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Direct differentiation of surface and bulk compositions of powder catalysts: application of electron-yield and fluorescence-yield NEXAFS to $Li_xNi_{1-x}O$

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We have applied near-edge X-ray absorption fine structure (NEXAFS) to characterize the surface and bulk properties of $Li_xNi_{1-x}O$ catalysts. In our experimental set-up, NEXAFS spectra of powder materials could be obtained by measuring the intensity of either electron-yield or fluorescence-yield. While the electron-yield method is sensitive only to the top few atomic layers, the fluorescence-yield method can detect species up to a few thousands angstroms deep into the bulk structure. The ability to distinguish surface and bulk compositions is demonstrated in studies of a number of $Li_{0.5}Ni_{0.5}O$ samples, of which the surface compositions vary as a function of preparation procedures. In addition, NEXAFS investigations following the reaction of $Li_xNi_{1-x}O$ with CH_4 have also been carried out and the results indicate that the initial surface reaction intermediates are Li_2CO_3.

Keywords: NEXAFS; surface composition; bulk composition; lithium nickel oxide

1. Introduction

As demonstrated by several research groups [1,2], lithium nickel oxides, $Li_xNi_{1-x}O$, are among the most selective type of catalysts for the conversion of methane to C_2 hydrocarbons. In an effort to understand the nature of the active sites for the oxidative coupling of methane, surface properties of $Li_xNi_{1-x}O$ powder catalysts have been investigated by using various experimental methods. For example, kinetic measurements to elucidate the reaction mechanisms and surface active sites have been carried out by Hatano and Otsuka [2], and also recently by Sun et al. [3]. Moggridge et al. [4] have applied the thermal desorption technique to investigate different surface oxygen species that could be the active sites for the oxidative coupling of methane. Bulk structures of $Li_xNi_{1-x}O$ ($x = 0.32$–0.40) have also recently been determined by Pickering et al. [5] using neutron powder diffrac-

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tion. In addition, investigations using planar model systems by evaporating Li onto well-characterized NiO clusters on Ni single crystal surfaces have been carried out by Badyal et al. [6] using photoemission spectroscopies and by Chen et al. [7] using surface vibrational techniques. One of the general conclusions from the catalytic studies of oxidative coupling of methane on lithium nickel oxides is that the activity and selectivity of this reaction depend strongly on the degree of Li-doping in the $Li_xNi_{1-x}O$ catalysts [1,3]. However, it is difficult to obtain a quantitative correlation between the x-values in $Li_xNi_{1-x}O$ and their catalytic activities, due to the possibility that *surface compositions of $Li_xNi_{1-x}O$ catalysts could be very different from the bulk stoichiometries.*

By using near-edge X-ray absorption fine structure (NEXAFS), we have observed that, depending on the preparation procedures, surface compositions of $Li_xNi_{1-x}O$ catalysts could indeed be significantly different from those of bulk structures. In our experimental set-up, NEXAFS spectra of near-edge features could be obtained by measuring the intensity of either electron-yield or fluorescence-yield. The electron-yield method is sensitive only to the top few surface layers because of the limited escape depth of electrons. On the other hand, the fluorescence-yield method can detect species up to a few thousands angstroms deep into the bulk structure due to the much deeper escape depth of energetic photons. In this paper, we will use $Li_{0.5}Ni_{0.5}O$ powder catalysts as a model system to demonstrate the capability of detecting different surface and bulk compositions by means of electron-yield and fluorescence-yield NEXAFS. For example, we found that the top few layers of freshly pressed $Li_{0.5}Ni_{0.5}O$ samples are in the form of Li_2CO_3. Though the surface Li_2CO_3 layers could be removed by a reaction with O_2 at 950 K, the resulting surface compositions could be either NiO or $Li_{0.5}Ni_{0.5}O$, depending on the gas-phase oxygen pressure during the reaction. Our results clearly demonstrate that, despite the rather dramatic differences in the surface compositions of these materials as detected by the electron-yield method, a bulk-technique such as the fluorescence-yield method is rather insensitive to the details of the top few surface layers. In addition, NEXAFS investigations of surface species following reactions of $Li_xNi_{1-x}O$ with CH_4 will also be discussed.

