# Journal of Catalysis 382 (2020) 22-30

Contents lists available at ScienceDirect

Journal of Catalysis

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

# Fabrication of Ni<sub>3</sub>N nanorods anchored on *N*-doped carbon for selective semi-hydrogenation of alkynes



JOURNAL OF CATALYSIS

Xiaozhen Shi<sup>a</sup>, Xin Wen<sup>a,\*</sup>, Shilin Nie<sup>a</sup>, Jie Dong<sup>a</sup>, Jingde Li<sup>b,\*</sup>, Yongqing Shi<sup>a</sup>, Huiling Zhang<sup>a</sup>, Guoyi Bai<sup>a,\*</sup>

<sup>a</sup> Key Laboratory of Chemical Biology of Hebei Province, College of Chemistry and Environmental Science, Hebei University, Baoding 071002, China <sup>b</sup> National-Local Joint Engineering Laboratory for Energy Conservation of Chemical Process Integration and Resources Utilization, School of Chemical Engineering and Technology, Hebei University of Technology, Tianjin 300130, China

# ARTICLE INFO

Article history: Received 13 August 2019 Revised 27 November 2019 Accepted 4 December 2019

Keywords: Nickel Nitride Semi-Hydrogenation Alkynes Z-Alkenes N-Doped Carbon

# ABSTRACT

Nickel is a highly active catalyst for the semi-hydrogenation of alkynes. However, the low selectivity of the alkene product caused by the over-hydrogenation reaction on Ni has hindered its practical applications. In this work, we report a new nickel nitride  $(Ni_3N)$ -catalyzed semi-hydrogenation of alkynes to the corresponding alkenes. The Ni<sub>3</sub>N nanorods were facilely fabricated via a direct pyrolysis of the solid mixture of nickel acetate tetrahydrate and melamine (Mlm). The Ni<sub>3</sub>N phase in the optimum catalyst (Ni<sub>3</sub>N/NC-6/5-550) is shown to be effective and stable in the semi-hydrogenation of alkynes, with a high yield and good selectivity for alkenes (Z/E ratios up to >99/1). Both terminal and internal alkynes bearing a broad scope of functional groups are readily converted into alkenes with good chemo- and stereoselectivity. Notably, it was found that the over-hydrogenation can be markedly suppressed even at high conversion of alkyne. Density functional theory (DFT) calculations reveal that the low interaction between the alkene product and the Ni<sub>3</sub>N might plays a critical role in the selectivity enhancement.

© 2019 Elsevier Inc. All rights reserved.

# 1. Introduction

Catalytic semi-hydrogenation of alkynes to alkenes is an important chemical process in fine chemical intermediates production and alkenes purification industry [1–9]. For decades, Pd-based catalysts have dominated this transformation [10–22], and the most widely used catalyst is known as Lindlar catalyst (Pd/CaCO<sub>3</sub> poisoned with Pb(OAc)<sub>2</sub> and quinoline). However, the high cost of Pd, toxic lead additives, and over-hydrogenation have limited its practical application for alkene production. Replacement of Pdbased catalyst with the non-precious metals (e.g. Ni, Co, Cu, Fe) has captured increasing attention due to the cost performance and resource availability [23-37]. One promising class of nonprecious metal catalysts for the semi-hydrogenation of alkynes is Ni-based catalysts [38–42], and recently graphitic shell encapsulated Ni [42], single Ni atoms [43], ligand-free Ni nanoparticles [44], confined cationic nickel [45], have been reported to show excellent catalytic activity towards alkynes semi-hydrogenation. Particularly, doping mono-metal catalysts with second element often leads to unique properties in the semi-hydrogenation of alkynes with respect to conventional catalyst [10-16,46-49], such as

Ni + P, Ni + Ga, Ni + Sn, Ni + B, Ni + Al, Ni + Zn, Ni + In, and Ni + Tl [49–56]. However, the doping effect of the second element on the catalytic performance was much less discussed. For example, Corma and co-workers reported that the selectivity for cisalkene can be tuned by the P atom in the nickel phosphide nanoparticles, which can be attributed to the blocking of the unsaturated Ni sites by P atoms [53]. By comparing two kinds of nickel phosphide catalyst, namely Ni<sub>2</sub>P and Ni<sub>5</sub>P<sub>4</sub>, Albani and co-workers demonstrated that the formation of spatially-isolated nickel trimers was responsible for the selectivity enhancement [50]. In a work carried out by Laursen et al., some strategies for designing the intermetallic compound catalyst composed of Ni and the boron group elements were reported [52]. Zhou and coworkers have demonstrated that the NiZn and NiGa alloys on AlSBA-15 showed high selectivity for alkene due to the geometric and electronic effects of the second element [56].

Nowadays, despite these achievements, the Ni-based catalysts still suffer from the low alkene selectivity or over-hydrogenation issues, which represent the key obstacle for alkynes semihydrogenation. It has been reported that the over-hydrogenation of alkene may be ascribed to two reasons: (i) the strong adsorption energy of alkene prolongs its resident time on the catalyst surface, increasing its likelihood for further hydrogenation reaction [57]; (ii) after the full conversion of alkyne, the accelerated overhydrogenation always takes place due to the lack of competitive



 <sup>\*</sup> Corresponding authors.
 *E-mail addresses:* wenxin767@hotmail.com (X. Wen), jingdeli@hebut.edu.cn (J. Li), baiguoyi@hotmail.com (G. Bai).

adsorption of alkyne species on the Ni active sites [58]. Such catalytic systems always require a strict-time monitoring especially at the high alkyne conversion. Accordingly, the optimum semihydrogenation catalysts for alkenes production should have the following features: (i) active for alkynes adsorption and hydrogenation; (ii) weak interaction with alkenes and higher activation energy barrier for alkenes hydrogenation. Thus, the searching for new efficient and practical catalytic system with these features is essential for synthesizing high-purity alkenes.

Nickel nitride (Ni<sub>3</sub>N) is an interstitial metallic compound, which has been widely studied as electrocatalyst [59,60]. However, the application of Ni<sub>3</sub>N in the heterogeneous catalysis is much less discussed [61,62]. The Ni atoms with the low plus valent (0.23 electrons) are isolated by N in the interstices. The strong interaction between Ni and N alters the electronic structure and the contraction of *d*-bands of Ni results in higher electron density near Fermi level [63]. On the one hand, the isolation of Ni active sites by the N atoms leads to a high barrier for the segregation of Ni atoms and the subsequent hydride formation, which may inhibit the overhydrogenation. On the other hand, the absorption energy of alkyne and alkene can also be tuned by the second elements. In this context, we proposed that Ni<sub>3</sub>N might be an efficient catalyst for alkyne semi-hydrogenation.

