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In situ EXAFS study of the nucleation and crystal growth of Ni particles on SiO_2 support

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Abstract

Ni/SiO_2 catalysts were prepared by wetness impregnation method (INi) and by a new two-step method ($ENien_{2.5/600}+INi_{2.5}$). The two-step method consists of formation of chemical glue, "nickel nuclei", having strong metal support interaction with SiO_2 and preparation of the "nickel reservoir" which has weak interaction with support. The nucleation and growth behaviors of such Ni/SiO_2 catalysts in the preparation stage were continuously monitored by in situ EXAFS spectroscopy. The in situ EXAFS spectra of INi catalyst began to change after 320°C and bulk NiO like structure was formed at 500°C heat treatment. The Ni/SiO_2 prepared with the two-step method had larger coordination number of Ni with silica support in the initial stage of in situ monitoring than that of INi catalyst, which showed the coexistence of Ni nuclei and Ni reservoir. The $ENien_{2.5/600}+INi_{2.5}$ had smaller particles of Ni compared with INi after high temperature calcination. The formation of small Ni particles could be attributed to the strong ion-support interaction of nickel nuclei with nickel reservoir in $ENien_{2.5/600}+INi_{2.5}$ catalyst. Slight particle growth occurred after 370°C calcination in Ni/SiO_2 prepared by two-step method. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: INi; ENien; EXAFS

1. Introduction

Supported metal catalysts consist of active phase (transition metal ions, oxides, or metal complexes) and support (metal oxides, zeolites or porous polymers). It has been suggested that the active phase-support interaction affects the dispersion of transition metals and the catalytic activity of the prepared catalyst [1–4].

Several studies have been reported to obtain the enhanced dispersion of active phase by controlling the metal-support interaction. Among those reports, the best understood method to obtain the highly dispersed catalysts is the proper selection of preparation conditions. Namely, pre-treatment gases, pre-treatment temperature, choice of metal precursor and morphology of support are important to control the dispersion of resulting catalysts. Zou and Gonzalez [1] reported the effect of pre-treatment on the dispersion of Pt/SiO_2 and Pd/SiO_2 catalysts prepared from amine precursors

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in basic solution. Starting from $[Pd(NH_3)_4]^{2+}$, this complex reacts with H_2 to form highly mobile intermediate species, $[Pd(NH_3)_2(H)_2]^0$, which leads to agglomeration of Pd particles. On the other hand, a pre-treatment with inert gases such as Ar or N_2 leads to highly dispersed Pd/SiO_2 catalysts, due to the formation of strongly bound Pd^{2+} species with SiO_2 support.

Another method to enhance the dispersion of supported metal catalyst is the change of electronic properties of noble metals by introducing non-reducible transition metal ions [5–10]. Yermakov et al. [5] and Yermakov [6] suggested that easily reducible Pt metal could be chemically anchored to the SiO_2 support by introducing non-reducible or partially reducible metal ions (Mo or W). In this system, non-reducible metals like Mo or W act as an anchoring site for the reducible metal. Sachtler and coworkers showed that small Pt and Rh particles in Y zeolite could be prepared by the addition of Fe and Cr ions. These Fe or Cr ions are electrostatically bound to the zeolite oxygen atoms, which act as anchoring sites and prevent the migration of Rh and Pt atoms. These reports emphasize the importance of pre-treatment conditions and chemical anchoring in obtaining enhanced metal-support interaction in the preparation steps. Despite the importance of these interactions, the effect of metal-support interaction on the preparation of highly dispersed catalyst are still ill-defined.

Recently, Che and Bonneviot [11,12,14], Che et al. [13] proposed the presence of ion-support interactions (ISI) at the interface of transition metal ions and support. ISI could be controlled either by changing the preparation method or by varying the treatment conditions. As a model system, Ni/SiO_2 catalysts was used to prove the effect of ion-support interaction on the nucleation and growth of Ni particle on a support using various preparation methods [15–18]. Depending on the preparation method (impregnation, ion-exchange or grafting), different types of Ni species can be prepared. Namely, the Ni/SiO_2 prepared from $[Ni(NH_3)_6]^{2+}$ complex gives rise to talc-like or serpentine-like nickelsilicate, whereas $[Ni(en)_3]^{2+}$ (en: ethylenediamine) inhibits the formation of nickelsilicate and leads to isolated Ni^{2+} species. To control the particle size of such Ni/SiO_2 catalysts, the nucleation step from the growth of metal particles were separated [19–21]. In this procedure, nickel nuclei having strong interaction with the support are prepared by ion-exchange or impregnation followed by washing. Then, the nickel reservoir, having weak interactions with support and providing nickel ions for the nickel particle growth on nickel nuclei, is deposited by impregnation. This two-step procedure leads to smaller particles after calcination and reduction. In the preparation of Ni/SiO_2 catalyst with two-step method, the presence of phyllosilicates and grafted Ni(II) species have been confirmed by TPR, FT-IR, EXAFS, TEM and TPR techniques [19–21]. However, the continuous monitoring of nucleation and growth of Ni particles with increasing temperature has not been investigated by in situ EXAFS.

Extended X-ray absorption fine structure (EXAFS) spectroscopy is a powerful method to characterize the local structure of supported metal catalysts at the atomic level. In heterogeneous catalysts, to preserve the physicochemical integrity of the sample during the acquisition of EXAFS data, in situ techniques have been developed [25]. In the early stage of in situ EXAFS studies of heterogeneous catalyst, the structural and electronic modification of the metallic phase during the calcination and the reduction could be monitored [26–28]. Recent development in the instrumentation of EXAFS spectroscopy allows the in situ measurement of phase changes and particle growth of supported metal catalyst. Sankar et al. [29] reported the combined in situ EXAFS and XRD study as a structural and kinetic tool studying the transitions and local environment change in ZnO/cordierite of high temperature. They showed that combined in situ EXAFS study could yield new insights into the structural chemistry at high temperature.

