On the behavior of the selective oxidation by LiNiO$_2$: Oxidative coupling of methane

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Abstract—The mobility of lattice oxygen and the fine structure of Li$_x$Ni$_{2-x}$O$_2$ ($0 \leq x \leq 1.0$) were investigated by thermogravimetric analysis and extended X-ray absorption fine structure, respectively. It was proven that the lattice oxygen of LiNiO$_2$ was mobilizable under reductive and oxidative atmosphere at 1033 K. The Ni–O bond lengths in NiO$_6$ slabs markedly changed at around $x = 0.65$. The results were in good agreement with the dependence of the selectivity for the OCM reaction on Li$_x$Ni$_{2-x}$O$_2$ catalysts. It was suggested from these data that the formation of active lattice oxygen species in LiNiO$_2$ should be induced by structural distortion in NiO$_6$.

INTRODUCTION

A synthesis of ethylene by the direct conversion of methane, i.e. the oxidative coupling of methane (OCM), has great significance in developing the chemical utilization of natural gas. Catalysts used for the OCM reaction are usually composed of metal oxides; but the reducible metal oxides such as NiO are so active that methane is easily oxidized further to carbon dioxide. It has been reported that LiNiO$_2$ [1] was active for the methane coupling reaction and its selectivity was comparable to those of supported catalysts such as Li/MgO [2] and Li/Sm$_2$O$_3$ [3]. It was suggested that the formation of active oxygen species and an anisotropic structure played a role in the selective methane activation on LiNiO$_2$ in which Li$^+$ and Ni$^{3+}$ layers were alternately and regularly arranged to oxygen layers [4]. It was assumed that the lattice oxygen in metal oxide contains two kinds of oxygen species at least. Thus, the lattice oxygen of LiNiO$_2$ easily forms methyl radical from methane, and that of NiO perfectly converts methane to carbon dioxide via a methyl

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radical. These reaction processes and active sites have not been clarified, though the structural features of LiNiO$_2$ and NiO should be important for the activation of methane and the reactivity control. Since the OCM reaction is operated in the high-temperature range, it is difficult to specify the origin of this reaction in detail. It is interesting to examine the behavior of activated lattice oxygen. From a fine structural point of view, it should be expected that the structural distortion attributed to the Jahn–Teller effect and/or the difference in the ionic radius between Ni$^{2+}$ and Ni$^{3+}$ ions resulted in NiO$_6$ slabs. In the present work, we examine the behavior of the lattice oxygen at high temperature by thermogravimetric analysis (TGA) and explore the Ni–O distance by extended X-ray absorption spectroscopy (EXAFS) to understand the origin of the activated lattice oxygen on LiNiO$_2$. The examination of the Ni–O bond length within NiO$_6$ slabs should be an approach to understand the origin of activated lattice oxygen for the OCM reaction.

**EXPERIMENTAL**

Li$_x$Ni$_{2-x}$O$_2$ ($0 \leq x \leq 1.0$) were prepared by a solid-state reaction from LiNO$_3$ and Ni(OH)$_2$. The powder samples were identified from the peak intensity ratio of X-ray diffraction patterns using a powder X-ray diffractometer (Rigaku RINT2000). Thermogravimetric analysis (TGA) of LiNiO$_2$ was carried out under methane and/or oxygen gas atmosphere using a Shimadzu TGA-51. EXAFS spectra at the Ni K-edge (8333 eV) were recorded on transmission mode using a Technos EXAC820 which a Ge(220) monochromator crystal at ambient temperature and atmosphere.

**RESULTS AND DISCUSSION**

Figure 1 shows X-ray diffraction patterns of Li$_x$Ni$_{2-x}$O$_2$ ($0 \leq x \leq 1.0$). No extra reflections resulting the presence of impurities were detected. Compared with XRD patterns, it was proven that the layered structure in which Ni$^{3+}$ layers and Li$^+$ layers were alternately and regularly arranged to oxygen ion layers had been formed in Li$_x$Ni$_{2-x}$O$_2$ with the range of $x > 0.6$.

TGA profiles of LiNiO$_2$ under methane gas atmosphere are shown in Fig. 2a. This measurement was performed at 1033 K where the OCM reaction on LiNiO$_2$ proceeded selectively. When the sample was contacted with methane, there was a slight weight increase at the beginning, which was followed by a large weight loss over a prolonged time. This weight loss was attributed to the loss of the lattice oxygen of the sample and the 24 mg of the oxygen loss indicated that about a half of the lattice oxygen had been removed. Figure 2b shows the variation of weight during the re-oxidation by oxygen. It is proven that the sample had rapidly been reproduced by oxygen gas, even if the amount of 10% of all lattice oxygen had been removed by methane. By the re-oxidation, it was possible also to confirm that the crystal structure of the sample had been reproduced to LiNiO$_2$ by the XRD