Herein, we report a straightforward protocol for the facile preparation of Ni<sub>3</sub>N nanorods supported on *N*-doped carbon (NC) via the direct pyrolysis of a mixture of nickel salt and melamine (Mlm). Notably, Ni<sub>3</sub>N nanorods can be *in situ* formed during the pyrolysis process under optimal conditions [Ni(OAc)<sub>2</sub>/Mlm, 6/5; pyrolysed at 550 °C], constituting a novel metallic nitride catalyst for the semi-hydrogenation of a variety of alkynes to their corresponding (*Z*)-alkenes. To the best of our knowledge, this is the first time that Ni<sub>3</sub>N is introduced as an efficient catalyst for alkyne semi-hydrogenation. Moreover, density functional theory (DFT) calculations confirmed that the improved selectivity for *Z*-alkene (1,2-diphenylethyne) over Ni<sub>3</sub>N/NC can be ascribed to its decreased adsorption energy and increased hydrogenation energy barriers when compared with those of Ni, providing a fundamental understanding of the hydrogenation mechanism at atomic level.

# 2. Experimental and computational details

# 2.1. Reagents and materials

Unless otherwise noted, all chemicals were of analytical reagent grade and used without any pre-treatment. Nickel(II) acetate tetrahydrate [Ni(AcO)<sub>2</sub>·4H<sub>2</sub>O], nickel nitrate hexahydrate [Ni (NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O] and Mlm were purchased from Aladdin Reagent Co. Ltd.. 1-(Phenylethynyl)-4-(trifluoromethyl) benzene, 1-fluoro-4-(phenylethynyl) benzene, 1-methyl-4-(phenylethynyl)benzene, and 1-(4-(phenylethynyl)phenyl)ethan-1-one were synthesized according to a reported method [64].

# 2.2. Catalyst preparation

The Ni<sub>3</sub>N/NC or Ni/NC catalysts were prepared using a basic pyrolysis process. In a typical run, the desired ratio of nickel acetate tetrahydrate and Mlm was first mixed thoroughly using an electric pulverizer. Then, the mixture (4.0 g) was pyrolysed in a furnace using a temperature-programmed method under a high purity N<sub>2</sub> atmosphere (total N<sub>2</sub> flow of 300 mL min<sup>-1</sup>) at room temperature for 10 min. Afterwards, the temperature was raised (2.3 °C min<sup>-1</sup>) to the desired temperature at low N<sub>2</sub> flow rates (31 mL min<sup>-1</sup>), held for 4 h, and then cooled to room temperature. The Ni<sub>3</sub>N/NC or Ni/NC catalysts were prepared by a solvent-free method via the direct pyrolysis of a solid mixture of nickel acetate

tetrahydrate and Mlm (Scheme 1). The effect of mass ratios of nickel acetate tetrahydrate and Mlm (Ni:Mlm = a/b), as well as the pyrolysis temperatures (T), were investigated. The resulting Ni catalysts prepared under different conditions are denoted as "Ni/NC-a/b-T" or "Ni<sub>3</sub>N/NC-a/b-T", accordingly.

Detailed information on the preparation of reference catalysts (Ni/SiO<sub>2</sub>, Ni/AC and Ni<sub>3</sub>N) are displayed in the Supplementary Material.

### 2.3. Catalyst characterization

The Ni content of the catalyst was measured by inductively coupled plasma optical emission spectrometry (ICP-OES) using a Vista MPX spectrometer. CO-chemisorption was performed on a Micromeritics AutoChem II 2920 chemisorber. X-ray diffraction (XRD) patterns were obtained using a Bruker D8-ADVANCE X-ray diffractometer using Cu Ka radiation at a scan step of 0.02°. Scanning electron microscopy (SEM) images were performed on a FEI Inspect F50 electron microscope. Transmission electron microscopy (TEM) images were acquired on a FEI Tecnai G2 F20 S-TWIN instrument at a voltage of 200 kV. The samples were first dispersed in ethanol and then deposited on a carbon-coated double copper grid, dried at 80 °C for 4 h. X-ray photoelectron spectroscopy (XPS) was recorded on a PHI 1600 spectrometer using Mg Ka X-ray source for excitation, in which the hydrocarbon C 1s line at 284.8 eV from adventitious carbon was used for energy referencing. The NMR spectra were measured with a Bruker DRX 600 MHz spectrometer using tetramethylsilane as the reference compound for <sup>1</sup>H and <sup>13</sup>C NMR. The reaction mixtures were analysed using Agilent 7820A gas chromatography with a 30 m HP-5 capillary column. Gas chromatography-mass spectrometry (GC-MS) was used to identify the products on a Thermo TRACE-1300GC-ISQ-LT instrument.

# 2.4. Semi-hydrogenation of alkynes

Catalytic tests of Ni<sub>3</sub>N/NC or Ni/NC were performed as follows: 1,2-diphenylethyne (5.38 mmol), Ni/NC or Ni<sub>3</sub>N/NC catalyst (7.8 mol%, based on ICP results) and solvent (70 mL) were mixed in a stainless-steel autoclave (100 mL) equipped with an electric heating system and a magnetically driven mechanical stirrer. The reaction system was flushed with hydrogen three times and pressurized with hydrogen (2.0 MPa), and then heated to 100 °C for hydrogenation. After the completion of reaction, it was allowed to cool to room temperature and the residual hydrogen was released. The solvent was removed under reduced pressure, and the crude products were purified by column chromatography on silica gel to withhold the catalyst.

For the substrate scope, the semi-hydrogenation of alkynes was conducted using a similar method. For a typical run: the alkyne (0.3 mmol), 7.8 mol%  $Ni_3N/NC-6/5-550$  and ethanol (3 mL) were placed in a glass vial (4 mL) with cap, septum, and needle, and then two glass vials were sealed in a stainless steel autoclave (100 mL) equipped with an electrical heating system, where a certain amount of ethanol was added to keep the same horizontal level of ethanol inside and outside the glass vials. Then, the reaction system was treated following the same steps as described above.