In the present study, the Ni/SiO_2 catalysts were prepared by a two-step method. Nickel in strong interaction with support, i.e. "nickel nuclei", was deposited first using ion-exchange of $[Ni(en)_3]^{2+}$ with SiO_2 followed by 600°C calcination. Then, nickel in weak interaction, i.e. "nickel reservoir", was introduced to the nickel nuclei. The nucleation and growth behaviors of Ni particles with increasing temperature were continuously monitored by in situ EXAFS spectroscopy. Based on in situ EXAFS results, nucleation and growth mechanisms for this preparation method were suggested.

2. Experimental

2.1. *Preparation of Ni/SiO$_2$ catalysts*

2.1.1. *Impregnation method*

The impregnation of silica (Spherosil XOA400, S_{BET}=400 m^2/g) with nickel was performed by incipient wetness impregnation (2 ml/g) with an aqueous solution of nickel nitrate (0.6 mol/l). Aqueous solution of nickel nitrate was put into contact with silica. The samples were kept at room temperature for 2 h and then dried at 90°C for 12 h. Sample with 5 wt% of nickel was prepared. The prepared catalyst is denoted as INi, where I stands for impregnated catalyst.

2.1.2. *Ni/SiO$_2$ preparation by a two-step procedure*

Step 1: *Preparation of "nickel nuclei"*: The tris (ethylenediamine)nickel(II) $[\mathrm{Ni(en)_3}]^{2+}$ was obtained by mixing nickel nitrate and ethylenediamine solution. The concentration ratio [en]/[Ni$^{\mathrm{II}}$] was higher than 3 in order to form the $[\mathrm{Ni(en)_3}]^{2+}$ complex. The pH of the solution was adjusted to 12. This solution (100 cm^3) of $[\mathrm{Ni(en)_3}](\mathrm{NO_3})_2$ was added to silica and continuously stirred at 25°C in a thermostated vessel for 48 h. Then, it was filtered and washed with a 0.24 M ethylenediamine solution at pH 12. The sample was dried at 90°C for 24 h and then calcined in air at 600°C for 2 h in order to decompose nitrate and (ethylenediamine)-nickel(II). The Ni loading of the prepared sample was about 2.5 wt%. The sample of $[\mathrm{Ni(en)_3}]^{2+}/\mathrm{SiO_2}$ is hereafter referred to as ENien$_{2.5/600}$.

Step 2: *Impregnation of the "nickel reservoir"*: The "nickel reservoir" was obtained by impregnation of silica containing "nickel nuclei " with nickel nitrate (2.5 wt%). The impregnating volume was 1 ml/g for the ion-exchanged sample. This sample is referred to as ENien$_{2.5/600}$+INi$_{2.5}$.

2.2. *In situ EXAFS of Ni/SiO$_2$ catalyst*

The in situ EXAFS spectra of Ni/SiO$_2$ catalysts were obtained on BL10B and BL7C of Photon Factory in National Laboratory for High Energy Physics (KEK) in Japan. The storage ring was operated with an electron energy of 2.5 GeV and a current between 250 and 360 mA. The in situ EXAFS spectra at Ni K-edge were measured in transmission mode using two ionization chambers. The energy was scanned with 2 eV steps from 8200–9200 eV. For good signal to noise ratio, the Ni/SiO$_2$ samples were pressed into self-supporting wafers and these wafers were placed in the in situ cell made by stainless steel with Kapton Windows. Fig. 1 shows the schematic diagram of the in situ EXAFS measurement apparatus. The in situ EXAFS spectra were measured continuously at increasing temperature from room temperature to

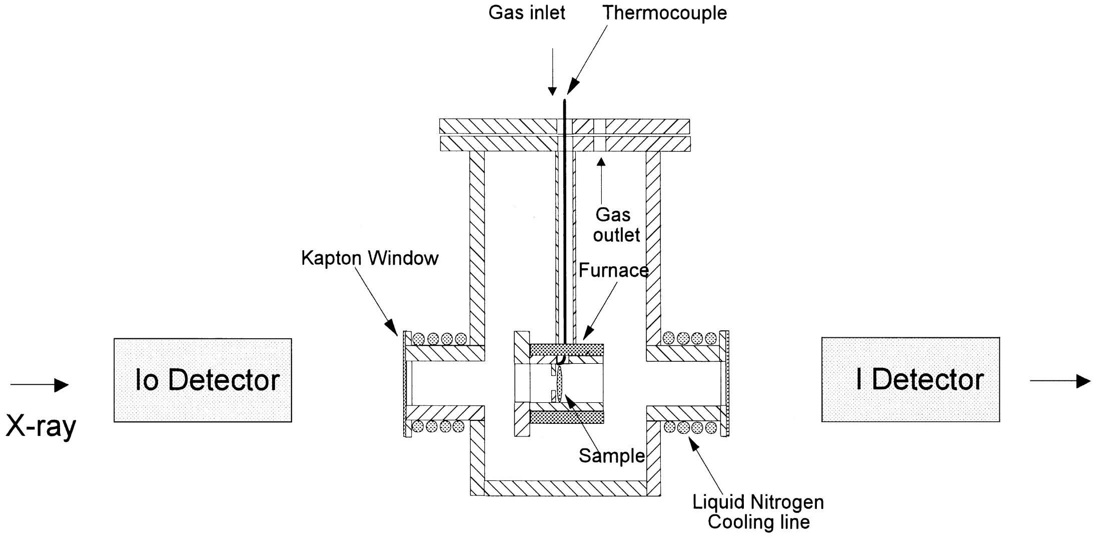

Fig. 1. Schematic diagram of the experimental arrangement used for in situ EXAFS measurement.

500°C in air atmosphere. The rate of temperature programming was 1.5°C/min. The liquid nitrogen was circulated around in situ cell to prevent heat transfer to the Kapton windows during cell operation at high temperature.

