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Adsorption of Propylene and Acrolein on a Bi–Mo–Si Oxide Catalyst*

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After vacuum treatment of Bi–Mo–Si oxides (in the range 20–430°C), IR spectroscopy reveals that MoO_3 is present on the surface. MoO_3 may be present in the starting pressed sample, but may also form from decomposition at high temperature of one of the two bismuth molybdates that constitute the mixed oxides. The presence of C_3H_6 in the gas phase influences the Mo=O bond of the MoO_3 at the surface. Acrolein adsorption occurs already at room temperature and causes the disappearance of the 990 cm^{-1} band assigned to the vibration of the Mo=O bond. Desorption at 225°C partially restores this band. The infrared spectra of the sample after acrolein adsorption also reveal the presence of firmly adsorbed and weakly adsorbed species. Bands assigned to C=O stretching vibrations and CH_2 saturated stretching and bending vibrations are seen, but not bands assigned to vibrations of the structure $[RCOO]^-$.

INTRODUCTION

In previous papers we evidenced the role of the metal oxygen double bond in oxidation catalysts (*1*). Now, in order to check more thoroughly the actual role of the Mo=O bond in these catalysts, we have studied the effect of vacuum treatment, and of propylene and acrolein adsorption on the surface structure of Bi–Mo–Si oxides by IR investigations.

EXPERIMENTAL PART

Materials

The Bi–Mo–Si oxides used consisted of 35 wt % of Bi–Mo–Si oxides (Bi/Mo = 1) and the remainder was silica (*2*). The surface area of the catalyst was 70 m^2/g. The samples were pressed at 3000 kg/cm^2 into thin self-supporting plates of thickness corresponding to 6 and 7 mg/cm^2. The plate was mounted to the sample holder of vacuum infrared cell and the spectra were recorded in the course of operations described below.

Propylene (purity 98%) was frozen at liquid nitrogen temperature in a vacuum apparatus with subsequent removal of impurities by vacuum treatment. Before adsorption measurements, the bulb with propylene was cooled down to −78°C to protect the gas phase from traces of water.

Acrolein was supplied by FLUKA (purity 98 wt %) and was degassed by alternate freezing and thawing in vacuum.

Oxygen was obtained by thermal decomposition of $KMnO_4$. Water vapor was frozen out at liquid nitrogen temperature.

Vacuum Apparatus and Spectroscopic Measurements

The vacuum apparatus was of the current type with two infrared cells described

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elsewhere (*3*, *4*). The ray trajectors in the cell were about 10 mm. Thermal treatment of samples was performed in the upper part of the cell outside the infrared beam. A vacuum between 10^{-5} and 10^{-6} Torr was reached. Pressure of adsorbate was measured by a McLeod gauge.

Spectra of samples at room temperature were run using double beam Perkin-Elmer 221 and 21 spectrometers. The system of two cells (one of the cells was placed in the reference beam of the spectrometer) enabled us to balance the spectra of the vapor phase. For expansion of the transmission scale, the attenuator beam was applied in the reference beam keeping the transmission for spectral regions 850–1050 cm^{-1}, 1250–2000 cm^{-1}, 2000–4000 cm^{-1} nearly the same for each run of experiments at wave numbers 1050, 2000, and 2600 cm^{-1}, respectively. In Figs. 1–5, transmission is expressed in arbitrary units.