The turnover frequency (TOF), which was defined as alkyne consumption per total active site per second, was calculated as follows:

$$TOF = \frac{A\alpha}{WNt}$$

where *A* is the amount of alkyne in the feedstock, mole;  $\alpha$  is the conversion of alkyne, %; *W* is the catalyst weight, g; and *N* is the



Scheme 1. Fabrication of Ni<sub>3</sub>N/NC nanohybrids for the selective semi-hydrogenation of alkynes.

number of active sites determined by CO chemisorption, mol  $g^{-1}$ ; *t* is the reaction time, s.

# 2.5. Computational method

The DFT calculations were performed using the VASP package [65,66]. The Perdew-Burke-Ernzerhof (PBE) functional was used for the exchange and correlation energy terms. The Ni and Ni<sub>3</sub>N catalysts were modeled using their (1 1 1) surfaces. The Ni (1 1 1) and Ni<sub>3</sub>N (1 1 1) surfaces were modeled using a (7 × 5) and (2 × 2) unit cell with four Ni-atomic layer slabs, respectively. The vacuum height was set to 15 Å. The bottom Ni layer was fixed in their bulk positions, whereas the remaining layers and the adsorbates were allowed to relax. A planewave cutoff energy was set to be 400 eV. The k-space was sampled using a 2 × 2 × 1 Mon-khorst–Pack grid. Structures were fully relaxed until the forces acting on the atoms were smaller than 0.03 eV/Å. On the basis of fully relaxed structures, adsorption energy (*E*<sub>ads</sub>) of the reactant and two intermediate surface species were calculated by the following equation:

$$E_{ads} = -(E_{X/slab} - E_X - E_{slab})$$

where  $E_{X/slab}$  represents the total energy of the adsorbate X bound to the Ni (1 1 1) and Ni<sub>3</sub>N (1 1 1) slabs,  $E_X$  is the energy of adsorbate alone,  $E_{slab}$  is the energy of the optimized Ni (1 1 1) or Ni<sub>3</sub>N (1 1 1) slab before adsorption. A more positive  $E_{ads}$  corresponds to a more stable adsorbate/slab system. The reaction transition states (TS) are determined using the climbing image nudged elastic band method (CI-NEB) and the TS was confirmed by its associated one imagery frequency [67].

# 3. Results and discussion

# 3.1. Catalyst characterizations

To understand the catalytic performance of these novel materials, detailed characterizations of selected catalysts were done. Fig. 1a shows the XRD patterns of the obtained catalysts prepared at 550 °C under different mass ratios (Ni:Mlm), 7/5, 6/5, and 5/5, respectively. For all samples, a broad diffraction peak at about 26.4° was observed, corresponding to the (0 0 2) crystalline g-C<sub>3</sub>N<sub>4</sub> formed during the thermal condensation process of Mlm [68]. In the cases of the pyrolysis temperature at 550 °C (Fig. 1a), the peaks in Ni/NC-7/5-550 at 44.5°, 51.8° and 76.4° can be assigned to the (1 1 1), (2 0 0) and (2 2 0) planes of the crystalline Ni (JCPDS No. 87-0712), suggesting that the nickel acetate decomposed to form metallic Ni during the pyrolysis process. In contrast, no peak related to crystalline Ni was observed in the samples of Ni<sub>3</sub>N/NC-6/5-550, and Ni<sub>3</sub>N/NC-5/5-550. Instead, six new peaks appeared at 39.2°, 41.6°, 44.6°, 58.5°, 71.1° and 78.0°, which were in agreement with the (1 1 0), (0 0 2), (1 1 1), (1 1 2), (3 0 0) and (1 1 3) crystal planes of the Ni<sub>3</sub>N phase (JCPDS No. 10-0280 and Table S1) [62,69]. The results suggested that, at 550 °C, the Ni<sub>3</sub>N phase can only be produced at a low Ni:Mlm ratio. Fig. 1b shows the XRD patterns of the catalysts developed at different pyrolysis temperatures but with a constant mass ratio (Ni:Mlm) of 6/5. One can see that the Ni<sub>3</sub>N phase can only be obtained at or below 550 °C, presumably due to the decomposition of the Ni<sub>3</sub>N phase at higher pyrolysis temperatures [61].

Fig. 2a and 2b show the SEM and TEM images of the optimum Ni<sub>3</sub>N/NC-6/5-550 catalyst, respectively. One can clearly see that the Ni<sub>3</sub>N nanorods were supported on the platelike g-C<sub>3</sub>N<sub>4</sub>. As presented in the high-resolution TEM (HRTEM) image (Fig. 2c), the nanorods exhibited a fringe space of 0.203 nm which can be indexed to the (1 1 1) lattice of Ni<sub>3</sub>N [70], further confirming the formation of Ni<sub>3</sub>N. The elemental mapping from energydispersive X-ray spectrometry (EDX) revealed that the Ni, N, C and O elements were uniformly distributed throughout the Ni<sub>3</sub>N/ NC-6/5-550 (Fig. 2d). Notably, by increasing the Ni:Mlm to 7/5 or the pyrolysis temperatures to 650 °C, the obtained Ni catalysts showed a clear core-shell structure (Figs. S1 and S2). The Ni cores have a rather broad size distribution and were embedded within the graphite-like C<sub>3</sub>N<sub>4</sub> shells. The formed C<sub>3</sub>N<sub>4</sub> shells might also tune the Ni<sub>3</sub>N or Ni electronically and hence are crucial for the selectivity enhancement in the semi-hydrogenation of 1a.

To further verify the formation of Ni<sub>3</sub>N phase in Ni<sub>3</sub>N/NC-6/5-550, the chemical state of the catalyst was investigated by XPS (Fig. 3a and b). In the Ni  $2p_{3/2}$  spectrum (Fig. 3a), the characteristic peak at the binding energy (BE) of 852.9 eV can be attributed to monovalent Ni<sup>+</sup> [71], indicative for the presence of Ni<sub>3</sub>N. The fitted peak located at 855.0 eV can be ascribed to the Ni 2p<sub>3/2</sub> of NiO, which was probably generated due to the surface atmospheric oxidation of Ni<sub>3</sub>N [63]. Moreover, the peaks at 859.5 and 862.2 eV (denoted as "Sat") can be assigned to the corresponding satellite peaks of Ni<sup>+</sup> and oxygen-binding Ni<sup>2+</sup>, respectively [70]. In Fig. 3b, the N 1s spectrum can be deconvoluted into four Nbonding configurations with binding energies of 397.2, 398.3, 399.3 and 400.9 eV. According to the previous report [15], the peak at 397.2 eV can be assigned to the N in Ni<sub>3</sub>N. The other peaks at 398.3, 399.3 and 400.9 eV can be attributed to the N of pyridinic N, pyrrolic N and graphitic N in the  $g-C_3N_4$  phase, respectively [72].

