XANES study of Li-MgO and Li-La_2O_3-MgO catalysts for oxidative coupling of methane

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To characterize the defect sites in the near-surface and bulk phase of Li-MgO and Li-La_2O_3-MgO, XANES at Mg K-edge and La L_3-edge was applied. For Li-MgO, it can be suggested that Li doping at a low content (2.5 wt%) brings about the formation of defect species only in the near-surface. This is due to the localization of doped Li ions in the surface, and thus the catalytically active species containing [Li^+-O^-] type center exist in the surface region. After OCM reaction, the defect species are formed in the near-surface over MgO and Li-MgO. By addition of La_2O_3 to Li-MgO (La/(Mg+La)=0.25), the structural change during the reaction is almost suppressed in the surface. In addition, the Li-La_2O_3-MgO shows higher C_2 selectivity than Li-MgO.

Keywords: La L-XANES; Mg K-XANES; Li-La_2O_3-MgO; defect species

1. Introduction

Li-promoted MgO (Li-MgO) catalyst has been used and applied widely in the selective oxidation of alkanes. In particular, Li-MgO catalysts for oxidative coupling of methane (OCM) reaction have been studied by many workers in 1980s (Ito *et al.*, 1985) because of high reactivity and C_{2+} selectivity (Lee *et al*., 1988). Catalytic active species of Li-MgO are recognized as unique oxygen-anion species, which were characterized by means of ESR mainly. With respect to Li-MgO, Li^+-O^- centers, which are in equilibrium with surface O^- centers via hole transport, were responsible for activation of CH_4 (Lunsford *et al.*, 1995). However, different oxygen-species such as O^{2-} or O_2^{2-} are proposed as active centers on other OCM catalysts (Otsuka *et al.*, 1987). Consistent active species for OCM reaction have not been decided. In fact, it would be difficult to characterize the active oxygen species in the reaction condition. On the other hand, it is accepted widely that vacant-hole sites such as F-centers are generated onto MgO not only in the surface but also in the bulk phase by promotion of Li^+ ions (Balint *et al.*, 1997). Thus, the characterization of Li-promoted MgO is important for elucidating the generation of vacancy sites in the bulk phase. But direct observation of vacancy sites in MgO is difficult by means of several spectroscopic studies. ESR study is only available for characterization of ESR-active oxygen anions. Although XRD study is available for characterizing the bulk phase on Li-MgO, crystallinity of MgO can only be evaluated. More information about the defect on Li-MgO is called for.

In this study, XANES was applied to the characterization of catalytically active species for OCM. Not only Li-MgO but also Li-La_2O_3-MgO catalysts, which showed higher activity than Li-MgO, were characterized. We applied the Mg K-edge XANES mainly for studying the local structure around Mg^{2+} ions. For XANES measurement at Mg K-edge, total electron-yield mode is used in this study. In this method, the penetration range of XANES is less than 38 nm because a component of electron-yield is mainly low energy secondary electrons. The structural information by Mg K-XANES is reflected in "near-surface region". To compare between XANES and XRD results, the formation of vacancy sites and crystallinity of MgO can be discussed in both surface region and bulk phase. La L_3-edge XANES spectra were measured in a transmission mode, and therefore, they reflect the information of bulk structure.

2. Experimental

The MgO sample was obtained by calcination of $Mg(OH)_2$ (Kojundo-Kagaku Kenkyusho Co.) at 873K for 3 h, and followed by cooling at ambient temperature for overnight. La_2O_3-MgO binary oxides were prepared by co-precipitation method. The mixture of hydroxides in aqueous solution was filtered, washed, dried overnight, and calcined at 873 K for 6 h. Li-promoted (2.5 wt% as Li) MgO or La_2O_3-MgO samples were obtained by impregnation of MgO or La_2O_3-MgO with an aqueous solution of $LiNO_3$ (Nacalai Tesque Co.) at 343 K, and then excess water was evaporated at 343 K to form a paste. Then the paste was dried at 353 K overnight and calcined at 873 K for 3 h. To avoid the exposure to air, the sample setting in all the measurements was as carried out under the flowing N_2 or He atmosphere by using a conventional dry glovebox or packing made of polypropylene film. The preparation of the sample for each measurement described below was carried out in this procedure.