2. Experimental

The NEXAFS experiments reported here were carried out at the U1 beamline of the National Synchrotron Light Source, Brookhaven National Laboratory. Details concerning the optics on the beamline, as well as the UHV chamber with facilities for high pressure reactions, have been described previously [8,9]. The NEXAFS spectra in the present study were recorded as a function of the incident X-ray photon energy in the vicinity of the lithium K-edge (35–85 eV), carbon K-edge (275–325 eV), oxygen K-edge (510–590 eV) and Ni L-edge (830–930 eV). The fluorescence-yield intensity was measured by using a differentially pumped, UHV-compatible proportional counter filled with 200 Torr of P-90 gas (90% methane, 10% argon) as counter-gas, as described previously [8,9]. In brief, the energetic photons related to the excitation of various near-edge features from the sample were intercepted by the proportional counter at a fixed solid angle and absorbed by the counter-gas, creating electron-ion pairs in the proportional counter. The charged particles were accelerated and the charge was multiplied by impact ionization of the counter-gas. The resulting pulse of electrons was then collected at the anode and amplified by a charge-sensitive amplifier [8]. The electron-yield intensity was recorded by a channeltron electron multiplier located near the sample holder. In order to reduce the intensity contribution from low-energy, secondary electrons from the subsurface regions, the entrance of the channeltron was biased by a negative voltage of 100 eV to repel these electrons. All NEXAFS results reported here were obtained by measuring the electron-yield and fluorescence-yield simultaneously, with the incident photon beam at a normal incidence angle with respect to the sample surface.

Lithium nickel oxide samples were prepared by solid state reactions of NiO with Li_2CO_3 in air following the method of Pickering et al. [10]. Bulk compositions and structures of $Li_xNi_{1-x}O$ samples were determined by X-ray diffraction, elemental analysis and neutron scattering. In the present study, powder samples of NiO, $Li_xNi_{1-x}O$ and Li_2CO_3 were pressed into stainless steel sample holders of about 1.3 cm in diameter and about 0.1 cm in depth. The powder samples were heated by resistively heating two tungsten wires (0.025 cm in diameter) spot-welded onto the sample holder; the sample temperature was measured by an alumel-chromel thermocouple. A very slow heating rate ($\leqslant$ 0.5 K/s) was used to ensure a uniform temperature profile for the pressed $Li_xNi_{1-x}O$ samples.

3. Results and discussion

3.1. SPECTROSCOPIC ASSIGNMENT OF OXYGEN K-EDGE FEATURES

Fig. 1 shows a comparison of electron-yield NEXAFS spectra of oxygen K-edge of NiO, Li_2CO_3 and $Li_{0.29}Ni_{0.71}O$ powder materials. The NiO and Li_2CO_3 powder surfaces were cleaned by briefly heating the samples in vacuum to 600 K; clean surfaces of $Li_{0.29}Ni_{0.71}O$ were obtained by reactions with 20 Torr of O_2 at 950 K, as will be discussed later. The electron-yield spectra in fig. 1 are identical to the corresponding fluorescence-yield spectra (not shown), indicating similar surface and bulk compositions after these cleaning procedures.

The peak positions and relative intensities of oxygen K-edge features of NiO powders (bottom spectrum) are very similar to previously reported NEXAFS spectra of NiO(100) single crystalline clusters produced on a Ni(100) surface [9,11,12]. The assignment of these O K-edge features has been discussed in detail in several publications [11–13]. Briefly, by using a symmetry-determined molecular-orbital

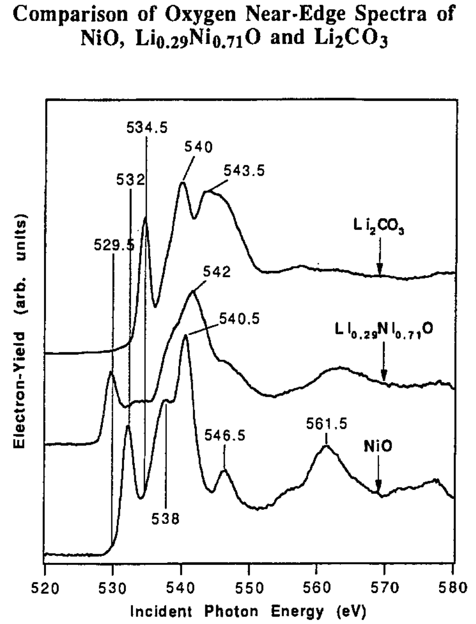

Comparison of Oxygen Near-Edge Spectra of NiO, $Li_{0.29}Ni_{0.71}O$ and Li_2CO_3

