Structural analysis of NiO nanocluster catalysts on SiO₂ by using XAFS measurements

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Abstract. NiO nanocluster catalysts were prepared on a SiO₂ support. Ni K-edge XAFS analysis revealed that the combined structure of NiO and Ni-silicate formed by using [Ni(NH₃)₆]²⁺ as a precursor, whereas pure NiO formed by using Ni-acetylacetonate or Ni-nitrate as a precursor. The obtained NiO nanocluster on Ni-silicate showed the catalytic activity for the oxidative coupling of thiophenol under air atmosphere. The combined structure of NiO and Ni-silicate showed the higher activity than pure NiO nanocluster did.

1. Introduction

Support plays important roles to the heterogeneous catalysts. Bulk gold seemed not to have the catalytic activity, however, supported gold nanoclusters enabled to produce the active gold nanocluster catalyst. [1]. As a result, researches on the nanocluster catalysis have become popular. Additionally, we have reported that Ni nanocluster catalysts supported on Al₂O₃ showed a Ni cluster size dependence on the WGSR (Water Gas Shift Reaction) [2]. Using a support for the heterogeneous catalysts has following benefits: i) preservation of the cluster size in any condition which causes a wide range of applicability for many reactions, ii) the support effect which can modify the nanocluster catalysis.

In many cases, developing the heterogeneous catalyst uses noble metals such as Pt and Pd because of their higher activity, whereas base metals are not so common. However, developing materials that substitute for noble metals is an urgent issue in terms of a sustainable chemistry. Nickel is one of the elements for this purpose, since it is abundant and cheaper than noble metals and it also has the activities for many reactions such as the hydrogenation of unsaturated compounds [3], the steam reforming of methane or ethane [4, 5], and so on. Moreover, the supported NiO catalyst is active for various reactions such as oxidative dehydrogenation of ethane [6] and that of naphthalene [7]. However, NiO used for oxidative reactions is less effective compared to other catalysts in many instances, and so there are few publications reporting about NiO catalysts. Using the support appropriately can produce the NiO nanocluster and allow us to utilize NiO as a catalyst more effectively.

We have succeeded in a preparation of the supported NiO nanocluster by using an alkoxide stabilizes Ni colloid which was the precursor and in showing the remarkable particle size effect for the oxidative coupling of thiophenol [8]. Our previous report focused on only relation between the NiO particle size and the catalytic activity. In this paper, we attempted to prepare NiO catalysts more...
simply without using stabilizer and to clarify the origin of this reaction from the viewpoint of the support effect.

In this paper fine surface analysis by XAFS measurements found that Ni-silicate that formed during catalyst preparation had promoting effect for oxidative coupling of thiophenol. The understanding structure-activity relationship is one of the most important factors in terms of development of sustainable heterogeneous catalytic processes. The insight of promoting effect Ni-silicate can lead to the development of new catalytic materials.

2. Experimental

2.1. Catalyst preparation

SiO₂ (Fuji Silysia Chemical Ltd., CARiACT P-10) supported catalysts were prepared by the impregnation method. NiO(amm)/SiO₂-T, NiO(ace)/SiO₂-T and NiO(nit)/SiO₂-T were obtained by using [Ni(NH₃)₆](NO₃)₂, Ni(acac)₂ and Ni(NO₃)₂ as a precursor, respectively, followed by heat treatment at T (K) in air. The heat treatment temperature was varied as 298, 573, 673 and 773 K. Ni loading regulated to 5 wt%. The abbreviation of amm, ace and nit means the precursor complex of ammine, acetylacetone and nitrate, respectively.

In order to compare the support effect, NiO(amm)/A.C.-T prepared by using [Ni(NH₃)₆](NO₃)₂ and active carbon (A.C.) as a precursor and a support, respectively.

A Ni-silicate was prepared by a similar way that M. V. Sivaiah et al. [9] reported: Sodium silicate (40 mmol), NiCl₂ (30 mmol) and HCl (36 wt%, 20 mmol) were stirred with water (500 mL) in a beaker. This mixture was treated by the hydrothermal synthesis in a Teflon sealed autoclave at 473 K for 96 hours. After the product was cooled to room temperature, it was washed with water and dried overnight. The chemical formula of the Ni-silicate was Si₄Ni₃O₁₁.

