# Structure of low coverage Ni atoms on the $TiO_2$(110) surface – Polarization dependent Total-Reflection Fluorescence EXAFS study –

Y. Koike[1], K. Ijima[2], W.-J. Chun[3], H. Ashima[3], T. Yamamoto[4], K. Fujikawa[1], S. Suzuki[3], Y. Iwasawa[5], M. Nomura[6], K. Asakura[1]*

[1]*Department of Quantum Science and Technology and Catalysis Research Center Hokkaido University, Sapporo, 001-0021, Japan*

[2]*Department of Electrical Engineering, Yamanashi University, Kofu 400-8511, Japan*

[3]*Catalysis Research Center and JST-CREST, Hokkaido University, Sapporo 001-0021, Japan*

[4]*Chemical Resources Laboratory, Tokyo Institute of Technology, Yokohama 226-8503, Japan*

[5] *Department of Chemistry, Graduate School of Science, The University of Tokyo, Tokyo 113-0081, Japan*

[6] *Photon Factory, Institute of Materials Structure Science, Tsukuba 305-0801, Japan*

* corresponding author Kiyotaka Asakura *Catalysis Research Center, Hokkaido University, Sapporo 001-0021, Japan Fax 81-11-706-9113: email askri@cat.hokudai.ac.jp*

Abstract

The structure of low coverage Ni atoms on the $TiO_2$(110) surface was studied using polarization dependent EXAFS. We found that Ni atoms interacted with oxygen atoms at the $\langle 1\bar{1}n \rangle$ step edges, where atomically dispersed Ni species were found with Ni-O distances at 0.199 ± 0.002 nm and 0.204 ± 0.003 nm in parallel and perpendicular directions to the

$TiO_2$(110) surface, respectively. The location corresponded to the virtual Ti site if the next $TiO_2$ layer was created on the topmost $TiO_2$ surface. The Ni location is mainly determined by the dangling bond directions of the surface oxygen atoms.

## 1. Introduction

Metal/oxide systems have been applied in many fields for catalysis, sensors, electric devices and thin film growths[1]. Interactions between metal and oxides are the most important factors to determine the electronic state and structure of the deposited metals and the physical and chemical properties of metal-oxide systems. The interaction of a *single atom* with the oxide surface is the simplest interaction, but the most fundamental one. However, great controversy exists even about the location of a metal atom on an oxide surface, *i.e.*, metal atoms initially interact with surface cations or surface anions. This point is crucial to determine the properties of the deposited metal.

$TiO_2$(110) is one of the most investigated single crystal surfaces[2]. Figure 1 shows a schematic drawing of the $TiO_2$(110) surface, which contains protruding oxygen atoms (bridging oxygen) and five-fold Ti atoms in the trough running along the [001] directions. The Group 10 elements (Ni, Pd, Pt) supported on $TiO_2$ are the most important catalytic and photocatalytic systems. Theoretical investigations have examined single atoms of Group 10 elements deposited on the $TiO_2$ (110) surface. Most of those studies have indicated that the metal interacts mainly with oxygen, especially bridging oxygen atoms[3–6]. On the other hand, experiments on metal clusters and $TiO_2$(110) such as XPS and STM have suggested that the metal preferably interacted with the five-fold Ti sites[7–10]. This contradiction might arise from the lack of direct information related to the bond between the single metal atom and the $TiO_2$ surface. We have applied polarization dependent EXAFS which can give 3 dimensional structure of the metal species on a single crystal surface.[11,–14]. PTRF-XAFS(polarization dependent total reflection fluorescence XAFS), a combination of total reflection fluorescence detection mode and polarization-dependent XAFS allows us to carry out the surface XAFS measurement of heavy elements with their coverage less than 0.1ML(ML=monolayer corresponding to 2 x $10^{14}$ atoms / $cm^2$) [15]. In this

work, we have studied Ni on $TiO_2$(110) at the low surface density of $1\times10^{13}$ atoms / $cm^2$ to obtain atomically dispersed Ni species. We have found a unique adsorption structure of atomically dispersed Ni. It is situated on the $\langle 1\bar{1}n \rangle$ step edge site of the $TiO_2$(110) surface with Ni-O bonds.