Fig. 1. Comparison of oxygen K-edge near-edge spectra of NiO, $Li_{0.29}Ni_{0.71}O$ and Li_2CO_3 powder materials. The NEXAFS spectra were obtained by measuring the intensity of electron-yield with a bias of −100 eV to the entrance of the channeltron multiplier.

model, various O K-edge features could be related to the creation of oxygen core holes via electronic transitions to the partially-filled or unfilled molecular orbitals of metal oxides [13]. The leading oxygen K-edge feature at 532 eV could be related to the electronic excitation to the $3e_g$ (Ni 3d + O 2pσ) orbitals of NiO. The atomic orbitals given in parentheses are those contributing dominantly to the corresponding molecular orbitals. Similarly, the 540.5 eV feature was assigned to the electronic transition to the $3a_{1g}$ (Ni 4s + O 2pσ) orbital and the 546.5 eV feature to the $4t_{1u}$ (Ni 4p + O 2pπ) orbitals of NiO, respectively [13]. The other two near-edge features at 538 and 561.5 eV are also characteristic near-edge features of single crystalline NiO and are related to the multi-electron configuration interactions [11,12].

Due primarily to their interesting magnetic properties, $Li_xNi_{1-x}O$ powders have been investigated by Kupier et al. using NEXAFS [14]. The NEXAFS spectrum of $Li_{0.29}Ni_{0.71}O$ catalysts (middle spectrum) is very similar to those reported by Kupier et al. [14]. The characteristic oxygen features are the sharp leading near-edge feature at 529.5 eV and a relatively broad feature centered around 542 eV. Similar to previous studies [14], we observe that the peak positions of these two oxygen features remain constant as the x-value increases in $Li_xNi_{1-x}O$ stoichiometries. The only major spectroscopic change is that the intensity ratio of these two features, 529.5 eV/542 eV, increases with Li-doping.

The NEXAFS spectrum of Li_2CO_3 powder materials in the oxygen K-edge region (top spectrum) is very similar to those reported for carbonates on a Ag(110) surface and for bulk $CdCO_3$ species [16,17]. The leading near-edge feature at 534.5 eV is characteristic of carbonate species, and is assigned to the electronic excitation to the π^* orbitals of carbonate [16]. The 540 and 543.5 eV features are related to the excitation to the σ^* orbitals. The corresponding NEXAFS data of Li_2CO_3 recorded in the carbon K-edge (spectra not shown) are also very similar to those reported for the bulk carbonate [16,17].

It is clear from the comparison in fig. 1 that each compound has a different set of oxygen near-edge features. This difference is especially characteristic in the excitation energy of the leading near-edge feature, with $Li_xNi_{1-x}O$ at 529.5 eV, NiO at 532 eV and Li_2CO_3 at 534.5 eV, respectively. The spectra given in fig. 1 provide the necessary spectroscopic background information for us to identify various surface and bulk compositions of $Li_xNi_{1-x}O$ catalysts, as will be discussed below.

3.2. DIFFERENT SURFACE AND BULK COMPOSITIONS OF $Li_{0.5}Ni_{0.5}O$ POWDERS

As stated in the Introduction, a direct differentiation of surface and bulk compositions could be achieved by comparing the NEXAFS spectra by means of electron-yield and fluorescence-yield. Such a comparison is given in fig. 2 for a freshly pressed $Li_{0.5}Ni_{0.5}O$ sample. By comparing fig. 2 with fig. 1, it is clear that the sur-

