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NOTES

On the Shift in the CH Stretching Bands of Methoxy Groups Chemisorbed on Metal Oxides

In a previous paper (*1*) we have studied the chemisorption of methanol on pure unsupported MoO_3 from room temperature to 110°C, a temperature range in which the catalyst is not reduced by methanol. Our study has shown that the frequencies of the CH stretching bands of chemisorbed methanol change as a function of temperature, and there exist at least three kinds of methanol on MoO_3. The present study shows the CH stretching bands of methanol chemisorbed on MoO_3 at temperatures above 150°C. The spectra were taken at reaction temperature during the reaction of 3.6% methanol in oxygen over molybdenum oxide.

Figure 1 shows the observed bands and Fig. 2 shows the positions of the main asymmetric and symmetric CH stretching bands (for the bands below 110°C, refer to the previous paper (*1*)). In the previous paper (*1*), the bands A in Fig. 2 were assigned to a methoxy group chemisorbed on an oxygen vacancy of terminal-bonded oxygen (Mo=O) (V_T), and the weak bands B to methoxy on an oxygen vacancy of bridged-bonded oxygen (Mo—O—Mo) (V_B). The bands C observed in the presence of gas-phase methanol were assigned to reversible methanol chemisorbed on terminal-bonded oxygen. Figure 1 shows the existence of formaldehye on the surface at temperatures above 210°C as observed by a band at 2787 cm^{-1}. At the present moment we do not have a proper assignment for the band observed at 2975 cm^{-1} at 210°C. Nevertheless, at temperatures above 150°C, there are abrupt frequency decreases in the positions of the bands which correspond to the bands A and B below 110°C, and the slope of the backgrounds becomes steeper owing to the reduction of the catalyst (the spectrum at 250°C is obtained by another catalyst disk). In the case of methoxy chemisorbed on silica (*2*) the positions of CH stretching bands taken at elevated temperature (up to 400°C) do not show any shift as a function of temperature.

It has been observed (*8*) that the surface of molybdenum oxide starts to be reduced above 100°C and reduction becomes appreciable above 150°C in the presence of methanol/oxygen mixtures. This implies that the frequency shifts at temperature around 150°C are probably related to the reduction of oxygen vacancies:

$$\underset{(\mathrm{Mo}\text{—}\square\text{—}\mathrm{Mo})}{V_B} \xrightarrow{+e} \underset{(\mathrm{Mo}\text{—}\boxed{e}\text{—}\mathrm{Mo})}{V_B^-} \xrightarrow{+e} \underset{(\mathrm{Mo}\text{—}\boxed{2e}\text{—}\mathrm{Mo})}{V_B^{2-}}$$

It seems useful to us to represent sites associated with Mo atoms which have terminal oxygens attached in fully oxidized MoO_3 in terms of vacancies, as in commonly done with the bridged sites. Thus we proceed as follows

$$\underset{\square\ \mathrm{Mo}^{6+}}{V_T} \xrightarrow{+e} \underset{\boxed{e}\ \mathrm{Mo}^{6+}\ \text{or}\ \mathrm{Mo}^{5+}}{V_T^-} \xrightarrow{+e} \underset{\boxed{2e}\ \mathrm{Mo}^{6+}\ \text{or}\ \mathrm{Mo}^{4+}}{V_T^{2-}}$$

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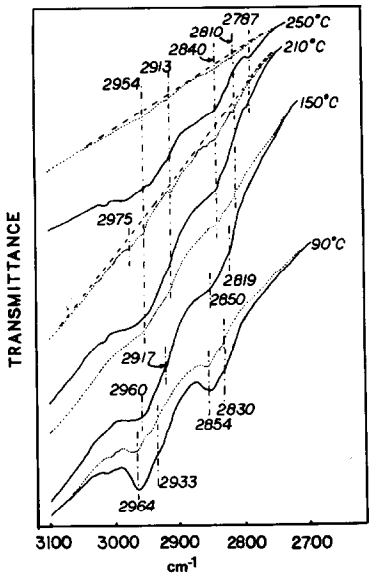


FIG. 1. Infrared spectra of chemisorbed methanol on molybdenum oxide in the CH stretching region. Spectra are taken at temperature indicated. —, 3.6% CH_3OH/O_2; · · · , after purging with helium for 20 min; ---, background.