## 2. Experimental

The PTRF-EXAFS system consists of three UHV chambers(base pressure = 5 x $10^{-8}$ Pa), *i.e*, a sample preparation chamber, an EXAFS measurement chamber, and a mobile sample transfer chamber[12]. An optically polished rutile $TiO_2$(110) single crystal (20 × 20 × 1 $mm^3$, Earth Jewelry Co., Japan) was pretreated at 1273 K for 3 h in air to remove carbon contaminations. The sample was further cleaned in the UHV preparation chamber by several cycles of $Ar^+$ sputtering and annealing at 873 K. These procedures yielded a sharp (1 × 1) LEED pattern and no C1s XPS peak. The Ni was evaporated from a tungsten filament that was wrapped with a Ni wire. The measurement chamber was equipped with a six-axis goniometer to adjust the total reflection conditions and the sample orientations The PTRF-EXAFS measurements were performed at BL9A of the Institute for Material Structure Science's Photon Factory (KEK-IMMS-PF), which was operated at 2.5 GeV and 400 mA. X-rays were monochromatized using a Si(111) double-crystal monochromator and focused using a pair of bent conical mirror[ 16 ]. The fluorescence signals were detected using a 19-element pure Ge solid-state detector (GL0110S; Canberra, USA). The $TiO_2$(110) has an anisotropic surface structure, as shown in Fig. 1. Therefore, PTRF-EXAFS measurements were carried out in three different orientations against the electric vector of incident x-rays, i.e., two parallel orientations to the surface: E//[001], $[1\bar{1}0]$ and perpendicular orientation to the surface E//[110]. The EXAFS analyses were carried out using REX 2000 and FEFF8.02[17]. The analytical error was estimated using the Hamilton ratio test[18]

## 3. Results and discussion

Figure 1 (a) shows possible adsorption sites – cation and anion adsorption sites-on the terrace of $TiO_2$(110). The cation adsorption site has two possibilities, *i.e.*, the five-fold Ti site in the trough and an oxygen point defect present on the bridging oxygen rows where the underlying Ti atoms are exposed and should interact with the incoming Ni. The anion adsorption sites are indicated in numerals(**1-5**) in the Fig.1(a). Other defects sites such as surface and subsurface Ti vacancies can be neglected because the $TiO_2$ is a n-type semiconductor.

Figure 2 shows Ni PTRF-EXAFS spectra with the coverage of $1 \times 10^{13}$ atoms/cm$^2$. The amplitudes of all observed EXAFS oscillations decay quickly, indicating the presence of oxygen atoms, not Ti or Ni atom as the nearest neighbor of Ni and its atomic dispersion. The curve fitting analysis shows that Ni-O distance is about 0.20 nm(0.199 nm for [001] and $[1\bar{1}0]$ directions and 0.204 nm for [110] direction.). The literature describes that atomically dispersed metal is located at the atop site of the five-fold Ti site(see Fig. 1(a))[2,8–10]. Nevertheless, the present EXAFS results reject the hypothesis of the five-fold Ti adsorption site for Ni. The oxygen defect (indicated by arrow in Fig.1(a)) is also excluded for the Ni adsorption site, where the Ti can interact with Ni[2,6,19].

We further analyzed EXAFS data by comparing the EXAFS data with theoretically calculated EXAFS. We postulated that Ni adsorbed on the anion sites of the unreconstructed terrace(sites **1**–**5** as shown in Fig. 1(a)). The Ni-O bonds in all directions are visible only at sites **3** and **4** because of the $\cos^2\theta$ dependence of EXAFS oscillation. However, we can not reproduce the observed EXAFS data based on these models. Figure 2(a) shows EXAFS oscillations calculated based on the Ni on the three-fold terrace site (site **3** in Fig. 1). The poor reproduction of the experimental spectra results from the short Ni-Ti (Ti atom under the bridging oxygen shown by A in Fig. 1(a)) distance, which always appears around 0.23 nm. Similar results are obtained for the model calculation of Ni adsorbed on site **4**, where Ni has a Ni-Ti (five-fold Ti) distance around 0.21 nm. Therefore, we have concluded that no stable adsorption sites are present on the terrace sites. Pang et al. proposed the K adsorption on the 3 fold terrace site corresponding to the site **3** by polarization dependent EXAFS.[20] They could not observe K-Ti