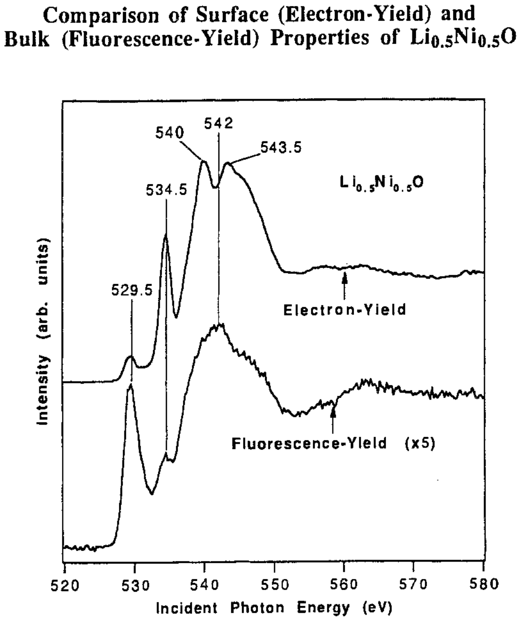


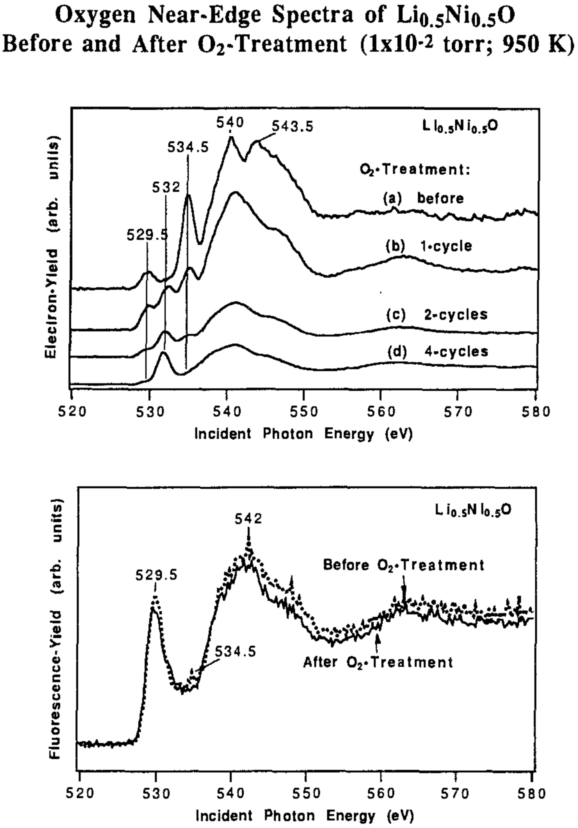
Fig. 2. Comparison of a simultaneous measurement of the electron-yield and fluorescence-yield of a $Li_{0.5}Ni_{0.5}O$ sample prior to heating or oxygen-treatment.

face composition (electron-yield) of this sample could be best described as Li_2CO_3, as indicated by the strong, characteristic near-edge features at 534.5, 540 and 543.5 eV.

On the other hand, the bulk structure of this sample is clearly lithium nickel oxide, as indicated in the fluorescence-yield spectrum by the two strong near-edge features at 529.5 and 542 eV, respectively. The positions of these two features are identical to those of $Li_{0.29}Ni_{0.71}O$ shown in fig. 1. The relative intensity ratio of these two features, 529.5 eV / 542 eV, is higher in fig. 2 because of the higher degree of Li-doping. We also observed that the 529.5 eV/542 eV intensity ratio is higher in the fluorescence-yield than in the electron-yield due possibly to different decay mechanisms for photons and electrons. More details concerning the quantitative intensity analysis of oxygen near-edge features as a function of Li-doping, by means of both electron-yield and fluorescence-yield NEXAFS, can be found elsewhere [15]. Even without any quantitative analysis, the comparison of the two spectra in fig. 2 clearly indicates that for this $Li_{0.5}Ni_{0.5}O$ sample, the surface composition is dominantly lithium carbonate while the bulk composition is lithium nickel oxide.

