



# Nondestructive construction of Lewis acid sites on the surface of supported nickel phosphide catalysts by atomic-layer deposition



Guoxia Yun<sup>a</sup>, Qingxin Guan<sup>a,\*</sup>, Wei Li<sup>a,b,\*</sup>

<sup>a</sup> College of Chemistry, State Key Laboratory of Elemento–Organic Chemistry, Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), Nankai University, Tianjin 300071, China

<sup>b</sup> Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Nankai University, Tianjin 300071, China

## ARTICLE INFO

### Article history:

Received 8 November 2017

Revised 20 January 2018

Accepted 12 February 2018

### Keywords:

ALD

Hydrodesulfurization

Hydrodearomatization

Hydrogenation

Nickel phosphide

## ABSTRACT

In this paper, we have developed a new strategy to construct the acidic sites on the surface of supported transition-metal phosphide catalysts, which could precisely control the deposition of the Al<sub>2</sub>O<sub>3</sub> atomic layer through atomic-layer deposition (ALD). A series of supported nickel phosphide catalysts decorated with Al<sub>2</sub>O<sub>3</sub> film were prepared and characterized. The results show that Al<sub>2</sub>O<sub>3</sub> film was deposited on the surface of the catalyst via Al–O–Si bonding, which does not affect or alter the characteristics of the as-prepared nickel phosphide phase. Most importantly, among all the Ni<sub>2</sub>P-based catalysts, the Ni<sub>2</sub>P/SiO<sub>2</sub>-ALD catalyst with 10 Al<sub>2</sub>O<sub>3</sub> layers possesses the optimal performance in hydrodesulfurization and hydrodearomatization reactions. In particular, superior hydrogenation performances were considered to be strongly related to a synergistic effect between nickel phosphide and the modulated acidic property. This precise stepwise ALD strategy opens a convenient route and provides a prospective design guideline for constructing high-performance hydrogenation catalysts.

© 2018 Elsevier Inc. All rights reserved.

## 1. Introduction

Transition-metal phosphides (TMPs), a class of interstitial metal compounds, have attracted worldwide interest for their unique physical and chemical properties. As alternative materials to noble metals, TMPs are inexpensive and have excellent antitoxic ability. They are widely used in catalytic hydrogenation [1–8], reforming of methane [9], electrochemical water splitting [10,11], electrode material [12–14], photocatalytic hydrogen evolution [15–18], and so on. In particular, TMP catalysts show superior activity and stability in the field of catalytic hydrogenation, which has inspired considerable research efforts in hydrodesulfurization (HDS) [19–22], hydrodenitrogenation (HDN) [23], hydrodeoxygenation (HDO) [6,24], and hydrodearomatization (HDA) [25]. For example, Lónyi et al. reported a new approach for the synthesis of highly active supported nickel phosphide catalysts through H<sub>2</sub> reduction of catalyst precursor gel for HDN of propylamine [26]. Oyama et al. reported Ni<sub>2</sub>P-based catalysts with excellent HDO activity

of 2-methyltetrahydropyran and provided insights on the unambiguous interactions between a cyclic ether with a TMP [27]. These works all have expanded ways for application or enhanced properties of TMPs.

It should be pointed out that the active phase and support are both critical for highly active hydrogenation catalysts. With regard to this, it has been reported that acidic supports can further promote hydrogenation in an HDS reaction and provoke an electron deficiency of the catalytic centers [28] so that the deactivation by coke deposition is lowered. Acidic supports also improve the catalytic activity of the catalyst particles by increasing their sulfur resistance and promoting their intrinsic activity [29]. The acidic sites of the support will adsorb the reactants during the hydrogenation reaction, and the dissociated hydrogen species can then migrate to nearby acidic sites, which could result in an improvement of the catalytic activity [30]. Although TMP catalysts possess high intrinsic activity, this is limited by acidic support during the synthesis of the supported catalysts, for example,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, which is widely used as a traditional HDS support. It is well known that, upon calcination, phosphate ion strongly associates with  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, thereby hindering the formation of the Ni<sub>2</sub>P phase and resulting in the formation of aluminum phosphate species at high temperature in the synthesis of the supported catalysts [31], such as AlPO<sub>4</sub>, at the surface of the support, which is an inactive species in HDS reactions. It can cause the loss of an active component and even

\* Corresponding authors at: College of Chemistry, State Key Laboratory of Elemento–Organic Chemistry, Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), Nankai University, Tianjin 300071, China (W. Li).