Curve fitting of EXAFS data was carried out by conventional fitting method reported by Teo and Lee [22,23]. The pre-edge region was fitted with a polynomial spline and then extrapolated with a polynomial spline. The extrapolated polynomial splines beyond the edge were subtracted from total absorption to give the elemental absorption μ(E). The k^3 weighted data in k-space, $k^3\chi(k)$ were Fourier transformed over a 3–12 Å^{-1}. The curve fittings were performed using reference compounds for the determination of the back-scattering phase and amplitude functions. Ni foil, NiO and Ni doped $Mg(OH)_2$ were chosen as reference compounds for the Ni–Ni, the NiO and the Ni–Si system. The FEFF6 code was also used for the amplitude and phase shift calculation [24].

3. Results

3.1. In situ EXAFS of Ni/SiO_2 prepared by incipient wetness impregnation

Fig. 2 shows the in situ EXAFS spectra of Ni/SiO_2 prepared by incipient wetness impregnation method (INi). The temperature was raised from room temperature to 500°C at a heating rate of 1.5°C/min. A single scan of EXAFS signal could be obtained within 15 min, and it took a 6 h to measure the entire EXAFS signal from room temperature to 500°C. In the EXAFS region of INi, the small peaks beyond the absorption edge (near 8340 eV) features begin to appear after 320°C calcination, and new oscillations of EXAFS signals (between 8500 and 8600 eV) are observed after 320°C heating. These in situ EXAFS spectra of INi catalyst reflect the coordination structure changes of Ni occurring after 320°C calcination. In situ EXAFS techniques enabled one to continuously monitor the coordination structure change of Ni during thermal treatment.

The radial structure functions of in situ EXAFS spectra of INi catalyst are shown in Fig. 3. The phase shift is not corrected in this figure. At low temperature, only the main peak around 2.0 Å is shown. As the temperature increases to 320°C, the magnitudes of second-shell interaction around 3.0 Å are increasing. Simultaneously, the intensities of peaks near 4–5 Å also increase, which reflects the formation of bulk metal oxide with increasing temperature.

At the initial stage of in situ monitoring, the first peak around 2.0 Å can be attributed to the interaction of $Ni(NO_3)_2xH_2O$ (where, x=4 or 2) [19]. While the second-shell interaction around 3.0 Å can be assigned to the mixed interaction of Ni–O and Ni–Ni bonds (Ni–O–Ni interaction) [31]. As the temperature is increased, the first-shell interaction decreased, whereas the second-shell interaction increased, consistent with the decomposition of nickel nitrate and the formation of NiO with increasing temperature. Therefore the second-shell interaction can be related to the growth of NiO. The radial structure function of EXAFS spectra of INi at 500°C is similar to that of NiO. The coordination number and the bond length of Ni–Ni interaction of INi_{500} obtained from best fitting results are 12 and 2.962 Å, respectively (Table 1). It implies the formation of bulk NiO after 500°C heat treatment in the impregnated Ni/SiO_2 catalyst.

Table 1
Structural parameters of reference compounds for EXAFS calculation and best fitting results of Ni/SiO_2 catalysts

Sample	Backscatterer	N[a]	R[b]	$\Delta\delta^{2}$[c]
Ni foil	Ni	12	2.492	–
NiO	O	6	2.09	–
	NI	12	2.94	–
$Ni(Mg)OH_2$	Mg	6	3.14	–
Nickel silicate[d]	Ni	6	3.07	−0.001
	Si	5	3.32	−0.001
INi_{500}	O	6	2.08	0.001
	Ni	12	2.96	0.003
$ENien_{2.5/RT}$	Ni	1.1	3.07	0.002
	Si	3.1	3.31	0.001
$ENien_{2.5/500}$	Ni	0.9	3.07	0.002
	Si	1.1	3.29	0.001
$ENien_{2.5/600}+INi_{2.5}$	Ni	2.8	3.06	0.002
at R.T.	Si	0.94	3.30	−0.001
$Enien_{2.5/600}+INi_{2.5}$	Ni	7.8	3.07	0.001
at 500	Si	0.94	3.27	0.002

Accuracies: N±10%, R±0.01, $\Delta\delta^2$±15%, [a] Coordination number, [b] bond length(), [c] Debye-Waller factor(^{2}), [d] 2:1 phyllosilicate (from reference of J. Am. Chem. Soc. 117 (1995) 2011).

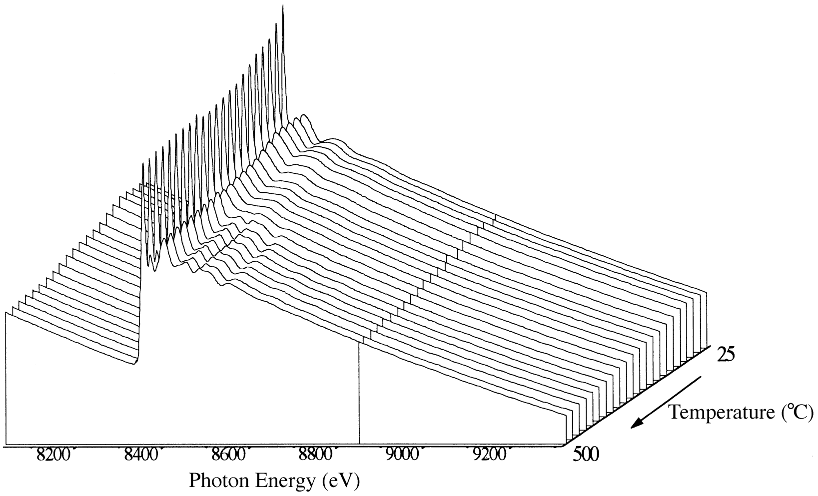

Fig. 2. The in situ EXAFS spectra of INi catalyst measured from room temperature to 500°C at Ni K-edge.