Fig. 2 also indicates that, despite the rather significant difference in the surface composition from the bulk stoichiometry, this difference is not detected by a bulk-sensitive technique such as fluorescence-yield NEXAFS. To further demonstrate the different detection sensitivities, we have applied the electron-yield and fluorescence-yield methods to follow the removal of surface lithium carbonates from $Li_{0.5}Ni_{0.5}O$ by heating in O_2. The formation of carbonate on $Li_xNi_{1-x}O$ surfaces, especially those surfaces with higher Li-dopings, has been observed in several previous studies [3,4]. Moggridge et al. [4] have reported a cleaning procedure that requires heating $Li_xNi_{1-x}O$ samples in a flow of oxygen (10^{-2} Torr of O_2 at sample surface) by repeated cycles of 5 min each at 950 and at 750 K. We have applied a similar procedure in our initial attempt to obtain clean $Li_xNi_{1-x}O$ samples. The $Li_{0.5}Ni_{0.5}O$ sample was annealed at 950 K for 5 min at the presence of 1×10^{-2} Torr of O_2; the sample was then cooled to and held at 750 K for 5 min in the presence of oxygen. The NEXAFS spectra following repeated cycles of this O_2-treatment are plotted in fig. 3. As shown in the upper panel of fig. 3, electron-yield NEXAFS spectra clearly indicate that the surface composition of the $Li_{0.5}Ni_{0.5}O$ sample is gradually converted from Li_2CO_3 to NiO as a result of reactions with 1×10^{-2} Torr of O_2. This is demonstrated by the disappearance of the Li_2CO_3 features at 534.5, 540 and 543.5 eV, and by the onset of the NiO feature at 532 eV. On the other hand, the fluorescence-yield spectra (lower panel of fig. 3) are very insensitive to the change in the surface compositions, with the spectra representing a $Li_{0.5}Ni_{0.5}O$ structure throughout the reaction with oxygen.

We found that surface composition of clean lithium nickel oxide, instead of NiO as shown in fig. 3, could indeed be obtained by reactions with oxygen. *However, a gas-phase O_2 pressure much higher than 1×10^{-2} Torr was required to obtain the stable lithium nickel oxide surface*, as shown in fig. 4. The NEXAFS spectra in



Oxygen Near-Edge Spectra of $Li_{0.5}Ni_{0.5}O$ Before and After O_2-Treatment ($1x10^{-2}$ torr; 950 K)

Fig. 3. Electron-yield (upper panel) and fluorescence- yield (lower panel) NEXAFS spectra recorded following the removal of surface Li_2CO_3 from $Li_{0.5}Ni_{0.5}O$ by reactions with 1×10^{-2} Torr of O_2 at 950 and 750 K. See text for details.

fig. 4 are recorded before and after the reaction of the $Li_2CO_3/Li_{0.5}Ni_{0.5}O$ sample at 950 K with 20 Torr of O_2 for 30 s; the sample was cooled in the presence of O_2 until below 600 K. As shown in the upper panel of fig. 4, the surface composition after this O_2-treatment is clearly converted to lithium nickel oxide, as indicated by the characteristic near-edge features at 529.5 and 542 eV, respectively. Again, the fluorescence-yield spectra (lower panel of fig. 4) are very insensitive to the change in the surface compositions.

The results shown in figs. 3 and 4 clearly indicate the importance of gas-phase oxygen in controlling the surface composition of $Li_{0.5}Ni_{0.5}O$ samples. The removal of surface Li_2CO_3 by oxygen could occur most likely via the following reaction:

$$2Li_2CO_3 + O_2 + 4NiO \rightarrow 4LiNiO_2 + 2CO_2(g) \ . \qquad (1)$$

However, the $LiNiO_2$ (or $2Li_{0.5}Ni_{0.5}O$) surface produced by the removal of Li_2CO_3 is thermally unstable in vacuum, and at $T \geqslant 950$ K it can undergo decomposition via the following reaction [4]:

