



In situ X-ray absorption fine structure analysis of redox reactions of nickel species with variable particle sizes supported on silica



Yusaku Yamamoto^a, Atsushi Suzuki^a, Naoki Tsutsumi^a, Masaki Katagiri^a, Shohei Yamashita^a, Yasuhiro Niwa^b, Misaki Katayama^a, Yasuhiro Inada^{a,*}

^a Department of Applied Chemistry, Graduate School of Life Sciences, Ritsumeikan University, 1-1-1 Noji-Higashi, Kusatsu 525-8577, Japan

^b Photon Factory, Institute of Materials Structure Science, High Energy Accelerator Research Organization, 1-1 Oho, Tsukuba 305-0801, Japan

ARTICLE INFO

Keywords:

Nickel catalyst
In situ XAFS
Redox reactions
Small particle

ABSTRACT

The chemical states of Ni species were systematically investigated using an *in situ* XAFS technique for a series of SiO₂-supported Ni catalysts with different Ni particle sizes. The Ni particles were refined by varying the Ni loading in the range between 0.10 and 5 wt% and by adding citric acid into the precursor solution. An *in situ* observation cell for fluorescence-yield XAFS measurements was developed for the dilute Ni catalysts. The chemical state of the supported Ni species converted between Ni(0) and NiO, and no other stable species were formed during the temperature-programmed oxidation and reduction processes. Refinement of the Ni particles resulted in decreasing the oxidation temperature and increasing the reduction temperature. These shifts were explained by the affinity of NiO to SiO₂, and more effective stabilization was thus anticipated for flattened small NiO particles with an increased contact area. In addition, the inhomogeneous distribution of small Ni particles observed for dilute catalysts was explained in terms of the precursor solution volume when nuclei of the precursor compound precipitated on SiO₂ during the drying process.

1. Introduction

Nickel species supported on a stable oxide material are promising metal catalysts required for a sustainable society. For example, supported Ni catalysts show catalytic activity for syngas production by steam reforming reaction, CO₂ reforming reaction, and partial oxidation of hydrocarbon [1–3]. The syngas is a basic raw material for the production of a variety of chemical compounds and for effective hydrogen generation by the combination with the water gas shift reaction. The generated hydrogen is an important energy source, and is also produced by the methane decomposition reaction catalyzed by Ni catalyst [4]. Numerous investigations have been continued to achieve the higher catalytic activities for such conversion processes, and the relatively low cost of catalytic systems using the Ni catalyst is strong motivation for replacing noble metal catalysts.

The size of the particles containing active Ni species in the catalyst greatly affects catalytic performance. A high surface area of supporting oxide materials contributes to disperse the supported Ni species, resulting in small particles on the Supporting materials [5,6]. The conditions used to treat the catalyst prior to the catalytic reaction may also contribute to decide the particle size. It has been reported that treatment under a reductive environment at elevated temperature

promotes the sintering of metallic Ni particles [7]. Furthermore, the procedure used to prepare Ni catalysts strongly affects the size of the produced Ni particles [8–11]. Formation of small Ni particles on the Supporting material is therefore important for enhancing catalytic activity. In addition to the metallic Ni catalyst, the unique characteristic has been reported for the NiO catalyst, *e.g.*, the oxidative coupling reaction of thiophenol is promoted by the NiO nanoparticles [12,13]. The small active particle can contribute not only to the catalytic activity but also to the suppression of the side product. It has been reported that the generation of carbon during the CO₂ reforming reaction of methane is suppressed when Ni catalyst with an average particle size of 15 nm is used [14]. Much attention has been paid to the particle size of supported Ni species to generate new catalytic functions and enhance catalytic activity.

One of the effective methods for preparing supported small metal particles is modified impregnation by adding an organic reagent to the precursor solution of the active metal species. Hong et al. found that the size of SiO₂-supported Co particles decreased as the proportion of sorbitol added to the Co precursor increased [15]. In the same way, highly soluble organic additives, such as glucose [16], sucrose [17], citric acid [16], and ethylenediaminetetraacetic acid [18], were used to prepare supported small metal particles. Bentaleb et al. have succeeded

* Corresponding author.