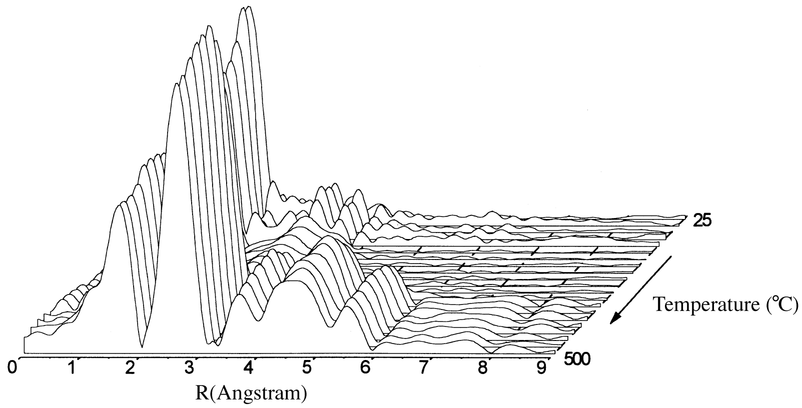

Fig. 3. The radial structure functions of in situ EXAFS spectra of INi catalyst with increasing temperature from room temperature to 500°C.

3.2. Ni/SiO$_2$ prepared by ion-exchange from an ethylene diamine solution

Fig. 4. shows the radial structure functions of in situ EXAFS spectra of ENien$_{2.5}$ catalyst with increasing temperature from room temperature to 500°C. The ENien$_{2.5}$ catalyst was prepared by ion-exchange with $[Ni(en)_3]^{2+}$ solution and followed by drying at 90°C (the Ni loading was 2.5 wt%). In the radial structure function of ENien$_{2.5}$ (the phase shift was not corrected in Fig. 4) at room temperature, the main peak around 1.9 Å is shown and the another peak around 2.7 Å is also shown. As the temperature is increased to 500°C, the intensities of these peaks are decreased.

The first-shell interaction of ENien$_{2.5}$ at room temperature can be attributed to the interaction of ethylenediamine coordinated around Ni atoms [17,20]. The second peak at ca. 2.7 Å might be attributed to the mixed interactions of Ni–O–Si and Ni–O–Ni bonds [17]. The best fitting results of EXAFS data of ENien$_{2.5}$ catalyst at room temperature (Table 1) show the 1.1 Ni and 3.1 Si exist as backscatters around Ni atoms. As the temperature of ENien$_{2.5}$ is increased

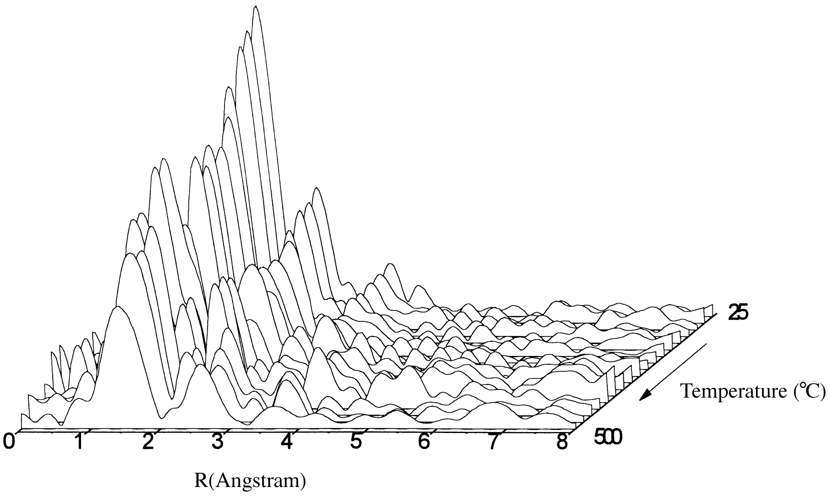

Fig. 4. The radial structure functions of in situ EXAFS spectra of ENien$_{2.5}$ catalyst with increasing temperature from room temperature to 500°C.

to 500°C (ENien$_{2.5/500}$), the coordination numbers of Ni and Si become 0.9 and 1.1, respectively. When the coordination numbers of Ni and Si of ENien$_{2.5/500}$ catalyst are compared with the structural parameters of reference compounds (Table 1). It can be said that they are different from those of nickel silicate or nickel oxide. In this respect, Che and coworkers [17], Che et al. [20] proposed that the formation of nickel silicate could be inhibited with the usage of a ligand such as ethylenediamine complex, and the isolated, grafted Ni(II) species was formed instead of nickel silicate. Our EXAFS fitting results indicate that the ENien$_{2.5}$ catalyst at room temperature (CN of Si=3.1, CN of Ni=1.1) has a dimmer structure of nickel, and ENien$_{2.5/500}$ (CN of Si=1.1, CN of Ni=0.9) is made up of isolated, grafted Ni species. In the ENien$_{2.5}$ catalyst, the coordination number of Ni during the pretreatment up to 500°C is not significantly changed, consistent with a strong interaction of Ni ions with the silica surface up to 500°C.

Fig. 5 shows the in situ EXAFS signals of ENien$_{2.5/600}$+INi$_{2.5}$ catalyst prepared by the two step-method. Namely, the 2.5 wt% of "nickel reservoir" is impregnated on the nickel nuclei (ENien$_{2.5/600}$). The in situ EXAFS signals of ENien$_{2.6/600}$+INi$_{2.5}$ catalyst show the existence of small peak in the near edge region even at room temperature. These peaks were only observed after 320°C heating on the INi catalyst. The radial structure functions of ENien$_{2.5/600}$+INi$_{2.5}$ are shown at Fig. 6. The intensities of first-shell interactions at ca. 1.9 Å are decreasing with increasing temperature. The intensity of second-peak (around 2.7 Å) at room temperature is somewhat stronger than that of impregnated catalyst, suggesting the co-existence of Ni nuclei and Ni reservoir during the initial stages of in situ EXAFS measurements. The intensities of second-shell interactions around 2.7 Å increased abruptly after heating to 370°C. The long range interaction beyond 4–5 Å is not greatly influenced by temperature, suggesting only mild particle growth of Ni in ENien$_{2.5/600}$+INi$_{2.5}$ catalyst after oxidation at 370°C.

