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Interaction mechanism of $Ni(NO_3)_2 \cdot 6H_2O$ and P123 in preparing highly-dispersed Ni/SBA-15 catalytic materials

Weiwei Yang, Huimin Liu, Yuming Li, Dehua He*

Innovative Catalysis Program, Key Lab of Organic Optoelectronics & Molecular Engineering of Ministry of Education, Department of Chemistry, Tsinghua University, Beijing 100084, China

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ABSTRACT

P123 (PEG-PPG-PEG triblock copolymer) was employed as a modifying agent to prepare highly-dispersed Ni/SBA-15 via a simple wetness impregnation method. A detailed molecular-level pathway had been illuminated to interpret the role of P123 during the catalyst preparation process with Raman, ^{1}H-NMR, UV–Vis, DLS, FTIR, and TPO measurements. There existed no interaction between $Ni(NO_3)_2 \cdot 6H_2O$ and P123 during impregnation and evaporation steps with the existence of H_2O in the media. The oxygen atoms of PEO blocks would coordinate with Ni^{2+}, NO_3^- and H_2O to form crown-ether-type complexes when the water was evaporated out from the solution during the drying step, which improved the dispersion and stabilization of the precursor. And the complexes ultimately inhibited the redistribution and affected the decomposition of $Ni(NO_3)_2 \cdot 6H_2O$ precursor during calcination. All in all, the above specific interaction between $Ni(NO_3)_2 \cdot 6H_2O$ and P123 would lead to a critical influence of P123 addition on the NiO dispersion on the support.

1. Introduction

Ni-based catalysts have aroused much attention for decades, especially due to the reasonable cost, availability and high activity in many catalytic reactions [1,2]. Mesoporous materials (*e.g.* SBA, MCM, KIT, FDU, AMS, and MSU, etc.) with high surface area, porosity and tunability, have been widely applied as supports for metals and metal oxides in catalysis fields [3]. Siliceous ordered mesoporous materials (*e.g.* SBA-15, etc.) supported Ni-based catalysts have been frequently reported as the catalysts for methane reforming [4,5], ethanol steam reforming [6,7], glycerol hydrogenolysis [8], and aromatic hydrogenation [9,10], etc. The catalytic activities of these specific catalysts depended greatly on the Ni dispersion. More specifically, larger fractional active sites could be exposed at the surfaces, accessible to reactants and available for catalysis, with higher metal dispersion [11,12].

Various catalyst preparation methods have been proposed to improve the Ni dispersion on mesoporous supports in the recent reports [13–19]. A Ni/SBA-15 catalyst with high Ni loading and homogenous Ni distribution was prepared by Murrieta et al. via a deposition-precipitation method [13]. Afterwards, Au's group employed a template ion-exchange (TIE) method to obtain a Ni/MCM-41 (TIE) catalyst with appropriate Ni dispersion and inside pores nickel-enrichment [14]. Moreover, Yang et al. invented a post-synthesis grafting method to prepare highly-dispersed Ni particles anchored by SBA-15 and MCM-41, in other words, nickel acetylacetonate was grafted controllably onto the surfaces of supports through atomic layer deposition [15]. Meanwhile, Williams et al. observed that the nano-Ni/SiO_2 catalyst prepared by sol-gel method possessed better Ni dispersion and higher surface areas compared with the Ni/SiO_2 impregnation catalyst [16,17]. Simultaneously, Srivastava et al. [18] and Kawamoto et al. [19] reported a one-step direct synthetic route to prepare highly loaded and well-dispersed NiO/SBA-15 catalyst for non-enzymatic sensing of glucose and producer gas conversion, respectively.

However, the high cost, low preparation efficiency, low loading efficiency and particular difficulty in scaling up of the methods mentioned above, limited the industrial application of these highly dispersed supported Ni-based catalysts. As we all know, impregnation method is of particular industrial practicability due to its low cost, high efficiency and simplicity [12]. Thus, the modified impregnation methods, assisted by adding appropriate amounts of specific modifying agents during the impregnation process,

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* Corresponding author.
E-mail address: hedeh@mail.tsinghua.edu.cn (D. He).

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attracted more and more attention recently. Cetyl trimethyl ammonium bromide (CTAB) [20], ethylene glycol (EG) [21,22], fatty acids (FAs) [12], oleic acid (OA) [23], β-cyclodextrin (β-CD) [4,24] and glucose [25] could assist the wetness impregnation process for highly-dispersed mesoporous material supported Ni-based catalysts. However, up to now there were no detailed reports about the mechanism study for modifying agents functioning in the catalyst preparation processes to improve the metallic dispersion. Therefore, it's quite necessary to establish a detailed investigation method to explore the mechanism.

Recently, we discovered a P123-assisted wetness impregnation method for preparing well-dispersed Ni/SBA-15 catalysts [26]. We found that the Ni dispersions on SBA-15 were dramatically improved with P123 addition during the impregnation process, while the optimized n_{P123}/n_{Ni} ratios were in the range of 0.002–0.02. Furthermore, the highly-dispersed Ni/SBA15-P123 (1/500), Ni/SBA15-P123 (1/100) and Ni/SBA15-P123 (1/50) catalysts exhibited higher activity, better stability and less carbon deposition than those catalysts prepared with no P123, insufficient P123 (1/X = 1/750) or superabundant P123 (1/X = 1/5) during the 50 h CRM reaction test [26].

In the present work, we investigated the promotional mechanism of P123 for improving Ni dispersion on SBA-15 with Raman, ^{1}H-NMR, UV–Vis, DLS, FTIR, and TPO. We rigorously collected and interpreted the characterization data obtained from each step during catalyst preparing process, which was as similar to the in-situ environment as possible. With these, we have established a comprehensive method to investigate the authentic interaction mechanism among $Ni(NO_3)_2 \cdot 6H_2O$, P123 and H_2O in P123-assisted catalyst preparation process.