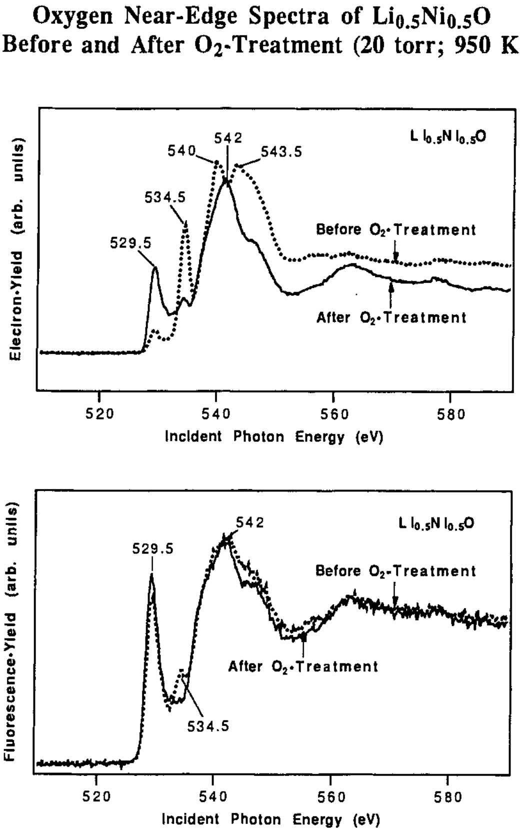

Oxygen Near-Edge Spectra of $Li_{0.5}Ni_{0.5}O$
Before and After O_2-Treatment (20 torr; 950 K)

Fig. 4. Electron-yield (upper panel) and fluorescence-yield (lower panel) NEXAFS spectra recorded before and after annealing $Li_{0.5}Ni_{0.5}O$ at 950 K in the presence of 20 Torr O_2.

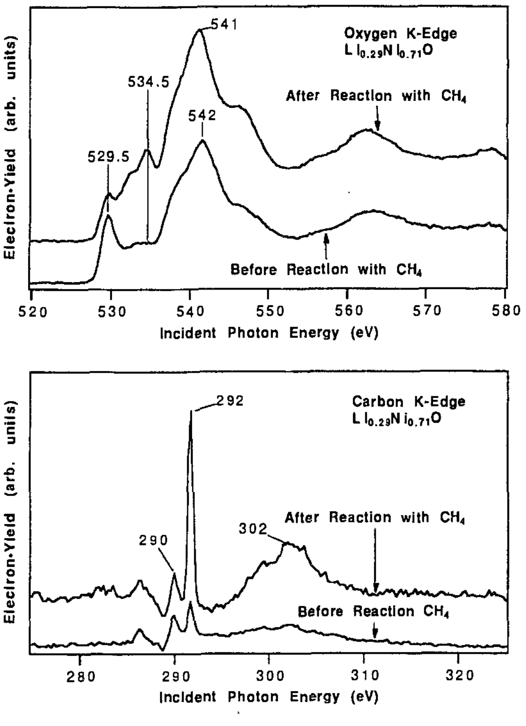
$$4LiNiO_2 = 4NiO + 2Li_2O(g) + O_2(g) \ . \tag{2}$$

This reaction is likely under equilibrium with gas-phase $O_2(g)$ and the degree of $LiNiO_2$ decomposition therefore depends strongly on the O_2 pressure. This would then explain the observations that the resulting surface composition is NiO under an O_2 pressure of 1×10^{-2} Torr (fig. 3) and is lithium nickel oxide under an O_2 pressure of 20 Torr (fig. 4).

The most important conclusion from the results shown in figs. 2–4 is the very different sensitivities of the electron-yield and fluorescence-yield methods. While the electron-yield method clearly indicates that the surface compositions are Li_2CO_3 (fig. 2), NiO (fig. 3) and lithium nickel oxide (fig. 4), the fluorescence-yield spectra show very little change from the $Li_{0.5}Ni_{0.5}O$ bulk structure. Other bulk-sensitive techniques, such as X-ray diffraction and neutron diffraction, should also be very insensitive to the details of the top few surface layers. Since the top few atomic layers are most likely responsible for the catalytic activities of most reactions, one must then be very cautious in drawing general correlations between bulk stoichiometries of catalysts and their catalytic activities. These results therefore demonstrate the usefulness of the NEXAFS by means of measuring both electron- and fluorescence-yields, since the combination of these two methods allows one to obtain the surface and bulk compositions simultaneously.