From the best fitting results of EXAFS data for ENien$_{2.5/600}$+INi$_{2.5}$ catalyst (Table 1), the coordination number of Ni–Ni at room temperature of in situ EXAFS experiment is 2.8. The coordination number of Ni–Ni starts to increase after 370°C calcination in ENien$_{2.5/600}$+INi$_{2.5}$ catalyst. The coordination number of Ni–Ni after 500°C calcination is 7.2, which shows the particle growth of Ni occurs above 320°C. In situ EXAFS fitting result enable us to monitor the growth pattern of Ni particle in presence of Ni nuclei. The Ni/SiO$_2$ catalyst prepared by two step-method has smaller particles of Ni compared with those prepared by impregnation method.

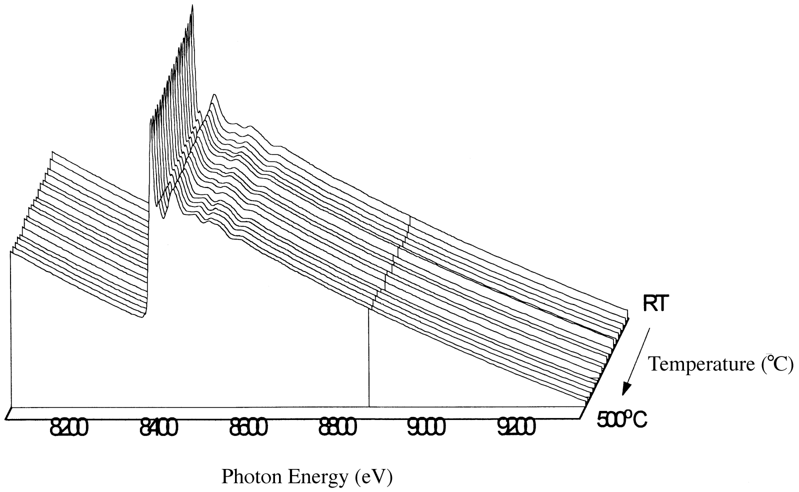

Fig. 5. The in situ EXAFS signals of ENien$_{2.5/600}$+INi$_{2.5}$ catalyst with increasing temperature from room temperature to 500°C.

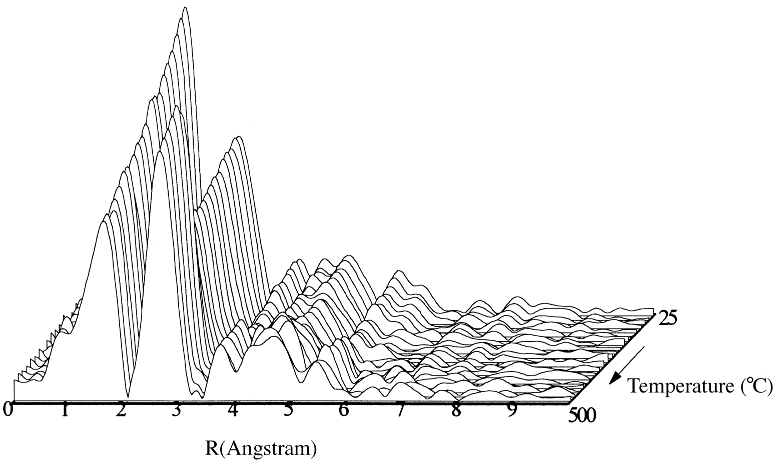

Fig. 6. The radial structure functions of in situ EXAFS spectra of ENien $_{2.5/600}$+INi$_{2.5}$ catalyst with increasing temperature from room temperature to 500°C.

4. Discussion

4.1. Effect of ligand structure on the preparation of Ni/SiO$_2$ catalyst

It is generally agreed that the surface reactions of support with transition metal ions are greatly influenced by the ligand properties (structure, mobility or accessibility) of transition metal ions and the surface charge of support. Hatheway and Lewis [32] showed that the adsorption of multidentate nitrogen ligand complex of Ni(II) on silica surface by ion-exchange process results in the complex ion's bonding to the surface. The subsequent reduction to the metal result in the preparation of highly dispersed supported metal catalyst. It implies the importance of ligand structure and accessiblity of transition metal ions in the preparation step.

In this study, a tris(ethylenediamine) nickel complex is used to prepare the nickel nuclei in the two-step