interaction. However, the K-O distance was 0.26 nm much longer than ours(0.20 nm) and K-Ti distance was 0. Therefore, in their case contribution of the Ti was small due to the $1/r^2$ dependence of the XAFS amplitude.

Other possibilities for Ni adsorption are substitution of Ti at surface or subsurface region and the step edge. We postulate the Ni is located at the 5-fold surface Ti or 6 fold subsurface Ti positions by removing the Ti atom. However, the calculated oscillations based on these models showed much larger EXAFS oscillations and we could exclude the substitution models. Finally we checked the step edges. Figure 1 (b) shows that $TiO_2$(110) has step edges, most of which run parallel to <001> or $<1\bar{1}n>$ (n=1,2,3 ….)[2,21]. Two structures have been proposed for the step running along the <001> step. Both are Ti-exposed structures. Figure 1(b) shows that one is a smooth Ti terminated step edge (<001>S), whereas the other has a rugged stepped edge <001>R. On the former site, Ni should have a direct Ni-Ti bond, whereas the rugged step edge can provide an adsorption site by replacing the protruding Ti atom (labeled as **B** in Fig. 1(b)) with a Ni atom. In this case, Ni is surrounded by three oxygen atoms, two coming from the upper terrace site and one from the lower terrace. However, in this structure, the average effective coordination numbers in two parallel directions to the surface ([001] and$[1\bar{1}0]$) should be equal to the perpendicular direction ([110]) because the height of the Ni atom is almost equal to that of the upper terrace, but this is not the case in observed data. The EXAFS amplitudes in the parallel directions are smaller than that in the perpendicular direction. Consequently, we can exclude the possibility of Ni adsorption on the <001> step. We tested the possibility for the $<1\bar{1}n>$ step edge. The $<1\bar{1}n>$ step edge has a characteristic adsorption site that is demarcated by ellipse **C** in Fig. 1(b) and the inset figure, which consists of two oxygen atoms: a bridging oxygen ($\mathbf{O_L}$) on the lower terrace and an oxygen ($\mathbf{O_U}$) of the upper terrace[2,21]. Figure 2(b) shows the manner in which we can reproduce observed spectra well when we put Ni atoms on this site. The detail model structure is illustrated in Fig. 3. We estimated the density of the adsorption site to 2-3 x $10^{13}$ sites / $cm^2$ based on the reported STM picture[2,21]. This value is larger than the Ni coverage studied here. The respective Ni-$O_L$ and $O_U$ distances are 0.204 ± 0.003 nm and 0.199 ± 0.002 nm. These lengths suggest that the bonding character is a strong chemical bond involving a

covalent character.

Interestingly this Ni location well corresponds to that for the Ti site in the $TiO_2$ unit cell. The next Ti cation is placed on the same position of the adsorbed Ni atom when we consider the next $TiO_2$ layer growing from the step edge and compare the Ni position and the $TiO_2$ structure. The Ni occupies the imaginary cation site of the $TiO_2$ layer. The Ni-$O_L$ distance is longer than that of Ni-$O_U$. This asymmetric structure can be explainable by the bulk structure of the rutile $TiO_2$ where corresponding Ti-O bonds have the same anisotropy. [2,22] We studied the adsorption structure of Ni on the $Al_2O_3(0001)$ previously using PTRF-EXAFS, which showed that the Ni was located at the imaginary Al site of the new $Al_2O_3$ layer[23]. Therefore, the imaginary cation site above the surface is inferred to be the most stable adsorption site for the foreign metal atoms. In other words, metal atoms are located at the site to which the dangling bonds of surface oxygen atoms are directed.

