[Letter]

**Oxygen Sensitivity of Intermetallic Compound Surface
Comprising Early Transition Metal**

Shinya Furukawa*, Genki Nishimura, and Takayuki Komatsu*
Course of Chemistry, School of Science, Tokyo Institute of Technology,
2-12-1 Ookayama, Meguro-ku, Tokyo 152-8551, JAPAN

(Received April 22, 2016)

Pd-based intermetallic compounds having early transition metals (Pd_3M ; $\text{M} = \text{Nb}$, Ti , and Zr) prepared by arc melting were characterized by X-ray photoelectron spectroscopy. When the ingot of Pd_3Zr was ground in N_2 with an oxygen concentration below 1 ppb, a large part of the surface maintained its original intermetallic state; however, for Pd_3Nb and Pd_3Ti , their surfaces were completely oxidized even in the N_2 atmosphere. This indicates the remarkably high oxygen sensitivity of the intermetallic compounds with early transition metal.

Keywords: Intermetallic compound, Early transition metal, Oxygen sensitivity, XPS, Palladium

1. Introduction

Intermetallic compounds are stoichiometric compounds of more than one metal element, which typically have specific crystal and electronic structures compared with those of the parent metals¹⁾. The use of intermetallic compounds as catalysts has received increasing attention²⁾. Intermetallic compounds that are expected to be promising catalysts comprise catalytically active elements, such as later transition metals (*e.g.*, Pt , Pd , Rh , Ni , and Co). Therefore, the counterpart metal should be an early transition or typical metal that is set apart from the later transition metals in the periodic table. Intermetallic compounds having typical elements have been widely studied and revealed as effective catalytic materials; for example, Pt_3Sn for alkane dehydrogenation³⁾, Pd_3Pb for methyl methacrylate synthesis⁴⁾ and amine oxidation⁵⁾, and PdGa for acetylene semihydrogenation⁶⁾. On the contrary, intermetallic compounds having early transition metals have rarely been studied as catalysts; hence, they are of great interest for catalytic chemistry.

This may be partly due to their surfaces being labile in air. As early transition metals have significantly high ionization tendencies, the surface of their intermetallic compounds seems to easily undergo oxidative decomposition in the presence of oxygen to form oxide phases. Moreover, such oxides are hard to be reduced by gaseous hydrogen at high temperatures (400–800 °C), the typical pretreatment for metallic catalysts. Therefore, experimental procedures, including the catalyst preparation and its transfer into a reactor or spectrometer, should be performed under oxygen-free conditions, such as under an ultra-high vacuum or pure inert gas atmosphere.

In this study, we prepared several Pd-based intermetallic compounds having early transition metals (Pd_3M , $\text{M} = \text{Ti}$, Zr , and Nb) and characterized their surface under an inert atmosphere with ppb levels of oxygen. We report remarkably high oxygen sensitivity of the early transition metals at the surface of the intermetallic compounds.

2. Experimental Details**2.1. Glove Box Conditions**

The inert gas atmosphere was prepared using an UNICO UL-800A glove box equipped with an MF-100 circulating gas purifier (for deoxygenation) and TORAY SD-450 O_2 sensor (range: 1 ppb–100 %). Dry nitrogen (Taiyo Nippon Sanso, 99.99995 %) was used as an inert gas. Standard working conditions typically result in an oxygen concentration of 500–600 ppb,

DOI: dx.doi.org/10.1627/jpi.59.160

前周期遷移金属を含む金属間化合物表面の酸素敏感性
古川森也*、西村元樹、小松隆之*

東京工業大学理学院化学系
152-8551 東京都目黒区大岡山 2-12-1

* Corresponding author, E-mail: furukawa.s.af@m.titech.ac.jp
E-mail: komatsu.t.ad@m.titech.ac.jp

which may be attributed to the purity of the supplied N_2 . In this study, ISO A-500HS oxygen absorbers (iron powder) were used to minimize oxygen concentration and air exposure. First, the supplied N_2 was purified through oxygen absorbers placed at the N_2 inlet. Second, the butyl rubber gloves were overlapped with extra gloves to prevent exposure of the sample to percolated oxygen. Several oxygen absorbers were put between the parent and extra gloves to trap the percolated oxygen. These efforts allowed an oxygen concentration below 1 ppb (indicated as 0 ppb) during experimental procedures.

