



**HAL**  
open science

# IR Study of the Adsorption and Isotopic Scrambling of Thiophene on CaO

A A Tsyganenko, F. Can, F. Maugé

► **To cite this version:**

A A Tsyganenko, F. Can, F. Maugé. IR Study of the Adsorption and Isotopic Scrambling of Thiophene on CaO. *Journal of Physical Chemistry B*, 2003, 107 (33), pp.8578 - 8587. 10.1021/jp034344y . hal-04164425

**HAL Id: hal-04164425**

**<https://hal.science/hal-04164425>**

Submitted on 26 Oct 2023

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# IR STUDY OF THE ADSORPTION AND ISOTOPIC SCRAMBLING OF THIOPHENE ON CaO

A.A. Tsyganenko<sup>a</sup>, F. Can<sup>b</sup>, F. Maugé<sup>b</sup>

<sup>a</sup> *Institute of Physics, St. Petersburg University, St. Petersburg 198504, Russia*

<sup>b</sup> *UMR CNRS 6506, ISMRA, University of Caen, 14050 Caen Cedex, France*

Thiophene, thiophene-2,5-*d*<sub>2</sub> and thiophene-*d*<sub>4</sub> adsorption on CaO activated at 723-973 K has been investigated at 170-300 K by means of IR spectroscopy and IR analysis of desorbed gas. Molecular adsorption of thiophene occurs on surface oxygen ions and basic OH groups by weak H-bond of CH groups with the lone electron pairs of oxygen. On the most basic oxygen ions of CaO activated at 973 K, thiophene dissociates already at 200 K with the formation of surface OH groups and thiophenide C<sub>4</sub>H<sub>3</sub>S<sup>-</sup> anions. This reversible dissociation accounts for the catalytic reaction of isotopic scrambling of thiophene-2,5-*d*<sub>2</sub> that takes place already at 220 K and leads to the appearance of all ten possible thiophene isotopomers in the desorbed gas. Experiments with thiophene coadsorption with CO enable one to associate the sites of thiophene dissociation with those cus oxygen ions that bound CO giving carbonite CO<sub>2</sub><sup>2-</sup> ions. Three kinds of such sites could be distinguished, that differ in the band positions of the resulting OH groups and in thermal stability of corresponding thiophenide anions.

## INTRODUCTION

Studies of thiophene adsorption and transformations on solid surfaces are of a great importance for the search of ways of sulphur removal from petroleum feedstocks. Detailed information about the adsorption sites and the structure of surface complexes could be obtained by means of IR spectroscopy. IR spectroscopy at variable temperatures is an excellent tool to study the interaction of molecules with the surface and mechanism of surface species transformations. Combined with adsorption of test molecules such as CO, this technique enables one to estimate the strength and concentration of surface sites and to follow their occupation or the creation of new sites after adsorption of other molecules [1].

Thiophene adsorption has been studied so far spectroscopically mostly on hydrotreatment (HDT) catalysts (see [2] and refs cited therein), on acid sites of oxides used as HYT supports, such as alumina [3-6], silica [7, 8] or of zeolites [8-11], both pure or modified by transition metal cations. Interaction of thiophene with basic sites has been practically not studied yet although the development of HDT catalysts supported on basic oxides is considered to be very promising for gasoline production. Therefore, the aim of this study was to elucidate the

mechanism of thiophene adsorption and transformations on CaO by means of IR spectroscopy at variable temperatures.

CaO surface does not manifest any Lewis or Brønsted acidity, and the OH groups of this oxide, whose surface location was confirmed by their sensitivity to the adsorption of CCl<sub>4</sub>, acetone [12], or ozone [13] do not show any tendency to form H-bond with the adsorbed molecules [14, 15]. After activation at about 1000 K, strong basic sites arise at CaO surface, capable to chemisorb CO producing very reactive carbonite CO<sub>2</sub><sup>2-</sup> ions [16], or to interact with ozone with the formation of surface ozonides [13]. Ammonia adsorption on such surface results in its dissociation with the formation of OH groups and NH<sub>2</sub><sup>-</sup> ions [17]. This reaction is believed to take place at the same basic oxygen atoms of CaO surface. Thus, this oxide is a good model system for studying adsorption on pure basic surface. Preliminary experiments have shown that thiophene in fact chemisorbs at 300 K on CaO [18], and here we report, as far as we know, a first detailed study of thiophene interaction with this oxide.

## EXPERIMENTAL

Batches of commercial Ca(OH)<sub>2</sub> were pressed into 20-50 mg/cm<sup>2</sup> pellets and treated directly in the cell. The stainless steel IR cell for measurements at 60-370 K has been described elsewhere [16, 19]. The cell enables sample treatment at 300-1000 K in vacuum or under controlled atmosphere to be carried out. The pellets were activated at 970 K in vacuum for 0.5 - 2 h. To obtain hydroxylated surface, the activated sample was let in contact with about 10 torr of water or D<sub>2</sub>O vapour at 300 K and then evacuated again at 723 K.

Normally, thiophene was added into the cell cooled by liquid nitrogen, then the temperature was raised until the appearance of the bands of adsorbed species and the following pressure increase indicates thiophene evaporation and adsorption. Then, the spectra were registered with progressively growing temperature up to 300 K. To study desorption, evacuation was carried out at low temperatures, at 300 K, or at elevated temperatures up to complete removal of surface species at 300-470 K.

To study the spectra of desorbed gases, the latter were let into a special glass cell, 175 mm long, with KBr windows. In order to keep the sample always at the desired temperature, the gas probes were taken without complete removal of He from the cell. For that, the cell was open to an isolated U-trap cooled by liquid nitrogen and gas, desorbed in certain temperature interval, was trapped. Then, the U-trap was disconnected from the cell, and gas, separated from He, was introduced into the gas cell. The pressure of analysed gas, as far as possible, was taken the same, close to 0.6 torr.