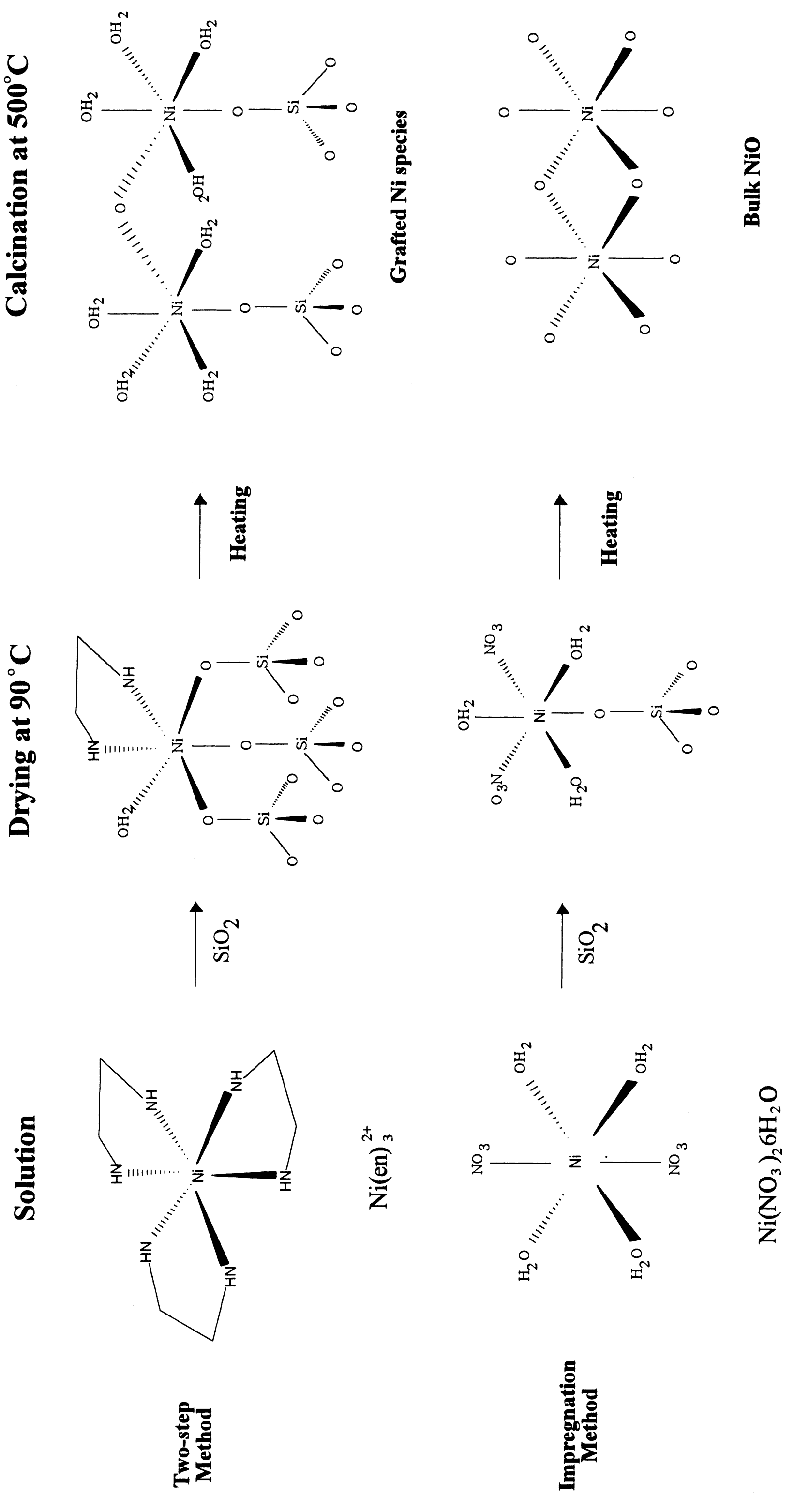

Fig. 7. Proposed structure of INi and ENien$_{2.5/600}$+INi$_{2.5}$ catalysts with increasing temperature.

method. Several studies have been reported the coordination structure and the thermodynamic stability of tris(ethylenediamine) nickel complex by UV-Vis, FT-IR and crystal field theory [33–36]. The absorption bands of $Ni(en)_3^{2+}$ complex observed in the frequency range 900–1180 nm come from the electronic transition $^3A_{2g} \rightarrow ^3T_{2g}$ of the octahedral bidentate Ni(II) complex [33,34]. On the other hand, a monodentate octahedral ligand structure can be proposed in the case of $Ni(NO_3)_2 6H_2O$ complex [34]. Therefore, the initial ligand structures of Ni complexes can be proposed in Fig. 7. These initial coordination structures, bidentate or monodentate, strongly affect the stability of Ni(II) ions during the preparation of Ni/SiO_2 catalysts.

It has been generally accepted that octahedral bidentate ligand are more stable than monodentate structures in solution state. Yang and Shul [30] showed that the octahedral bidentate ligand structure of $RuCl_3$ dissolved in ethylene glycol is more stable than tetrahedral $RuCl_3$ in aqueous solution. They suggested that the thermal stability and dispersion of Ru particles in Ru/Al_2O_3 catalyst were strongly dependent on the initial ligand structure. In this experiment, the coordination of Ni(II) by ethylenediamine favored the bidentate ligand structure in basic solution (pH=12). This Ni(ethylenediamine) complex having bidentate chelate rings are more thermo-dynamically stable than those containing monodentate ligands such as H_2O or NH_3 [20].

The enhanced stability of nickel ethylenediamine ligand protects the nickel cation and this ligand inhibits the reactions with silica. In contrast, monodentate nickel ligands like H_2O or NH_3 can easily react with silica to form phyllosilicates. The coordination numbers of Si and Ni in $ENien_{2.5/RT}$ catalyst obtained from EXAFS fitting result suggest the formation of isolated Ni species at the initial stage of in situ experiment (Fig. 7). The ethylenediamine groups are still coordinated to Ni after drying at 90°C. Ethylenediamine begins to decompose after 300°C calcination and it is completely removed after 600°C calcination. High temperature calcination (600°C) leads to the formation of grafted Ni species as shown in Fig. 7. This grafted Ni species have a strong support interaction with a support and acts as "nickel nuclei" during Ni particle growth.

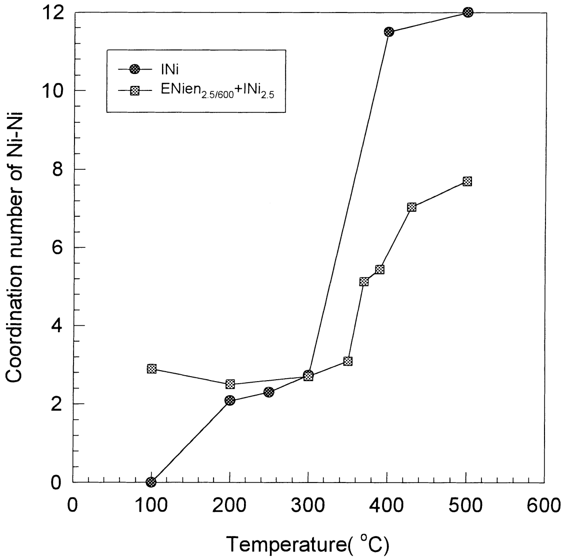

Fig. 8. The coordination numbers of Ni interaction of INi and ENien $_{2.5/600}$+$INi_{2.5}$ catalysts obtained from EXAFS fitting result with increasing temperature.

