

INFRARED STUDY OF PYRIDINE OXIDATION ON Fe-Mo-O CATALYST

L. KUBELKOVÁ and P. JÍRŮ

*Institute of Physical Chemistry,
Czechoslovak Academy of Sciences, Prague 2*

Received May 4th, 1971

Surface complexes of pyridine on $\text{Fe}_2(\text{MoO}_4)_3\text{-MoO}_3$ catalyst activated at 400°C and changes in their composition, caused by oxidation of pyridine at 200°C and 400°C , were studied by means of infrared spectroscopy. Experimental data showed the formation of Brønsted acidic centres on the catalyst as a result of the oxidation reaction. These centres interacted with pyridine giving pyridium ions. Only pyridine bonded to the surface *via* electrons of the nitrogen atom was found to be present prior to oxidation. The formation of Brønsted acidic centres may be probably ascribed to adsorbed water which was one of the products of the pyridine oxidation.

In the recent study of the catalytic oxidation reactions, the attention was also devoted to the $\text{Fe}_2(\text{MoO}_4)_3\text{-MoO}_3$ catalyst (Fe-Mo-O) with respect to its activity and selectivity in methanol oxidation to formaldehyde. Among others, pyridine was employed for studying active centers on its surface. Pyridine preadsorbed on the Fe-Mo-O catalyst inhibits the oxidation as well as the adsorption of methanol. These facts led to the conclusion² that both pyridine and methanol interact probably with the same type of surface centres. The Fe-Mo-O catalyst activated in oxygen at 400°C was found to catalyze the oxidation of pyridine at temperatures higher than 200°C under the formation of N_2 , H_2O , CO and CO_2 (see²).

We thought is useful to complete the mass spectrometric data on the composition of the gaseous phase also by the study of the influence of the oxidation reaction on the pyridine surface complexes by means of infrared spectroscopy.

EXPERIMENTAL

The Fe-Mo-O catalyst with the surface area of $6.9\text{ m}^2/\text{g}$ and composition corresponding to 17.5 wt% Fe_2O_3 and 82.5 wt% MoO_3 was pulverized and subjected to 2000 kg/cm^2 pressure to make plates of $18\text{--}20\text{ mg/cm}^2$ "thickness". The sample was activated in the infrared cell⁴ by heating at 400°C under vacuum and by oxidation for 18 h at the same temperature (pressure of O_2 : 20–25 Torr). After removal of oxygen from the cell at room temperature, the spectrum of the sample was recorded (Zeiss, Jena UR-10 infrared spectrometer, spectral slit width: $4\text{--}12\text{ cm}^{-1}$). Then the pyridine interaction with the catalyst at room temperature and the oxidation of pyridine in presence of oxygen in the gas phase at 200° and 400°C followed. The corresponding spectra were always recorded after cooling the sample down to room temperature. The absorption bands of the gas phase were eliminated from the spectra by putting the second cell into the reference beam of spectrometer. The spectra of the surface species given in Fig. 1 were obtained by subtraction of the spectrum (in absorbance scale, A) of activated sample from the

spectra of the sample after interaction with pyridine or after the oxidation of pyridine. Detailed description of the experimental arrangement, the data about the purity and preparation of the reagents are published elsewhere³.

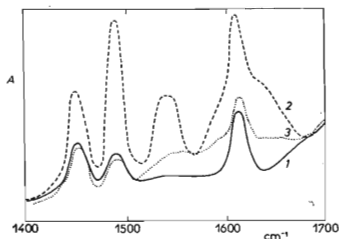


FIG. 1

IR Spectra of Pyridine Complexes Adsorbed on Fe-Mo-O Catalyst

1 After interaction with pyridine (12 Torr) at room temperature for 90 min; 2 after 60 min of oxidation at 200°C; 3 after subsequent 90 min of oxidation at 400°C. Initial values of pressures for 2 and 3: pyridine 12 Torr, O₂ 24 Torr.

RESULTS AND DISCUSSION

The spectra of the Fe-Mo-O surface complexes (Fig. 1) are presented in the region 1700–1400 cm⁻¹ where the bands of pyridine and of pyridinium ion (PyH)⁺ ring vibrations appear. Band assignment was performed according to literature data^{5,6}. Pyridine is adsorbed on the activated catalyst at room temperature under participation of the lone pair of electrons on the nitrogen atom (1610, 1487 and 1447 cm⁻¹ bands). As it has been shown earlier^{2,3}, the adsorption centres on the surface in this case are most probably vacancies in the coordination shell of cations. The properties of the catalyst are probably affected by water, produced during the oxidation of pyridine at 200°C, *i.e.*, acidic protonic centres are formed. These centres interact with pyridine giving (PyH)⁺ ions (1640, 1610, 1540 and 1487 cm⁻¹ bands). The simultaneous increase of the 1447 cm⁻¹ band, assigned to pyridine bonded to the surface *via* nitrogen atom, can be explained by assuming pyridine interaction with OH groups formed on the catalyst after the release of the proton from adsorbed water³. It also seems probable that oxygen influences the number of active centres as well as their properties³ by keeping the catalyst in the oxidized state. This may result in the intensity changes of spectral bands. The decrease of the intensity of all bands of adsorbed pyridine complexes after the oxidation of pyridine at 400°C might be caused by the consumption of pyridine during the reaction.

At the same time, however, neither the effect of further changes in the properties of catalyst during the oxidation can be excluded. As for other adsorbed complexes than those mentioned above (*e.g.* CO, CO₂, N₂), the only competent statement is that their bands were not found in the spectra under the described experimental conditions.

We can conclude that oxidation of pyridine at higher temperatures leads to changes in the composition of surface complexes. This may be accounted for to the effect of water produced in the oxidation reaction. Water interacts with the catalyst under the formation of protonic centres.

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Translated by V. Čermáková.