Formation of Defects in Near-Surface Region over Li or Mn-Doped MgO Studied by Mg K-Edge XANES

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The near-surface region of Li or Mn-doped Mg was characterized by Mg K-edge XANES spectroscopy. The oxygen defects were formed in near-surface region when the content of Li or Mn ion is relatively low. The amount of the defects in near-surface region does not depend on the crystallinity.

A Li-doped MgO is known as a catalyst for selective oxidation of alkanes, in particular, for oxidative coupling of methane (OCM).[1-4] It is accepted that the catalytically active species for OCM are [Li^+-O^-] centers which are in equilibrium with surface O^- centers *via.* hole transport[4,5] because vacant-hole sites are formed by Li-doping in both surface and bulk. The defects in/on MgO can be investigated by electron spin resonance (ESR)[6-8] and DC conductivity.[9] In case of Mn-MgO and alkaline-doped Mn-MgO systems, the presence of defects has also been observed by ESR.[10-13] The defects in/on Li or Mn-doped MgO strongly relate to the redox catalytic activity. However, observation of vacancy site distribution over cation-doped MgO includes some difficulties. ESR is one of the useful techniques but is available for characterization of oxygen anions and/or trapped electrons. By X-Ray diffraction (XRD), crystallinity of MgO can only be evaluated. Direct observation of the structure around lattice Mg ions should be required. With this regard we employed X-Ray absorption near edge structure (XANES) spectroscopy at Mg K-edge to characterize the lattice Mg ions of cation-doped MgO. To XANES measurement, we applied a total electron yield mode sensitive to near-surface region less than 38 nm.[14,15]

A MgO sample was prepared by calcination of $Mg(OH)_2$ (Kojundo-Kagaku Kenkyusho Co.) at 873K for 3h, and followed by cooling at ambient temperature for overnight. Li- or Mn-doped MgO samples were prepared by impregnation of $Mg(OH)_2$ with aqueous solution of $LiNO_3$ or $Mn(NO_3)_2$•$6H_2O$ (Nacalai Tesque Co.) at 343K, and then evaporated at 343K to form a paste. The paste was dried at 353K for overnight and calcined at 873K for 3h. X-Ray experiment was performed at BL-7A at UVSOR, in the Institute for Molecular Science, Okazaki, Japan, with a ring energy 750 MeV and a stored current 120 - 220 mA. Each sample was mounted on a carbon-tape and attached on a beryllium-copper dynode at the first-stage of an electron multiplier placed into a vacuum chamber. The spectrum was recorded in a total electron yield mode at room temperature, using a beryl two-crystal monochromator. The photon energy was calibrated at Al K-edge (1559 eV). XRD patterns were recorded with a Rigaku Geiger-Flex 2102 X-ray diffractometer using Ni-filtered Cu-$K\alpha$ radiation. Each sample was mechanically mixed with NaCl for Li-MgO or KCl for Mn-MgO as an internal standard. In XRD patterns shown in Figure 3, diffraction peaks by the internal standard was removed.

XANES spectra of Li- and Mn-doped MgO samples are shown in Figure 1. In case of Li-doped MgO, the spectra of high Li-doped samples (above 5.0 wt%) are almost similar to that of MgO shown in Figure 2, indicating that rock salt MgO structure is dominant in near-surface region. On the other hand, the spectrum for the sample with 2.5 wt% Li-doping is different from those of MgO and higher Li-doped samples. But the 2.5 wt% Li-MgO includes bulk MgO with a high crystallinity confirmed by XRD. Therefore, structural change should be brought about in near-surface and coexistence of rock salt and other structure can

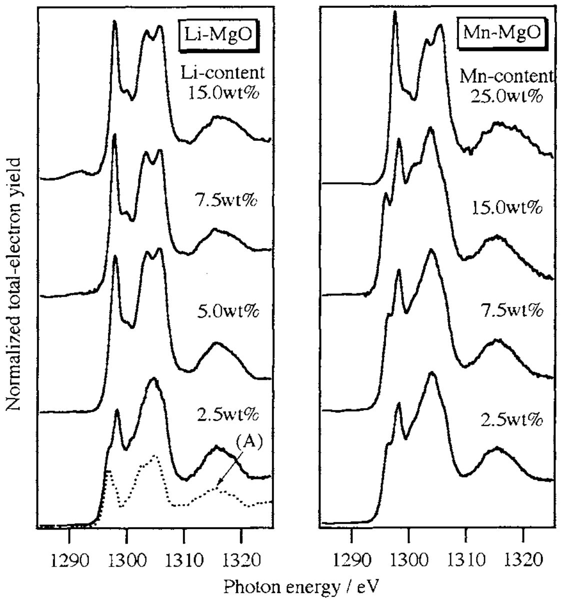

Figure 1. Mg K-edge XANES of Li- (left) and Mn- (right) doped MgO. A dotted line (A) is a subtracted spectrum of MgO with 55% intensity from 2.5 wt% Li-MgO.