2.2 Catalyst Preparation

Pd-based intermetallic compounds (Pd_3M , $M = Ti, Zr, Nb$) were prepared by arc melting of a mixture of Pd (Kojundo Kagaku, 99.9 %) and the second metal (Soekawa Chemical, 99.9 %) under an Ar atmosphere using a SANVAC SV-A434 vacuum arc-melting furnace. The resultant ingots were transferred into the glove box and ground into a fine powder. For grinding, the oxidized shell part of the ingot was discarded and the core part was collected as a naked sample. As a control experiment, grinding in air with a subsequent reduction treatment was also conducted. The ingot of the intermetallic compound that was ground in the air was treated by H_2 in a separable glass tube connected to a gas circulation system (under 60 kPa H_2 at 800 °C for 1 h). The sample in the sealed glass tube was transferred into the glove box without exposure to air.

2.3. Characterization

X-ray photoelectron spectra (XPS) of the intermetallic compounds were recorded with an ULVAC PHI 5000 VersaProbe spectrometer. The ground catalyst powder was pressed into a pellet and placed on a sample holder for the spectrometer in the glove box. This sample holder was transferred into the spectrometer without being exposed to air using a portable transfer vessel. Spectra were obtained with an Al $K\alpha$ X-ray source using C 1s as a reference for binding energy. The crystal structures of the prepared intermetallic compounds were examined in the air by powder X-ray diffraction (XRD) with a Rigaku RINT2400 using a Cu $K\alpha$ X-ray source.

3. Results and Discussion

The powder ground in air was analyzed by X-ray diffraction. For all samples, the desired intermetallic phases (Pd_3Nb , Pd_3Ti , and Pd_3Zr ; space group, $I4/mmm$, $P6_3/mmc$, $P6_3/mmc$, respectively) were formed in single phases (Fig. 1). The samples were then characterized by

X-ray photoelectron spectroscopy (XPS). Prior to the measurement, the sample ground in air was treated under H_2 at 800 °C for 1 h. The sample was moved into the spectrometer using a portable transfer vessel

Vertical lines indicate the references: ICDD PDF; #00-042-1257 (Pd_3Nb), #00-035-1361 (Pd_3Ti), #01-072-2945 (Pd_3Zr).

Fig. 1 XRD Patterns of Pd-based Intermetallic Compounds

(a) Ground in air, followed by H_2 treatment at 800 °C for 1 h. (b) Ground in N_2 in the presence of <1 ppb O_2 . (c) The sample (b) after sputtering.

Fig. 2 Nb 4d XPS of Pd_3Nb

without being exposed to air.

Figure 2 shows the Nb 3d XPS of Pd₃Nb after various treatments. The sample ground in air (a) shows dominant peaks at 207.4 eV and 210.2 eV, assigned to fully oxidized Nb⁵⁺ (Nb₂O₅)^{7,8}. A small portion of Nb⁴⁺ (NbO₂; 205.0 eV and 208.9 eV)⁷ and Nb²⁺ (NbO; 203.8 eV and 206.4 eV)⁸ species were also observed. These results demonstrate that the surface Nb atoms comprising Pd₃Nb are easily oxidized by air and that the oxidized species cannot be reduced to the metallic state by hydrogen treatment, even at 800 °C. The Pd₃Nb sample ground in N₂ (b) showed dominant peaks assigned to NbO. After sputtering of the oxidized shell (c), new peaks appeared at 203.8 eV and 205.6 eV, corresponding to intermetallic Pd₃Nb. No contribution of Pd₃Nb was observed in the unsputtered sample, indicating that the surface Nb atoms comprising Pd₃Nb were completely oxidized, even in the presence of ppb level oxygen. The corresponding Pd 3d XPS showed that the Pd species was in its metallic state for each sample (data not shown). Based on these results, it can be said that aerobic oxidation of Pd₃Nb resulted in decomposition to a composite of metallic Pd and Nb oxides.

Figure 3 shows the Ti 2p XPS of the Pd₃Ti intermetallic compound. Similarly to Pd₃Nb, the sample

(a) Ground in air, followed by H₂ treatment at 800 °C for 1 h. (b) Ground in N₂ in the presence of <1 ppb O₂. (c) The sample (b) after sputtering.