E-mail address: yinada@fc.ritsumei.ac.jp (Y. Inada).

in preparing the Ni catalyst with the particle size of 3–4 nm in the presence of citric acid [16]. It has been proposed that the increased viscosity of the precursor solution due to the organic additive promotes dispersion of the supported Ni particles, and that size-controlled Ni species can be prepared by this method.

Small Ni particles are also obtained by decreasing the loading of the supported Ni species [19]. The reduced amount of Ni species per unit surface area of the Supporting material can lead to dispersion of the Ni particles. Although the apparent catalytic activity is diminished due to the reduced amount of active species, catalytic selectivity may be enhanced by the reduced particle size. Ueno *et al.* have reported the selectivity of propanol for the hydrogenation of propionaldehyde using Ni/SiO₂ catalyst with variable Ni loadings of between 2 and 26 wt% [20]. They concluded that a catalyst particle diameter of less than 5 nm is achieved with reduced Ni loading and is a key factor in enhancing selectivity. The characterization of such reduced loading Ni catalysts is important for understanding the catalytic properties and enhancing the functions of the Ni catalyst.

Knowledge of the chemical state of supported metal species is required for understanding catalytic performance. The reactant and product species present in the actual reaction environment affect the chemical state of the active metal species. Speciation of the active metal species under the reaction conditions provides useful guidelines for catalyst design and for optimizing catalytic reaction conditions. X-ray absorption fine structure (XAFS) is a powerful tool for analyzing the electronic state and local structure of the target metal element, especially for supporting metal catalysts [21]. The *in situ* XAFS observation under the reaction gas atmosphere at elevated temperatures provides direct information about the active metal species [22,23]. In previous studies of SiO₂-supported Ni and Co catalysts, the chemical state of the active species and its dynamic changeover were thoroughly investigated using an *in situ* XAFS technique [24–26]. It has been demonstrated that the chemical state of the supported Ni species reversibly and quantitatively converts between NiO and metallic Ni, and that the overall conversion reaction consists of surface redox steps and internal oxygen migration [25]. It has also been revealed that the oxidation temperature of supported Ni(0) particles is dependent on the Ni loading, whereas the reduction temperature of NiO is almost constant at about 623 K for Ni catalysts with loadings ranging from 5 to 15 wt%, for which the average Ni particle size between 17 and 42 nm. It is therefore necessary to clarify the effect of much smaller Ni particles on the chemical state to understand why supported small Ni particles exhibit high catalytic activity.

In situ XAFS measurements are usually carried out in transmission mode, and a suitable sample concentration is necessary to achieve good statistics for X-ray absorption. It is thus difficult to measure the XAFS spectrum of dilute metal catalysts under such reaction conditions. Fluorescence detection significantly improves the sensitivity of the XAFS technique and thus *in situ* XAFS measurements in the fluorescence-yield mode are useful in the study of dilute supported catalysts. In this study, we developed an *in situ* observation cell for fluorescence XAFS measurements in order to characterize supported Ni catalysts with loadings below 1 wt%.

The aim of the present study was to clarify the chemical state of supported small Ni species with different particle size under a reactive gas environment. SiO₂-supported Ni catalyst with a particle size of less than 10 nm was prepared by the impregnation method. The particle size was controlled by adding citric acid and by varying the Ni loading. The prepared samples were characterized by X-ray fluorescence (XRF) analysis, X-ray diffraction (XRD), and transmission electron microscopy (TEM). The *in situ* speciation of the supported Ni species in H₂ and O₂ atmospheres was carried out using the XAFS technique. The particle size effects of redox temperatures were systematically analyzed for dilute Ni catalysts using the developed *in situ* observation cell for fluorescence-yield XAFS measurement. The mechanism of formation of small Ni particles in the dilute catalyst is discussed.

