



Heterogeneous nickel catalyst for selective hydration of silanes to silanols

Ken-ichi Shimizu^{a,*}, Katsuya Shimura^a, Naomichi Imaiida^b, Atsushi Satsuma^b

^a Catalysis Research Center, Hokkaido University, N-21, W-10, Sapporo 001-0021, Japan

^b Department of Molecular Design and Engineering, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan

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ABSTRACT

Selective catalytic hydration of silanes to silanols is studied by Ni metal nanoparticles (NPs) on activated carbon (Ni/C) prepared by in situ H₂-reduction of NiO-loaded activated carbon (NiO/C). The catalytic activity of Ni/C increases with decrease in the average Ni particle size. Ni/C with the smallest size (7.6 nm) exhibits a high selectivity for silanols, high turnover number (TON) of 9300, and excellent reusability. Studies on the structure–activity relationship show that metallic Ni species on the surface of small Ni metal particles are catalytically active species. Based on mechanistic studies, a catalytic cycle involving the activation of Et₃SiH as the rate limiting step is proposed.

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1. Introduction

In view of the sustainable chemistry, the development of recyclable heterogeneous non-noble metal catalyst to replace the noble-metal catalysts is an important objective in the catalysis research. Despite the fact that Ni catalysts, such as sponge Ni (Raney Ni), have been used as a promoter or heterogeneous catalyst for hydrogenation of various compounds, advances in the field of heterogeneous non-noble metal catalyzed organic synthesis is still in its infancy. Recently, Ni NPs catalysts have been introduced as a new class of heterogeneous catalysts to overcome some economic and ecological problems [1–4]. As summarized in recent reviews by Yus et al. [1] and Lipshutz et al. [2], Ni NPs catalyze several organic transformations which are typically implemented by noble metal-based catalysts. Our ongoing interest in the supported metal nanoparticles catalysis in organic synthesis [5] combined with these pioneering studies motivated us to investigate possibilities of supported Ni NPs as cheaper alternatives to the well established noble-metal catalysts in organic reactions.

Silanols have found widespread use in organic synthesis and in industry as building blocks for silicon-based polymeric materials [6,7]. Among various preparation methods of silanols, recent attention has been focused on the oxidation of organosilanes with water under neutral conditions by noble-metal catalysts. Homogeneous (Ir [8], Re [9,10], Rh [11], Ru [12,13], Pt [14], Ag [15]) and heterogeneous (Ru [16,17], Ag [18], Pd [19,20], Au [21–23]) noble-metal

catalysts were developed. Homogeneous [24] and heterogeneous [20,25] catalysts based on Cu or Ni were also reported, but their activity was lower than the noble-metal catalysts. We report herein our findings on the selective hydration of silanes to silanols by Ni/C prepared by H₂-reduction of NiO/C. The effects of particle size and oxidation states of Ni species on the intrinsic activity per surface Ni sites are studied to clarify the structure of active Ni species. Mechanistic studies are conducted to discuss a possible reaction mechanism.

2. Experimental

2.1. General

Commercially available organic compounds (from Tokyo Chemical Industry or Kishida Chemical) were used without further purification. Raney Ni (B113W, Ni > 90%) was supplied from Evonik Industries. Ni powder was purchased from Kishida Chemical. The GC (Shimadzu GC-14B) and GCMS (Shimadzu GCMS-QP2010) analyses were carried out with a DB-1 capillary column (Agilent J&W) using nitrogen as the carrier gas. ¹H NMR spectra were recorded in CDCl₃ with TMS as an internal standard at ambient temperature on JEOL JNM-ECX 400 operating at 400 MHz.

2.2. Catalyst preparation

Active carbon (296 m² g⁻¹) was purchased from Kishida Chemical. TiO₂ (JRC-TIO4, 50 m² g⁻¹), CeO₂ (JRC-CEO3, 81.4 m² g⁻¹), MgO (JRC-MGO-3, 19 m² g⁻¹), and SiO₂–Al₂O₃ (JRC-SAL-2, Al₂O₃ = 13.75 wt%, 560 m² g⁻¹) were supplied from Catalysis

* Corresponding author. Fax: +81 11 706 9163.