According to a theoretical calculation, the atop site of bridging oxygen atoms might be the most stable site on the terrace[3]. However, the single Ni-bridging oxygen bond is not sufficiently strong to fix it on the atop site. Consequently, Ni can hop to the next bridging oxygen atoms and diffuse along the [001] direction. The Ni atoms can find other Ni to form clusters before reaching the step edges if the surface density of Ni is sufficiently high. At less than the critical coverage, the Ni atoms can reach the step edge site without forming cluster.

## 4. Conclusions

This paper first described that atomically dispersed Ni interacts with the oxygen atoms at the step edges that are parallel to the $\langle 1\,\bar{1}\,n\rangle (n = 1,2,3,)$ directions of the $TiO_2(110)$ surface. The Ni location is the imaginary Ti site and the bond distances are respectively 0.199 ± 0.002 nm and 0.204 ± 0.003 nm in the parallel and perpendicular directions. These results suggest that the atomically dispersed Ni adsorption is strongly affected by the -O dangling bond. We are now extending the work to confirm the validity of these conclusions to other noble metals such as Pd, Pt, Cu, Ag and Au, which are less strongly-interacted with oxygen atoms.

## Acknowledgments

The EXAFS measurements were performed under the approval of Program Advisory Committee (PAC) Proposal Nos. 2000G276 2002G270, 2003G097, 2004G285, 2005G203. This work was supported financially by the Core Research Evolution in Science and Technology (CREST) of the Japanese Corporation for Science and Technology (JST), Promotion for Joint Research between Universities and the Industry Program Project "A new EXPEEM", Program No. 20702026 of JST and a Grant-in-Aid for Scientific Research, Category S (No. 16106010) of the Japan Society for Promotion of Science (JSPS).

## References

1 H.-J. Freund, Surf.Sci 500 (2002) 271.

2 U. Diebold, Surf. Sci. Rep. 48 (2003)53.

3 P. L. Cao, D. E. Ellis, V. P. Dravid, J. Mater. Res. 14 (1999) 3684.

4 T. Bredow, G. Pacchioni, Surf. Sci. 426 (1999) 106.

5 J. F. Sanz, N. C. Hernandez, A. Marquez, Theor. Chem. Acc. 104 (2000) 317.

6 K.Okazaki , Y. Morikawa, S. Tanaka, K.Tanaka, M.Kohyama, J. Mater. Sci., 40 (2005)3075.

7 H. Onishi, T. Aruga, C. Egawa, Y. Iwasawa, Surf. Sci. 233 (1990) 261.

8 C. Xu, X. Lai, G. W. Zajac, D. W. Goodman, Phys. Rev. B 56 (1997) 13464.

9 K. D. Schierbaum, S. Fischer, M. C. Torquemad, J. L. de Segovia, E. Roman, J. A. Martin-Gago, Surf.Sci. 345 (1996) 261.

[10] S. Takakusagi, K. Fukui, R. Tero, F. Nariyuki, Y. Iwasawa, Phys.Rev.Lett. 91 (2003) 066102.

[11] Y. Iwasawa (ed.), X-ray Absorption Fine Structure for Catalysts and Surfaces, World Scientific, Singapore, 1996.

[12] W. J. Chun, K. Asakura, Y. Iwasawa, J. Phys Chem. B 102 (1998) 9006.

[13] W. J. Chun, K. Asakura, Y. Iwasawa, Chem. Phys. Lett. 288 (1998) 868.

[14] W. J. Chun, Y. Tanizawa, T. Shido, Y. Iwasawa, M. Nomura, K. Asakura, J.Synchrotron Rad. 8 (2001) 168.

[15] Y. Tanizawa, T. Shido, Y. Iwasawa, M. Nomura, W.-J. Chun, K. Asakura, J.Phys.Chem. 107 (2003) 12917

[16] M. Nomura, A. Koyama, Nucl. Instrum.meth.A 467(2001) 733.