Mg K-edge XANES spectra were collected on a facility of BL-7A station of soft X-ray beam line at UVSOR, in the Institute for Molecular Science, Okazaki, Japaf stored current. At the Mg K-edge (1303.0 eV), tf stored current. At the Mg *K*-edge (1303.0 eV), the resolution of the photon-energy was better than 0.5 eV. Because the penetration range is less than 38 nm into the bulk (Erbil *et al*., 1988), the XANES spectra reflect the structure of the samples in "near-surface region". Each sample was mounted on a carbon-tape, and then attached on a beryllium-copper dynode, which was set to the first-stage of electron multiplier placed into a vacuum chamber. After the chamber had been evacuated ($< 3.0 \times 10^{-7}$ Torr), the spectrum was recorded in a total electron yield mode at room temperature, using a beryl double-crystal monochromator (d = 0.79825 nm). The energy was calibrated by using Al metal-foil at Al K-edge (1559 eV).

La L_3-edge XANES spectra were collected on a facility of BL-7C beamline at the Photon Factory in the High Energy Accelerator Research Organization (KEK-PF), Tsukuba, Japan, with 2.5 GeV of ring energy and 200-330 mA of stored current. Each sample was packed in a polyethylene film, and measured in a transmission mode at room temperature, using a Si(111) double-crystal monochromator (d = 0.313551 nm). The photon energy was calibrated by Cu metal-foil at Cu K-edge (8979 eV).

The OCM reaction was carried out using a fixed-bed flow reactor. The catalyst (0.5 g) was placed in a ceramic tube reactor. Each catalyst sample was pretreated at 1023 K for 1 h in an O_2(2.3%)/He stream before the OCM reaction. The reactor was then kept at 1023 K in a He stream for 10 min. After pretreatment, a gas

Table 1
Catalytic activity for OCM reaction over 2.5 wt% Li-doped / non-doped MgO and La_2O_3-MgO. (Reacted at 1023 K for 6 h.)

Catalyst	CH_4 Conv. /%	Selectivity / % C_2	Selectivity / % $CO+CO_2$	C_2 Yield / %
MgO	19.5	23.0	77.0	4.5
Li-MgO	11.8	69.9	30.1	8.2
La_2O_3-MgO				
La 25 mol%	15.5	9.5	90.5	1.5
La 50 mol%	15.3	11.6	88.4	1.8
La 75 mol%	16.5	15.4	84.6	2.5
La_2O_3	24.0	37.7	62.3	9.0
Li-La_2O_3-MgO				
La 25 mol%	13.7	68.6	31.4	9.4
La 50 mol%	10.2	70.5	29.5	7.2
La 75 mol%	11.7	70.0	30.0	8.2
Li-La_2O_3	11.8	69.9	30.1	8.2

mixture containing CH_4(9.4%)/O_2(2.3%)/He was fed to the reactor for the OCM reaction at 1023 K. The total flow-rate was 66.5 $cm^3\ min^{-1}$ (SV = 7980 $cm^3\ g^{-1}\ h^{-1}$) in both the pretreatment and reaction. The flow rate of the gases was controlled by means of mass-flow controllers (KOFLOC 3650). The product were analyzed periodically by two online gas-chromatographs (Shimadzu GC-3BT and GC-4C) with columns packed with Porapak-Q (3m, 333 K) and Unibeads-C (2m, 353 K).

3. Results and Discussion

3-1 Catalytic activity for OCM

Table 1 shows the catalytic reactivity for OCM over Li-doped and non-doped MgO and La_2O_3-MgO. MgO shows relatively low activity for producing C_2 compounds (OCM reaction). By addition of Li onto MgO, the C_2 selectivity becomes very high. It indicates the formation of active species for OCM. In this case, C_2 yield reached 8.2 %. On the other hand, La_2O_3-MgO binary oxides with various molar ratio showed very low activity for OCM. La_2O_3 catalyst gave higher C_2 yield than Li-MgO, however, it is not a valuable OCM catalyst because of low C_2 selectivity (37.7 %). By Li-doping onto La_2O_3, high OCM reactivity as same as Li-MgO was exhibited. In the case of Li-doped La_2O_3-MgO, higher OCM reactivity was brought about in all the molar ratios of La. This feature is similar to that of MgO and La_2O_3. It is noted that Li-La_2O_3-MgO with 25 mol% La showed the maximum C_2 yield (9.4 %), which is higher than Li-MgO and Li-La_2O_3. This tendency has an interest in the relation between the generation of OCM reactivity and its structural effects given by a mixture of MgO and La_2O_3. It is important to study the active species for OCM on Li-doped La_2O_3-MgO. Therefore, characterization of catalytically active species for OCM is performed by means of Mg K- and La L_3-edge XANES mainly.