2. Experimental section

2.1. Preparation of Ni catalyst

The supported Ni catalysts were prepared by the conventional impregnation method, which is the most widely used and simple preparation procedure for the metal catalysts. The preparation condition was selected based on the previous research [25]. The SiO₂ (Fuji Silysia Chemical Co., Ltd., Japan) with a specific surface area of 192 m² g⁻¹ was used as the Supporting material. Ni(NO₃)₂·6H₂O was dissolved in deionized water and SiO₂ powder was suspended in the solution. The mixture was dried at 343 K for 72 h, then the obtained powder was calcined at 873 K in air for 3 h. Four Ni catalysts were prepared by varying the Ni loading, ranging from 0.1 to 1.4 wt%. The actual Ni loadings determined by XRF analysis were 0.10, 0.13, 0.73, and 1.4 wt%. The calcined samples were treated under a dilute H₂ flow (10 vol% in Ar, total flow rate of 200 cm³/min) at 873 K for 3 h to reduce the supported Ni species. A part of the reduced sample was oxidized under a dilute O₂ flow (10 vol% in Ar, total flow rate of 200 cm³/min) at 873 K for 3 h to prepare the NiO species supported on SiO₂. The samples prepared by this procedure are referred as “x wt% IMP”, where x denotes the Ni loading.

An additional Ni catalyst was prepared by the modified impregnation method in the presence of citric acid in the precursor solution. A stoichiometric amount of citric acid relative to Ni was initially added into an aqueous solution of Ni(NO₃)₂·6H₂O, then SiO₂ powder was added and the mixture was dried at 343 K for 72 h. The calcination temperature was 873 K, and the obtained sample was reduced and oxidized at 973 K under dilute H₂ and O₂ atmospheres, respectively. The Ni loading was set to be 5 wt%. The sample prepared by this method is referred as “5 wt% IMPCA”.

2.2. Characterization of Ni catalyst

XRF analysis of dilute Ni catalysts was performed using a Supermini X-ray fluorescence spectrometer (Rigaku, Japan). Pd K α radiation (0.5855 Å) was used as the X-ray source and Ni K α fluorescence intensity was detected. XRD measurements were carried out with an Ultima IV diffractometer (Rigaku, Japan) using Cu K α radiation (1.5418 Å). Diffraction intensities were recorded over the 2 θ range between 10° and 80°. TEM observations were performed on reduced samples using a JEOL2010 microscope (JEOL, Japan).

2.3. *In situ* XAFS measurements

In situ XAFS measurements at the Ni K edge were performed at the BL-9C and BL-12C stations of the Photon Factory (KEK, Japan). A Si(111) double-crystal monochromator was used at both stations, and the higher-order reflections were removed by detuning the parallelism of the monochromator.

A flow-type cell was used for XAFS measurements in transmission mode of the 5 wt% IMPCA sample [27]. The temperature-programmed reduction (TPR) and oxidation (TPO) processes were carried out at up to 973 K under H₂ and O₂ flows diluted by He (10 vol%), respectively. The total flow rate was 200 cm³/min. The temperature of the sample was increased at a rate of 10 K/min. The measurement time for one XAFS spectrum was 60 s, and the XAFS measurements were repeated at intervals of 60 s.

In situ XAFS measurements for low loading samples were carried out in fluorescence-yield mode. A schematic diagram of the developed *in situ* observation cell is shown in Fig. 1. The powder sample is mounted in a stainless-steel tube (i.d. 7 mm) and placed at an angle of 45° with respect to the incident X-ray beam. The fluorescent X-rays emitted from the sample were counted with a single pixel Ge solid-state detector. Contamination of the fluorescent X-rays by Ni in the cell body was independently checked using SiO₂ powder as the sample; the

Download English Version:

<https://daneshyari.com/en/article/7757878>

Download Persian Version:

<https://daneshyari.com/article/7757878>

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