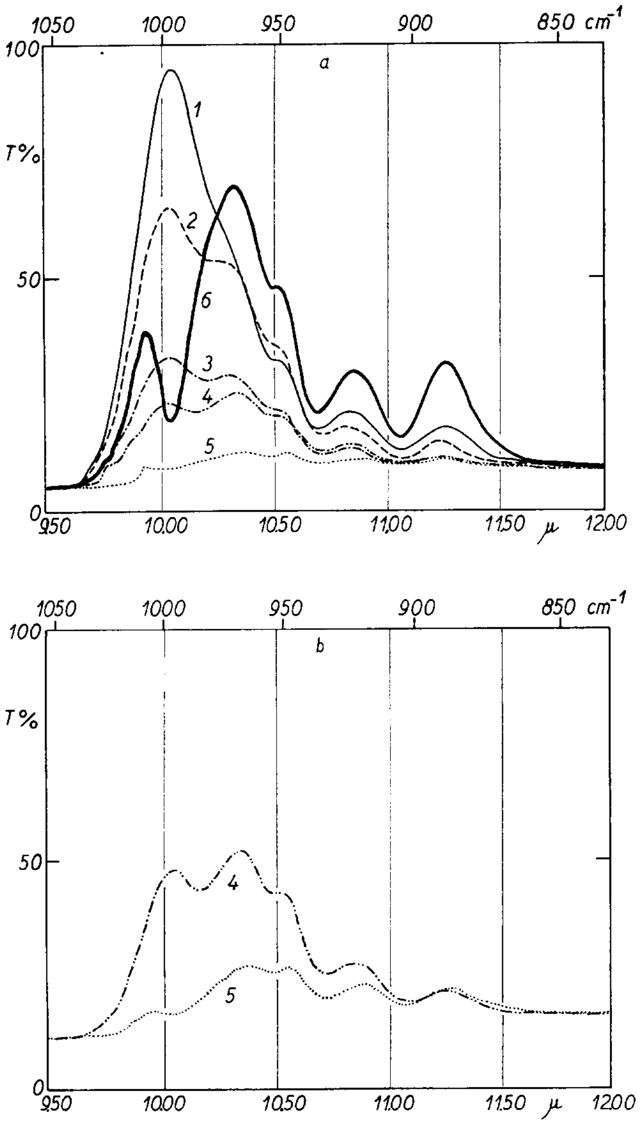

FIG. 1. IR Spectra of Bi–Mo–Si oxide catalyst: (1) in air; (2) after a 3-hr vacuum treatment at room temperature; after a 1-hr vacuum treatment at: (3) 125°C; (4) 225°C; (5) 430°C; and (6) after a 1.5 hr oxidation at 420°C (P_{O_2} = 44 Torr); (a,b) spectra were run with different attenuator beam.

RESULTS AND DISCUSSION

Vacuum Treatment

The spectra of the sample after vacuum treatment at different temperatures up to 430°C are given in Fig. 1a and b, in which only the spectral region 850–1050 cm^{-1} is reported.

A 3-hr vacuum treatment of Bi–Mo–Si catalyst at room temperature only causes the disappearance of the band at 1625 cm^{-1} connected with the decrease of intensity of the 3320 cm^{-1} band and with shifting of its position to 3420 cm^{-1}. It follows that during such treatment, the main part of the physically adsorbed water is desorbed. After a 1-hr vacuum treatment at 125°C, the whole of the physically adsorbed water is removed from the surface (the band at 3420 cm^{-1} disappears). OH surface groups persist even after vacuum treatment at 430°C (band 3650 cm^{-1}). By vacuum treatment at room temperature a band at 980 cm^{-1} was evidenced (Fig. 1). This band persists at higher temperature.

On increasing the temperature at which vacuum treatment of the catalyst is done, the transmission of the sample decreases while the color of the catalyst turns black. Simultaneously, the position of the 980 cm^{-1} band shifts to 990 cm^{-1} (see Fig. 1b). After 1.5 hr of oxidation of the sample at 420°C, with 44 Torr of O_2, the intensity of the 990 cm^{-1} band strongly increases (see Fig. 1a). By comparing the band position of our sample in the spectral region 850–1050 cm^{-1} with those of Bi–Mo oxides (Bi/Mo = 1), Bi–Mo–Si oxides (Bi/Mo = 1), pure MoO_3, and MoO_3 supported on silica, obtained with KBr disc technique, we assign the bands at 950, 930, and 900 cm^{-1} to vibrations of Bi–Mo oxides and of the bands at 980–990 cm^{-1} to vibrations of Mo=O of MoO_3. Moreover, IR data given by Batist *et al.* (*5*) and Dewing (*6*) enable us to prove the presence in our mixed oxides catalyst of Bi molybdates with Bi/Mo ratio at 2:3 (bands at 950–930–900 cm^{-1}).

The MoO_3 found in the sample could be present in the starting pressed sample, but was not revealed by KBr technique. However, it is possible that additional MoO_3 is also formed by vacuum treatment at high temperature.

Thermal treatment with oxygen at 420°C reveals that the amount of MoO_3 present in our catalysts increased at 420°C; the decrease of intensity of the bands at 950–930 and 900 cm^{-1} observed led us to think that MoO_3 was formed from the decomposition of the Bi/molybdate with Bi/Mo = 2:3.

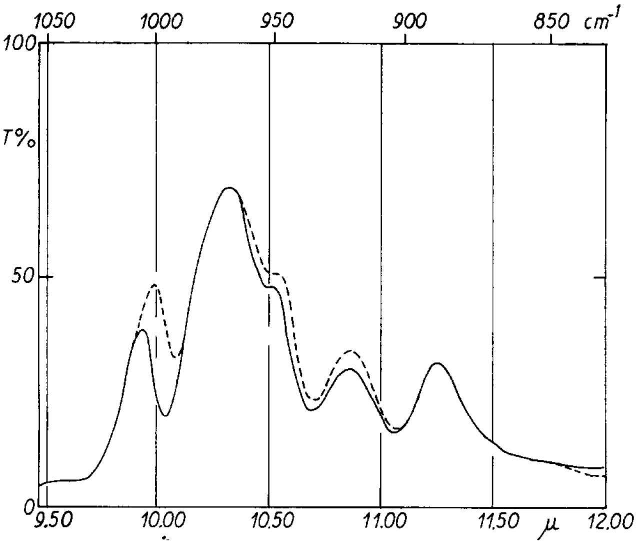

FIG. 2. IR Spectra of Bi–Mo–Si oxide catalysts: (—) after a 1.5 hr oxidation at 420°C (P_{O_2} = 44 Torr); (- - -) after C_3H_6 adsorption at room temperature (P_{O_2} = 80 Torr).

