

Surface Structure of Ni species on TiO₂(110) by Polarization-dependent Total Reflection Fluorescence EXAFS (PTRF-EXAFS)

Yuichiro KOIKE¹, Kaoru IJIMA², Keisuke FUJIKAWA¹, Wang-Jae CHUN^{1,3},
Kiyotaka ASAKURA¹, and Yasuhiro IWASAWA⁴

¹Catalysis Research Center Hokkaido University and ³CREST-JST, Kita 21-10, Kita-ku, Sapporo 001-0021, Japan

²Department of Electronic Engineering, Yamanashi University
Takeda, Kofu 400-8510, Yamanashi, Japan.

⁴Department of Chemistry, Graduate School of Chemistry, The University of Tokyo, Hongo, Tokyo 113-0033, Japan..

Introduction

Metal-oxide interaction has been widely studied because it is one of important issues in many fields such as catalysts, sensors, and electronic devices. Development in SPM (Scanning probe microscopy) and surface X-ray technique have provided the registry, morphology and texture of the deposited metal. However, the problem about the bond structure between the metal and metal oxide is still under debate. We have not had sufficient answers to the following fundamental questions, yet:

- 1) Do metal atoms preferably interact with O²⁻ ?
- 2) Or do metal atoms interact with cation?

Polarization-dependent surface EXAFS is a suitable technique and we have determined the structures of the Cu and the Mo oxide on TiO₂ (110) by this technique [1, 2]. In this paper we will report the structure of Ni on TiO₂(110) surface at low coverage to get an answer to the questions described above.

Experimental

A TiO₂(110) surface was cleaned by Ar⁺-sputtering and 873 K-annealing cycles which gave a clean (1x1) LEED pattern. The Ni was evaporated from a tungsten filament which was wrapped with a Ni wire. The amount of Ni was monitored by XPS. Polarization dependent XAFS was measured at BL9A beam line in a total reflection fluorescence mode. The sample was kept under 10⁻⁸ Pa. The fluorescence X-ray was detected by a Canberra 19-element SSD.

Results and Discussion

Figure 1 shows the PTRF-XAFS oscillations for 0.02, 0.03, 0.3 ML. Envelope of the EXAFS oscillations of 0.02 and 0.03 ML indicated the presence of Ni-O bonding while 0.3 ML showed mainly Ni-Ni bonding. At each coverage, the oscillations from the parallel directions e.g. [001] and [1 $\bar{1}$ 0] directions were similar. In contrast, there was clear polarization-dependence between parallel and perpendicular; [110] directions. For 0.03, 0.02 ML, the larger amplitude in [110] direction was observed. It might be corresponding to the larger contribution of Ni-O in this direction. These results gave us a clear answer to

the question described above, that Ni atoms preferably interact with O²⁻, not with Ti⁴⁺. This answer was the same as in case of Ni on α -Al₂O₃ (0001) surface where Ni atoms dispersed monoatomically on the 3-fold oxygen site and no Ni-Ni bond was detected at 0.04 ML[3]. However, Ni-Ni distance was found in Ni/TiO₂(110) at 0.03 ML. This may be due to the fact that there is no oxygen sites on the TiO₂(110) terrace which can provide 3 fold adsorption site for Ni without the close contact of Ti⁴⁺ cations. The adsorption site of Ni at 0.02 ML might be the defect sites such as step sites which has no Ti nearest neighbor. The adsorption site will be saturated around that coverage and Ni-Ni formation was observed. This finding is surprising and also important. Many surface scientists especially working with STM techniques often postulate that the adsorption site of metal atoms on TiO₂(110) should be 5-fold Ti⁴⁺, though theoretical works say metal preferably adsorbs on oxygen sites. Thus the model structures given by STM must be revised so as to be consistent with XAFS observations and theoretical predictions.

References

- [1] W.-J. Chun, *et al.*, *J.Phys.Chem.* **102**, 9006 (1998).
- [2] Y. Tanizawa, *et al.*, *J.Synchro.Rad* **8**, 508 (2001).
- [3] K. Ijima *et al.*, *Chem,Phys.Lett.*, **384**, 134 (2004).

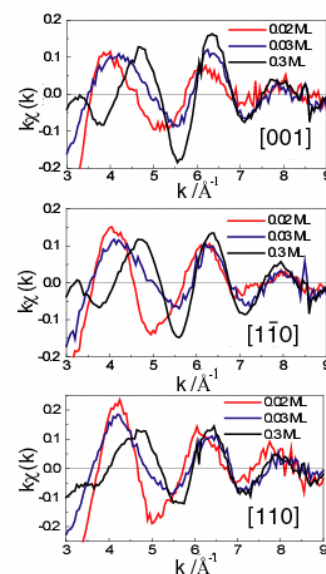


Fig. 1 PTRF-EXAFS oscillations of 0.02, 0.03 and 0.3 ML Ni on TiO₂ (110).