On the CH Stretching Bands of Surface Alcoholates Formed on Metal Oxides—A Reply to Morrow, Thomson and Wetmore

In their letter, Morrow, Thomson and Wetmore (*1*) discussed the assignments of the CH stretching bands of surface alcoholates. They stated that since the degeneracy of an asymmetric ν_{CH} mode is removed in the methyl group attached to oxygen, a single asymmetric ν_{CH} mode of the methyl group is no longer preserved in surface methoxide. This was experimentally illustrated by the spectrum of surface methoxide formed on silica. From the spectra of methoxy CH_3O– and dideuterated methoxy CHD_2O– groups, they concluded that while the band due to a symmetric ν_{CH} mode could be assigned, those due to asymmetric ν_{CH} mode was somewhat more complicated. The spectrum of methoxy group CH_3O– observed by Morrow, Thomson and Wetmore (*1*) was practically the same as those observed by other workers (*2, 3*). However, in the experiments performed by Morrow, Thomson and Wetmore excess methanol was evacuated at room temperature so that physically adsorbed methanol may be present together with methoxide. This may complicate the spectra. Actually, Borello, Zecchina and Morterra (*2*) reported that methanol strongly and physically adsorbed on silica could be removed by evacuation at temperatures over 200°C.

In spite of these complexities of the spectra, however, it is reasonable to conclude that a single asymmetric ν_{CH} mode does not always exist in surface methoxide as Morrow, Thomson and Wetmore (*1*) noted.

In the spectra of bulk methoxides, generally three strong bands are seen which are referred to as ν_a, ν_b and ν_c bands, respectively, in the decreasing order of wave number. The exceptions are aluminum and germanium methoxides in 12 different bulk methoxides. The ν_a band was generally assigned to the overtone of the CH bending mode whereas ν_b and ν_c bands were asymmetric and symmetric modes, respectively. As Morrow, Thomson and Wetmore suggested, a more detailed investigation should be carried out for the assignments of the bands.

The surface methoxides so far obtained on silica (*2, 3*) and germania (*4*) exhibited three strong bands in the ν_{CH} region and the ν_b band was found to be most intense. When methanol was brought in contact with magnesia or calcium oxide at room temperature, methoxide was formed.* The features of the spectra were similar to those observed on silica and germania (*7*). With reference to the work by Morrow, Thomson and Wetmore (*1*), Borello, Zecchina and Morterra (*2*) and Low and Harano (*3*), the ν_c band can be assigned to a symmetric ν_{CH} mode although ν_a and ν_b bands can not be assigned in a strict sense. For surface boron (*3*), zinc (*5*) and aluminum methoxides (*6*), two strong bands were observed. The bands located at a higher wave number were stronger in the former two methoxides hence they could be assigned to the ν_b band and to the ν_c band, respectively. As for the latter methoxide, we could not estimate the intensities of the two bands from the spectrum in the literature (*6*) but from the correlation we previously reported (*8*) they could also be assigned to ν_b and ν_c bands. Figure 1 shows the positions of strong ν_{CH} bands of surface methoxides observed by several authors. The most intense band is marked with a thick line. Similar plots are

* Tench, Giles and Kibblewhite [*Trans. Faraday Soc.* **67**, 854 (1971)] recently reported that the ν_{CH} bands of methoxide on magnesia were observed at 2920, 2860 and 2807 cm[-1] in excellent accord with our results.

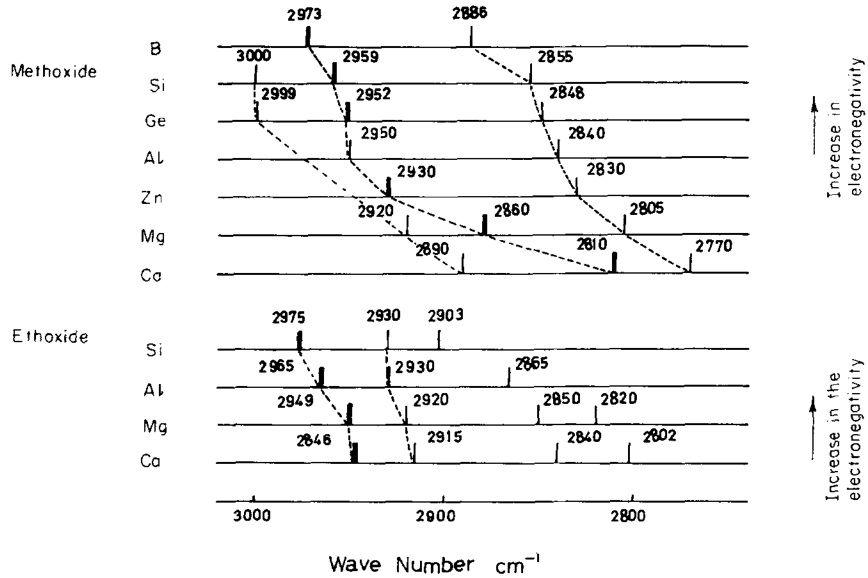

Fig. 1. The CH stretching bands of surface alcoholates formed on metal oxides. The band with highest intensity represents with a thick line. Some results are from the literature: methoxides on SiO_2 and B in SiO_2 (*3*); methoxide on GeO_2 (*4*); methoxide on ZnO (*5*); methoxide on Al_2O_3 (*6*); methoxides on MgO and CaO, and ethoxides on SiO_2 and CaO (*8*); ethoxide on Al_2O_3 (*9*) and ethoxide on MgO (*10*). Ethoxide was formed on magnesium oxide at room temperature. The feature of the spectrum was similar to that observed by Kagel and Greenler [*J. Chem. Phys.* **49**, 1638 (1968)] although the positions of the bands in ν_{CH} region were not given by these authors.

also shown for surface ethoxides. As shown in Fig. 1, it is apparent that all strong bands in the ν_{CH} region shift in the same direction when metal oxide differs. In this respect, even though no single asymmetric ν_{CH} mode is preserved, the positions of the bands in the ν_{CH} region can be well correlated with the electronegativity of metal in metal oxides. As was discussed in the previous work (*8*), it is suggested that on a less electronegative oxide surface alkoxy-group is anionic whereas covalently bound alkoxides are formed on a more electronegative oxide.

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N. Takezawa
H. Kobayashi

Department of Chemical Process Engineering
Hokkaido University
Sapporo, Japan
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