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Metal Structure on the Defected TiO_2(110) Surface

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Introudction

Metal catalyst is often used as nano particles stabilized by the high surface area oxide supports like TiO_2, SiO_2 and Al_2O_3. Metal nanoparticles are chemically interacting with the supporting oxides and the electronic structures of the nanoparticles are modified. But the nature of the chemical interaction is still veiled in mystery because we have no tool to obtain the metal-oxide interaction directly. Recently we have developed polarization dependent fluorescence XAFS(PTRF-XAFS) which enables us to determine the metal-oxide bonding information directly. TiO_2 (110) is the most well known oxide and metals are put on this surface. In our previous paper we carried out PTRF-XAFS measurements on the Ni on a flat TiO_2 (110) surface and found Ni was fixed at the oxygen atoms of the step edge at low coverage while the self-regulated cluster with Ni-O bond at 0.22 nm was formed at high coverage.[1-3] However, many papers have reported that the oxygen defect of TiO_2 (110) has a strong interaction with metals where Ni-Ti bond should be present. We investigated defective surface which was prepared by sputtering and low temperature annealing in order to confirm the Ni defect interaction. We found that Ni structure was modified in the presence of defect but we do not obtain any evidence for the formation of Ni-Ti bond.

Experimental

TiO_2 (110) surface was cleaned by Ar^+ ion sputtering and annealed at 873 K. After obtaining a clean (1×1) LEED pattern, we sputtered Ni with an Ar^+ ion but annealed at 673 K in order to obtain a defective surface. Such treatment gave a diffuse LEED pattern. Ni was deposited on the TiO_2 (110) surface by a vacuum evaporation. PTRF-XAFS was measured at Photon Factory's BL-9A in the three different polarization directions under ultra high vacuum. [2,3] The Si(111) double crystal monochromator was used and the fluorescence signal was detected by a 19 element SSD. The data analyses were carried out by REX 2000.

Results

Fig. 1. shows the PTRF-XAFS spectra for Ni/TiO_2 (110). The coverage was about 0.05 ML. The XAFS oscillation of Ni foil was given as a reference.

We found polarization dependence in the spectra. If the Ni-Ti interaction was present, Ni oscillation in the [110] direction (perpendicular polarization) should involve the Ni-Ti interaction but curve fitting analyses indicated that the Ni-O interaction between the Ni and support surface. In contrast the oscillation in the [001]. The analyses indicated the Ni-Ni bonding with its coordination number 1.5 The results indicated that the Ni trimer aligned along the [001] was selectively formed on the TiO_2 (110) surface. The defect may prevent the migration of Ni species and rather small cluster was formed on the surface. We are now carrying out more detailed analysis

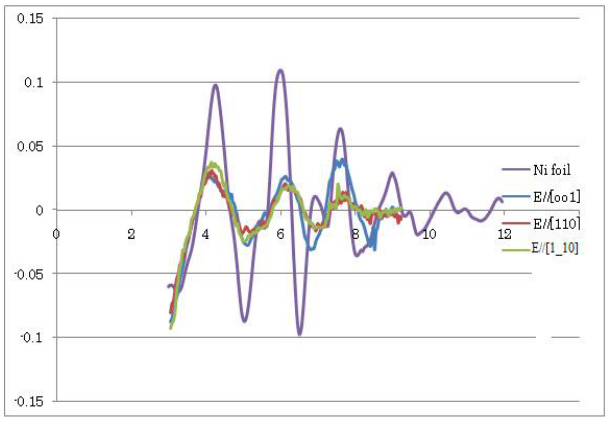

Fig.1 Polarization dependent XAFS oscialltaions for the sample two 0.07ML

References

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[3] Y. Koike, et al. J.Phys.Chem.C. **112**, 4667 (2008).