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IR INVESTIGATION OF THIOPHENE HYDROGENOLYSIS ON γ-Al_2O_3

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The adsorption of thiophene on γ-Al_2O_3 in the temperature range from 20 to 450 °C has been studied. It is demonstrated that hydroxyl groups of the surface are not only adsorption sites but also reactants leading to the formation of saturated surface structures. The hydrogenation of surface structures up to a hydrogen pressure of 11 atm was followed IR-spectroscopically in a specially designed cell. The rates of hydrogenation of these species were found to be different.

Изучена адсорбция тиофена на γ-Al_2O_3 при температурах от 20 до 450 °С. Показано, что OH-группы поверхности являются не только центрами адсорбции, но и вступают во взаимодействие, в результате которого образуются насыщенные поверхностные структуры. За процессом гидрирования поверхностных структур при давлении водорода до II атм наблюдали ИК спектроскопически с помощью специально сконструированной кюветы. Установлено, что скорость гидрирования этих форм различна.

The conversions of thioorganic compounds on different catalysts have been investigated earlier /1-6/, but the conclusions on the mechanism, made on the basis of the reaction products and the catalyst structure are contradictory or not fully justified.

In recent years IR spectroscopy has found increasing use in mechanistic investigations with thioorganic compounds, because it permits different forms of adsorption to be observed experimentally /7-11/.

Most spectroscopic studies are restricted to interactions between adsorbed molecules and a catalyst, but the catalytic reactions of the various adsorbed species involved in hydrogenation and hydrogenolysis under industrial conditions have not been investigated. Therefore, we have studied the hydrogenolysis of thiophene, one of the most stable thioorganic compounds. For this purpose a specially designed cell-reactor was used, which allowed to record the spectrum during the reactions (at temperatures up to 450 °C and hydrogen pressures up to 20 atm).

EXPERIMENTAL

γ-Al_2O_3 powder obtained by the thermal decomposition of aluminium hydroxide was pressed into thin plates at 20 kg/mm^2. The resulting plate was 20 mg/cm in thickness. To remove organic impurities and adsorbed gases the sample surface was treated in air at 500 °C for 2 hrs and at 400 °C in vacuum. Before adsorption thiophene was degassed repeatedly. IR spectra were recorded in the regions of 1200–2 000 and 2 500–3 800 cm^{-1} on a UR-20 spectrometer converted for work at high temperatures. The slit width was 8 cm^{-1} at 1 000 cm^{-1}

The adsorption of thiophene at 20 °C is accompanied by the appearance of two groups of peaks in the spectrum: at 1260, 1410, 1580, 3 110 cm^{-1} and at 1470, 2 860, 2 930 cm^{-1} (Fig. 1). The bands of the first group are analogous to those in the spectrum of liquid thiophene. The band at 1260 cm^{-1} can be assigned to the vibration of the C–S bond in the thiophene ring /12, 13/, and the bands at 1410

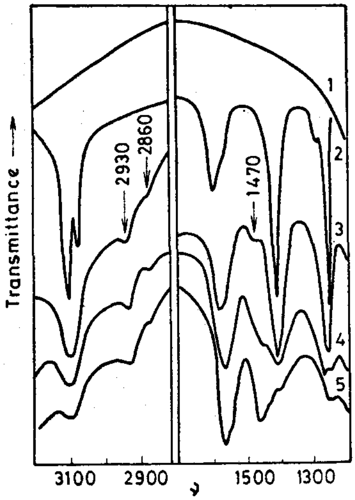

Fig. 1. IR spectra of thiophene adsorbed on γ-Al_2O_3: (1) background of the sample; (2) liquid thiophene; (3) adsorption of thiophene at 20 °C and (4) at 400 °C; (5) desorption of thiophene at 400 °C

and 1 580 cm^{-1} to the skeletal vibrations of the ring /14, 15/. The bands at 1470, 2 860 and 2 930 cm^{-1} belong to the deformation and stretching of the CH_2 group /16/.

To study the effects of temperature on adsorbed forms of thiophene on γ-Al_2O_3, the sample was heated to 400 °C and the cell evacuated to remove adsorbed thiophene (curves 4 and 5) which is desorbed into the gas phase under these conditions. During this process the bands at 1470, 2 860, 2 930 and 3 100 cm^{-1} persist. This fact indicates the formation of a rather strong bond between adsorbed thiophene and the γ-Al_2O_3 surface; the band at 1 580 cm^{-1} shifts to 1 570 cm^{-1} and the 1 260 cm^{-1} band splits into two: at 1250 and 1265 cm^{-1}.

The measurement of band intensities (optical density) at different stages of desorption has shown that the relative intensity of the 1470 and 1 570 cm^{-1} bands remains constant while the intensities of the 1250 and 1265 cm^{-1} bands fall to 1/15 of their original values in comparison with the above bands. This fact indicates the existence of different species of adsorbed thiophene.

Taking into account previous investigations by Ligin et al. /10/ and Nicolson /7,8/, we may draw the conclusion that there are several forms of adsorbed thiophene species on the surface of γ-Al_2O_3. One of them leaves the stretching vibrations of the CH group unchanged (3 100 cm^{-1}) and thus characterizes the one-point adsorption of thiophene, owing to the unshared $3p^2$ electrons of the sulfur atom. The second form of adsorption may be connected with rising peaks at 1470, 2 860 and 2 930 cm^{-1}, which relate to the stretching mode and to the symmetric and asymmetric deformation of the CH_2 group, respectively. The appearance of these bands is probably due to the formation of saturated structures with the hydrogen of surface OH groups, with retention of the thiophene ring.