Commercial thiophene, as well as thiophene- $d_4$  (99 atom % D) and thiophene-2,5- $d_2$  (98.9 atom % D) produced by CDNISOTOPES were used. Commercial CO, O<sub>2</sub> and He before letting into the cell, were always purified by passing through a trap cooled with liquid nitrogen.

Transmission IR spectra were recorded with 4 cm<sup>-1</sup> spectral resolution by NICOLET 710 and NICOLET Nexus spectrometers, spectra of gases were run by an Avatar THERMONICOLET spectrometer.

## RESULTS AND DISCUSSION

### *Adsorption of thiophene- $h_4$*

In the spectrum of CaO, as it was already mentioned in [13], the band of surface OH groups is presented by two peaks at 3710-3703 cm<sup>-1</sup>, poorly resolved at 300 K that move to higher wavenumbers, up to 3722 and 3710 cm<sup>-1</sup> on lowering the temperature up to 77 K. If the pretreatment temperature is below 773 K, one more weak band could be seen at about 3610 cm<sup>-1</sup>, that according to [20] belongs to the OH groups of type V, that is bound to 5 surrounding Ca ions, while the double peak at about 3710 cm<sup>-1</sup> is due to more basic type I hydroxyls. Both bands could be seen in fig. 1 (curve 1) in the spectrum of the sample pretreated at 723 K, registered after cooling the cell by liquid nitrogen. Thiophene adsorption at about 220 K and pressure of about 0.2 Torr in equilibrium results in almost complete perturbation of the OH groups that absorb at 3722 and 3710 cm<sup>-1</sup>, while new strong band of perturbed hydroxyls could be seen, that in the spectrum registered at 77 K occurs at 3700 cm<sup>-1</sup> with a shoulder at about 3687 cm<sup>-1</sup> (curve 2). The position of this band is not quite constant. When first thiophene molecules reach the surface, the band appears at 3675 cm<sup>-1</sup>, then it shifts to about 3700 cm<sup>-1</sup> and reveals almost no dependence on the coverage or temperature. Two other bands arise in the OH frequency region at 3616 and 3485 cm<sup>-1</sup>. The former could be removed together with the band at 3700 cm<sup>-1</sup> by evacuation at about 220 K simultaneously with the restoration of the initial OH bands, while the latter remain in the spectrum up to 300 K, and could only be removed by prolonged pumping at ambient temperature.

Strong bands of adsorbed thiophene appear at 3100, 3083, 3072 and 722 cm<sup>-1</sup>, positions of other bands shown in fig. 1 do not differ from those presented in Table 1 for sample pretreated at 973 K. It should be noted that the band at 1408 cm<sup>-1</sup> appears with well resolved shoulder at 1400 cm<sup>-1</sup>, shown in a special insert in fig. 1. Most of thiophene bands disappear together with those of OH groups at 3700 and 3616 cm<sup>-1</sup> after pumping at 220 K or

above. Some other bands are more resistant and remain together with the OH band at 3485  $\text{cm}^{-1}$  up to about 300 K. These are the bands at 3055, 3010, 2995, 803, 783 and 698  $\text{cm}^{-1}$ .

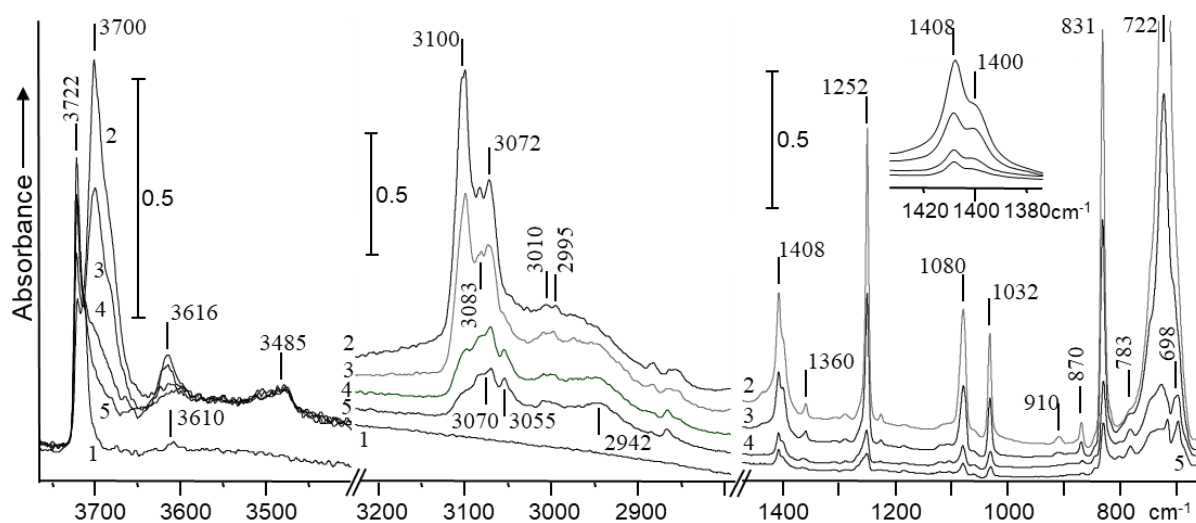


Figure 1. IR spectra of thiophene- $h_4$  adsorbed on CaO pretreated at 723 K. (1) Sample cooled up to 77 K, (2) after addition of thiophene- $h_4$  and heating the cell up to 200 K and (3-5) after progressive removal of adsorbate by raising the sample for 10-35 s into the warm part of the cell kept at 300 K. All the spectra are registered at 77 K.