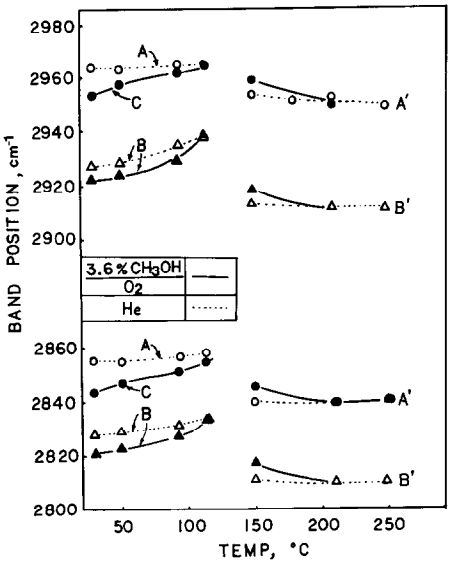


FIG. 2. Frequency shift in the CH stretching bands of chemisorbed methoxy groups as a function of reaction temperature. The bands A and B were assigned to the methoxy groups on V_T and V_B sites, respectively, in the previous paper (*1*). The bands above 2900 cm^{-1} are CH asymmetric stretching, and those below 2900 cm^{-1} are CH symmetric stretching. Typical precision of shift is ±2 cm^{-1}.

For instance, Mo^{5+} is physically the same as Mo^{6+}. These are two symbols for the same state and do not correspond to the configuration of the electrons, which is unknown to us.

Takezawa and Kobayashi (*9, 10*) have correlated the frequencies of the CH stretching bands of methoxy groups formed on several other pure oxides with the electronegativity of the oxide. However, for metal oxides with variable cation charge, as for molybdenum oxide, it is not possible to get the value of the electronegativity on Pauling's scale since the value exists only for metal elements. Moreover the same plot now does not show a good correlation after more data are added in, especially in the case of acidic oxides (Fig. 3).

In an attempt to improve the correlation and to identify the sites for the methoxy chemisorbed at temperatures above 150°C, we developed a new parameter defined as

$$\phi = (I_p)(Z^2/R^3)^{3/4}/1000.$$

Here Z is the cation charge, I_p is the ionization potential (in volts), and R is the radius (Å) of the metal ion with a charge Z. These three parameters characterize the cationic

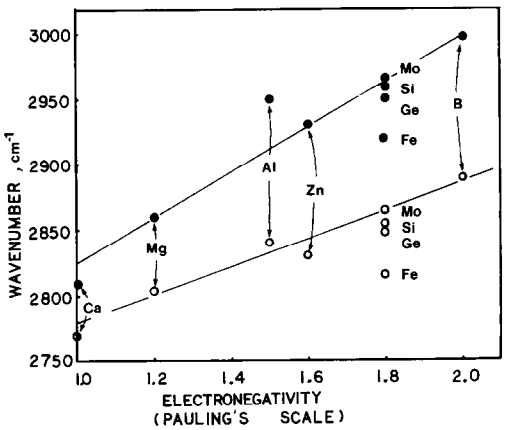


FIG. 3. Plot of the asymmetric and symmetric CH stretching bands of chemisorbed methoxy vs the electronegativity of metal oxides. B_2O_3(6); MoO_3, the band A in Fig. 2; GeO_2(3); SiO_2(2); Fe_2O_3(4); ZnO(7); Al_2O_3(5); MgO and CaO(8). ○, CH symmetric stretching band; ●, CH asymmetric stretching band.

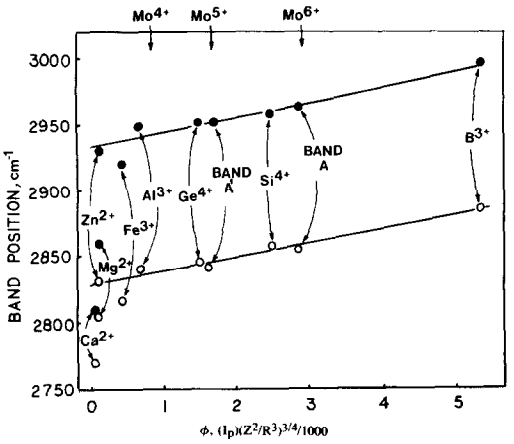
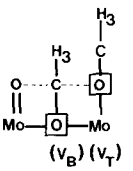