#### 3.2. Optimization of reaction conditions

Table 1 summarized the catalytic performance of the asprepared Ni<sub>3</sub>N/NC or Ni/NC catalysts in the semi-hydrogenation of 1,2-diphenylethyne **1a**. The results showed that Ni<sub>3</sub>N/NC-6/5-550 (Table 1, entry 2) exhibited the highest conversion (99%) and excellent selectivity (98%) for (*Z*)-stilbene **2a** in ethanol using molecular hydrogen (2.0 MPa) as hydrogen source at 100 °C. In case of higher mass ratio 7/5 (Table 1, entry 1), both conversion and selectivity were lower than those of 6/5. In contrast, in case



Fig. 1. XRD patterns of the as-developed catalysts prepared under different conditions (a) prepared at 550 °C under different mass ratios (Ni:Mlm): 7/5, 6/5, and 5/5; (b) prepared under the mass ratio (Ni:Mlm) of 6/5 at different pyrolysis temperatures: 850, 750, 650, 550 and 450 °C.



Fig. 2. (a) SEM, (b) TEM, (c) HRTEM images and (d) elemental maps of the Ni<sub>3</sub>N/NC-6/5-550 catalyst.

of lower mass ratios 5/5 (Table 1, entry 3), the selectivity slightly increased to 99%, but the conversion of **1a** decreased to 81%. Although the catalysts pyrolysed at 650 °C (Table 1, entry 5) and 750 °C (Table 1, entry 6) were active, the selectivities for stilbene and the Z/E ratio were much lower than those of Ni<sub>3</sub>N/NC-6/5-550. Furthermore, those catalysts pyrolysed at even lower (450 °C, Table 1, entry 4) and higher (850 °C, Table 1, entry 7) temperatures gave significantly lower conversion in this transformation. With respect to the TOF value, a negative correlation was observed between the activity and the feed ratio of Mlm in the mixture of nickel acetate tetrahydrate and Mlm (Table 1, entry 1-3). In contrast, the activity showed a positive correlation with the temperature (Table 1, entry 2, 4-7). These phenomena can be attributed to the fact that the carbon layer on the catalyst surface gradually thinned with the decreasing of the feed ratio of Mlm in

the precursor (Fig. S1), or the increasing of pyrolysis temperature (Fig. S2), which can increase the exposure of the activity sites, and thus enhance the activity. However, Ni/NC-6/5-850 showed a low activity due to the severe aggregation of Ni nanoparticles (Fig. S2).

In order to compare the selectivity for alkene, control experiments were carried out using NC support,  $SiO_2$  supported Ni (Ni/SiO<sub>2</sub>), activated carbon supported Ni (Ni/AC) and unsupported Ni<sub>3</sub>N as reference catalysts (Table 1, entries 8-11). In the absence of the Ni<sub>3</sub>N or Ni phase, the NC support gave the lowest conversion of only 4% in 5 h (Table 1, entry 8). Although Ni/SiO<sub>2</sub> and Ni/AC showed high activities in the semi-hydrogenation of **1a** with the conversion up to 99%, the selectivity for stilbene was much lower than that of Ni<sub>3</sub>N/NC-6/5-550 (Table 1, entries 9 and 10). Using pure Ni<sub>3</sub>N, the selectivity for stilbene was increased to 71% with



**Fig. 3.** XPS spectra of (a) Ni  $2p_{3/2}$ , and (b) N 1s of the Ni<sub>3</sub>N/NC-6/5-550 catalyst.

# Table 1Semi-hydrogenation of 1,2-diphenylethyne over Ni-based catalysts.

//Ph	$ \xrightarrow{\text{Ni-based catalyst (7.8 mol%)}}_{\text{EtOH, 100°C, H_2 (2 MPa)}} \qquad $							
Ph								
1a		2a 3a	4a					
Entry	Catalyst	Ni loading of catalyst (wt %)	Conv. <sup>a</sup> (%)	Sel. For stilbene <sup>b</sup> (%)	$Z/E^{c}$	$TOF^{d}(s^{-1})$		
1	Ni/NC-7/5-550	51.0	89	90	89/11	0.293		
2	Ni <sub>3</sub> N/NC-6/5-550	36.3	99	98	98/2	0.110		
3	Ni <sub>3</sub> N/NC-5/5-550	20.7	81	99	98/2	0.067		
4	Ni <sub>3</sub> N/NC-6/5-450	11.4	71	96	97/3	0.034		
5	Ni/NC-6/5-650	55.2	99	89	91/9	0.308		
6	Ni/NC-6/5-750	63.8	97	97	95/5	0.975		
7	Ni/NC-6/5-850	71.3	8	96	94/6	0.059		
8	NC	_	4	98	95/5	-		
9 <sup>e</sup>	Ni/SiO <sub>2</sub>	14.3	97	37	91/9	-		
10 <sup>f</sup>	Ni/AC	14.3	99	22	95/5	-		
11	Ni <sub>3</sub> N	-	99	71	93/7	-		

Reaction conditions: 1a (5.38 mmol), 7.8 mol% Ni (based on ICP results), ethanol (70 mL), 5 h, 100 °C, initial P(H<sub>2</sub>) = 2.0 MPa.

<sup>a</sup> Determined by GC.

<sup>b</sup> Selectivity for (*Z*)- and (*E*)-stilbene.

<sup>c</sup> Relative percent ratio of (*Z*)-stilbene **2a** and (*E*)-stilbene **3a**.

<sup>d</sup> The TOF was calculated based on conversion lower than 30% and the number of active sites (Table S2).

<sup>e</sup> 2 mol% Ni, 80 °C, 10 min.