Table 1 Band positions of thiophene- $h_4$ , thiophene-2,5- $d_2$  and thiophene- $d_4$  in the gas state [21] and adsorbed on CaO pretreated at 973 K.

| thiophene- $h_4$  |                                     |                       | thiophene-2,5- $d_2$ |                     |                       | thiophene- $d_4$  |                 |                       |
|-------------------|-------------------------------------|-----------------------|----------------------|---------------------|-----------------------|-------------------|-----------------|-----------------------|
| gas <sup>21</sup> | weak ads                            | strong ads            | gas <sup>21</sup>    | weak ads            | strong ads            | gas <sup>21</sup> | weak ads        | strong ads            |
|                   | 3690 (3616) <sup>a</sup> (OH)       | 3560, 3485, 3430 (OH) |                      | 2665 (OD)           | 2630, 2580, 2535 (OD) |                   | 3690, 3616 (OH) | 2630, 2580, 2535 (OD) |
| 3128              | 3110(sh),<br>3100-3090 <sup>b</sup> | 3095, 3084 3054       | 3101, 3088           | 3088, 3078,<br>2957 | 3081, 3055, 3000      | 2343              | 2331            | 2314, 2270            |
| 3088              | 3075                                | 3010, 2995            | 2368, 2336           | 2316                | 2314, 2284            | 2290              | 2283            | 2235, 2226            |
| 1547              |                                     | 1475                  | 1500                 |                     |                       | 1462              | 1453            | 1423                  |
| 1408,             | 1408, (1400),                       |                       | 1398, 1310           | 1393 1304,<br>1250  | 1382, 1283            | 1376,             | 1373, 1235      |                       |
| 1358              | 1360                                |                       |                      |                     |                       | 1248              |                 |                       |
| 1253              | 1253                                | 1290                  | 1215                 | 1213, 1182          | 1227, 1145            | 1061,             | 1145, 1112,     | 964                   |
|                   |                                     |                       |                      |                     |                       | 1034              | 1080, 1029      |                       |
| 1079              | 1081                                | 1185                  | 1044                 | 1045                | 1081                  | 896,              | 892, 844        | 860                   |
|                   |                                     |                       |                      |                     |                       | 846               |                 |                       |
| 1032              | 1030                                | 1063                  | 918                  | 915                 |                       | 785               | 783             | 840                   |
| 838               | 831                                 | 845, 813, 803         | 884, 818             | 881, 827            | 847                   | 731               | 727, 710 (sh)   | 718                   |
| 712               | 733-722                             | 706-690, 640          | 754, 584             | 749                 | 717-695, 652          | 531               |                 | 691                   |

Thiophene- $h_4$  adsorption at low temperature on preliminary deuterated surface of CaO pretreated at 723 K, where the double peak at 2746-2740  $\text{cm}^{-1}$  and a weak maximum at 2661  $\text{cm}^{-1}$  could be seen instead of corresponding OH bands at 3722-3710 and 3610  $\text{cm}^{-1}$ , leads to exactly the same spectrum of the adsorbed thiophene. The band of perturbed OD groups arises at 2730  $\text{cm}^{-1}$ , while the diminution of 2661  $\text{cm}^{-1}$  band, is accompanied by the appearance of a slightly stronger maximum at 2667  $\text{cm}^{-1}$ . The band at 3485  $\text{cm}^{-1}$  arises, but no corresponding deuterated band could be seen, at least at low temperatures.

Thiophene adsorption on CaO pretreated at 973 K does not perturb completely the band of surface OH groups. At highest coverages, that could be achieved at about 200 K, one can easily see the perturbation (figure 2), when the intensity of initial bands diminishes and new absorption appears at lower wavenumbers, first at about 3675-50  $\text{cm}^{-1}$ , then with the increasing coverage strong maximum occurs at 3690  $\text{cm}^{-1}$ . However, unlike CaO pretreated at 723 K, where both OH components diminish substantially, for the samples activated at 973 K the high-frequency maximum at 3722  $\text{cm}^{-1}$  remains almost intact, and the intensity decrease is well observable only for the low-frequency OH species that absorb at 3710  $\text{cm}^{-1}$ . The band at 3616  $\text{cm}^{-1}$  does not appear, but besides the band at 3485  $\text{cm}^{-1}$ , two more new OH bands arise at 3560 and 3430  $\text{cm}^{-1}$ .

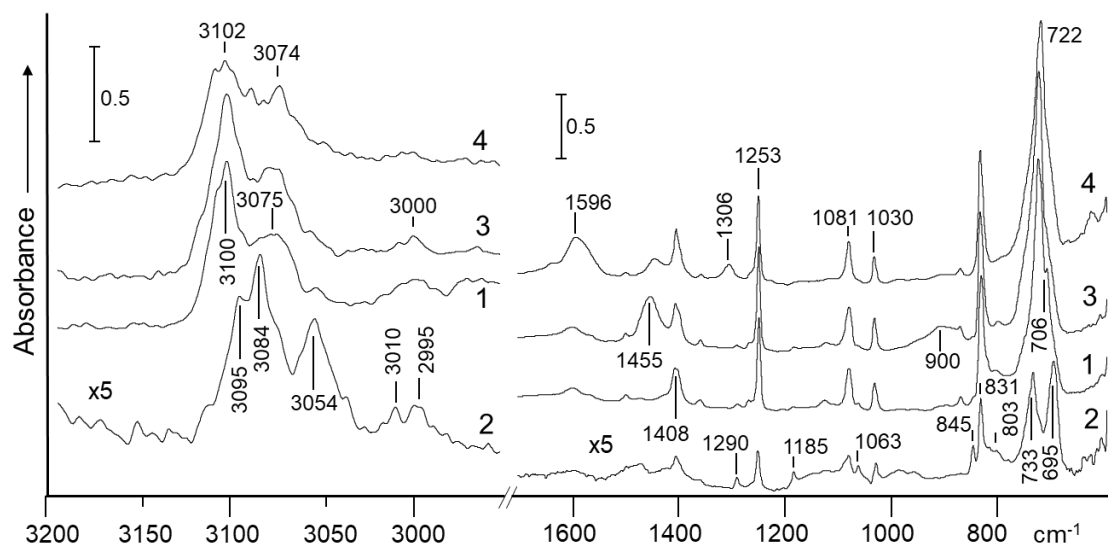


Figure 2. IR spectra of thiophene-*h4* adsorbed on CaO pretreated at 973 K: (1) after addition of thiophene-*h4* and heating the cell up to 200 K, (2) after removal of weakly bound molecules by quickly (1 min) heating the sample up to 300 K, (3) after CO addition at 77 K to the sample with thiophene adsorbed as in stage 1, and (4) after subsequently raising the temperature up to 205 K. Spectra 1-3 are registered at 77 K.