3-2 Mg K- and La L_3-edge XANES

Figure 1 shows the Mg K-edge XANES spectra of MgO, Li-MgO and Li-La_2O_3-MgO. It is noted that the spectrum of Li-MgO is different from that of MgO. This indicates definitively that Li-doping at 2.5 wt% brings about a structural change in the near-surface region. This phenomenon was also observed for Mn-doped MgO, as described in the previous report (Aritani *et al.*, 1999). From the XRD results, the Li-MgO contains a bulk MgO phase with higher crystallinity than MgO. Therefore, structural change should occur in the near-surface region, and the coexistence of rock salt structure due to MgO and other structural components can be realized. However, the spectral feature is not similar to that of $Mg(OH)_2$ (in Figure 1 in a dotted line) or other typical reference materials. For the XANES of Li-MgO, it is noted that the edge energy obtained by first derivative XANES spectrum is positioned at 1296.0 eV. This value is a little lower than that of MgO (1296.9 eV) but is higher than that of Al_2MgO_4 (1294.5 eV). If the local structure consists of hepta-coordinated ones only, the edge energy should be higher than that of MgO with O_h symmetry. (Tanaka *et al.*, 1996) It is likely that the Li doping perturbs the Oh local symmetry and/or the filling of the 22g level, changing the XANES spectral shape. On the assumption that the spectrum contains components due to rock salt MgO and another unidentified species, we can suggest that the component due to this latter species can be estimated by subtraction of MgO-based spectral components from the spectrum of 2.5 wt% Li-MgO system. The detail of this discussion has been reported in the another paper (Aritani *et al.*, 2000). In contrast, the spectra of La_2O_3-MgO and Li-La_2O_3-MgO are almost similar to that of MgO, indicating the existence of rock salt MgO in majority.

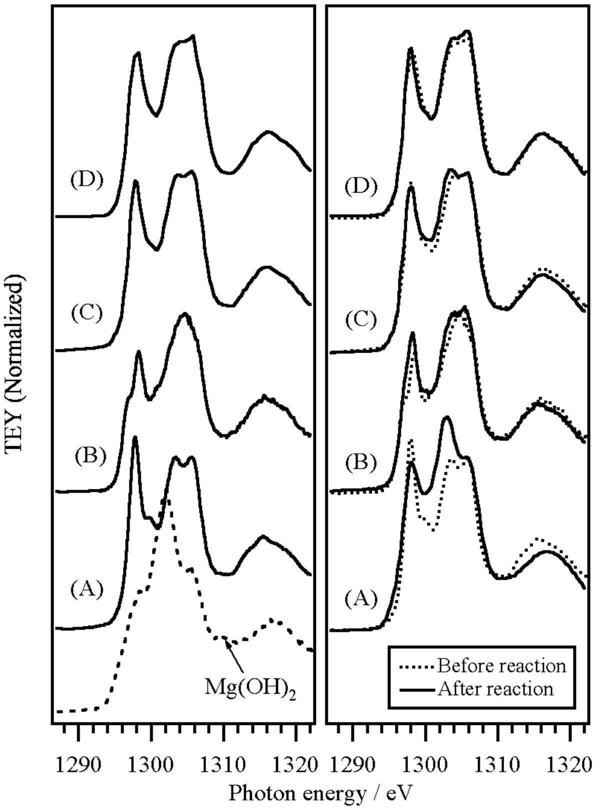

Figure 1
Mg K-edge XANES of the catalysts before (left hand) and after (right hand) the OCM reaction at 1123 K for 6 h. The catalyst samples were MgO (A), Li-MgO (B), La_2O_3-MgO (C) and Li-La_2O_3-MgO (D). La ratio (=La/(La+Mg) is 25 mol%.

As shown in Figure 1 in the right hand, the difference of XANES spectra of these samples before and after the OCM reaction was compared. In the case of MgO, the XANES spectrum after the

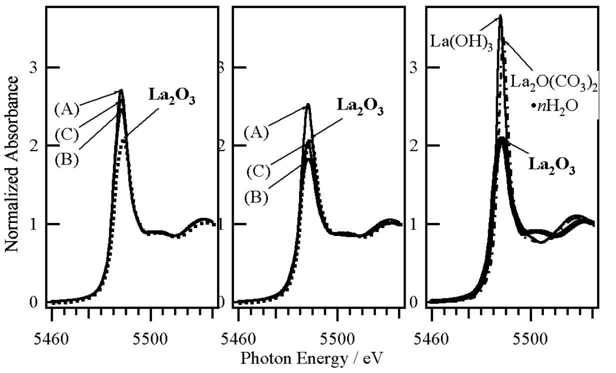

Figure 2
La L_3-edge XANES spectra of La_2O_3-MgO (left), Li-La_2O_3-MgO (center) and reference La-materials (right). The La molar ratio is 25 (A), 50 (B) and 75 (C) mol%.