<sup>f</sup> 2 mol% Ni, 80 °C, 3 min.

a 99% conversion (Table 1, entry 11), verifying the enhanced selectivity for stilbene over the Ni<sub>3</sub>N catalyst. After introducing NC support in the Ni<sub>3</sub>N catalyst (Ni<sub>3</sub>N/NC-6/5-550, Table 1, entry 2), the selectivity was further increased to 98% with a 99% conversion, indicating that the NC support is also beneficial for the selectivity enhancement in alkyne semi-hydrogenation [27,48,73]. In comparison with reference catalysts, the selectivity for alkene at high conversion follows the order of Ni<sub>3</sub>N/NC > Ni<sub>3</sub>N > Ni. In addition, effect of solvents was also examined with the optimum catalyst Ni<sub>3</sub>N/ NC-6/5-550. It was found that the semi-hydrogenation of **1a** proceeded sluggishly in a range of solvents, including *N*,*N*-dimethyl formamide, acetonitrile, tetrahydrofuran, toluene, ethyl acetate and dioxane, compared to ethanol (Table S3). Combined, these experimental results demonstrated that the Ni<sub>3</sub>N phase is the most active species in the selective semi-hydrogenation of **1a**.

# 3.3. Kinetic profile and DFT study

The kinetic profile for the semi-hydrogenation of **1a** over  $Ni_3N/NC-6/5-550$  is shown in Fig. 4. It can be seen that  $Ni_3N/NC-6/5-550$  afforded a 99% conversion and 96% selectivity for **2a** within 5 h. Notably, high chemo- and stereoselectivity was maintained even during prolonging reaction times up to 12 h. The excellent catalytic performance of  $Ni_3N/NC-6/5-550$  was also



Fig. 4. Time course of the semi-hydrogenation of 1a over Ni<sub>3</sub>N/NC-6/5-550.

evaluated by a control experiment (Scheme 2), in which a mixture of **1a** (4%) and a large excess of **2a** (96%) was hydrogenated at 100 °C under 2.0 MPa of H<sub>2</sub> in the presence of Ni<sub>3</sub>N/NC-6/5-550. The results showed that only trace amounts of **3a** isomer and over-hydrogenated product **4a** were detected after full conversion



Scheme 2. Control experiment: the hydrogenation of a mixture of 1a and 2a over Ni<sub>3</sub>N/NC-6/5-550.

of **1a**, demonstrating that the isomerization and overhydrogenation of **2a** were inhibited in this catalytic system involving Ni<sub>3</sub>N/NC-6/5-550. The superior chemo- and stereoselectivity of Ni<sub>3</sub>N/NC-6/5-550 makes it an excellent candidate for the purification of alkenes by the selective semi-hydrogenation of any alkyne impurity, without the need for strict reaction monitoring.

In order to clarify the role of Ni<sub>3</sub>N in the selectivity enhancement in alkyne semi-hydrogenation, DFT calculations were performed. Specifically, using 1,2-diphenylethyne (1a)hydrogenation as the model reaction, the adsorption energy of intermediate species produced during its semi-hydrogenation on Ni (1 1 1) and Ni<sub>3</sub>N (1 1 1) surfaces were calculated (Fig. 5). These intermediate species include the first (Z-int and E-int) and second hydrogenation products (Z-stilbene and E-stilbene). The results showed that, for the 1,2-diphenylethyne reactant, its adsorption on Ni (1 1 1) surface (1.81 eV) was much stronger than that (0.23 eV) on Ni<sub>3</sub>N (1 1 1), suggesting that Ni might be more active for the hydrogenation reaction, and in accordance with the result of control experiment (Ni/SiO<sub>2</sub>). Moreover, Ni<sub>3</sub>N (1 1 1) exhibited lower adsorption towards the intermediate Z-int, E-int, Z-stilbene and E-stilbene species as well. For example, on Ni (1 1 1), the semi-hydrogenation product Z-stilbene and E-stilbene has adsorption energies of 0.99 and 2.50 eV, respectively. However, on Ni<sub>3</sub>N (1 1 1), their corresponding E<sub>ads</sub> was only 0.10 and 0.31 eV, respectively. The lower adsorption energies of stilbene products observed on Ni<sub>3</sub>N (1 1 1) indicated that desorption of stilbene into gas phase was preferred, suppressing its further hydrogenation and therefore improve the selectivity of stilbene. Moreover, the hydrogenation kinetics of 1,2-diphenylethyne towards stilbene production were also investigated. Fig. 6 presents the transition states (T.S) and corresponding activation energies for the forward/backwards of the hydrogenation reaction on Ni (1 1 1) and Ni<sub>3</sub>N (1 1 1) surfaces. Overall, the energy barriers of these hydrogenation steps were very similar on both surfaces except for the Z-stilbene production step, for which the energy barrier on Ni<sub>3</sub>N (1 1 1) was 1.44 eV higher than that on Ni (1 1 1). The high adsorption energy and the relatively low energy barrier on Ni (1 1 1) surface indicated that Ni was more active for the hydrogenation reaction than Ni<sub>3</sub>N. However, this would also lead to over-hydrogenation during reaction. On the other hand, the reaction kinetics on Ni<sub>3</sub>N (1 1 1) might be slightly slow. However, the low adsorption energy of stilbene indicated that, upon the formation of stilbene product, it would release from the Ni<sub>3</sub>N surface, making it a promising catalyst towards the semi-hydrogenation of alkynes. These calculation results agree well with the experimental observations. As shown in Table 1, the hydrogenation reaction proceeded rapidly on Ni (10 min). However, the selectivity for stilbene production is higher on Ni<sub>3</sub>N-based catalyst (71-98%) than Ni (37%).

# 3.4. Substrate scope

With the most active catalyst and optimal conditions in hand, the semi-hydrogenation of various alkynes was also studied to evaluate the versatility of Ni<sub>3</sub>N/NC-6/5 catalyst. The results summarized in Table 2 confirm that a broad range of functional groups. such as fluoro, chloro, bromo, cyano, trifluoromethyl, methyl, ethyl, propyl, alkyl, thienyl, ester and hydroxy, in both terminal and internal alkynes are tolerated in this semi-hydrogenation protocol. Terminal alkynes with either phenylic or aliphatic substituents can be smoothly hydrogenated to afford the corresponding alkenes exclusively with up to > 99% conversion (Table 2, entries 1-8). A substrate bearing a thienyl substituent displayed low reactivity under standard conditions, probably due to the coordination with the metal catalyst [74], but still afforded a 91% conversion with 93% selectivity while prolonging the reaction time to 11 h (Table 2, entry 8). On the other hand, a series of internal alkynes was readily hydrogenated to the desired (Z)-alkene products. Aromatic substrates containing both electron-donating and



Fig. 5. The most stable adsorption configurations of the surface species invloved in 1,2-diphenylethyne hydrogenation reaction on Ni (1 1 1) and Ni<sub>3</sub>N (1 1 1) surface models. Orange (Ni), gray (C), blue (N), white (H).