Like in the case of CaO pretreated at 723 K, bands of adsorbed thiophene could be separated in two groups: those which disappear after evacuation at about 220 K together with the bands of perturbed hydroxyls, and those that correspond to more strongly held species. To show this difference, the bands are presented in two separate columns in Table 1, denoted as "weak" and "strong" adsorption, respectively. The former bands arise and start to grow at about 180 K as soon as temperature is raised enough for thiophene evaporation, and have almost the same frequencies as after adsorption on CaO pretreated at 723 K. As a certain dissimilarity caused by higher pretreatment temperature, one could mention the absence of the band near 1400  $\text{cm}^{-1}$  in the spectrum of sample activated at 973 K.

Bands of weakly adsorbed thiophene do not differ much from those of liquid thiophene in their shape, position and relative intensities. There are few bands, however, that reveal considerable difference in their positions with respect to free molecules. At 200 K, the most intense bands of adsorbed thiophene in the C-H stretching region occur at  $3100\text{ cm}^{-1}$  with a shoulder at  $3110\text{ cm}^{-1}$ , and at  $3075\text{ cm}^{-1}$ , far below the positions of the same vibrations for the gas phase (see the table), and with the decreasing coverage the differences increase. The strongest IR band of thiophene, corresponding to the out-of-plane C-H bending vibration appears first at  $722\text{ cm}^{-1}$ , and moves to  $733\text{ cm}^{-1}$  with the decreasing coverage. It is, thus, displaced by about  $21\text{ cm}^{-1}$  to higher wavenumbers with respect to the value of  $712\text{ cm}^{-1}$  known for gas [21] or  $714\text{ cm}^{-1}$  [22] for liquid thiophene.

As the coverage decreases, the  $706\text{ cm}^{-1}$  band, first observed as a shoulder of the  $722\text{ cm}^{-1}$  band (fig. 2 curve 1), moves to lower wavenumbers up to  $695$  (curve 2) and further to  $690\text{ cm}^{-1}$ , where it could be seen at 300 K together with other bands of "strongly" adsorbed species. Cooling the sample to 77 K after removal of gaseous thiophene does not change the band positions, while repeated adsorption or pumping at about 200 K demonstrate the reversibility of the above changes in the spectra. This confirms that the observed shifts of bands due to both "weak" or "strong" adsorption are in fact caused by coverage variations, but not by the temperature increase.

Prolonged evacuation at about 230 K leads to almost complete disappearance of the  $733\text{ cm}^{-1}$  peak together with other bands of weakly adsorbed molecular thiophene, but only slightly diminishes the intensities of other bands, listed in the column "strong adsorption" in the table 1, including that at  $690\text{ cm}^{-1}$ . These bands are not typical of thiophene in any aggregate state, and, evidently, are due to some product of thiophene chemisorption. To see better the weak bands of these products, the absorbance scale for the curve 2 in fig. 2 is 5-fold expanded.

In the CH stretching region, strong band of molecular form at  $3100\text{ cm}^{-1}$  with the shoulder at  $3110\text{ cm}^{-1}$  and broader band at  $3075\text{ cm}^{-1}$  shift to lower wavenumbers with the decreasing amount of adsorbate, until they disappear together with the band at  $733\text{ cm}^{-1}$ . As seen from the spectra presented in fig. 2 curves 1 and 2, the C-H stretching region is complicated due to the superimposed absorption of the remaining traces of the shifted bands of molecular form and almost coinciding bands of several chemisorbed products, much more abundant after pretreatment at 973 K. The most typical bands of chemisorbed products can be well distinguished in the low frequency region. The scaling coefficient for the curve 2 is chosen in such a way, so that the bands of molecular form after expansion are still weaker

than those in curve 1. Bands of strongly adsorbed species, on the contrary, are enhanced due to expansion. Among the latter, peaks at 3084, 3054, 3010, 2995, 1472, 1290, 1185, 1063, 845  $\text{cm}^{-1}$  could easily be distinguished.

Removal of gaseous thiophene by pumping for several minutes at 240 - 270 K results in the disappearance of the OH band at 3430  $\text{cm}^{-1}$  together with the intensity decrease of other strongly adsorbed thiophene bands. Prolonged evacuation at 270 - 300 K leads to simultaneous decrease of the OH band at 3485  $\text{cm}^{-1}$  and bands at 2995 and 803  $\text{cm}^{-1}$ , that disappear completely after evacuation at 370 K. The bands at 3095, 3054, 3010, 1290, 1185, 1063, 845, 813 and 690  $\text{cm}^{-1}$  resist evacuation at 370 K, but could be removed completely together with the OH band at 3560  $\text{cm}^{-1}$  by evacuation at 420 K. After that, only slightly increased absorption below 3700  $\text{cm}^{-1}$  remains in the spectrum, however the treatment of such thiophene-contacted sample in oxygen at 973 K leads to dramatic increase of absorption between 1220 and 1100  $\text{cm}^{-1}$  that evidently is due to sulphate ions [23] and testify, thus, for the presence of some quantity of sulphur that still remains in the sample.

#### ***Adsorption of thiophene- $d_4$ and thiophene-2,5- $d_2$***

Adsorption of deuterated thiophene enables us to distinguish well the bands of OH groups perturbed by adsorbed molecules from those formed due to dissociative chemisorption. When thiophene- $d_4$  is admitted to CaO sample pretreated at 723 K, intensity diminution of OH bands at 3722 and 3610  $\text{cm}^{-1}$  is accompanied by appearance of bands at 3700 and 3616  $\text{cm}^{-1}$ , like in the case of usual thiophene- $h_4$ . The band at 3485  $\text{cm}^{-1}$ , however, does not appear. A weak maximum at 2580  $\text{cm}^{-1}$  arises instead in the OD region after raising the temperature up to about 230 K.