2. Experimental section

2.1. Sample preparation

SBA-15 supported Ni-based catalysts, Ni/SBA15-P123 (1/X), were prepared via a P123-assisted wetness impregnation method [26]. More specifically, a certain amount of $Ni(NO_3)_2 \cdot 6H_2O$ and P123 (molar ratio $n_{P123}/n_{Ni} = 1/X$) were dissolved in deionized water, then SBA-15 was added afterwards and stirred for 12 h. After impregnation, a rotary evaporation was conducted at 60 °C and −0.1 MPa to remove the water from the above mixture. The obtained solid samples were dried in static air at 110 °C for 12 h. The dried $Ni(NO_3)_2 \cdot 6H_2O$/SBA15-P123 (1/X) samples were denoted as 'Ni/SBA15-P123 (1/X)-Uncal', while 'P123 (1/X)/SBA15-Uncal' represented the samples without $Ni(NO_3)_2 \cdot 6H_2O$ addition. Subsequent calcination treatments were carried out from room temperature (R.T.) to 650 °C with a ramp of 2 °C/min.

2.2. Sample characterization

The Raman spectroscopy measurements were employed to investigate the interaction mechanism among $Ni(NO_3)_2 \cdot 6H_2O$, P123 and H_2O using a HORIBA Jobin Yvon LabRAM HR Evolution instrument with a 514 nm laser. Appropriate amounts of $Ni(NO_3)_2 \cdot 6H_2O$ and P123 were added into deionized water and stirred for 12 h at room temperature, and the procedure of sample preparation was remained the same for the following ^{1}H-NMR,

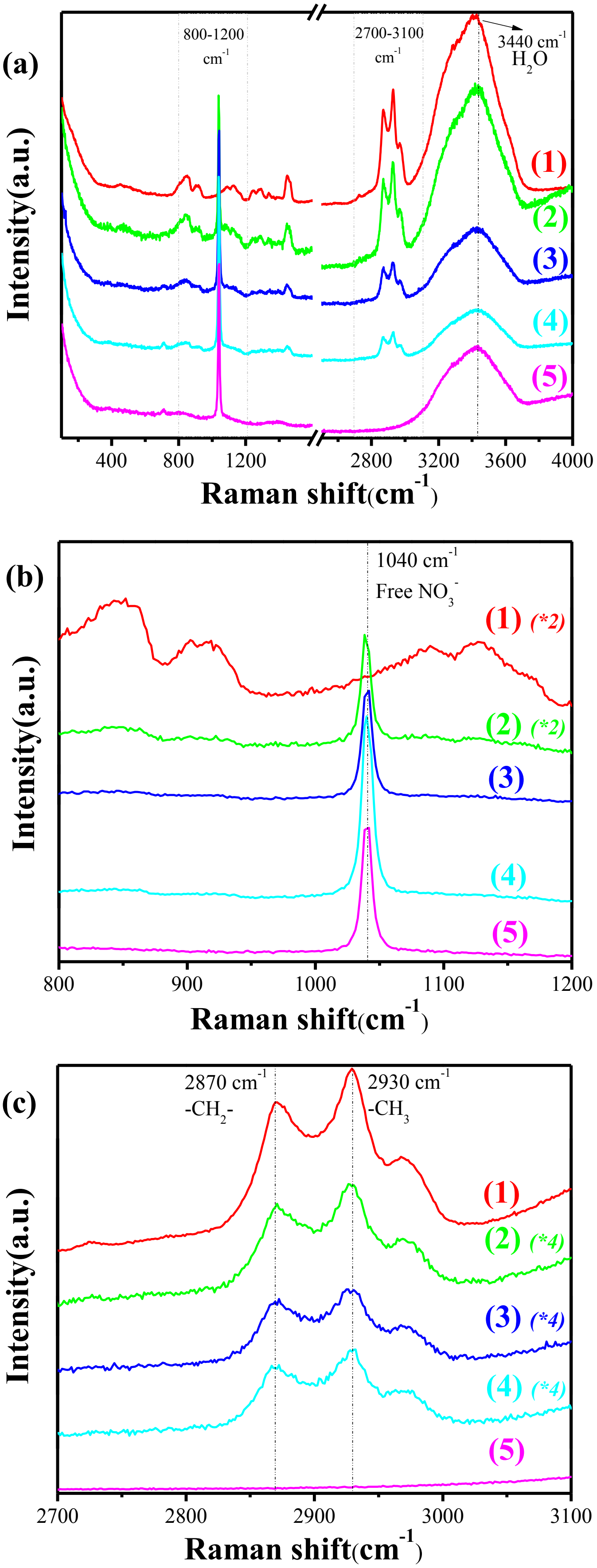

Fig. 1. Raman spectra of aqueous systems. (1) P123 + H_2O, (2) $Ni(NO_3)_2 \cdot 6H_2O$–P123 (1/10) +H_2O, (3) $Ni(NO_3)_2 \cdot 6H_2O$–P123 (1/30) +H_2O, (4) $Ni(NO_3)_2 \cdot 6H_2O$-P123 (1/50) +H_2O, (5) $Ni(NO_3)_2 \cdot 6H_2O$ + H_2O. (a) Full spectrum (100–4000 cm^{-1}), (b) Part spectrum (800–1200 cm^{-1}), (c) Part spectrum (2700-3100 cm^{-1}). (The detailed concentration information has been listed in Table 3).