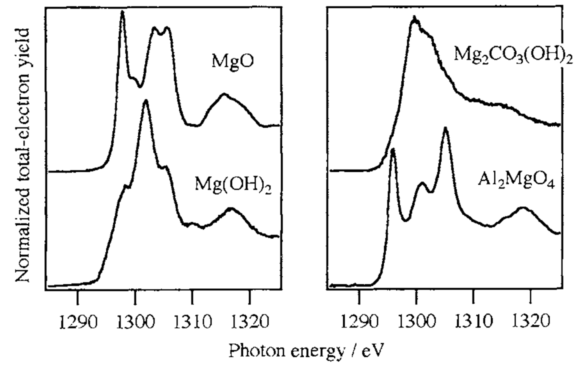

Figure 2. Mg K-edge XANES of reference compounds.

be realized by a limited amount of Li doping. In XANES spectrum of 2.5 wt% Li-MgO, a shoulder peak at 1297 eV should be noted which characterizes the unknown species in near-surface. In XANES spectra of typical metal compounds, it has been reported that the position of an edge peak can be found at lower energy side when the cations are in lower coordinations.[16,17] This characteristics is also found for Mg compounds as shown in Figure 2. The spectrum of Al_2MgO_4, which has a spinel structure where a Mg cation occupies a tetrahedral site, exhibits an edge peak at 1296 eV. Therefore, the shoulder peak at 1297 eV suggests that the unknown species involves coordinatively unsaturated Mg cations. On the basis of the assumption that the spectrum of 2.5 wt% Li-MgO consists of those of rock salt MgO and the unknown species, we tried to extract the spectral component due to the unknown species by subtraction of weighted MgO-based component from the spectrum of 2.5 wt% Li-MgO. An example of the resultant spectrum is depicted as a dotted curve (A) in Figure 1, which was obtained by subtraction of 0.55-weighted MgO spectrum. Other weight gave obscure or unlikely spectrum. An intriguing point is that the feature of the spectrum is very similar to that of MgO although it is shifted by 1 eV lower than that of MgO. The feature was quite different from those of $Mg(OH)_2$, $Mg_2CO_3(OH)_2$, and Al_2MgO_4 in Figure 2. Because XANES feature is dominated by local structure around an absorption atom, the similarity of the spectral feature means the similar structure. A Mg atom in the unknown species is presumably located at a specific site like an edge or a corner which can be formed adjacent to oxygen vacancies. The formation of the vacant defects and the introduction of Li can enhance the base strength which stabilizes the lowest levels of unoccupied states resulting in the shift of the XANES spectrum of the unknown species to low energy side.

Similar phenomenon was observed for Mn-doped MgO. At lower Mn contents between 2.5 and 15.0 wt%, each spectrum contains both the components of MgO and the unknown species while at 25.0 wt% Mn-doping, the spectrum consists of MgO component mainly. We also guess that the oxygen defects in near-surface are present at lower Mn-doping.

XRD patterns are shown in Figure 3. In case of Li-MgO, a crystallinity of MgO is enhanced with Li-doping up to 5.0 wt%. This supports the reports by many groups that addition of small amount Li ions to MgO promotes crystallization of MgO and a steep decrease in surface area. At high Li contents above 7.5 wt%, the MgO crystallinity is reduced and $LiOH•H_2O$ and Li_2CO_3 were detected. Combining the the results of XANES and XRD, it is suggested that doped Li promotes the formation of oxygen defects which are localized in near-surface at a low content (2.5 wt%) and at higher contents, Li may exist not only in near-surface but also in the bulk, and a crystallinity of MgO is reduced. But defects in near-surface are hardly formed at higher Li contents. Lunsford et al. reported that intensity of an ESR signal of $[Li^+-O^-]$ sites increased with an increase in Li-doping below 15.0 wt%, which are present in near-surface.[18] Therefore, we proposed that the formation of the $[Li^+-O^-]$ site is accompanied by the appearance of oxygen defects at lower Li-doping, and at higher Li- doping, it dissolved into MgO.

In case of Mn-MgO, XRD patterns exhibit similar tendency to those of Li-MgO. At contents below 5.0 wt%, the crystallinity of MgO is enhanced with Mn-doping while at contents above 5.0 wt%, crystallinity of MgO is reduced and coexistence of MgO and Mg_6MnO_8 is found. From the results of XRD and XANES, we suppose that oxygen defects are generated during the formation of Mg_6MnO_8 which contains a similar local structure to MgO.

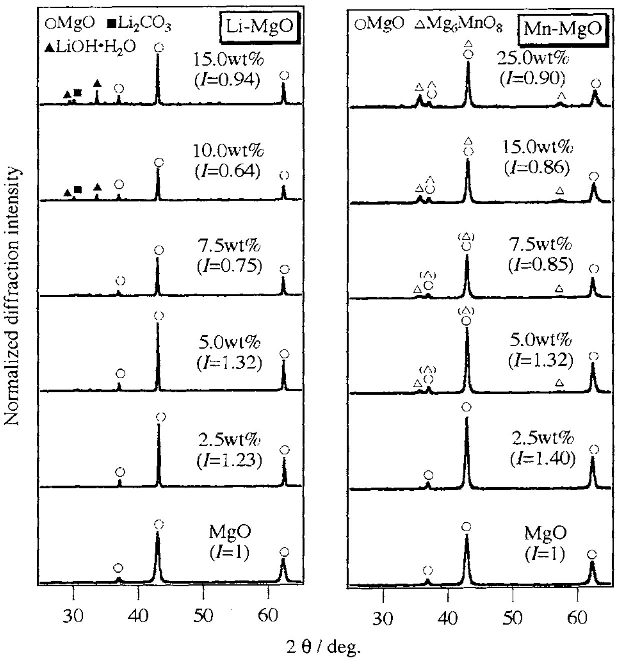

Figure 3. XRD patterns of Li- (left) and Mn- (right) doped MgO. *I* shows the diffraction intensity ratio of sample *vs.* MgO.

It is concluded that structural change of MgO in near-surface is brought about at a low content of Li- or Mn- doping. The critical doping amount lies between 2.5 - 5.0 wt% (13.0 - 23.4 atom%) in Li-MgO, and between 15.0 - 25.0 wt% (11.4 - 19.7 atom%) in Mn-MgO. The atomic range is similar to each other. The amount of defects does not depend on the crystallinity of MgO.

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