Spectrum of thiophene- $d_4$  adsorbed on CaO pretreated at 973 K is illustrated in fig. 3. When thiophene- $d_4$  is introduced at 77 K into the cell and the temperature increases up to about 180 K, first bands of adsorbed molecules (see table 1) arise together with the appearance of the OD bands at 2630, 2580, 2535  $\text{cm}^{-1}$ . Simultaneously, the band of perturbed OH groups, much more intense than the band of initial hydroxyls, appears at 3675  $\text{cm}^{-1}$  and moves first up to 3695  $\text{cm}^{-1}$  with the increase of surface coverage at about 200 K, then back to 3690  $\text{cm}^{-1}$  when the temperature approaches 300 K. No OH bands, however, could be seen between 3650 and 3200  $\text{cm}^{-1}$ .

As in the case of usual thiophene, removal of the gas phase reveals the difference between the bands of weakly bound molecular thiophene and stronger held chemisorbed products. The bands of the latter in the low frequency region are very weak, that is why in Fig 3 the absorbance scale for spectra 2 and 3, obtained after evacuation, are ten-fold expanded.



In this case the visible intensity of bands of the weak molecular adsorption is steadily diminishing from spectrum 1 to 3. The bands of chemisorbed thiophene, on the contrary, are enhanced in the curve 2 due to the expanded scale and keep almost the same intensity in spectrum 3. Real band intensity for strongly held chemisorbed species, turns also to diminish notably from spectrum 1 to 2, but in much smaller extent than the intensity of bands of weak molecular adsorption.

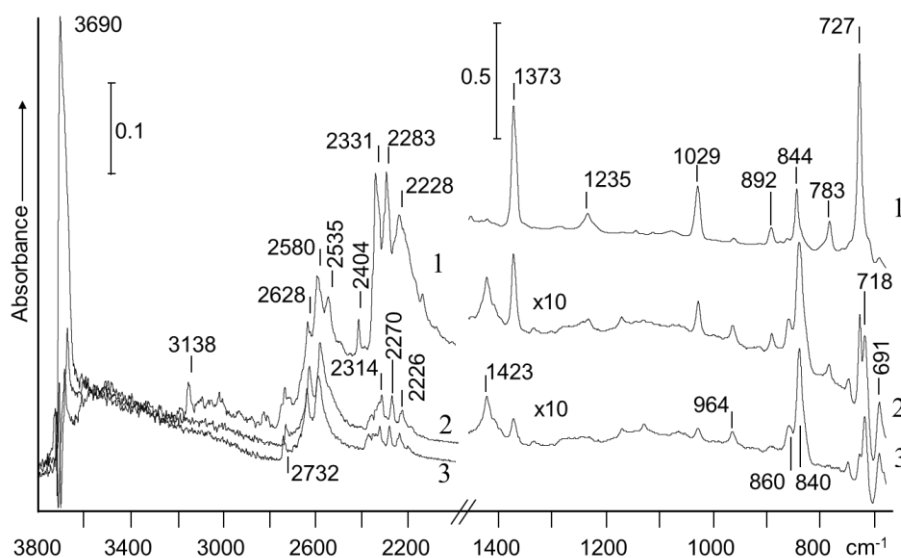


Figure 3. IR spectra of thiophene- $d_4$  adsorbed on CaO pretreated at 973 K: (1) after addition of thiophene- $d_4$  and heating to 270 K, (2) after freezing off gaseous thiophene for 7 min, and (3) after pumping for 10 min at 280 K

Detailed analysis of spectra presented in fig 3 enables us to separate bands of chemisorbed species at 860, 840 and 718  $\text{cm}^{-1}$  from closely located 844 and 727  $\text{cm}^{-1}$  bands due to molecular adsorption. Bands at 3138 and 2404  $\text{cm}^{-1}$  (fig.3, curve 1) that disappear together with other bands of molecular thiophene, have too high frequency to be attributed, respectively, to the CH vibrations of partially deuterated thiophene molecules or to CD stretching vibration of thiophene- $d_4$ , and evidently, belong to combination modes of adsorbed molecules. As in the case of usual thiophene, the low-frequency CD stretching band of the product that remains at the place of a strong band at 2228  $\text{cm}^{-1}$  after its removal by pumping at about 270 K, is split in two components at 2235 and 2226  $\text{cm}^{-1}$ , from which the latter is the first to diminish on evacuation together with the OD band at 2580  $\text{cm}^{-1}$ . Note that another band in the OD region observed at 2535  $\text{cm}^{-1}$  disappears even earlier, together with the bands of molecularly adsorbed thiophene.

Analysis of gas desorbed from the surface at 200-210 or 250-280 K shows that, in both cases, it is practically pure thiophene- $d_4$  without notable traces of other isotopic compounds.

Adsorption of small doses of thiophene-2,5- $d_2$  on CaO surface at 300 K, alongside with the bands of adsorbed thiophene, leads first to the appearance of the OD band at 2630  $\text{cm}^{-1}$ , then one more maximum shows up at 2580  $\text{cm}^{-1}$  together with the OH band growing at 3675  $\text{cm}^{-1}$  until finally, after the equilibrium pressure of thiophene gas reaches about 1 torr, the OH bands at 3560 and 3485  $\text{cm}^{-1}$  become visible. In the spectrum of adsorbed thiophene, increase of the adsorbate pressure leads to dramatic complications, in particular, a great number of new peaks arise below 1000  $\text{cm}^{-1}$ .

As in the case of unsubstituted thiophene, evacuation results in sequential disappearance of the shoulders due to the perturbed hydroxyls at 3690  $\text{cm}^{-1}$  together with the bands that should be attributed to the weakly bound thiophene, and then, at elevated temperatures, of the bands of newly created OH and OD groups and of chemisorbed thiophene.