FIG. 4. Same as Fig. 3, but as a function of ϕ. References are the same as those in Fig. 3. The bands A and A′ are obtained from Fig. 2 (see also Fig. 1 and previous paper (*1*)).

sites with more discrimination than the single electronegativity, so that the parameter ϕ now has different values for Si, Ge, and Fe, for instance. The data upon which Fig. 3 is based are used to find the correlation shown in Fig. 4. The two exponents were founded by trial and error, choosing values to give the straight lines shown. The extremely basic oxides MgO and CaO are not interesting catalysts for the partial oxidation of methanol, so we have not given weight to the data for these oxides. The parmeter ϕ seems to furnish a good basis for the correlation of ν_a and ν_s for various acidic oxides. Although ϕ may be related to a tendency to attract electrons (acidity), we are considering here the cationic sites, so that ϕ does not necessary change monotonically in the direction of the acidity of the oxides as a whole.

The values for bands A and A′ now lie on the curve of Fig. 4 where A is associated with Mo^{6+} (at $T < 100$°C), and A′ is associated with Mo^{5+} (at $T > 150$°C). These results show that the most abundant active site on molybdenum oxide during the partial oxidation reaction of methanol is Mo^{5+} (V_T^-), an oxygen vacancy with one trapped electron. The reduction of the terminal-bonded oxygen vacancy V_T on molybdenum oxide effectively changes Mo^{6+} to Mo^{5+} during reaction at temperatures above 150°C. This causes the CH stretching bands of chemisorbed methoxy to shift to lower frequencies. Therefore, in Fig. 2, the shifts from the frequencies of the bands A and bands B at low temperature to those of the bands A′ and bands B′ above 150°C result from the reduction of the V_T and V_B sites to V_T^- and V_B^-. Likewise, the deviation to lower frequency of α-Fe_2O_3 in Fig. 4 is probably caused by the coexistence of Fe^{2+}.

Since we have not accounted for the effect of the anion, deviation can also be caused by the change and configuration of neighboring oxygens around the chemisorbed methoxy. This is probably the reason why the extremely basic MgO and CaO show deviation, and the CH bands of methoxy groups chemisorbed on the vacancy of the bridged oxygen Mo—O—Mo (V_B) on molybdenum oxide (the bands B and B′ in Fig. 2) locate at much lower frequencies than those on the vacancy of terminal oxygen Mo=O (V_T) (the bands A and A′ in Fig. 2). Therefore the shift from the frequencies of the bands A and bands A′ to those of the bands B and bands B′ in Fig. 2 can be explained by the effect of neighboring oxygen. Methoxy chemisorbed on V_B has a high probability to be influenced by neighboring oxygens, resulting in the weakening of the CH bonding in methoxy.



The formation of dehydration products such as dimethyl ether and dimethoxymethane, which has been observed during partial oxidation of methanol to formaldehyde (*11, 12*), probably proceeds by this type of methoxy on the oxygen vacancy of Mo—O—Mo, since the carbon in the methoxy is able to interact easily with

neighboring oxygen, resulting in the weakening of the CO bond in the methoxy.

When methoxy chemisorbs on the most acidic Mo^{6+}, it is not so active for the production of formaldehyde, because of the weak chemisorption bond and the strong CH bond. Most of the methoxy desorbs as methanol after purging with helium as observed in a previous paper (*1*). The methoxy on less acidic Mo^{5+} produces formaldehyde owing to the moderate bond strength in the CH, and our results in Figs. 1, 2, and 4 show that the most abundant species at reaction temperatures above 150°C is Mo^{5+}, the oxygen vacancy of Mo=O with one electron trapped. There is a high probability of CO production by the methoxy on least acidic Mo^{4+} because of the weakened CH bond.

It is also interesting to note that in the case of metal oxides with ϕ greater than 1.5, the transformation of chemisorbed methoxy into formate at high temperature has not been observed (see the corresponding references in Fig. 3). On the oxides with ϕ less than 1.0, which are active for the formation of formate, CO and CO_2, the infrared band of formate has been observed at temperature above 150–250°C. Examples are SnO_2 (*13*), Al_2O_3 (*5*), Cr_2O_3 (*14*), MgO (*15*), ZnO (*7*).

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