2.2. Characterization and catalytic reaction

Ni K-edge XAFS data were collected at BL-9C of KEK-PF (Proposal No. 2014G575) with Si(111) double crystal monochromator in a transmission mode at room temperature.

Oxidative coupling of thiophenol under air atmosphere was carried out as follows: Thiophenol (5.0 mmol), biphenyl (0.63 mmol) and acetonitrile (25 mL) in Schlenk tube were stirred with the catalyst (0.029 g) in a water bath at 303 K for 0.5 h. The molar ratio of thiophenol/catalyst was 200 based on the Ni amount. The yield was determined by GC (Shimadzu, GC-2025) with a capillary column (Hewlett Packard, Ultra 2, 25 m x 0.20 mm, 0.33 µm) and an FID detector.

![Scheme 1. Oxidative coupling of thiophenol](image)

3. Results and discussion

Figure 1 shows the Ni K-edge XANES of NiO catalysts and reference compounds. The valence and chemical species of the nickel species on the supported NiO catalysts were determined from these spectra.

XANES shapes of all catalysts were similar to that of bulk NiO (dotted line a), which indicates that nickel species on these catalysts consisted of NiO. However, a presence of other nickel species cannot be excluded. Indeed, there are two shoulders at 8346 eV (α-peak) and 8350 eV (γ-peak) on three types of NiO(amm)/SiO₂, besides β-peak which is a characteristic of NiO, and Ni-silicate that is a reference compound also showed two weak peaks at same energy (α- and γ-peak). Furthermore, formation of Ni-silicate was reported when [Ni(NH₃)₆]²⁺ was supported on SiO₂ [10, 11]. Therefore, two weak peaks of three kinds of NiO(amm)/SiO₂ were assigned to the Ni-silicate, and it can be concluded that Ni-silicate formed with NiO on our NiO(amm)/SiO₂ catalysts. Additionally, the similarity of XANES
shapes of three types of NiO(amm)/SiO₂ indicates that Ni-silicate formed with NiO on all of these and the ratio of these nickel species was mostly the same.

Figure 2 shows the FT of Ni K-edge EXAFS oscillations for NiO catalysts and reference compounds and Table 1 shows the model parameters of reference compounds and the curve fitting results of the nearest Ni-(O)-Ni.

NiO particles on NiO(nit)/SiO₂-673 were as large as bulk NiO since the coordination number (CN) of Ni-(O)-Ni was 12. On the other hand, CNs of the other catalysts were much smaller than that of bulk NiO, which indicates that NiO particles on these catalysts were very small, namely, these were NiO nanoclusters. Also, the peaks of the nearest Ni-(O)-Ni of three types of NiO(amm)/SiO₂ were at the same position with that of the Ni-silicate. This fact also indicates that Ni-silicate was on NiO(amm)/SiO₂ catalysts. Moreover, the CNs of NiO(amm)/SiO₂ catalysts were larger than that of Ni-silicate (CN = 6) means that not only Ni-silicate but also NiO was on these catalyst. Additionally, these CNs increased with the treatment temperature and it can be said that NiO particles grew with the temperature elevation.

Figure 1. Ni K-edge XANES of NiO catalysts and reference compounds: (a) Ni foil, (b) bulk NiO, (c) NiO(nit)/SiO₂-673, (d) NiO(ace)/SiO₂-673, (e) NiO(amm)/A.C.-573, (f) NiO(amm)/SiO₂-773, (g) NiO(amm)/SiO₂-573, (h) NiO(amm)/SiO₂-298, (i) bulk Ni-silicate.

Figure 2. FT of Ni K-edge oscillations for NiO catalysts and reference compounds: (a) bulk NiO, (b) NiO(nit)/SiO₂-673, (c) NiO(ace)/SiO₂-673, (d) NiO(amm)/A.C.-573, (e) NiO(amm)/SiO₂-773, (f) NiO(amm)/SiO₂-573, (g) NiO(amm)/SiO₂-298, (h) bulk Ni-silicate. Imaginary part (dotted lines) and absolute value (solid lines).