4.2. *Particle growth behavior of Ni/SiO_2 as a function of preparation method*

The in situ EXAFS experiment enables us to continuously monitor the particle growth behavior with heat treatment under air atmosphere. Our in situ EXAFS results show the particle growth behavior of Ni is strongly dependent on the preparation method. Fig. 8 clearly shows that the particle growth behavior obtained from in situ EXAFS of Ni/SiO_2 catalysts as a function of preparation method. At the initial stage of in situ EXAFS experiment, the Ni/SiO_2 prepared with two-step method has a larger coordination number of Ni(CN of Ni=3.0) compared with impregnated Ni/SiO_2 catalysts (CN of Ni=0). This result shows that particle growth of nickel nuclei on grafted Ni already takes place in a two-step process during drying at 90°C after impregnation of Ni precursor. Louis et al. [19] has proposed that at 90°C nickel nitrate in impregnated nickel sample is decomposed into basic nitrate $[Ni(NO_3)_2 2Ni(OH)_2]$ containing hydroxyl group and particle growth occurs via a condensation reaction between hydroxyl groups of nickel nitrate and water coordinated to grafted nickel of the nickel nuclei. Therefore, the $ENien_{2.5/600}$+$INi_{2.5}$ catalyst has a larger coordination number of Ni than that of INi catalyst on initial stage of in situ EXAFS experiment. On the other hand, the impregnated sample (INi) shows no Ni–Ni interaction at the initial stage which showing the mononeric dispersion of Ni species.

As the temperature increases, the coordination number of Ni in INi catalyst increases after 320°C heating and the coordination number of Ni reaches 12 after 500°C calcination. Apparently, bulk NiO forms by the impregnation method due to the high mobility of Ni species. On the other hand, in the Ni/SiO_2 prepared by two-step method has strong Ni nuclei and the initial coordination number of Ni (CN of Ni=3.0) is maintained up to 370°C, but the coordination number of Ni is increasing after 370°C and it becomes 7.8 after 500°C calcination. The impregnatd sample shows a rapid increase of Ni–Ni interaction with heating. When we compare the two-step process, the sudden increase of Ni–Ni interaction starts from 300°C. It suggests that the mobility of Ni species having weak interactions with support is affected by the Ni nuclei that provide the chemical glue. As a result, Ni/SiO_2 prepared by two-step method ($ENien_{2.5/600}+INi_{2.5}$) formed small particles compared with impregnation method after 500°C heat treatment.

The fact that the growth mechanism of Ni particles can be described as shown in Fig. 9. In Ni/SiO_2 prepared with impregnation method, the nickel would exist as $Ni(NO_3)_2(H_2O)$. As the temperature is increased to 320°C, the nitrate decomposes and bulk NiO particles are obtained after heating. In Ni/SiO_2 prepared by two-step method, the particle growth has already occurred on a nucleation site during drying. The particle growth on the Ni reservoir can be pre-

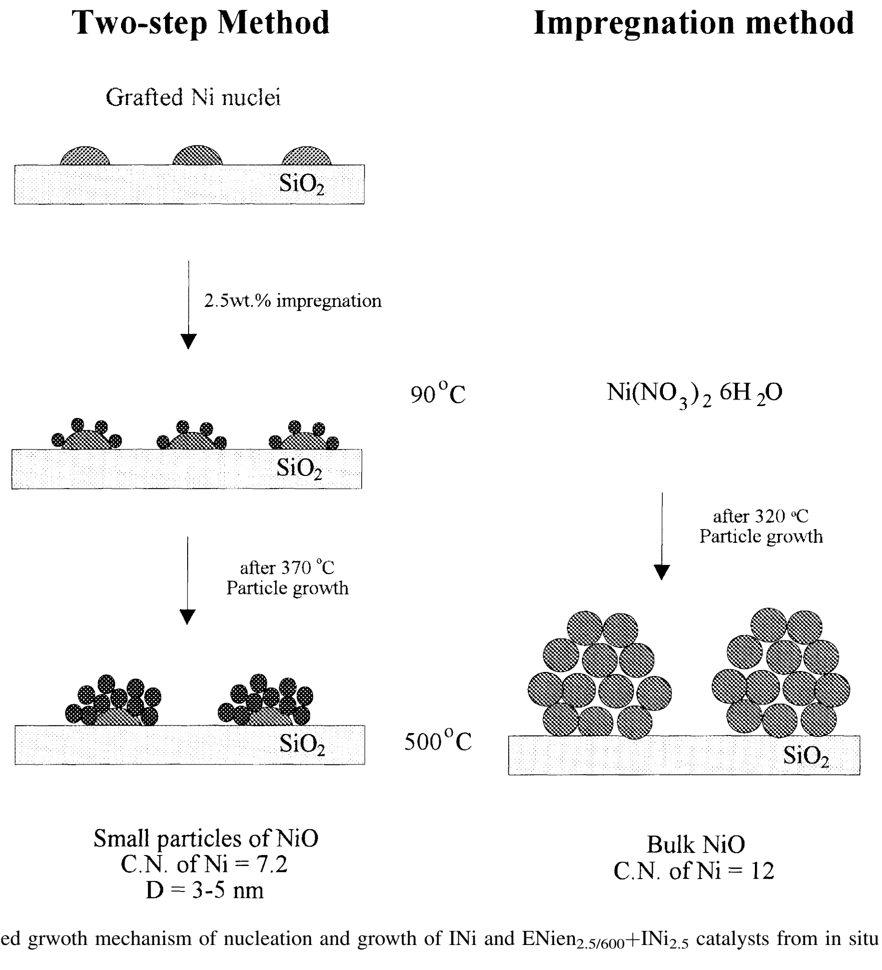

Fig. 9. Proposed grwoth mechanism of nucleation and growth of INi and $ENien_{2.5/600}+INi_{2.5}$ catalysts from in situ EXAFS data.

vented upto 370°C, because of the effect of strong ion support interactions between Ni and SiO_2. The grafted Ni species form strong interaction with the nickel reservoir, which prevents the migration and growth of Ni particle upto 370°C. After higher heating, the agglomeration of Ni particles occurred because of the low thermal stability of this Ni/SiO_2 prepared with two-step method. Also, it has been suggested that for a given amount of impregnated nickel and an increasing amount of nickel nuclei, the particle concentration increases and the average particle size decreases [20]. This means that it is possible to obtain smaller Ni particles even of higher loadings if we can provide large number of nuclei. It suggests that particle growth of Ni mainly occurs on the nickel nuclei. Therefore, the two-step method is effective to obtain small particles compared with conventional impregnation method.