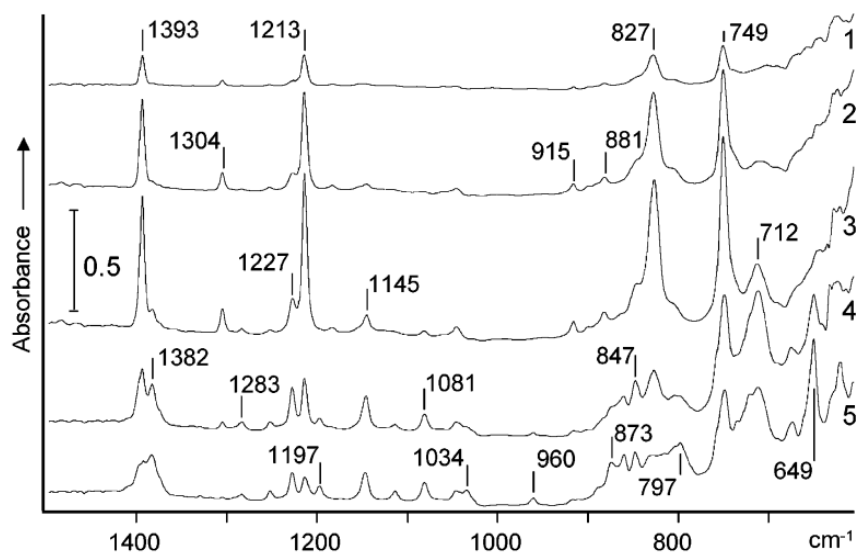


Figure 4. IR spectrum of CaO pretreated at 973 K after addition of thiophene-2,5- $d_2$  and raising the temperature up to at 174 (1), 183 (2), 194 (3), 210 (4), and 218 K (5).

Data on low-temperature adsorption of thiophene-2,5- $d_2$  on CaO pretreated at 973 K, presented in fig 4, provide more detailed information and enable one separate at least three groups of bands. The first to appear at about 180 K are the bands at 1393, 1304, 1213, 827, 749  $\text{cm}^{-1}$ , and some others (see the table) that are close enough to the values reported for free thiophene-2,5- $d_2$  [21]. Intensities of these bands decrease after heating above 200 K (curves 4, 5). Evacuation at 200 K or higher results in their disappearance together with the restoration of the bands of surface hydroxyl groups disturbed by thiophene adsorption. Another group of bands, very weak in the beginning, grows in the presence of adsorbate up to 210 K, is still intense at 218 K (curve 5), and resist pumping at temperatures up to 230 K. These are the

bands at 1382, 1227, 1145, 1081, 847  $\text{cm}^{-1}$  and one more band at 717-695  $\text{cm}^{-1}$  with the coverage-sensitive position like that of the band at about 700  $\text{cm}^{-1}$  in the spectrum of thiophene- $h_4$ . Several other bands, both removable or not by pumping at about 230 K, grow slowly if the sample is kept in the presence of thiophene above 200 K or increase rapidly (at the expense of other bands) if the sample is heated up to 300 K for a short time. Some of these bands, such as those at 1197, 1034, 960, 873, 797 and 649  $\text{cm}^{-1}$ , can be seen in curves 4 and 5 (fig4). Finally, these bands become more intense and numerous, and this leads to the dramatic complication of the spectrum, observed after adsorption of thiophene-2,5- $d_2$  at 300K. This phenomenon does not have any analogy in the spectra of unsubstituted thiophene or thiophene- $d_4$  adsorbed on CaO. Its explanation one could see in the effect of isotopic exchange that may be expected in the system with reversible thiophene dissociation evidenced by the appearance of surface OD species after adsorption of deuterated molecules. To verify this hypothesis, the below experiments with IR analysis of the desorbed gas have been carried out.

### ***Gas analysis***

The isotopic content of the desorbed gas was monitored during gradual heating of the sample after addition of about 40  $\mu\text{moles}$  of thiophene-2,5- $d_2$  into the cell at 77K. At certain temperatures, doses of desorbed gas were taken by freezing in the trap without removing the gaseous helium. Simultaneously, spectra of adsorbed species were registered as above. Figure 5 shows the spectra of gas desorbed from the sample pretreated at 973 K. For comparison, spectra of pure gaseous thiophene- $h_4$ , thiophene- $d_4$  and thiophene-2,5- $d_2$  registered at the same conditions are also presented in the same figure. Spectrum of gas desorbed at 194-200 K (not shown in the figure) almost does not differ from that of pure thiophene-2,5- $d_2$ . Only slightly increased peak at 701  $\text{cm}^{-1}$  indicates of the increased amount of thiophene-2- $d_1$ , which was present as a minor impurity in the spectrum of initial thiophene-2,5- $d_2$ . Temperature increase by less than 10 degrees (curve 4) results in a great enhancement of this peak and appearance of several new bands including those at 712 and 532  $\text{cm}^{-1}$  that could be identified as the Q branches of the strongest bands of thiophene- $h_4$  and thiophene- $d_4$ . Several more bands appear in the gas desorbed at 210-216 K (curve 5). After raising the temperature up to 230 K (curve 6), when strong complication of the spectrum of adsorbed species occurs, in the spectrum of desorbed gas initial bands of thiophene-2,5- $d_2$  and band of thiophene 2- $d_1$  become weaker and bands at 811, 801, 787, 669, 645, 613 and 578  $\text{cm}^{-1}$  turn to be substantially enhanced. According to the literature data [21] these bands should be ascribed to

thiophene-3,4-*d*<sub>2</sub>, thiophene-2,5-*d*<sub>2</sub>, thiophene-3-*d*<sub>1</sub>, thiophene-2,3-*d*<sub>2</sub>, thiophene-3,5-*d*<sub>2</sub>, thiophene-2,3,4-*d*<sub>3</sub> and thiophene-2,3,5-*d*<sub>3</sub>, respectively. Thus, spectra of desorbed gas reveal the presence all ten different isotopic modifications of thiophene with different deuterium content in the desorbed gas, testifying for complete isotopic scrambling.