Table 1. Model parameters of reference compounds and curve fitting results of Ni-(O)-Ni coordination for NiO catalysts and yield of oxidative coupling of thiophenol

| Catalyst | FR² (nm) | CN³ | r⁴ (nm) | dE⁵ (eV) | DW⁶ (nm) | R⁷ (%) | Yield⁸ (%) |
|----------|----------|-----|---------|----------|----------|--------|------------|
| Ni-silicate (model)³ | - | 6 | 0.307 | 0 | 0.006 | - | 0.2 |
| NiO(amm)/SiO₂-298 | 0.233-0.322 | 7.3±1.2 | 0.311 | 4.54 | 0.00730 | 0.012 | 39 |
| NiO(amm)/SiO₂-573 | 0.233-0.322 | 7.4±1.2 | 0.311 | 4.76 | 0.00790 | 0.026 | 22 |
| NiO(amm)/SiO₂-773 | 0.233-0.322 | 8.0±1.3 | 0.310 | 5.33 | 0.00900 | 0.171 | 4.4 |
| NiO(ace)/SiO₂-673 | 0.215-0.307 | 5.0±0.8 | 0.300 | 1.17 | 0.00830 | 0.132 | 2.1 |
| NiO(nit)/SiO₂-673 | 0.212-0.328 | 7.0±1.2 | 0.298 | -1.87 | 0.00950 | 1.449 | 0.2 |
| Ni-silicate (model)³ | - | 12 | 0.295 | 0.459 | 0.00600 | 0.090 | 0.0 |
| bulk NiO (model)³ | - | 12 | 0.295 | 0 | 0.006 | - | 0.0 |

¹ Filtering range, ² coordination number, ³ bond distance, ⁴ difference between model compound and experimental threshold energies, ⁵ Debye-Waller factor, ⁶ R-factor, ⁷ diphenyl disulfide yield at 303 K for 0.5 h, ⁸ reference [11]. FT range: 30-140 nm⁻¹.
Table 2 shows the yield of diphenyldisulfide (catalytic activity) and $CN$ of Ni-(O)-Ni. Three types of NiO(amm)/SiO$_2$ and NiO(amm)/A.C.-573 showed the catalytic activity for the oxidative coupling of thiophenol and the other catalysts did not. In case of NiO(amm)/A.C.-573, it is considered that the very small size of NiO ($CN = 5.0$) showed the catalytic activity, although this activity was quite low. On the other hand, NiO(nit)/SiO$_2$-673 and NiO(ace)/SiO$_2$-673 did not have the catalytic activity probably due to NiO particles were not small enough. One of the most interesting things is that three types of NiO(amm)/SiO$_2$ showed higher activity than NiO(amm)/A.C.-573 and NiO(ace)/SiO$_2$-673, in spite of the larger $CN$. In light of the discussion of XAFS measurements, it is reasonable to suppose that the coexistence of Ni-silicate with NiO is the key factor in order to produce the activity for this reaction.

The things predicted from these results are that Ni-silicate that has the OH group layer contributed the coverage of SH bond of thiophenol and promote the oxidative coupling of thiophenol or that formation of Ni-silicate caused an unique structural change of NiO particles, which lead to high catalytic activity. The active species for this reaction was the NiO nanocluster and its size affected the catalytic activity.

**Conclusion**

The supported NiO catalysts were prepared by using three kinds of nickel species ([Ni(NH$_3$)$_6$]$^{2+}$, Ni(acac)$_2$ or Ni(NO$_3$)$_2$) as a precursor.

Obtained catalysts were used for the oxidative coupling of thiophenol and three types of NiO(amm)/SiO$_2$ and NiO(amm)/A.C.-573 showed the catalytic activity for this reaction while the other catalysts did not. Through the results of the XAFS measurements and the catalytic reaction, we concluded that very small NiO particles (NiO nanoclusters) were needed to cause the catalytic activity and the Ni-silicate promoted it.

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