Fig. 6. Geometric structures of the transition state and corresponding forward/backward activation energies of the species and elementary reactions in 1,2-diphenylethyne semi-hydrogenation reaction on Ni (1 1 1) and Ni<sub>3</sub>N (1 1 1) surface models. Orange (Ni), gray (C), blue (N), white (H).

# Table 2 Nitride nickel-catalysed semi-hydrogenation of various alkynes.

Entry	Substrate	Time (h)	Conv. <sup>a</sup> (%)	Sel. For alkene (%) <sup>b</sup>	$Z/E^{c}$
1		1	>99	87	-
2		1.5	>99	92	-
3	Br-	4	92	94	-
4		4	>99	85	-
5	F <sub>3</sub> C-	2	96	87	-
6	~ ~ ~ //	1.3	>99	83	-
7		0.83	>99	80	-
8		11	91	93	-
9	$\langle \rangle = \langle \rangle$	5	99	98	98/2
10		4.7	>99	95	95/5
11		2	96	95	96/4
12 <sup>d</sup>		11	>99	97	91/9
13		9.5	44	97	96/4
14 <sup>d</sup>		14.5	>99	96	95/5
15 <sup>e</sup>		7	>99	95	96/4
16	CF3	6	>99	94	97/3
17	$\langle  \rangle = \langle  \rangle$	3	>99	89	95/5
18 <sup>f</sup>		3.7	>99	82	93/7
19		2	95	83	93/7
20	но, он	10	76	>99	>99/1
21 <sup>e</sup>	$\rightarrow = \leftarrow$	11	>99	99	>99/1
22		2	>99	96	>99/1

Reaction conditions: substrate (0.3 mmol), 7.8 mol% Ni<sub>3</sub>N/NC-6/5-550, ethanol (3 mL), 100 °C, initial *P*(H<sub>2</sub>) = 2.0 MPa.

<sup>a</sup> The conversion and selectivity were determined by GC.

<sup>b</sup> Selectivity for (*Z*)- and (*E*)-stilbene.

<sup>c</sup> Relative percent ratio of (*Z*)-alkene and (*E*)-alkene.

<sup>d</sup> 120 °C, initial  $P(H_2) = 3.0$  MPa.

<sup>e</sup> 120 °C, initial  $P(H_2) = 4.0$  MPa.

<sup>f</sup> Ethyl (Z)-3-phenylacrylate was detected due to the transesterification.



Fig. 7. (a) Influence of cycle number on the catalytic performance of Ni<sub>3</sub>N/NC-6/5-550; (b) TEM image and XRD pattern (inset) of recycled Ni<sub>3</sub>N/NC-6/5-550.

electron-withdrawing groups (Table 2, entries 9-18) provided the corresponding (*Z*)-alkene products in good conversion and with satisfactory selectivity. In particular, ketones were compatible with the reaction conditions (Table 2, entry 13), and no homologous product was detected even under harsh conditions (Table 2, entry 14). In contrast, substrates bearing an ester group afforded relatively lower alkene selectivities (Table 2, entries 17–19). Notably, the reaction of aliphatic alkynes, either dialkylacetylenes or alkynols, proceeded smoothly to provide the corresponding alkenes in excellent yield with *Z/E* ratios above 99:1 (Table 2, entries 20 and 21), probably due to their difficulty in accessing the active site of Ni<sub>3</sub>N on the polar support [75]. In summary, the above results demonstrate the general applicability of the Ni<sub>3</sub>N/NC-6/5 catalyst toward the semi-hydrogenation of a range of alkynes.

# 3.5. Stability test

Finally, the recoverability and reusability of the Ni<sub>3</sub>N/NC-6/5-550 catalyst was evaluated in the semi-hydrogenation reaction of **1a**. The used catalyst can be readily isolated by precipitation, and then be successfully cycled for 5 successive runs without loss of its initial catalytic activity (Fig. 7a). In addition, the lattice parameter and morphology of the recycled Ni<sub>3</sub>N/NC-6/5-550 remain unchanged after the recycling process (Fig. 7b), indicating the good stability of Ni<sub>3</sub>N catalyst.

# 4. Conclusion

In summary, we have developed a novel method for the facile fabrication of *N*-doped carbon supported nickel nitride (Ni<sub>3</sub>N/NC) via a direct pyrolysis of a solid mixture of nickel acetate tetrahydrate and Mlm. Notably, Ni<sub>3</sub>N has been demonstrated as the active species in the semi-hydrogenation of alkynes. The Ni<sub>3</sub>N/NC-6/ 5-550 catalyst thus obtained showed high activity, excellent selectivity for (*Z*)-alkenes and good functional group tolerance in the semi-hydrogenation of both internal and terminal alkynes. We have experimentally demonstrated and theoretically confirmed that the selectivity for alkene in semi-hydrogenation of alkynes can be markedly enhanced using the Ni<sub>3</sub>N/NC-6/5-550 catalyst. Furthermore, this non-precious metal catalyst showed good stability, making it an excellent candidate for further applications.

# **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Acknowledgements

The authors thank Professor Laurence M. Harwood for his kind help in preparing this manuscript. Financial support by the National Natural Science Foundation of China (21676068, 21706049 and 21376060), the Natural Science Foundation of Hebei Province (B2016418005, B2019201341) and the Hebei University construction project for comprehensive strength promotion of Midwest colleges and universities is gratefully acknowledged.

# Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcat.2019.12.005.

