC surface. Color codes: W (light blue), C (brown), Ni (green), N (blue), H (light pink), and O (red). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Scheme 1. Mechanism of nitrobenzene reduction proposed by Haber.

Subsequently, the reduction mechanism for nitrobenzene was investigated. As shown in Scheme 1, the reduction mechanism for nitrobenzene proposed by Haber has been widely accepted, a direct route via reactions 1–3, and an indirect pathway via reactions 1, 2, and 4–7. Under our test conditions, the products were not only catalyst-dependent, but also affected by the molar ratio between nitrobenzene and N<sub>2</sub>H<sub>4</sub>. The main product can change from aniline to hydrazobenzene with increased NB/N2H4·H2O molar ratio  $(1:13 \rightarrow 8:13)$ . In Fig. 5, the most stable adsorbed configuration for each intermediate is presented, and all structures preferred to adsorb on the catalytic surface in parallel mode rather than vertical mode. To illustrate the selective reduction of NBs in the presence of Ni/WC, we compared the reaction energies (Table 2) on different catalytic surfaces by following the elementary steps in Scheme 1 [25]. The direct formation of aniline proceeds through three successive hydrogenation steps, which are calculated as -1.34, 0.47, and -2.10 eV on the Ni-WC surface (Table 2). These energies are found to be much more favorable than on pure Ni and WC. Particularly, the transformation of Phono to PhNHOH species on Ni and WC is calculated to be thermodynamically unfavorable due to the high reaction energies, with values of 1.06 and 2.24 eV, respectively. This may result in the catalytic activity order Ni-WC > Ni > WC.

Alternatively, the reduction of nitrobenzene may proceed along the indirect route, generating azobenzene and hydrazobenzene intermediates. As illustrated in Table 2, the condensation reaction,

#### Table 2

Reaction energies (eV) of different reaction steps occurring on WC (0 0 1), Ni (1 1 1), and Ni-WC (0 0 1) composite.

| Reaction steps                            | Reaction energy ( $\Delta E$ , eV) |       | /)    |
|---|------------------------------------|-------|-------|
|   | WC                                 | Ni    | Ni-WC |
| 1. $PhNO_2 \rightarrow Phono$             | -0.44                              | -1.12 | -1.34 |
| 2. Phono $\rightarrow$ PhNHOH             | 2.24                               | 1.06  | 0.47  |
| 3. PhNHOH $\rightarrow$ PhNH <sub>2</sub> | -0.69                              | -1.40 | -2.10 |
| 4. PhNHOH + PhNO $\rightarrow$ PhN = NOPh | 0.00                               | -0.67 | -0.30 |
| 5. PhN = NOPh $\rightarrow$ PhN = NPh     | -0.75                              | -1.51 | -1.28 |
| 6. PhN = NPh $\rightarrow$ PhNHNHPh       | 2.69                               | 1.44  | 0.53  |
| 7. PhNHNHPh → PhNH <sub>2</sub>           | -1.09                              | -0.99 | -2.67 |

step 4, was calculated to be thermodynamically feasible on all three catalyst models, with  $\Delta E$  of 0.00, -0.67, and -0.30 eV on WC, Ni, and Ni-WC, respectively. However, the further hydrogenation of PhN = NPh to PhNHNHPh is considerably restricted by the high reaction energies on WC (2.69 eV) and Ni (1.44 eV), whereas it is only 0.53 eV on the composite catalyst. This indicated that Ni-WC is still more active than the two isolated components. To give an explanation for the obtained activity order, we further analyzed the adsorption energy changes for the main products. As represented in Table S14, the adsorption energy of PhNHNHPh on Ni-WC (-2.04 eV) was much weaker than that on Ni (-2.63 eV) and WC (-2.92 eV). This indirectly demonstrated that the desorption of PhNHNHPh from Ni-WC could occur relatively easily, leading to more accessible active sites for the further reaction and thus improving the catalytic activity.

Based on the above analysis, synergy between Ni and WC resulted in highly efficient reduction of nitroarenes. Both the *direct* and *indirect* ways are revealed to be thermodynamically favorable on the Ni-WC catalyst; thus the concentration of H played an important role in the catalytic selectivity. When the NB/N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O molar ratio is 1:13, the overabundance of H will promote the reaction via direct or hydrogenation of PhNHNHPh to mainly produce PhNH<sub>2</sub>, resulting in selectivity toward PhNH<sub>2</sub>. Conversely, with more NB involved (8:13), the indirect way is more likely to produce PhNHNHPh, as obtained in experiment.

# 4. Conclusions

In summary, we report a multifacial Ni-WC/C catalyst that can realize high-yield and highly selective reduction of nitroarenes into aniline (AN) or hydrazobenzene (HAB) derivatives just by controlling the molar ratio of nitroarene to hydrazine hydrate. In a typical catalytic experiment, the 1:13 M ratio of NB/N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O led to a 98% yield of AN product, while the 8:13 M ratio of NB/N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O produced 94% HAB. A series of control experiments and DFT calculations verify that the distinct Ni/WC interfaces can induce a synergistic effect, significantly modulating the electronic structure of the Ni-WC/C catalyst, and endowing the catalysts with switchable selectivity and high activity for the hydrogenation reduction of nitroarenes. This work suggests a new strategy for developing multi-interfacial catalysts with a remarkable synergistic effect for the selective reduction of nitroarenes.

#### Acknowledgments

This work is supported by the National Science and Technology Major Project Fund (2011ZX02707), the National Natural Science Foundation of China (21771033, 21671036, 51725204, 51572179, 21771132), the Fundamental Research Funds for the Central Universities (grant no. 2412018BJ001, 2412018QD005 and 2412018ZD007). Scientific Development Project of Jilin Province (grant no. 20190201206JC), the Foundation of Jilin Educational Committee (grant no. JJKH20190268KJ), the China Postdoctoral Science Foundation funded project (No. 2018M631849), the Opening Project of Key Laboratory of Polyoxometalate Science of Ministry of Education. The authors declare no competing financial interests.

#### Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcat.2019.06.023.

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