

In-situ valence band UPS of lithium nickel oxide for selective methane oxidation

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Introduction

Lithium nickel oxide (LiNiO_2) has been studied as a model catalyst for an oxidative coupling of methane (OCM). High temperature performance of $\text{Li}_x\text{Ni}_{2-x}\text{O}_2$ ($0 \leq x < 0.65$) mainly oxidize methane to carbon dioxide, while $\text{Li}_x\text{Ni}_{2-x}\text{O}_2$ ($0.65 \leq x \leq 1.0$) selectively convert methane to C_2 hydrocarbon such as ethane or ethylene [1]. There are anticipated to be two kinds of surface function which are a partial oxidation site and a perfect oxidation site. On the other hand, the structure of $\text{Li}_x\text{Ni}_{2-x}\text{O}_2$ at $x \approx 0.65$ changed hexagonal type from cubic type, so it was made to be a structural lattice boundary. It was suggested that the hexagonal layered structure of LiNiO_2 related with the formation of the selective activation sites. Then, we have investigated the valence band structure of LiNiO_2 . The upper valence band UPS has five structures which are discriminated at $E_b < 15$ eV as denoted by characters A-E in Figure 1-(a). These valence band structures were assigned to two Ni3d states (A and B), two O2p states (C and D) and Ni3d satellite (E). It was suggested that the proportion of the two O2p and two Ni3d states were related to the function of the selective methane oxidation [2]. In this report, ultraviolet photoelectron spectra (UPS) of LiNiO_2 were measured at high temperature and low pressure with CH_4 and/or O_2 , in-situ UPS measurement, in order to discuss the electronic structure on the selective methane oxidation.

Experimental

Polycrystalline LiNiO_2 sample were prepared by solid phase reaction. The mixtures of LiNO_3 and Ni(OH)_2 were ground, pelletized and heated at 873 K and 1073 K in an Alumina tube furnace. The LiNiO_2 sample was identified by means of X-ray diffraction measurement system (RINT2000, Rigaku Co. Ltd). The measurements of ultraviolet photoelectron spectra were carried out at the beam line 7A, 7B in KEK-PF. The base pressure of the measurement chamber was 5×10^{-7} Pa. The sample pellets were fixed on Ta substrate that was also utilized as a resistant heater. The surface purification of the samples was carried out by the argon ion sputtering. The measurements of in-situ UPS were carried out with heating at 923K and/or CH_4 gas of 5×10^{-4} Pa.

Results and Discussion

Figure 1 shows the upper valence band UPS of LiNiO_2 obtained $h\nu = 30$ eV with heating at 923K and with CH_4 gas at 923K. Five structures are discriminated in the spectra of (b) and (c) as denoted by characters A'-E'. These spectra were similarly shifted to higher binding energy. The intensity of the two Ni3d states decreased, when the sample was heated at 923K. The two O2p states C' and D' were clearly distinguishable in comparison to spectrum (a). The intensity ratio of C' and D' in spectrum (b) was almost unity. When CH_4 gas was spouted on LiNiO_2 , the intensity of lower binding energy O2p state C' was decreased clearly. Then, it seems that the lower energy O2p bonding electron of LiNiO_2 plays in dehydrogenation process of methane molecule. The role of the OCM reaction may be decided by the density and the binding energy of O2p states of surface lattice oxygen.

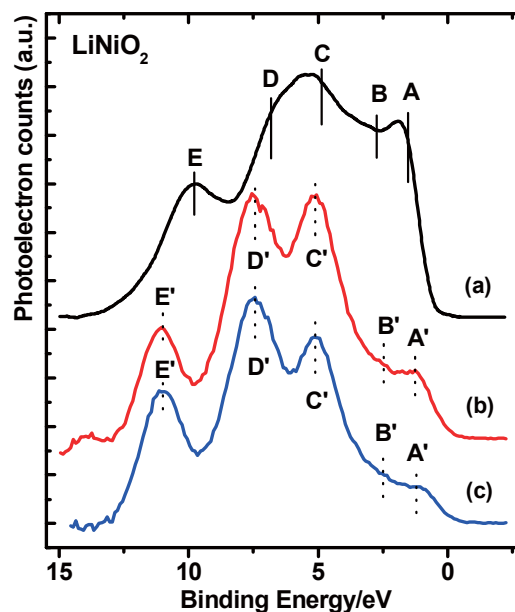


Figure 1. The valence band UPS of LiNiO_2 (a) at room temperature after argon ion sputtering [1], (b) with heating at 923K and (c) with CH_4 of 5×10^{-4} Pa at 923K. The energy zero is the top of valence band.

References

- [1] T. Miyazakia et al., J. Jpn. Appl. Phys., 38, 51 (1999).
- [2] T. Miyazakia et al., Appl. Cat. A, 338, 79 (2008).