## References

- K. Chernichenko, A. Madarász, I. Pápai, M. Nieger, M. Leskelä, T. Repo, Nat. Chem. 5 (2013) 718–723.
- [2] R. Chinchilla, C. Nájera, Chem. Rev. 114 (2014) 1783–1826.
- [3] M. Crespoquesada, F. Cárdenaslizana, A.L. Dessimoz, L. Kiwiminsker, ACS Catal. 2 (2012) 1773–1786.
- [4] J.A. Delgado, O. Benkirane, C. Claver, D. Curulla-Ferré, C. Godard, Dalton Trans. 46 (2017) 12381–12403.
- [5] C. Oger, L. Balas, T. Durand, J.-M. Galano, Chem. Rev. 113 (2013) 1313–1350.
- [6] Y. Zhang, X. Wen, Y. Shi, R. Yue, L. Bai, Q. Liu, X. Ba, Ind. Eng. Chem. Res. 58 (2019) 1142–1149.
- [7] S. Zhou, L. Gao, F. Wei, S. Lin, H. Guo, J. Catal. 375 (2019) 410–418.
- [8] C. Riley, S. Zhou, D. Kunwar, A. De La Riva, E. Peterson, R. Payne, L. Gao, S. Lin, H. Guo, A. Datye, J. Am. Chem. Soc. 140 (2018) 12964–12973.
- [9] R. Lin, D. Albani, E. Fako, S.K. Kaiser, O.V. Safonova, N. López, J. Pérez-Ramírez, Angew. Chem. 131 (2019) 514–519.
- [10] Y. Liu, A.J. McCue, C. Miao, J. Feng, D. Li, J.A. Anderson, J. Catal. 364 (2018) 406– 414.
- [11] D. Albani, M. Shahrokhi, Z. Chen, S. Mitchell, R. Hauert, N. López, J. Pérez-Ramírez, Nat. Commun. 9 (2018) 2634.
- [12] R. Guo, Q. Chen, X. Li, Y. Liu, C. Wang, W. Bi, C. Zhao, y. Guo, M. Jin, J. Mater. Chem. A 7 (2019) 4714–4720.
- [13] A.J. McCue, A. Guerrero-Ruiz, I. Rodríguez-Ramos, J.A. Anderson, J. Catal. 340 (2016) 10–16.
- [14] X. Zhao, L. Zhou, W. Zhang, C. Hu, L. Dai, L. Ren, B. Wu, G. Fu, N. Zheng, Chem 4 (2018) 1080–1091.
- [15] A.J. McCue, A. Guerrero-Ruiz, C. Ramirez-Barria, I. Rodríguez-Ramos, J.A. Anderson, J. Catal. 355 (2017) 40–52.
- [16] Y. Liu, A.J. McCue, J. Feng, S. Guan, D. Li, J.A. Anderson, J. Catal. 364 (2018) 204– 215.
- [17] X. Li, Y. Pan, H. Yi, J. Hu, D. Yang, F. Lv, W. Li, J. Zhou, X. Wu, A. Lei, L. Zhang, ACS Catal. 9 (2019) 4632–4641.
- [18] F. Liguori, P. Barbaro, J. Catal. 311 (2014) 212–220.
- [19] Y. Kuwahara, H. Kango, H. Yamashita, ACS Catal. 9 (2019) 1993–2006.
- [20] D. Teschner, E. Vass, M. Hävecker, S. Zafeiratos, P. Schnörch, H. Sauer, A. Knop-Gericke, R. Schlögl, M. Chamam, A. Wootsch, A.S. Canning, J.J. Gamman, S.D. Jackson, J. McGregor, L.F. Gladden, J. Catal. 242 (2006) 26–37.
- [21] S. Wang, Z.-J. Zhao, X. Chang, J. Zhao, H. Tian, C. Yang, M. Li, Q. Fu, R. Mu, J. Gong, Angew. Chem., Int. Ed. 58 (2019) 7668–7672.
- [22] F. Huang, Y. Deng, Y. Chen, X. Cai, M. Peng, Z. Jia, P. Ren, D. Xiao, X. Wen, N. Wang, H. Liu, D. Ma, J. Am. Chem. Soc. 140 (2018) 13142–13146.

- [23] K. Tokmic, A.R. Fout, J. Am. Chem. Soc. 138 (2016) 13700-13705.
- [24] K.K. Tanabe, M.S. Ferrandon, N.A. Siladke, S.J. Kraft, G. Zhang, J. Niklas, O.G. Poluektov, S.J. Lopykinski, E.E. Bunel, T.R. Krause, J.T. Miller, A.S. Hock, S.T. Nguyen, Angew. Chem., Int. Ed. 53 (2014) 12055–12058.
- [25] P.-H. Phua, L. Lefort, J.A.F. Boogers, M. Tristany, J.G. de Vries, Chem. Commun. (2009) 3747–3749.
- [26] F. Studt, F. Abild-Pedersen, T. Bligaard, R.Z. Sørensen, C.H. Christensen, J.K. Nørskov, Science 320 (2008) 1320–1322.
- [27] F. Chen, C. Kreyenschulte, J. Radnik, H. Lund, A.-E. Surkus, K. Junge, M. Beller, ACS Catal. 7 (2017) 1526–1532.
- [28] C. Chen, Y. Huang, Z. Zhang, X.-Q. Dong, X. Zhang, Chem. Commun. 53 (2017) 4612-4615.
- [29] E. Richmond, J. Moran, J. Org. Chem. 80 (2015) 6922-6929.
- [30] E. Korytiakova, N.O. Thiel, F. Pape, J.F. Teichert, Chem. Commun. 53 (2017) 732-735.
- [31] O.G. Salnikov, H.-J. Liu, A. Fedorov, D.B. Burueva, K.V. Kovtunov, C. Coperet, I.V. Koptyug, Chem. Sci. 8 (2017) 2426–2430.
- [32] A. Fedorov, H.-J. Liu, H.-K. Lo, C. Copéret, J. Am. Chem. Soc. 138 (2016) 16502– 16507.
- [33] T.N. Gieshoff, A. Welther, M.T. Kessler, M.H.G. Prechtl, A. Jacobi von Wangelin, Chem. Commun. 50 (2014) 2261–2264.
- [34] M. Tejeda-Serrano, J.R. Cabrero-Antonino, V. Mainar-Ruiz, M. López-Haro, J.C. Hernández-Garrido, J.J. Calvino, A. Leyva-Pérez, A. Corma, ACS Catal. 7 (2017) 3721–3729.
- [35] X. Qi, X. Liu, L.-B. Qu, Q. Liu, Y. Lan, J. Catal. 362 (2018) 25-34.
- [36] N. Kaeffer, K. Larmier, A. Fedorov, C. Copéret, J. Catal. 364 (2018) 437–445.
  [37] N. Kaeffer, H.-J. Liu, H.-K. Lo, A. Fedorov, C. Copéret, Chem. Sci. 9 (2018) 5366–
- 5371.
- [38] M.D. de los Bernardos, S. Pérez-Rodríguez, A. Gual, C. Claver, C. Godard, Chem. Commun. 53 (2017) 7894-7897
- [39] Y. Chen, C. Li, J. Zhou, S. Zhang, D. Rao, S. He, M. Wei, D.G. Evans, X. Duan, ACS Catal. 5 (2015) 5756–5765.
- [40] H. Konnerth, M.H.G. Prechtl, Chem. Commun. 52 (2016) 9129–9132.
- [41] K. Murugesan, C.B. Bheeter, P.R. Linnebank, A. Spannenberg, J.N.H. Reek, R.V. Jagadeesh, M. Beller, ChemSusChem 12 (2019) 3363–3369.
- [42] K. Murugesan, A.S. Alshammari, M. Sohail, M. Beller, R.V. Jagadeesh, J. Catal. 370 (2019) 372–377.
- [43] X. Dai, Z. Chen, T. Yao, L. Zheng, Y. Lin, W. Liu, H. Ju, J. Zhu, X. Hong, S. Wei, Y. Wu, Y. Li, Chem. Commun. 53 (2017) 11568–11571.
- [44] X. Wen, X. Shi, X. Qiao, Z. Wu, G. Bai, Chem. Commun. 53 (2017) 5372–5375.
- [45] Y. Chai, G. Wu, X. Liu, Y. Ren, W. Dai, C. Wang, Z. Xie, N. Guan, L. Li, J. Am. Chem. Soc. 141 (2019) 9920–9927.
- [46] S.C. Smith, D.F. Rodrigues, Carbon 91 (2015) 122–143.
- [47] M. Zhao, Chem.-Asian J. 11 (2016) 461–464.
- [48] L. Shen, S. Mao, J. Li, M. Li, P. Chen, H. Li, Z. Chen, Y. Wang, J. Catal. 350 (2017) 13–20.

