

In-situ XPS of lithium nickel oxide for selective methane oxidation

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Introduction

Hexagonal lithium nickel oxide (H-LiNiO₂) has a catalytic active for the oxidation coupling of the methane (OCM). High temperature performance of H-Li_xNi_{2-x}O₂ (0 ≤ x < 0.65) with hexagonal structure mainly oxidize methane to carbon dioxide while C-Li_xNi_{2-x}O₂ (0.65 ≤ x ≤ 1.0) with cubic structure convert methane to C₂ hydrocarbon such as ethane or ethylene. It was suggested that the hexagonal layered structure in solid solution related with the formation of the selective activation sites. In this study, we prepared H-LiNiO₂ and their partial metal substitution compounds: hexagonal Li-Ni mixed metal oxides (H-LiNi_{0.95}M_{0.05}O₂; M=Al, Mn, Ti) and measured X-ray photoelectron spectra (XPS). Specifically, the XPS of these samples were measured at 1023K under CH₄ gas. We discussed the relationship between the electronic structure of the surface lattice oxygen and the selective oxidation of methane.

Experimental

Polycrystalline H-LiNiO₂ and H-LiNi_{1-x}M_xO₂ (M=Al, Mn, Ti, x=0.05) were prepared by solid phase reaction. The mixtures of LiNO₃ and metal nitrate were mixed, pelletized and heated at 1073 K in an alumina tube furnace. The synthesized samples were identified by means of X-ray diffraction measurement system (RINT2000, Rigaku Co. Ltd). The XPS were measured at BL7A of KEK-PF. The base pressure of the XPS measurement chamber was 5 × 10⁻⁷ Pa. The sample pellet was fixed on Ta metal substrate which was also utilized as heater equipment. The XPS measurements of these samples were carried out at 1023K under CH₄ gas of 5 × 10⁻³ Pa.

Results and Discussion

Figure 1 shows the XPS of O1s core level of LiNi_{0.95}M_{0.05}O₂ (M=Al, Mn, Ti), LiNiO₂ and NiO at 1023K. There is a peak of NiO but are two peaks of H-LiNiO₂ and H-LiNi_{1-x}M_xO₂ (M=Al, Mn, Ti, x=0.05), which are labelled A and B, in this region. Before the comparison of these spectra, each XPS is normalized at the peak top position of structure A. The partial metal substitution changes the intensity ratio of peak A (531eV) and B (528eV). The C₂-selectivity of the samples was the order of LiNi_{0.95}Al_{0.05}O₂ ≥ LiNiO₂ ≈ LiNi_{0.95}Mn_{0.05}O₂ > LiNi_{0.95}Ti_{0.05}O₂. The larger the intensity ratio of A/B, the more the C₂-selectivity may be high. It is possible that the peak A and B may be corresponding to a partial oxidation site and a perfect oxidation site, respectively.

Figure 2 shows a intensity change of the XPS O1s of LiNiO₂ under CH₄ gas of 5 × 10⁻³ Pa at 1023K. The initial

C₂-selectivity of virgin sample of LiNiO₂ has 99%, however, it rapidly decrease to 68%. The XPS O1s in Figure 2 indicate to decrease the intensity of peak A and increase that of peak B. The decrease of C₂-selectivity corresponds to change from a generation site of C₂-hydrocarbon to that of carbon dioxide. These findings suggest that the peak A is partial oxidation site (soft oxidant) and the peak B is perfect oxidation site (hard oxidant) of methane.

From the XPS O1s of H-LiNi_{1-x}M_xO₂ (M=Al, Mn, Ti, x=0.05) and H-LiNiO₂, it suggests that the partial oxidation site on metal oxide surface formed in the hexagonal layered Li-M-O lattice. The selective oxidation of methane might be decided by the formation of two oxygen states and its proportion on metal oxide surface.

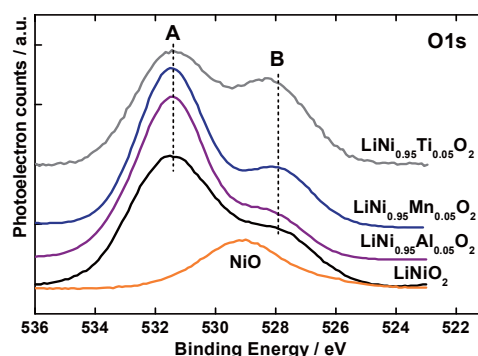


Figure 1. XPS O1s of LiNi_{0.95}Al_{0.05}O₂, LiNi_{0.95}Mn_{0.05}O₂, LiNi_{0.95}Ti_{0.05}O₂, LiNiO₂ and NiO at 1023K.

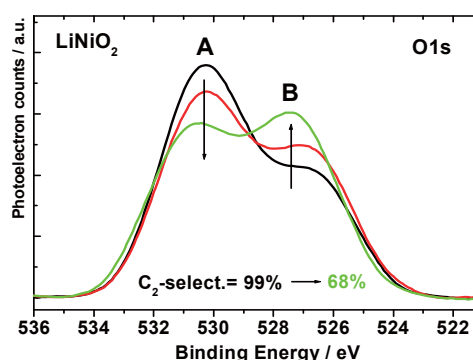


Figure 2. The intensity change of XPS O1s of virgin sample LiNiO₂ (—) at 750°C, (—) in CH₄ after 40 min and (—) in CH₄ after 100 min at 1023K. The UPS measurement was carried out under 5 × 10⁻³ Pa of CH₄.

References

- [1] T. Miyazaki, et al., Appl. Cat. A, 338, 79 (2008).
- [2] T. Miyazaki, et al., PF Activity Report 2009.