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# Synthesis of nickel nanoparticles with excellent thermal stability in micropores of zeolite

Hitoshi Inokawa<sup>a</sup>, Makoto Maeda<sup>b</sup>, Shunsuke Nishimoto<sup>c</sup>,  
Yoshikazu Kameshima<sup>c</sup>, Michihiro Miyake<sup>c</sup>, Takayuki Ichikawa<sup>d</sup>,  
Yoshitsugu Kojima<sup>d</sup>, Hiroki Miyaoka<sup>a,\*</sup>

<sup>a</sup> Institute for Sustainable Sciences and Development, Hiroshima University, 1-3-1 Kagamiyama, Higashi-Hiroshima 739-8530, Japan

<sup>b</sup> Natural Science Center for Basic Research and Development, Hiroshima University, 1-3-1 Kagamiyama, Higashi-Hiroshima 739-8530, Japan

<sup>c</sup> Graduate School of Environmental and Life Science, Okayama University, 3-1-1 Tsushima-Naka, Kita-ku, Okayama 700-8530, Japan

<sup>d</sup> Institute for Advanced Materials Research, Hiroshima University, 1-3-1 Kagamiyama, Higashi-Hiroshima 739-8530, Japan

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## ABSTRACT

Nickel (Ni) nanoparticles were synthesized in micropores of zeolite by the adsorption and decomposition of a sublimated Ni organometallic compound,  $\text{Ni}(\text{C}_5\text{H}_5)_2$ , to invent metallic catalysts with nanosize, which are smaller than 5 nm and keep the nanosize at high temperature. In the decomposition process, Ni species were partially decomposed by ultraviolet light irradiation and fixed in zeolite pores prior to thermal reduction under  $\text{H}_2$  flow. Note that the Ni nanoparticles showed an excellent thermal stability, because they kept the high dispersion with diameters smaller than 5 nm even after heating at 400 °C. On the other hand, the Ni particles supported on zeolite by a conventional method, which is an incipient wetness impregnation process, became larger than 10 nm after heating at the same temperature. The synthesized Ni nanoparticles acted as a metallic catalyst because they showed higher selectivity for  $\text{H}_2$  generation than  $\text{C}_2\text{H}_4$  generation during ethanol steam reforming reaction.

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## 1. Introduction

Metallic catalysts industrially play important roles in various fields to control chemical reactions [1,2]. In particular, noble metals, which are represented by Pt, Rh, and Ru, have been applied because of their high catalytic activities [2,3]. On the other hand, transition metals, e.g., Fe, Co, and Ni have also

been investigated with the expectation to be utilized instead of noble metals to reduce cost and save resources [4–8]. For instance, Ni has been investigated hard as a catalyst for  $\text{H}_2$  production from hydrocarbons and biomass, and used for industrial steam methane reforming reaction [5,6,8,9]. The performance of transition metals, however, has not yet been adequate as compared with that of noble metals. Thus, to

\* Corresponding author. Tel.: +81 82 424 4604.

E-mail address: [miyaoka@h2.hiroshima-u.ac.jp](mailto:miyaoka@h2.hiroshima-u.ac.jp) (H. Miyaoka).

improve their catalytic performance, methods that can be used to control the particle size of metals have been investigated because it significantly affects their performance [10,11]. In particular, nanoparticles smaller than 5 nm in diameter show greater performance because of their higher surface energy and ratio of atoms [10,11]. Some techniques to synthesize nanoparticles on supports have been investigated, e.g. for instance impregnation [12,13], deposition precipitation [13,14], strong electrostatic adsorption [15], and chemical vapor deposition [16,17]. A few approaches resulted in successful preparation of nanoparticles of base metals smaller than 5 nm [15,18].

Nanoparticles, however, have a serious problem that they become larger with sintering during some treatments and reactions with heating at high temperature, resulting in their deactivation. Though Bozbag et al. reported Ni nanoparticles of about 5 nm in diameter dispersed on carbon aerogel after reduction at 170 °C, it is also indicated that the nanoparticles could become larger than 5 nm at higher temperature than 200 °C in particular under reduction condition [18]. Therefore, the development of techniques to prevent their sintering and keep their size at high temperature has been required. To resolve this problem, we designed a catalyst supported by micropores of zeolite, which would maintain the nanosize smaller than 5 nm after heating to several hundreds of °C, for example, beyond 300 °C for H<sub>2</sub> production from ethanol [19–22]. Zeolite is a functional material with characteristic structural properties, which are three-dimensionally ordered micropores, high heat resistance, and relatively high hardness. Thereby, it has attracted attention as catalyst and/or catalyst support [23,24]. It is expected that zeolite will be an appropriate support of nanoparticles in terms of the stability and diffusion of reactants for catalytic reactions [25]. A synthesis method for nanoparticles in zeolite has already been reported in a case of noble metals [26]. Nijis et al. prepared Ru nanoparticles by reducing Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> introduced to zeolite micropores by an ion exchange process [26]. This method is not suitable for base metals such as Fe, Co, and Ni because of their high ionization tendency, although noble metals such as Pt and Ru can be reduced easily by this method.