E-mail addresses: [qingxinguan@nankai.edu.cn](mailto:qingxinguan@nankai.edu.cn) (Q. Guan), [weili@nankai.edu.cn](mailto:weili@nankai.edu.cn) (W. Li).

damage the surface texture of catalysts, which decreases the activity of the catalyst. Thus, their practical applications still suffer from great challenges. There are two main ways to solve this problem: (i) reduce the synthesis temperature of the catalyst [32,33], and (ii) introduce other oxide supports [34]. For the former, the kind of TMP catalysts that could be synthesized is limited. For the latter, acidic sites on the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surface are greatly reduced. Hence, it remains a significant challenge to synthesize TMP on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support.

To overcome these disadvantages, new technologies and catalyst preparation methods are urgently needed to meet the challenges of producing enough and better quality ultra-clean liquid hydrocarbon fuels to fulfill the world's transportation needs. Efforts to resolve this issue are currently underway. Atomic-layer deposition (ALD) is a powerful technique for depositing nanoparticles or thin films and has outstanding advantages. ALD has good universality and is regarded as a well-established coating technique that inherently allows for atomic-scale thickness control [35]. These impressive features have expanded its application in the synthesis of both metal and metal oxide catalytic materials. Recently, a plethora of research articles have reported that ALD can also be used as an advanced catalyst design method for tuning the acidity and/or improving catalytic performance [36,37]. Martens et al. reported ALD of aluminum (ALD-Al) to be an elegant technique for introducing aluminum in nanoporous materials and demonstrated an enhancement of the acidity and acid catalytic activity of US-Y zeolite and Zeolite-4 hierarchical material for decane hydroconversion [38].

Subsequently, the successful introduction of tetrahedral aluminum in the all-silica COK-14 zeolite by the ALD-Al method was also reported by Martens et al., and this research demonstrates the catalytic activation of OKO-type zeolites for hydrocracking of n-decane. This is the first example of generating acid sites in a purely siliceous zeolite by ALD-Al [39].

Notably, Dumesic et al. proposed a facile one-pot coating method for the synthesis of mesoporous niobia employing ALD of niobia within the pores of a mesoporous SBA-15. The mesoporous niobia produced by 19 cycles has been studied for dehydration of 2-propanol and 2-butanol, showing catalytic activity superior to commercial niobia (HY-340). This research gives a new concept for the design of highly efficient and multifunctional nanocatalysts [40].

Different from published results, in this paper, we developed a new strategy to not only fabricate nickel phosphide on an acidic support but also construct the acidic sites on the surface of highly active supported nickel phosphide catalysts, which could precisely control the deposition of a well-defined Al<sub>2</sub>O<sub>3</sub> atomic layer by means of ALD technology (Fig. 1). Herein, this straightforward method can be employed for surface acid construction of various supported TMP catalysts. To gain a better understanding of how it works, various supported nickel phosphide catalysts were constructed using ALD technology. The results of the characterization

and activity test show that this method can greatly enhance the activity of supported nickel phosphide catalysts.

## 2. Experimental section

### 2.1. Materials

Nickel nitrate (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O), aluminum nitrate (Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O), and ammonium dihydrogen phosphate (NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>, 99%) were purchased from Tianjin Guangfu Technology Development Co. Ltd., China. Trimethylaluminum (TMA, 2.0 M in toluene) was obtained from Aladdin Industrial Corporation. SiO<sub>2</sub> was purchased from Tianjin Chem. Sci. Co. Ltd., China. It had a specific surface area of 206 m<sup>2</sup> g<sup>-1</sup>, a pore volume of 0.8 cm<sup>3</sup> g<sup>-1</sup>, and a BJH average pore size of 15.96 nm. SBA-15 was purchased from Nanjing XFNANO Materials Tech Co. Ltd., China.  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was obtained by the calcination of pseudoboehmite (Shandong Aluminum Plant, PR China) at 600 °C for 2 h. All of the materials were analytical grade and utilized without further purification.

