

ACKNOWLEDGMENTS

We are greatly indebted to Dr. E. J. Wells for helpful discussion and encouragement at many points. We thank the National Research Council of Canada for an operating grant, and the New Jersey Zinc Co. for the sample of ZnO used.

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Received September 13, 1971

The Shift of CH Stretching Band of Surface Alcoholate on Metal Oxides

The frequency of the various types of vibration in molecules is influenced by internal or external environments (1, 2). The infrared spectra of adsorbed species should, therefore, be closely related to the nature of the catalyst. Kiselev (3) showed recently that the absorption band originating in free hydroxyl groups on a silica surface shifted to lower frequencies when hydrogen bonding occurred with organic compounds, and the shift of the band increased with the increase of the heat of adsorption of these compounds. Cook (4) found that the frequency of —C=O stretching vibration in xanthone shifted due to the interaction with metal halides; the acidity of the halides was correlated with the shift.

In the present note, the authors show

that the absorption bands due to CH asymmetric stretching vibration in a terminal methyl group is strongly influenced by the nature of metal oxides when surface normal alcoholates are formed on the oxides.

EXPERIMENTAL

Experiments were carried out in a manner similar to that in our previous work (5). Magnesium oxide sample (Kishida Chem. Co. Ltd., Guaranteed grade) was prepared by compacting the powder at a pressure of 210 kg/cm² in a steel die to form a self-supporting disc of about 50 mg/cm².

Before the run, the disc was degassed at 700°C for 30 min and then heated in oxygen under a pressure of 5 cm Hg for 1 hr

at the same temperature. Thereafter, the disc was degassed again at 700°C for 1 hr. Cabosil silica and calcium oxide from calcium hydroxide (Kanto Chem. Co. Ltd., Guaranteed grade) were also treated in the same manner before the adsorption.

All reagents: methanol, ethanol, *n*-propanol and *n*-butanol (Nakarai Chem. Ltd. Guaranteed grade) were degassed several times before the run.

The spectra were recorded with a Nippon Bunko (Japan Spectroscopic Co. Ltd.) Model IR-G infrared spectrophotometer.

RESULTS AND DISCUSSION

When alcohols were adsorbed on metal oxides, surface hydroxyl and alcoholates were formed. The wave number $\tilde{\nu}_{as}(\text{CH}_3)$ of the asymmetric CH stretching vibration of the terminal methyl group in surface alcoholates shifted to lower values as compared with that of corresponding alcohols. For example, when ethanol was adsorbed on

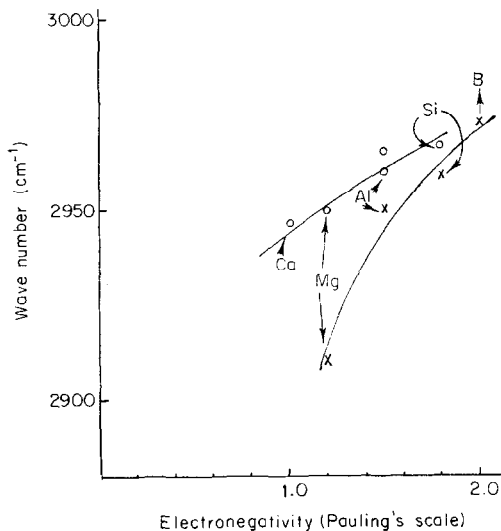


Fig. 1. The wave numbers of CH asymmetric stretching vibration in a methyl group in surface normal alcoholates formed on various metal oxides as a function of the electronegativities (Pauling's scale) of metals in the oxides. (O), surface ethoxides; (X), surface methoxides. Some results were from refs. 5 (ethoxide on MgO), 6 (methoxides on SiO₂ and B in SiO₂), 7 (methoxide on Al₂O₃), 8 (ethoxide on Al₂O₃, upper point) and 9 (ethoxide on Al₂O₃, lower point).

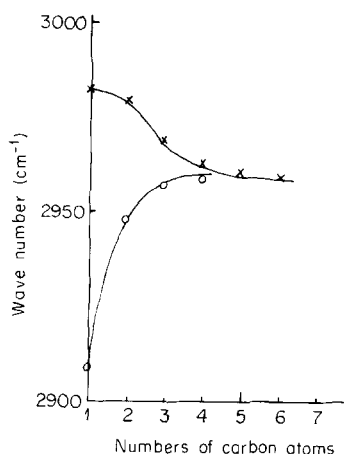


Fig. 2. The wave numbers of CH asymmetric stretching vibrations in terminal methyl group in surface normal alcoholates on MgO and in corresponding alcohols as a function of the number of constituent carbon atoms. (O), alcoholates; (X), alcohols. The results of ethoxide are from the data of ref. 5.

calcium oxide, the wave number $\tilde{\nu}_{as}(\text{CH}_3)$ shifted from 2975 cm⁻¹ to 2946 cm⁻¹. In Fig. 1, the wave numbers $\tilde{\nu}_{as}(\text{CH}_3)$ observed on various metal oxides are plotted against the electronegativities of the metals in metal oxides. Some results for surface methoxides of Si (6) and B (7), and ethoxides of Mg (5) and Al (8, 9) obtained by other workers are also plotted. The value of the wave number $\tilde{\nu}_{as}(\text{CH}_3)^*$ is increased with the increase in electronegativity. The positions of the bands of surface methoxides are strongly influenced by the electronegativity. Figure 2 shows the results of the adsorption of various normal alcohols on magnesium oxide. When the wave numbers $\tilde{\nu}_{as}(\text{CH}_3)$ in surface alcoholates thus formed are compared with those in corresponding alcohols, the effect of a magnesium atom upon the positions of the bands decreases gradually with the increase of carbon number.

From these results, it is concluded that the wave number $\tilde{\nu}_{as}(\text{CH}_3)$ of a surface

*The wave numbers in CH stretching vibrations of CH₂ groups and the CH symmetric stretching vibration of CH₃ groups could not be determined accurately due to overlapping.

alcoholate on metal oxides is strongly affected by the electronegativity of the constituent metal atom, and its effect propagates along the C-C-O bond.

Bent (10) has shown recently that bond shortening occurs when electronegative substituents are introduced into molecules. Since the effect of the metal in the oxides propagates along the C-C-O bond, the carbon atom in the methyl group is more electronegative for a surface alcoholate on an electronegative metal oxide. In such a case, the CH bond of the methyl group can be shortened. According to Gordy (11), the bond stretching force constant k of the bond AB is empirically expressed as $k = aN(x_A x_B / d^2)^{3/4} + b$, where a and b are constants. N and d represent the bond order and the bond length, respectively. x_A and x_B are electronegativities of A and B, respectively. It follows, therefore, that the force constant of the CH bond of a methyl group in a surface alcoholate increases as the electronegativity of the metal in the oxides increases. As shown in Fig. 2, the wave number $\tilde{\nu}_{\text{as}}(\text{CH}_3)$ shifted to higher wave numbers with the increase of carbon number of normal alcoholates. If one assumes that the metal in the oxides is electron releasing to the carbon atom in the methyl group through the C-C-O bond, the electronegativity of the carbon atom still increases with the increase in that of the metal, and it increases with the increase of carbon number in surface alcoholates. In this respect, the results in Fig. 2 are qualitatively accounted for on the same basis as those in Fig. 1. However, this is still speculative.

From the present work, it is concluded that the nature of adsorbed species on the oxides is closely related to that of the bulk of the catalyst.

ACKNOWLEDGMENTS

This work was supported by a Grant of the Ministry of Education which one of the present authors (N.T.) gratefully acknowledges.

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Received September 21, 1971