- [49] H. Zhou, X. Yang, L. Li, X. Liu, Y. Huang, X. Pan, A. Wang, J. Li, T. Zhang, ACS Catal. 6 (2016) 1054–1061.
- [50] D. Albani, K. Karajovic, B. Tata, Q. Li, S. Mitchell, N. López, J. Pérez-Ramírez, ChemCatChem 10 (2018) 1–9.
- [51] Y. Liu, X. Liu, Q. Feng, D. He, L. Zhang, C. Lian, R. Shen, G. Zhao, Y. Ji, D. Wang, G. Zhou, Y. Li, Adv. Mater. 28 (2016) 4747–4754.
- [52] Y. Song, S. Laursen, J. Catal. 372 (2019) 151-162.
- [53] S. Carenco, A. Leyva-Pérez, P. Concepción, C. Boissière, N. Mézailles, C. Sanchez, A. Corma, Nano Today 7 (2012) 21–28.
- [54] C. Li, Y. Chen, S. Zhang, J. Zhou, F. Wang, S. He, M. Wei, D.G. Evans, X. Duan, ChemCatChem 6 (2014) 824–831.
- [55] K. Schutte, A. Doddi, C. Kroll, H. Meyer, C. Wiktor, C. Gemel, G. van Tendeloo, R. A. Fischer, C. Janiak, Nanoscale 6 (2014) 5532–5544.
- [56] L. Yang, S. Yu, C. Peng, X. Fang, Z. Cheng, Z. Zhou, J. Catal. 370 (2019) 310–320.
- [57] Y. Liu, J. Zhao, J. Feng, Y. He, Y. Du, D. Li, J. Catal. 359 (2018) 251–260.
- [58] W. Long, N.A. Brunelli, S.A. Didas, E.W. Ping, C.W. Jones, ACS Catal. 3 (2013) 1700–1708.
- [59] M. Shalom, D. Ressnig, X. Yang, G. Clavel, T.P. Fellinger, M. Antonietti, J. Mater. Chem. A 3 (2015) 8171–8177.
- [60] F. Gillot, J. Oro-Sole, M.R. Palacin, J. Mater. Chem. 21 (2011) 9997–10002.
- [61] G. Clavel, V. Molinari, A. Kraupner, C. Giordano, Chem.-Eur. J. 20 (2014) 9018– 9023.
- [62] M. Shalom, V. Molinari, D. Esposito, G. Clavel, D. Ressnig, C. Giordano, M. Antonietti, Adv. Mater. 26 (2014) 1272–1276.
- [63] K. Xu, P. Chen, X. Li, Y. Tong, H. Ding, X. Wu, W. Chu, Z. Peng, C. Wu, Y. Xie, J. Am. Chem. Soc. 137 (2015) 4119–4125.
- [64] G. Chen, X. Zhu, J. Cai, Y. Wan, Synth. Commun. 37 (2007) 1355–1361.
- [65] G. Kresse, J. Furthmüller, Comp. Mater. Sci. 6 (1996) 15-50.
- [66] G. Kresse, J. Furthmüller, Phys. Rev. B 54 (1996) 11169–11186.
- [67] G. Henkelman, B.P. Uberuaga, H. Jónsson, J. Chem. Phys. 113 (2000) 9901– 9904.
- [68] S. Kumar, T. Surendar, A. Baruah, V. Shanker, J. Mater. Chem. A 1 (2013) 5333– 5340.
- [69] M. Chen, J. Qi, D. Guo, H. Lei, W. Zhang, R. Cao, Chem. Commun. 53 (2017) 9566–9569.
- [70] F. Xie, H. Wu, J. Mou, D. Lin, C. Xu, C. Wu, X. Sun, J. Catal. 356 (2017) 165–172.
  [71] Y. Wang, L. Chen, X. Yu, Y. Wang, G. Zheng, Adv. Energy Mater. 7 (2017)
- 1601390.
- [72] D. Guo, R. Shibuya, C. Akiba, S. Saji, T. Kondo, J. Nakamura, Science 351 (2016) 361–365.
- [73] X. Li, W. Zhang, Y. Liu, R. Li, ChemCatChem 8 (2016) 1111-1118.
- [74] S. Fu, N.Y. Chen, X. Liu, Z. Shao, S.P. Luo, Q. Liu, J. Am. Chem. Soc. 138 (2016) 8588–8594.
- [75] E. Vasilikogiannaki, I. Titilas, G. Vassilikogiannakis, M. Stratakis, Chem. Commun. 51 (2015) 2384–2387.