E-mail address: kshimizu@cat.hokudai.ac.jp (K.-i. Shimizu).

Society of Japan. SiO₂ (Q-10, 300 m² g⁻¹) was supplied from Fuji Silysia Chemical Ltd. ZrO₂ (60 m² g⁻¹) was prepared by hydrolysis of zirconium oxynitrate 2-hydrate in distilled water by gradually adding an aqueous NH₄OH solution (1.0 mol dm⁻³), filtration of precipitate, washing with distilled water three times, drying at 100 °C, and calcining at 500 °C. γ-Al₂O₃ (with surface area of 124 m² g⁻¹) was prepared by calcination of γ-AlOOH (Catapal B Alumina purchased from Sasol) at 900 °C for 3 h. NiO/C was prepared by an impregnation method; a mixture of carbon (9.5 g) and an aqueous solution of Ni(NO₃)₂·6H₂O (0.17 M, 50 cm³) were evaporated at 50 °C, followed by drying at 100 °C for 12 h, calcination in air at 300 °C for 1 h. Before each catalytic experiment, Ni/C catalysts were prepared by in situ pre-reduction of NiO/C in a glass (pyrex or quartz) tube under a flow of H₂ (20 cm³ min⁻¹) at 500–700 °C for 0.5 h. Typically, the Ni/C catalyst pre-reduced at 500 °C with Ni loading of 5 wt% was used as a standard catalyst.

2.3. Characterization of catalysts

Ni K-edge X-ray absorption fine structure (XAFS) measurements were performed in transmission mode at the BL01B1 in the SPring-8 (Proposal No. 2011B1137). The storage ring was operated at 8 GeV. A Si(1 1 1) single crystal was used to obtain a monochromatic X-ray beam. The catalyst pre-reduced in a flow of 100% H₂ (20 cm³ min⁻¹) for 30 min at 500 °C was cooled to room temperature in the flow of H₂ and was sealed in cells made of polyethylene under N₂, and then the XAFS spectrum was taken at room temperature. The analyses of X-ray absorption near-edge structures (XANES) and extended X-ray absorption fine structure (EXAFS) were performed using the REX version 2.5 program (RIGAKU). The Fourier transformation of the *k*³-weighted EXAFS oscillation from *k* space to *r* space was performed over the range 30–140 nm⁻¹ to obtain a radial distribution function. The inversely Fourier filtered data were analyzed with a usual curve fitting method in the *k* range of 30–140 nm⁻¹. The parameters for the Ni–O and Ni–Ni shells were provided by the FEFF6. The number of free parameters for curve fitting can be estimated as $P_{free} = 2\Delta k \Delta R/\pi \approx 14$, indicating that we can model the EXAFS data with three shells.

X-ray diffraction (XRD) patterns of the powdered catalysts were recorded with a Rigaku MiniFlex II/AP diffractometer with Cu K α radiation. Ni particle size distributions of Ni/C catalysts were determined by using a JEOL JEM-2100F TEM operated at 200 kV.

2.4. Catalytic tests

Metal-loaded catalysts were prepared by the H₂-reduction of the metal oxide-loaded precursors (such as NiO/C) at 500 °C for 0.5 h, followed by cooling it in H₂ to room temperature. Then, a mixture of silane (1.0 or 5.0 mmol), water (16 mmol) and acetone (1.6 g) was injected to a pre-reduced Ni catalyst (typically 0.3 mol% Ni with respect to silane) in the glass tube, and the mixture was stirred. Then, an injection needle was inserted to the rubber. Thus, the reaction vessel was open to air and H₂ was released outside of the reactor. For the kinetic experiments, initial rates of the silanol formation were determined by changing the initial concentration of Et₃SiH and H₂O in the reaction mixture. The products were confirmed by comparison of their GC retention times, GC–MS spectra, and ¹H NMR spectra with those of authentic data. Conversion of silane and yields of products were determined by GC using *n*-octane as an internal standard. GC analysis of the gas phase product was carried out by Shimadzu GC-6A with TCD detector, molecular sieve 5A column and Ar carrier.