[17] A. L. Ankudinov, B. Ravel, J. J. Rehr, S.D. Conradson, Phys. Rev. B 58 (1998) 7565.

[18] W. C. Hamilton, Acta Crysta. 18 (1965) 502.

[19] Y. Wang, G. S. Hwang, Surf. Sci. 542 (2003)72.

[20] C. L. Pang, C. A. Muryn, A. WOodhead, H. Raza, S. A. Haycock, V. R. Dhanak, G. Thornton, Surf.Sci. 583 (2005) L147.

[21] U. Diebold, J. Lehman, T. Mahmoud, M. K. Kuhn, G. Leonardelli, W. Hebenstreit, M. Schmid, P. Varga, Surf.Sci. 411 (1998) 137.

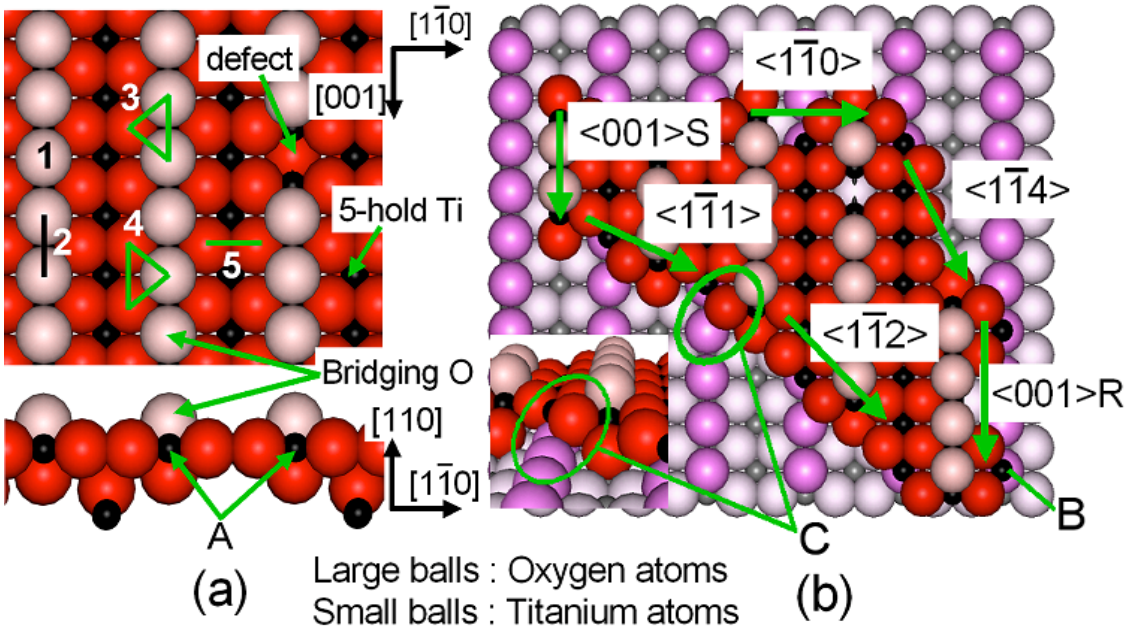
[22] E. A. Grant, Rev. Mod. Phys. 31 (1959) 646.

[23] K. Ijima, Y. Koike, W.-J. Chun, Y. Satio, Y. Tanizawa, T. Shido, Y. Iwasawa, M. Nomura, K. Asakura, Chem,Phys.Lett. 384 (2004) 134-38.

Fig. 1: Ball models of $TiO_2$(110). Large balls correspond to oxygen atoms and small ones correspond to Ti atoms. (a) Top and side views of the $TiO_2$(110)-(1 × 1) surface. Arrows indicate the bridging oxygen, five-fold Ti cation and oxygen point defect. The numbers in the figure denote the possible Ni adsorption sites on the anions of terrace. The six-fold Ti cation, which is under the bridging oxygen, is labeled as "A". (b) $TiO_2$(110) with a single-height step along the <1$\bar{1}$n> and <001> directions. Two types of step edges along the <001> direction, *i.e.*, smooth and rugged structures are shown as <001>S and <001>R, respectively. A calculated adsorption site at <001>R step edges is labeled as "B". The green ellipse labeled by "C" indicates the proposed Ni adsorption site at the step edges along <1$\bar{1}$n> direction. The inset shows an enlarged side view around the adsorption site "C".