In this work, we investigated the process of synthesizing Ni particles in zeolite by introducing and decomposing an organometallic compound of Ni. The surface of zeolite is mostly composed of micropores and exhibits coulombic attraction caused by cations and the negative charge of the framework structure. Thus, some molecules such as H<sub>2</sub>O, CO, CO<sub>2</sub>, and hydrocarbons which have dipole or quadruple moments and are smaller than the channels of zeolite, can be adsorbed in the pores of zeolite [25]. In fact, it was reported that ferrocene, which is an organometallic compound expressed as Fe(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>, can be introduced into the pores of zeolite by adsorption [27–30]. Ferrocene belongs to the metallocene group, which is composed of cations, which are Fe<sup>2+</sup>, Co<sup>2+</sup>, and Ni<sup>2+</sup>, inserted between two cyclopentadienyl anions. Thus, it is expected that nanoparticles of catalytic materials such as Fe, Co, and Ni with metallic states can be formed in zeolite pores by introducing their organometallic compounds into the zeolite pores and their reduction via the decomposition of organic ligands, where this process would be easier than a conventional reduction method at cation sites

via an ion exchange process. The Ni nanoparticles maintaining the nanosize (<5 nm in diameter) at high temperature are expected to be useful as a novel catalyst for reforming reactions of hydrocarbons and alcohols to produce H<sub>2</sub> [5,9]. The variation of the organometallic compound of Ni during the synthesis process and the catalytic properties of the synthesized Ni particles were examined in detail by various experimental and analytical methods to characterize the Ni particles. From the obtained results, we proposed an innovative method of synthesizing the nanoparticles in zeolite.

## 2. Experiments

### 2.1. Sample preparation

Faujasite-type zeolite (Wako chemical, Japan) with a SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio of 5.5 and Na<sup>+</sup> as a cation, which is generally called zeolite Y, was heated under vacuum condition at 600 °C for 20 h to remove adsorbents such as water and carbon dioxide in advance. The zeolite was mixed with an Ni organometallic compound, Ni(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> (Sigma–Aldrich, USA), in a glove box filled with purified Ar, and placed in a quartz tube. After evacuating the tube, the mixture was heated at 130 °C for 8 h to enable Ni(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> molecule adsorption in the zeolite pores by sublimation. The Ni(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>-adsorbing zeolite was exposed to ultraviolet (UV) light generated by a 300 W Xe lamp at room temperature for 72 h to partially decompose the organic ligand. Finally, the mixture after UV irradiation was reduced under H<sub>2</sub> flow at 400 °C to decompose organics completely. The catalyst synthesized by the above procedure is expressed as Ni<sub>CH</sub>.

For comparison with a conventional method, Ni particles were supported on zeolite Y by an incipient wetness impregnation process. Zeolite powder was added to a NiCl<sub>2</sub> solution, and then the suspension was heated with stirring to remove water. After evaporation, zeolite with NiCl<sub>2</sub> was calcined at 400 °C for 3 h in air and reduced at 400 °C under H<sub>2</sub> flow. The zeolite with Ni particles prepared by a conventional impregnation method is expressed as Ni<sub>imp</sub>.

### 2.2. Characterization

The microstructure of Ni particles was examined using a transmission electron microscopy (TEM) system (JEM-2010, JEOL) at Natural Science Center for Basic Research and Development, Hiroshima University, equipped with an energy-dispersive X-ray spectrometer (EDS), operated at an acceleration voltage of 200 kV.

Ni content was semiquantitatively analyzed by X-ray fluorescence spectroscopy (XRF, ZSX-Primus II, Rigaku, Japan). For XRF analysis, samples were calcined at 600 °C for 3 h in air to remove organics and anions.

To estimate the specific surface areas and pore volumes of samples, adsorption and desorption isotherms of N<sub>2</sub> on the catalysts at 77 K were measured using a sorption analyzer (BELSORP18SP, BEL JAPAN, Japan), and the results were analyzed by Brunauer–Emmett–Teller (BET) method. For the measurement, samples were reduced at 400 °C for 1 h under 3% H<sub>2</sub>/Ar flow.

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