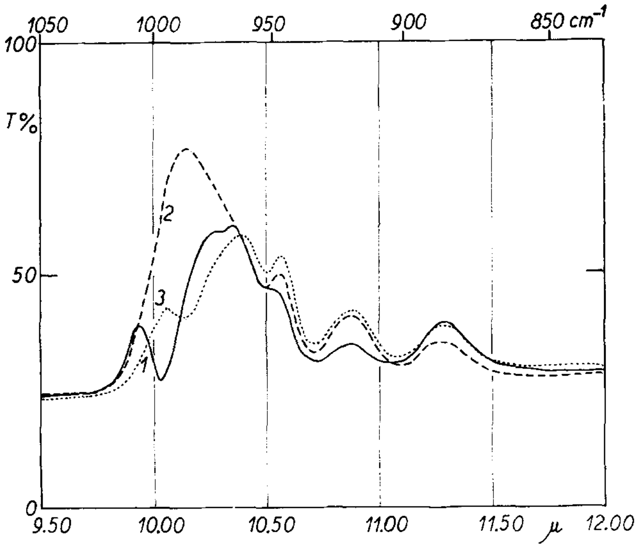

FIG. 3. IR Spectra of Bi-Mo-Si oxide catalyst: (1) after a 1.5 hr oxidation at 420°C (P_{O_2} = 44 Torr); (2) after a 2.5 hr adsorption of acrolein at room temperature ($P_{C_3H_4O}$ = 15 Torr) and after a subsequent 0.5 hr vacuum treatment at the same temperature; and (3) after a 1-hr desorption of surface species at 235°C.

Adsorption of Propylene

Bands of surface complex with propylene could not be seen at normal temperature or after 0.5-hr treatment at 165 and 225°C. But changes in the spectral region 850–1050 cm^{-1} were detected (Fig. 2). After adsorption of propylene at room temperature, the band of Mo = O vibration at 990 cm^{-1} was shifted to 985 cm^{-1} and its intensity decreased; heating to higher temperature did not lead to any further changes.

The changes observed after contacting the sample with propylene allow us to state that propylene interacts with MoO_3 present on the surface of the Bi–Mo–Si oxide.

Adsorption of Acrolein

After adsorption of acrolein on Bi–Mo–Si oxides at room temperature, both weakly adsorbed species (desorbable at room temperature) and firmly adsorbed species (desorbable only by heating the sample to higher temperatures) were observed. The same experiments made on silica (Cabosil) shows the same bands in the IR spectra of surface species with the same position as in our sample, but the amount of firmly bound species (per cm^2) was much less on the surface of Cabosil than in Bi–Mo–Si oxides. This fact suggests that also the Bi–Mo oxides component plays a role on the formation of adsorbed species.

During the adsorption of acrolein at room temperature the band at 990 cm^{-1}, corresponding to Mo=O of the MoO_3, disap-

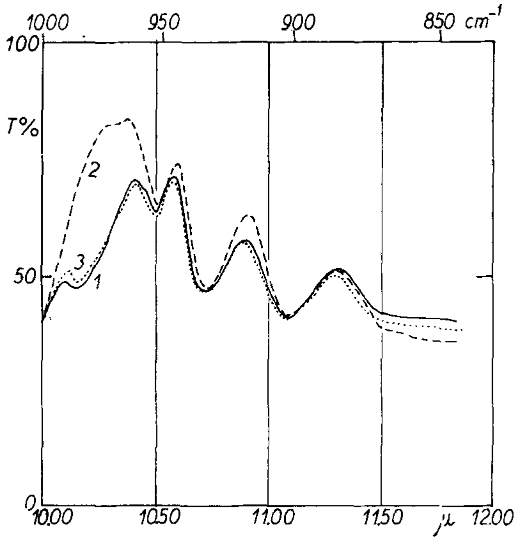

FIG. 4. IR Spectra of Bi-Mo-Si oxide catalyst: (1) after a 1-hr desorption of acrolein at 320°C; (2) after readsorption at room temperature; and (3) after further 1-hr desorption at 320°C.