### 2.2. Catalyst preparation

#### 2.2.1. Supported nickel phosphide catalysts

A series of supported nickel phosphide catalysts were successfully synthesized using our previously published metal phosphate direct reduction method [41]. It mainly includes the following steps [1]: first, the oxide precursor was prepared by incipient wetness impregnating supports with a mixed aqueous solution of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>, followed by drying at 120 °C for 4 h, and then calcination at 500 °C for 2 h in air [2]; the oxide precursor was reduced at 600 °C for 2 h under flowing H<sub>2</sub> (60 mL min<sup>-1</sup>) to obtain the nickel phosphide catalyst. Finally, the product was cooled to ambient temperature under flowing H<sub>2</sub> and was passivated in 1% O<sub>2</sub>/N<sub>2</sub> for 1 h. In all the supported catalysts, the initial mole ratio of Ni/P was 1.25, the loading of Ni<sub>2</sub>P was 20 wt%, and the support included SiO<sub>2</sub>, SBA-15, and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

#### 2.2.2. ALD on supported nickel phosphide catalysts

ALD technology has been extensively studied in the field of coating [42]. Fig. 2 illustrates the scheme of the ALD reactor and the reaction mechanism of ALD-deposited Al<sub>2</sub>O<sub>3</sub> film. In this work, the supported nickel phosphide catalyst is a powder material. ALD of supported nickel phosphide catalysts was prepared following the below procedure. Briefly, the ALD reactor was a tubular furnace structure in which the catalyst was located in the middle of the reaction tube and blocked with glass fiber at both ends. The TMA and H<sub>2</sub>O were contained in 25 mL glass bottles and connected to the reactor via a stainless-steel valve. TMA and H<sub>2</sub>O were alternately entrained in the N<sub>2</sub> carrier flow using gas switching valves. The Al<sub>2</sub>O<sub>3</sub> film was deposited at 150 °C in an ALD reactor using alternating exposures of TMA and H<sub>2</sub>O. The conformal Al<sub>2</sub>O<sub>3</sub> ALD film growth proceeded according to two self-limiting surface reactions.

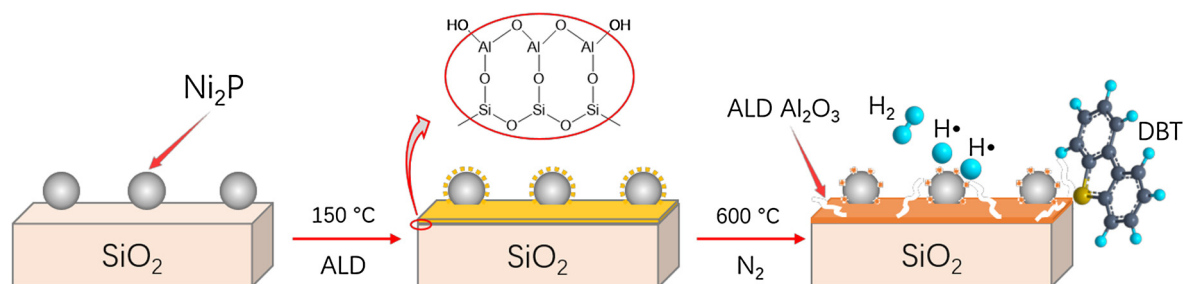


Fig. 1. Scheme of constructing of acidic sites on the surface of Ni<sub>2</sub>P/SiO<sub>2</sub> catalyst using ALD.

Download English Version:

<https://daneshyari.com/en/article/6526669>

Download Persian Version:

<https://daneshyari.com/article/6526669>

[Daneshyari.com](https://daneshyari.com)