

Atomic and electronic structures of intermetallic compound catalysts

Kazuki NOZAWA

Department of Physics and Astronomy, Kagoshima University
1-21-35, Korimoto, Kagoshima 890-0065

In this fiscal year we have studied the initial stage of oxidation of Ni₃Al(210) and PdZn(111) surfaces. All calculations are carried out using VASP with the PAW method and the PBE exchange-correlation functional.

It was reported that Ni₃Al is highly active for hydrogen production from methanol and methane, and its catalytic performance is considered to be attributed to the selective oxidation and hydroxylation of Al and the formation of metallic Ni particles at low oxygen partial pressures[1]. An X-ray photoelectron spectroscopy study shows Al oxide is formed preferentially in the beginning of the oxidation process, and Ni oxides start to form at 1.6 ML oxygen coverage[2]. We first searched for the stable adsorption sites at 0.25 and 0.5 ML. In both cases, it turned out that the most stable adsorption site is a pseud-threefold site surrounded by two Al atom at the top layer and one Ni atom at the second layer. The adsorption geometry is similar to the result reported for NiAl(110)[3], but this structure is not consistent with the XPS experiment showing no sign of Ni oxides formation at this coverage. Inspired by the previous study[3], we introduced some antisite defects in the oxidized surface, and it is found that antisite defect stabilizes the surface when they form a specific structure. According to the simulated STM images using the Tersoff-Hamann approximation, this structure shows a unique image easily distinguished from other structures with different antisite arrangement or without the defect.

Although pure Pd is not active for methanol steam reforming (MSR), PdZn exhibits comparable catalytic activity and selectivity to the conventional Cu catalyst in MSR. Recently, some groups reported that ZnO formed during the reaction is essential for the catalytic performance of PdZn. However, this is not straightforward because Zn has no d-state around the Fermi level implying the chemical inactivity of ZnO. We first determined the stable adsorption structure of oxygen on PdZn(111), and investigated the electronic structure of this system. We previously reported that bulk PdZn has a similar electronic structure to Cu[5], but the Pd 4d-band of PdZn is broadened when oxygen is adsorbed. It was also found that Zn-d states appear below the Fermi level when oxygen adsorbs on the most stable site.

References

- [1] D. H. Chun *et al.*, J. Catal. **243** (2006)99, Y. Xu *et al.*, J. Phys. Chem. C **114** (2010)6047.
- [2] Y. Xu *et al.*, Appl. Surf. Sci., **39** (2017)18.
- [3] A. Y. Lozovoi *et al.*, Phys. Rev. Lett., **85** (2000)610.
- [4] K. Yamaguchi, Master Thesis (Kagoshima University, 2020).
- [5] A. P. Tsai *et al.*, Acc. Chem. Res. **50** (2017)2879.