The spectral region of 3 000–3 800 cm^{-1} was studied to elucidate the question about the participation of hydroxyl groups of the aluminium oxide surface in the formation of chemisorbed thiophene compounds. The spectra show that thiophene adsorption at room temperature decreases the band intensity of isolated OH groups in the region of 3 680–3 800 cm^{-1} /17/ and also in the region of 3 300 cm^{-1} (Fig. 2, curve 2).

Upon heating the sample of adsorbed thiophene to 400 °C (curves 3–6), a high frequency band appears in the spectrum, owing to isolated OH groups. At the same time the 3 620 and 3 580 cm^{-1} bands disappear. This indicates that the formation of CH_2 groups on the surface is due to the hydrogen of hydrogen-bonded OH groups. To prove this point, the adsorption of thiophene on a hydrogenated γ-Al_2O_3 surface has been studied. After adsorption, only the bands analogous to those of liquid thiophene

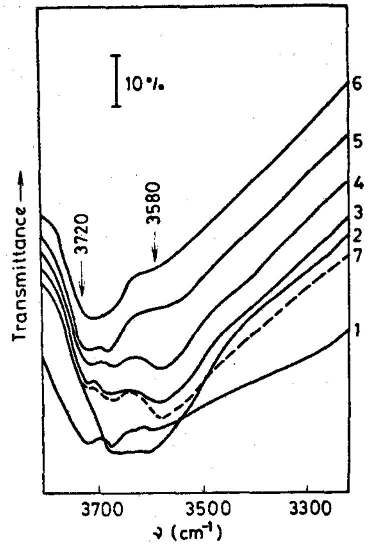

Fig. 2. IR spectra of the OH groups of γ-Al_2O_3. (1) after thiophene adsorption: at 20 °C (2), 100 °C (3), 200 °C (4), 300 ° (5) and 400 °C (6); (7) after introducing hydrogen into the cell at 400 °C

are observed with an additional band at 3 100 cm^{-1}, which is characteristic of thiophene adsorbed through the sulfur atom, this form can be easily removed upon heating to 100 °C.

In order to investigate the hydrogenolysis of chemisorbed thiophene, purified hydrogen was admitted into the cell under a pressure of 5 atm (at lower pressures no appreciable hydrogenolysis would take place even at 450 °C). Figure 3 shows the hydrogenation of chemisorbed thiophene at different pressures. At 300 °C and a hydrogen pressure of 5 atm (curve 2) besides the initial ones, new bands appear at 1305 and 1360 cm^{-1}, i.e. in the region of deformational vibrations. They can be assigned to vibrations of trans-CH=CH- and CH_3 groups, respectively /16/. In the region of stretching vibrations, very closely spaced bands are observed at 2 800-3 000 cm^{-1} and an intensive band at 3 018 cm^{-1}, assigned to stretching vibrations of

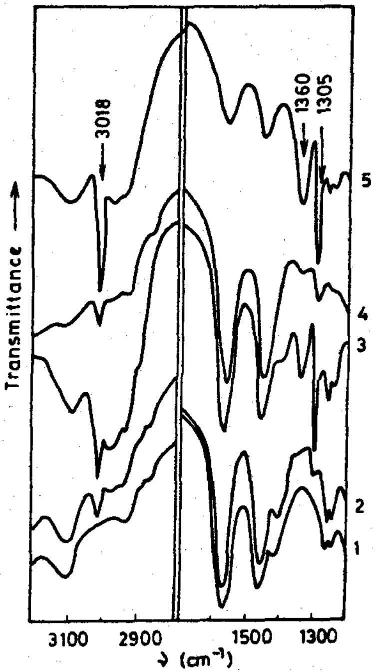

Fig. 3. Variation of the IR spectrum of adsorbed thiophene during hydrogenolysis. (1) Adsorption of thiophene at 400 °C; (2) hydrogenation at 300 °C at 5 atm; (3) at 11 atm and (4) after evacuation of the gas phase, hydrogenation at 400 °C at P_{H_2} = 5 atm

the -CH=CH- group. Upon increasing P_{H_2} to 11 atm, the intensities of these bands increase with a simultaneous decrease in the intensities of the 1 250 and 1 265 cm^{-1} bands, the bands at 1470 and 1 570 cm^{-1} are more stable. This fact proves that different species of adsorbed thiophene undergo hydrogenation to different extents at 300 °C, as can be seen most clearly from the spectrum of the sample evacuated after the reaction (Fig. 2, curve 4). All the bands of adsorbed thiophene decrease in intensity upon increasing the temperature up to 400 °C.

During hydrogenation of adsorbed thiophene some changes take place also in the region of stretching vibrations of the OH groups. The hydroxyl band at 3 580 cm^{-1}

appears again (Fig. 2, curve 7). This provides additional evidence for its participation in the formation of a chemisorbed surface compound. This fact invalidates the assumption that the disappearance of the OH groups is not connected with the effect of temperature. Identification of the reaction products was made by means of the 1270, 1305, 1360, 2 800-3 000 and 3 018 cm^{-1} bands. The appearance of the vibrations of –CH=CH– and CH_2–groups in the spectrum indicates the formation of butene /18/ in the gas phase.

The predominant formation of butenes upon the hydrogenation of adsorbed thiophene was also proved chromatographically.

Thus the investigation of thiophene adsorption in a wide temperature range has shown that, together with physical adsorption, strongly chemisorbed thiophene species are also observed on the γ-Al_2O_3 surface, OH groups being involved in their formation. The hydrogenation of these surface species proceeds at different rates.

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