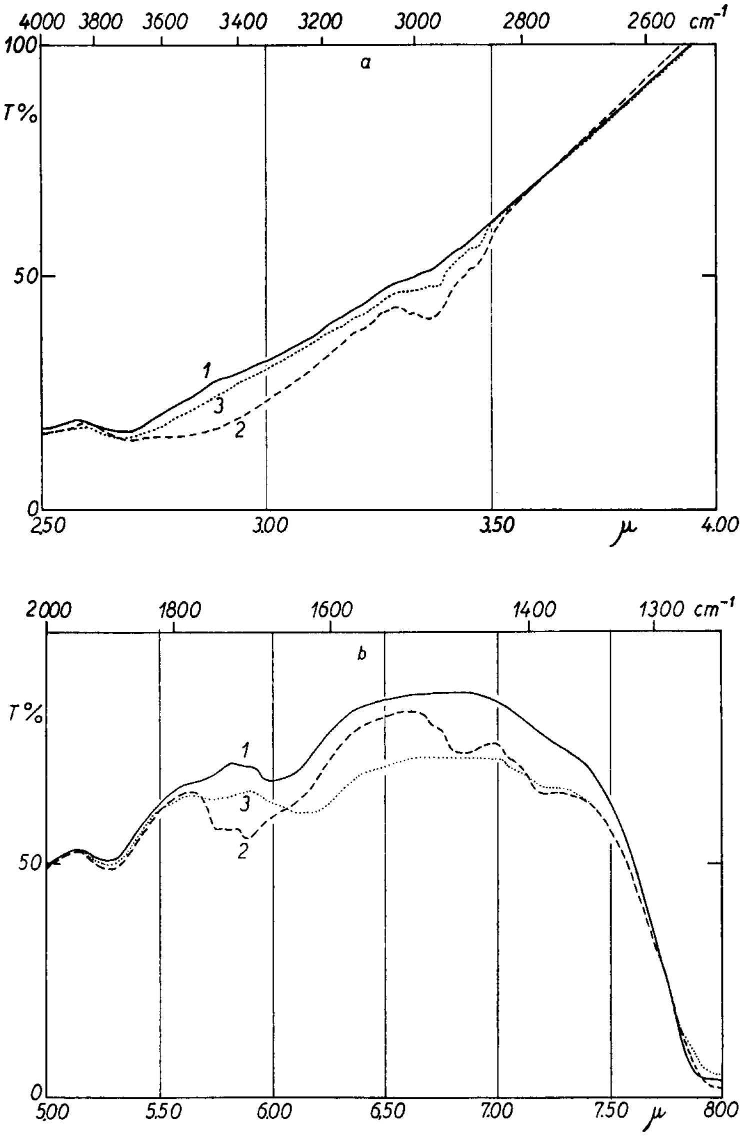

FIG. 5a,b. IR Spectra of Bi–Mo–Si oxide catalyst: (1) after a 1.5 hr oxidation at 420°C (P_{O_2} = 44 Torr); (2) after a 2.5 hr adsorption of acrolein at room temperature ($P_{C_3H_4O}$ = 75 Torr) and after a subsequent 0.5 hr vacuum treatment at the same temperature; and (3) after a 1-hr desorption of surface species at 235°C

pears (Fig. 3); on the other hand, the other bands characteristic of Bi–Mo oxides do not vary considerably. Only after a 1-hr heating of the sample at 225°C and condensing the desorbed species in a nitrogen liquid trap does a band at 985 cm^{-1} corresponding to Mo=O appear again, and simultaneously the bands of the adsorbed species nearly disappear. Further desorption for 1 hr at 320°C does not cause important changes of the 985 cm^{-1} band.

By adsorbing again at room temperature the previously desorbed species, the band at 985 cm^{-1} disappears and it appears again after heating the sample to 320°C (Fig. 4). After reoxidation of the catalyst at 420°C, the spectrum of the sample was quite the same as that of the starting sample with band at 990 cm^{-1}.

The infrared spectra in the region 1250–4000 cm^{-1} of the sample after acrolein adsorption (2.5 hr) and after further 0.5 hr desorption of weakly adsorbed species are reported in Fig. 5a and b. These spectra show the presence of OH groups and H bonds (broad absorption in the region 3600–3400 cm^{-1}), of C=O stretching vibrations (absorption near 1700 cm^{-1}) and CH_2 saturated stretching and bending vibrations (band at 2925, 2850, and 1460 cm^{-1}). The bands belonging to the structure $[R–COO]^-$, as observed by Sachtler and co-workers (*7*) in the case of benzaldehyde adsorption on $SnO_2–V_2O_5$, were not detected.

From this experiment we can deduce that in the formation of adsorbed species on the surface, MoO_3 is involved and reacts by losing its metal oxygen double bond character.

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