Fig. 3 Ti 2p XPS of Pd₃Ti

ground in air (a) showed dominant peaks assigned to Ti⁴⁺ (TiO₂: 458.8 eV and 464.5 eV)⁹. The sample ground in N₂ (b) showed various peaks corresponding to TiO₂, Ti₂O₃ (456.8 eV and 462.5 eV)⁹, TiO (455.2 eV and 461.1 eV)⁹, and intermetallic Pd₃Ti (454.9 eV and 460.8 eV)¹⁰. Considering that the Pd₃Ti phase has a minor contribution to the whole spectrum, the outermost surface of the sample seems to be covered with the oxide phases. Although the TiO₂ phase almost disappeared upon sputtering (c), a significant amount of Ti₂O₃ phase remained in addition to the bulk Pd₃Ti phase. The Pd 3d XPS of Pd₃Ti showed peaks assigned to monometallic Pd or intermetallic Pd₃Ti (data not shown). The absence of Pd oxide phases indicates the oxidative decomposition of the intermetallic Pd₃Ti into metallic Pd and Ti oxides, as observed for Pd₃Nb. Thus, for Pd₃Nb and Pd₃Ti, the surface of the intermetallic compound could not tolerate the ppb level oxygen, demonstrating their remarkably high oxygen sensitivity. Conversely, for Pd₃Zr, a different situation was observed. As shown in **Fig. 4**, although the sample ground in air showed peaks of ZrO₂¹¹, the sample ground in N₂ showed a large contribution of peaks that correspond to the intermetallic Pd₃Zr phase. No divalent ZrO species¹¹ were observed in this spectrum. These results indicate that a large part of the Pd₃Zr

(a) Ground in air, followed by H₂ treatment at 800 °C for 1 h. (b) Ground in N₂ in the presence of <1 ppb O₂. (c) The sample (b) after sputtering.

Fig. 4 Zr 3d XPS of Pd₃Zr

surface keeps its original state under the N₂ atmosphere with a ppb level of oxygen. Thus, the sensitivity to oxygen of the intermetallic compounds depends on the individual intermetallic compounds.

4. Conclusion

In summary, we performed XPS analysis of Pd-based intermetallic compounds having early transition metals that were prepared under a ppb-level oxygen atmosphere. The obtained results suggest an intrinsic difficulty in maintaining the original state of the intermetallic compound surface having early transition metals using standard glove box techniques. A surface science technique such as *in-situ* cutting of an intermetallic crystal under high vacuum would be useful for studying the non-oxidized compounds; however, such a procedure is hardly applicable to commonly used catalytic conditions. Therefore, a much more strict protocol allowing a ppt level oxygen with minimum percolation through the gloves may be required for glove box techniques to be valid for studies dealing with intermetallic compounds having early transition metals as catalysts.

References

- 1) Westbrook, J. H., Fleischer, R. L., "Magnetic, Electrical and Optical Properties and Applications of Intermetallic Compounds," Wiley, New York (2000).
- 2) Komatsu, T., Onda, A., *Catal. Surv. Asia*, **12**, 6 (2008).
- 3) Furukawa, S., Tamura, A., Ozawa, K., Komatsu, T., *Appl. Catal. A: General.*, **469**, 300 (2014).
- 4) Yamamatsu, S., Yamaguchi, T., Yokota, K., Nagano, O., Chono, M., Aoshima, A., *Catal. Surv. Asia*, **14**, 124 (2010).
- 5) Furukawa, S., Suga, A., Komatsu, T., *Chem. Commun.*, **50**, 3277 (2014).
- 6) Armbruster, M., Kovnir, K., Behrens, M., Teschner, D., Grin, Y., Schlögl, R., *J. Am. Chem. Soc.*, **132**, 14745 (2010).
- 7) Bahl, M. K., *J. Phys. Chem. Solids*, **36**, 485 (1975).
- 8) Jha, M., Ramanujachary, K. V., Lofland, S. E., Gupta, G., Ganguli, A. K., *Dalton Trans.*, **40**, 7879 (2011).
- 9) Saied, S. O., Sullivan, J. L., Choudhury, T., Pearce, C. G., *Vacuum*, **38**, 917 (1988).
- 10) Bzowski, A., Sham, T. K., *Phys. Rev. B*, **48**, 7836 (1993).
- 11) Degonzalez, O., Garcia, E. A., *Surf. Sci.*, **193**, 305 (1988).