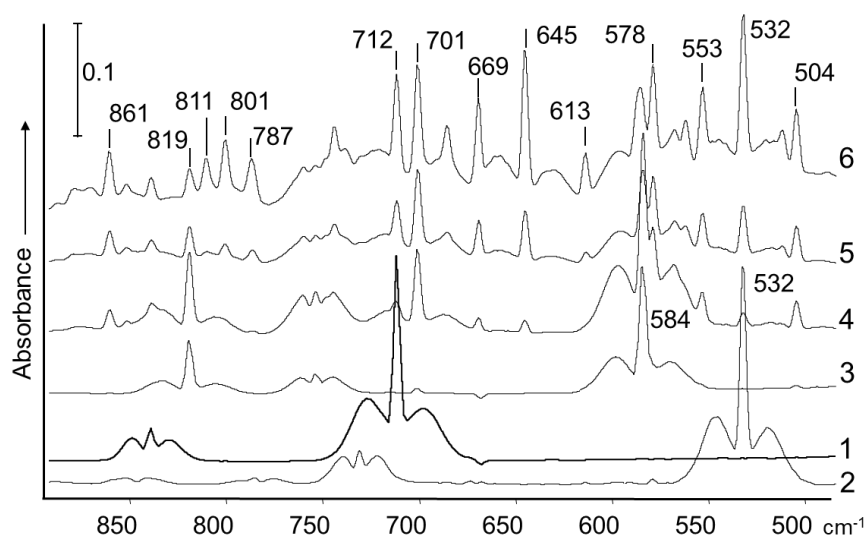


Figure 5. IR spectra of gaseous thiophene-*h*4 (1); thiophene-*d*4 (2); thiophene-2,5-*d*2 (3); and of the gas desorbed at 200-203 K (4), 210-216 K (5), and 230 K (6) from CaO activated at 973 K and exposed to thiophene-2,5-*d*2.

The same experiment with CaO pretreated at 723 K after water adsorption shows that in this case the scrambling also takes place, but the reaction is much slower and it needs longer time and higher temperature to obtain spectra comparable with that presented in curves 5 and 6, figure 5.

### ***Influence of coadsorbed CO***

To find out if the sites that account for thiophene chemisorption and isotopic scrambling are the same that react with CO to form "carbonite"  $\text{CO}_2^{2-}$  ions, coadsorption of these two molecules on CaO has been studied. Two kinds of experiments have been carried out: preliminary poisoning of surface sites by chemisorbed CO or CO addition to the sample with preliminary chemisorbed thiophene. The most basic sites that have the concentration of about  $0.3 \text{ nm}^{-2}$  could easily be saturated by adsorption of small quantities of CO at 300 K [16]. For that, about  $10 \mu\text{mol/g}$  of CO was adsorbed, that lead to carbonite bands at 1480, 885 and  $745 \text{ cm}^{-1}$ . Adsorption of the repeated dose does not lead to any increase of their intensities, thus testifying for the complete saturation of the corresponding basic sites.

Subsequent addition of thiophene to the cell cooled up to 77 K and raising the temperature up to about 200 K results in the spectrum almost identical to that obtained after thiophene adsorption on pure sample and in a gradual intensity decrease of carbonite bands. Just the same, adsorption of thiophene-2,5- $d_2$  at CaO with preadsorbed CO leads to the appearance of all the three OD bands simultaneously with the disappearance of carbonite bands already at about 190 K. However, after removal most of thiophene by prolonged evacuation at 300 K, repeated CO addition results in the appearance of same, although less intense bands of carbonites.

To avoid possible displacement of CO from basic sites by stronger adsorbed thiophene, in another experiment after addition of small portion of CO the resulting carbonites were oxidised by oxygen admitting at 300 K. In this case the OH band at 3560  $\text{cm}^{-1}$  as well as the concurrently appearing bands of thiophene products at 3010 and 813  $\text{cm}^{-1}$  do not appear at all or have very low intensity even after raising the temperature up to 300 K, however, bands at 3485 and 3430  $\text{cm}^{-1}$  appear as usually. Adsorption of thiophene-2,5- $d_2$  on such samples with poisoned basic sites leads to the spectra without OD band at 2630  $\text{cm}^{-1}$ .

Analysis of gas desorbed after thiophene-2,5- $d_2$  adsorption on CaO sample pretreated at 973 K, shows that after poisoning by CO with subsequent oxidation the scrambling also occurs, however, comparison of the spectra taken at the same conditions shows that the rate of this reaction decreases.

The effect of preliminary added thiophene on the spectra of adsorbed CO is illustrated above in figure 2. CO addition to the sample with thiophene adsorbed in excess, as at the stage presented by curve 2, leads to the carbonite bands at 1455, 900  $\text{cm}^{-1}$  and a shoulder at about 740  $\text{cm}^{-1}$ . Temperature increase diminishes their intensities and results in the appearance of new bands of carbonite transformation products at 2032, 1596 and 1306  $\text{cm}^{-1}$ , almost the same as in the absence of adsorbed thiophene.