3.3. REACTION OF $Li_xNi_{1-x}O$ WITH METHANE

To understand the surface compositions of lithium nickel oxides during the oxidative coupling of methane, we have applied the NEXAFS technique to characterize the surface species after reactions of $Li_xNi_{1-x}O$ with CH_4. NEXAFS results of the carbon and oxygen K-edge features before and after the reaction of a $Li_{0.29}Ni_{0.71}O$ sample with CH_4 are compared in fig. 5. The sample was reacted with 20 Torr of CH_4 at 950 K for 8 min; it was cooled in the presence of methane to 600 K, and then cooled in vacuum to 300 K. By comparing the upper panel of fig. 5, the most obvious changes in the oxygen K-edge features are the reduction of the $Li_xNi_{1-x}O$ feature at 529.5 eV and the onset of the Li_2CO_3 feature at 534.5 eV, indi-



Near-Edge Spectra of $Li_{0.29}Ni_{0.71}O$ Before and After Reaction with Methane (8 minutes; 20 torr; 950 K)

Fig. 5. Electron-yield NEXAFS spectra of carbon K-edge (lower panel) and oxygen K-edge (upper panel) features recorded before and after reaction of $Li_{0.29}Ni_{0.71}O$ with CH_4. The reaction was carried out at 950 K for 8 min in the presence of 20 Torr CH_4.

cating the conversion of surface from $Li_{0.29}Ni_{0.71}O$ to Li_2CO_3. The formation of surface lithium carbonates is more clearly shown in the lower panel of fig. 5, where the carbon K-edge features are compared before and after the reaction. The strong carbon near-edge features at 292 and 302 eV are identical to our NEXAFS spectra of Li_2CO_3 powders (not shown), and these two features can be readily assigned to the electronic excitations to the π^* and σ^* orbitals of carbonates, respectively [16]. The weak carbon near-edge features observed on the $Li_{0.29}Ni_{0.71}O$ sample prior to the reaction with CH_4 are related to the residual carbonate impurities on the sample, and the concentration is estimated to be below 0.2 monolayer. Experimental efforts to quantify the carbonate coverage are currently under way.

The formation of carbonates under the experimental conditions used here is limited to the top few surface layers, since the fluorescence-yield spectra in the oxygen K-edge (not shown) are almost identical before and after the reaction with CH_4. The observation of lithium carbonates on the $Li_xNi_{1-x}O$ catalysts suggests strongly that one has to be very careful in evaluating the *initial* C_2-hydrocarbon selectivity, $[C_2/(C_2 + CO_x)]$, in the oxidative coupling of methane. Since CO_x species produced by surface oxidations would most likely be retained on the catalysts as lithium carbonates during the initial stages of reactions, one has to consider the *overall* carbon balance, including that in the form of Li_2CO_3, for the estimation of selectivities to C_2-products. Failure to do so would obviously give rise to an initial C_2-selectivity that is much higher than the real value. This has been observed and quantified in recent transient experiments [3], which show that the true initial selectivity of $Li_{0.5}Ni_{0.5}O$ is about 78% instead of the 100% selectivity reported earlier by Otsuka et al. [2]. More details related to the NEXAFS investigations of reactions of $Li_xNi_{1-x}O$ with CH_4, CO_2, O_2 and H_2 will be given elsewhere [15].

4. Conclusions

Based on the results presented above, the following conclusions can be made concerning the NEXAFS characterization of the $Li_xNi_{1-x}O$ catalysts by means of electron-yield and fluorescence-yield methods:

(1) Depending on the preparation procedures, the surface compositions of $Li_xNi_{1-x}O$ could be significantly different from the bulk stoichiometries. We have demonstrated that the combination of the electron-yield and fluorescence-yield methods is a powerful tool in distinguishing such a difference in the surface and bulk compositions. These experimental methods could be applied to differentiate the surface and bulk compositions of other powder materials.

(2) Though the impurity Li_2CO_3 layers on $Li_xNi_{1-x}O$ catalysts could be removed by a reaction with O_2 at 950 K, the resulting surface compositions could be either NiO or $Li_xNi_{1-x}O$, depending on the oxygen pressure during the reaction. Higher oxygen pressure favours the lithium nickel oxide compositions.

(3) Surface lithium carbonates are produced after the initial reaction of

$Li_xNi_{1-x}O$ with CH_4 at 950 K. The detection of carbonate formation suggests that one has to consider the overall carbon balance, including that in the form of Li_2CO_3, in the estimation of initial selectivities to C_2-hydrocarbon species in the oxidative coupling of methane.

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