5. Conclusions

In this experiment, the nucleation and growth of Ni/SiO_2 catalysts prepared by different preparation methods were characterized by in situ EXAFS spectroscopy. The in situ EXAFS was proved to be powerful to monitor particle growth behavior during thermal treatment. The formation of nickel nuclei having strong interaction with silica can be prepared by the use of stable Ni(ethylenediamine) complexes. The bulk NiO is formed in the impregnated Ni/SiO_2 catalyst, whereas the small particles of Ni can be prepared by the two-step method. The formation of small particle can be attributed to the strong ion-support interaction between nickel nuclei and nickel reservoir.

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References

[1] W. Zou, R.D. Gonzalez, Catal. Today 15 (1992) 443.
[2] S.J. Tauster, S.C. Fung, R.L. Garten, J. Am. Chem. Soc. 100 (1978) 170.
[3] S. Alerasool, R.D. Gonzalez, J. Catal. 124 (1990) 204.
[4] K. Tohji, Y. Udagawa, S. Tanabe, T. Ida, A. Ueno, J. Am. Chem. Soc. 106 (1984) 5172.
[5] Y. Yermakov, B. Kuznetsove, Y. Ryndin, J. Catal. 42 (1976) 73.
[6] Y. Yermakov, Catal. Rev. Sci. Eng. 13 (1976) 77.
[7] M. Tzou, H. Jiang, W. Sachtler, Appl. Catal. 20 (1986) 231.
[8] M. Ichkawa, T. Fukushima, T. Yokoyama, N. Kosugi, H. Kuroda, J. Phys. Chem. 90 (1986) 1222.
[9] A. Fukuoka, M. Ichikawa, J. Hriljac, D. Shriver, Inorg. Chem. 26 (1987) 3643.
[10] A. Fukuoka, T. Kimura, N. Kosugi, H. Kuroda, Y. Minai, Y. Sakai, T. Tominga, M. Ichikawa, J. Catal. 126 (1990) 434.
[11] M. Che, L. Bonneviot, Z. Phys. Chem. 152 (1987) 113.
[12] M. Che, L. Bonneviot, Pure Appl. Chem. 60 (1988) 1369.
[13] M. Che, O. Clause, L. Bonneviot, in: J. Phillips, M. Ternan (Eds.), Proceedings of the Ninth International Congress on Catalysis, The Chemical Institute of Canada, Ottawa, 1988, p. 1750.
[14] M. Che, L. Bonneviot, in: T. Inui (Ed.), In Successful Design of Catalysis. Future Requirements and Development, Elsevier, Amsterdam, 1988, p. 147.
[15] L. Bonneviot, O. Legendre, M. Kermarec, D. Olivier, M. Che, J. Colloid Interface Sci. 134 (1990) 534.
[16] M. Che, D. Masure, P. Chaquin, J. Phys. Chem. 97 (1993) 9022.
[17] O. Clause, L. Bonneviot, M. Che, H. Dexpert, J. Catal. 130 (1991) 21.
[18] O. Clause, L. Bonneviot, M. Che, J. Catal. 138 (1992) 195.
[19] C. Louis, Z.X. Cheng, M. Che, J. Phys. Chem. 97 (1993) 5703.
[20] M. Che, Z.X. Cheng, C. Louis, J. Am. Chem. Soc. 117 (1995) 2008.
[21] Z.X. Cheng, C. Louis, M. Che, in: L. Guczi et al. (Eds.), Proceedings of the Tenth International Congress on Catalysis Elsevier, Amsterdam, 1993, p. 1785.
[22] B.K. Teo, EXAFS: Basic Principles and Data Analysis, Springer, Berlin, 1985.
[23] D.C. Koningsberger, R. Prins, X-ray Absorption: Principles, Applications and Techniques of EXAFS, SEXAFS and XANES, Wiley, New York, 1988.
[24] J. Rher, J. Mustre de Leon, S. Zabinsky, R. Albers, J. Am. Chem. Soc. 113 (1991) 5135.
[25] F.W. Lytle, P.S.P. Wei, R.B. Greegor, G.H. Via, J.H. Sinfelt, J. Chem. Phys. 70 (1979) 4849.
[26] M. Ichikawa, T. Fukushima, T. Yokoyama, N. Kosugi, H. Kuroda, J. Phys. Chem. 90 (1986) 1222.
[27] B.S. Clausen, B. Lengeler, B.S. Rasmussen, J. Phys. Chem. 89 (1985) 2319.
[28] D.G.J. Castner, P.R. Watson, I.Y. Chan, J. Phys. Chem. 94 (1990) 819.
[29] G. Sankar, P. Wright, S. Natarajan, J.M. Thomas, G. Greaves, A. Dent, B. Dobson, C. Ramsdale, R. Jones, J. Phys. Chem. 97 (1993) 9550.
[30] J.C. Yang, Y.G. Shul, Catal. Lett. 36 (1996) 41.
[31] K.I. Pandya, W.E. O'Grady, D.A. Corrigan, J. McBreen, R.W. Hoffman, J. Phys. Chem. 94 (1990) 21.
[32] B.J. Hathaway, C.E. Lewis, J. Chem. Soc. A (1969) 1176.
[33] C.K. Jorgensen, Acta Chem. Scand. 11 (1957) 399.
[34] W. Monch, W. Fernelius, J. Chem. Educ. 38 (1961) 192.
[35] L. Swink, M. Atoji, Acta Cryst. 13 (1960) 639.
[36] D.L. Leussing, Inorg. Chem. 2 (1963) 77.