Fig. 2: PTRF-EXAFS spectra of Ni/$TiO_2$(110) at the Ni coverage: $1 \times 10^{13}$ atoms/cm$^2$ (black dotted lines) and calculated ones (red solid lines).
(a) and (b) show the difference calculated PTRF-EXAFS spectra based on a model structure of Ni adsorbed on the site 3 and the proposed adsorption structure at the step edge, respectively.
(1) E//[001](// surface), (2) E//[1$\bar{1}$0](// surface) and (3) E // [110] (⊥ surface).

Fig. 3: A proposed adsorption structure of Ni atoms at step edges "C" on $TiO_2$(110). Large balls represent oxygen atoms, medium ones represent Ni atom, and small ones Ti atoms. The bond length unit is nanometers.



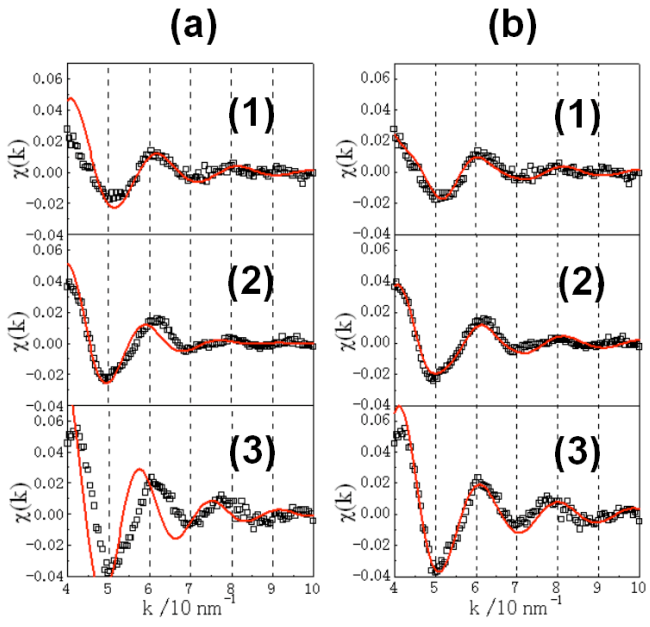




Figure 2 Y. Koike

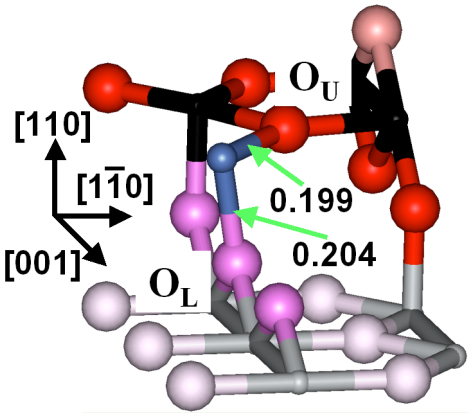



Figure 3　Y. Koike

| Site | N*(ratio) | | |
|---|---|---|---|
| | [001] | $[1\bar{1}0]$ | [110] |
| 1 | 0(0) | 0(0) | 3(1) |
| 2 | 3.3(1.2) | 0(0) | 2.7(1) |
| 3 | 3.3(1.1) | 2.6(0.84) | 3.1(1) |
| 4 | 3.1(1.1) | 3.0(1.0) | 2.9(1) |
| 5 | 0(0) | 3.3(1.2) | 2.7(1) |
| 6 | 0.8(0.26) | 2.0(0.65) | 3.1(1) |
| C | 1.3(0.45) | 1.8(0.62) | 2.9(1) |