reaction strongly suggests the coexistence of hydroxide species with MgO. It suggests that hydration of surface Mg was brought about. For Li-MgO, the increase of MgO component can be seen after the reaction, suggesting the decrease of defect species. It is summarized that the structural changes occurred during the OCM reaction on MgO and Li-MgO. On the other hand, the XANES spectra of La_2O_3-MgO and Li-La_2O_3-MgO before and after the reaction are almost similar to each other. This result indicates that Mg ions with rock salt structure show little change during the reaction. Thus, the coexistence of La_2O_3 with MgO has an effect of stabilization of rock salt MgO structure in the surface region. According to the MgO-based OCM catalyst, this result supports that one of the conditions for exhibiting high OCM reactivity is the stable rock salt structure in not only bulk phase but also surface region.

To clarify the structural effect of La_2O_3, La L_3-edge XANES (in a transmission mode) has been applied. The XANES spectra of La_2O_3-MgO and Li-La_2O_3-MgO with several La ratios are shown in Figure 2. One white-line is seen in the L_3-XANES region, which is due to La 2*p*-5*d* electron transition mainly. It is reasonable that the ligand-field splitting of 5*d* orbital reflects the spectral feature of the white line. The feature of 5*d*-splitting may affect the peak intensity and width. For instance, the distortion level of local symmetry of octahedron (La-O_6)-like structure is La_2O_3 < $La(OH)_3$. In this case, the white line intensity is quite different, La_2O_3 < $La(OH)_3$, as shown in Figure 2, because of adjacent band of split 5*d* orbital. For the second derivatives of XANES as shown in Figure 3 at least two peaks can be seen in La_2O_3, suggesting the existence of split bands. In contrast, only one peak was seen in $La(OH)_3$. This supports the explanation about the symmetry.

For non-doped La_2O_3-MgO, the intensity of the white-line peaks (in Figure 2) is slightly larger than La_2O_3 in the whole La ratio, however, the split peak can be seen in the derivative XANES (in Figure 3). This suggests the coexistence of La_2O_3 mainly and $La(OH)_3$-like species partly. In the case of Li-doped La_2O_3-MgO except for La 25 mol% one, the white-line peaks are smaller than non-doped ones. For La 25 mol% Li-La_2O_3-MgO, the intensity is almost as same as non-doped one. This sample is the most reactive for OCM, as described in Table 1. It is suggested that the Li ions affect the formation of La_2O_3-like local structure. However, poorly crystallized La_2O_3 species are formed in La 25 mol% sample. In this case, the high conversion of CH_4 is given over the OCM. After the OCM reaction, $La(OH)_3$ phase can be seen even by XRD in Li-La_2O_3-MgO samples. But Li-La_2O_3 gives relatively high reactivity, as shown in Table 1. From these results, it can be concluded that Li-La_2O_3-MgO in 25mol% La has a rock salt MgO phase, whose stability is enhanced by coexistence of poorly crystallized La_2O_3 species, which bring about the high CH_4 conversion. Because hydrated MgO species give low reactivity but hydrated La_2O_3 species are independent on the reactivity by promotion of Li, 25 mol% La sample shows a high reactivity for OCM. It is concluded that Li-doped binary oxide catalyst consists of highly crystallized MgO and poorly crystallized La_2O_3 species affect the activity for production of C_2 compounds.

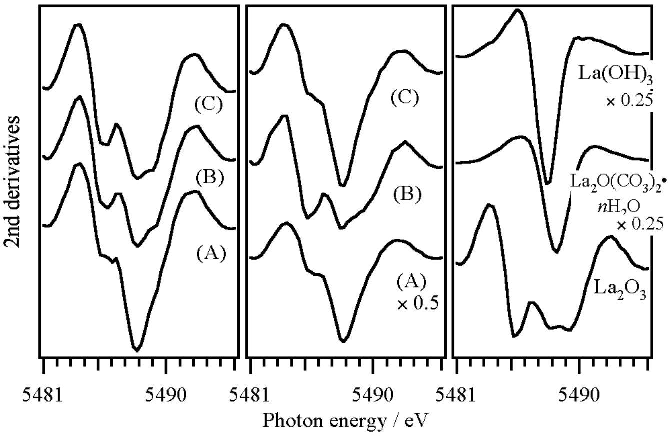

Figure 3
Second derivatives of XANES spectra of La_2O_3-MgO (left), Li-La_2O_3-MgO (center) and reference La-materials (right). The La molar ratio is 25 (A), 50 (B) and 75 (C) mol%.

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