Table 1

Hydration of triethylsilane by supported metal (5 wt%) catalysts and reference catalysts.^a

Entry	Catalyst	Yield/%
1 ^b	Raney Ni	1
2 ^b	Ni powder	1
3	NiO/C	0
4	Ni/C	37
5 ^c	Ni/C-air	0
6	Cu/C	1
7	Co/C	1
8	Fe/C	1
9 ^d	C	0
10	Ni/TiO ₂	25
11	Ni/SiO ₂	5
12	Ni/CeO ₂	5
13	Ni/ZrO ₂	4
14	Ni/SiO ₂ -Al ₂ O ₃	1
15	Ni/Al ₂ O ₃	1

^a Conditions: catalyst (M: 0.3 mol%), Et₃SiH (1 mmol), H₂O (16 mmol) in acetone (1.6 g), 25 °C, 0.5 h. The catalysts pre-reduced in H₂ at 500 °C were used without exposure to air except for entries 3 and 5.

^b Ni = 1 mol%.

^c Pre-reduced Ni/C was exposed to air at room temperature after H₂-reduction at 500 °C.

^d Active carbon = 0.10 g.

3. Results and discussion

First, various non-noble metal catalysts were tested for the selective hydration of triethylsilane (Et₃SiH, **1a**) to triethylsilanol (Et₃SiOH, **2a**) as shown in Table 1. Conventional Ni catalysts (Raney Ni and Ni powder) and NiO/C were inactive for the formation of **2a**. The active carbon was inactive, which excluded a contribution of the support itself as a catalyst. The Ni/C catalyst was prepared by the H₂-reduction of NiO/C at 500 °C for 0.5 h, followed by cooling it in H₂ to room temperature. Then, the reaction mixture was injected to the pre-reduced catalyst inside the glass tube through a rubber, and then the mixture was stirred under air at 25 °C. Ni/C effectively catalyzed the selective hydration of **1a** to **2a**. Ni/C showed higher activity than Cu, Co, and Fe-loaded carbon (entries 6–8) and Ni-loaded metal oxides (entries 10–15) under the same pre-reduction and reaction conditions.

The precursor NiO/C and the catalyst Ni/C were characterized by spectroscopic characterizations. The XRD pattern of NiO/C (Fig. 1) showed a line due to NiO. The Ni K-edge XANES spectrum of NiO/C was nearly identical to that of NiO (Fig. 2A). As shown in Table 2, the curve-fitting analysis of EXAFS (Fig. 2B) confirmed the

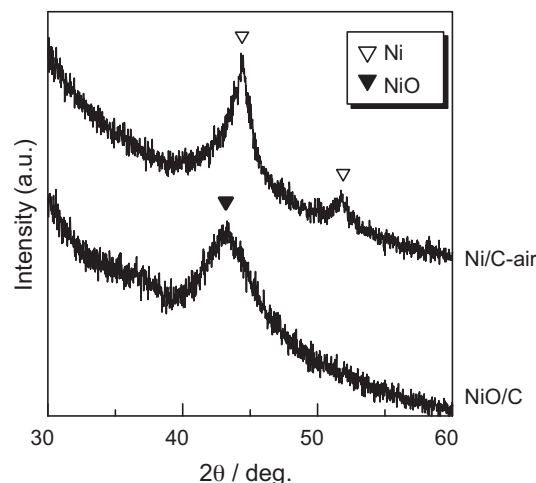


Fig. 1. XRD patterns.

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