The same effect was observed with preadsorbed thiophene-2,5- $d_2$ . If most of the molecular form of adsorption is removed by pumping at 205 K, three OD bands produced by thiophene chemisorption are clearly seen at 2630, 2580 and 2535  $\text{cm}^{-1}$ . Subsequent addition of about 3 Torr of CO at 77 K and further raising the temperature results in the spectra very close to those obtained for pure CaO [16]. Strong band of molecular CO at 2153  $\text{cm}^{-1}$  disappear after heating up to 170 K. Bands of carbonites arise at 1465, 890 and 732  $\text{cm}^{-1}$  as soon as CO is adsorbed at 77 K, remain unchanged up to 170 K, then diminish and disappear completely at 220-240 K. From about 110 K the band at 2032  $\text{cm}^{-1}$  arises together with other bands of dioxoketenes (1340 and 992  $\text{cm}^{-1}$ ), grow and reach maximal intensities at 160-200

K, and then diminish, but still visible at 273 K. Bands of further CO chemisorption products at about 1600, 1306, 1175 and 1110  $\text{cm}^{-1}$  increase constantly in from 77 to 300 K. It seems that the presence of chemisorbed thiophene practically does not influence CO adsorption, and results only in slight shifts of band positions. However, CO addition causes certain changes in the spectrum of thiophene adsorption products. In particular, the OD band at 2535  $\text{cm}^{-1}$  that normally resist pumping at 205 K, started to diminish in the presence of CO already at 77 K and disappear completely after raising the temperature up to 140 K. Two other OD bands remain in the spectrum up to 273 K.

## **Discussion.**

### ***Molecular adsorption of thiophene***

Spectrum of thiophene adsorbed in molecular form on CaO does not differ much from that of liquid or gaseous thiophene. The most sensitive to adsorption are the stretching and out-of plane bending vibrations of C-H groups (3126 and 712  $\text{cm}^{-1}$  for gas phase) that for the adsorbed molecules are shifted to lower and higher wavenumbers, respectively. The shift decreases with the increasing coverage and depends on the conditions of sample pretreatment. For samples outgassed after contact with water at 723 K, the 712  $\text{cm}^{-1}$  band is shifted by not more than 11  $\text{cm}^{-1}$ , while for the sample preactivated at 973 K the shift of this band reaches 21  $\text{cm}^{-1}$  that is well above values typical of physisorption.

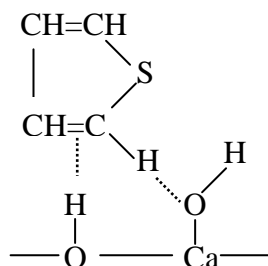
Another important spectral manifestation of molecular adsorption is reversible perturbation of surface hydroxyl groups by weakly bound thiophene. Appearance of new bands of perturbed OH groups at 3700-3675  $\text{cm}^{-1}$  is accompanied by simultaneous reversible diminution of the bands of unperturbed hydroxyls and could be observed on addition of both usual or deuterated thiophene. On the other hand, the same shift occurs with the OD groups of deuterated samples when normal thiophene is adsorbed. This proves that new bands are in fact due to the perturbed, and not to newly created hydroxyls.

The observed frequency shifts of OH and OD stretching vibrations caused by thiophene adsorption are about 22 and 17  $\text{cm}^{-1}$ , respectively, while neither interaction with stronger bases such as pyridine [14,15] or acetone [12], nor adsorption of more inert molecules like  $\text{CCl}_4$  [12], CO [24], benzene, n-hexane, nitrogen, oxygen [25], produce any remarkable shift of these bands. This result could be elucidated if we take into account high basicity of these hydroxyl groups that are able to form complexes with weak acids. So, ozone adsorption shifts OH and OD bands of CaO by 21 and 15  $\text{cm}^{-1}$ . We can suppose that thiophene could also act as an acid, forming weak H-bond by C-H group with the oxygen

atom of hydroxyl, leading to a slight lowering of the OH stretching frequency. Such explanation is in coherence with the low-frequency shift of C-H stretching from 3128 up to 3100  $\text{cm}^{-1}$  and with increased frequency of out-of-plane bending mode of adsorbed thiophene from 712 up to 723  $\text{cm}^{-1}$ , observed for samples dehydrated at 723 K. Even lower position of CH stretching (up to 3090  $\text{cm}^{-1}$ ) and higher value of bending band (up to 733  $\text{cm}^{-1}$ ) observed for samples activated at 973 K at low surface coverages, could naturally be explained by the same mechanism of thiophene interaction with basic oxygen atoms formed on CaO surface upon dehydroxylation.

Somewhat unexpected is different ability of 3722-3710  $\text{cm}^{-1}$  hydroxyls to be perturbed by adsorbed thiophene for the samples activated at different temperatures. Usually, adsorption of test molecules on all the surface OH groups is not possible because of steric limitations for the hydroxylated surfaces of metal oxides with high concentration of OH groups. Hydroxyl groups of same oxides pretreated at high temperatures are more accessible for adsorption because of their lower concentration, and could be perturbed almost completely by adsorbed CO, benzene or other proton-accepting molecules. For thiophene adsorbed on CaO, on the contrary, much more complete perturbation of both the 3722 and 3710  $\text{cm}^{-1}$  bands occurs if the sample is outgassed at 723 K. After activation at 973 K the high-frequency component at 3722  $\text{cm}^{-1}$  remains unperturbed if thiophene is adsorbed at the same conditions. To our mind, the reason is in the formation of great quantity of basic oxygen sites. Preferable adsorption of thiophene on these stronger sites results in steric hindrances for interaction of other molecules with basic OH groups.

The band at 3616  $\text{cm}^{-1}$  which appears after thiophene adsorption on samples pretreated at 723 K should also be due to the perturbed OH groups, since it arises both after adsorption of usual or deuterated thiophene. It does not appear in the spectra of samples activated at 973 K where the band at 3610  $\text{cm}^{-1}$  is absent before adsorption. For the deuterated surface the same kind of perturbation can be observed for OD groups with the band at 2661  $\text{cm}^{-1}$  that shifts to 2667  $\text{cm}^{-1}$  after addition of thiophene, both usual or deuterated. It should be noted that simultaneously, in the spectrum of adsorbed thiophene the shoulder at 1400  $\text{cm}^{-1}$  could also be observed. Such a shift of C=C stretching band to lower wavenumbers is characteristic of H-bond with the  $\pi$ -electron system of the ring. We have to conclude, thus, that some of adsorbed thiophene molecules, maybe the same which interact with oxygen atoms of type I OH-groups, form a weak H-bond by their  $\pi$ -electron system with protons of OH groups that absorb at 3610  $\text{cm}^{-1}$ :



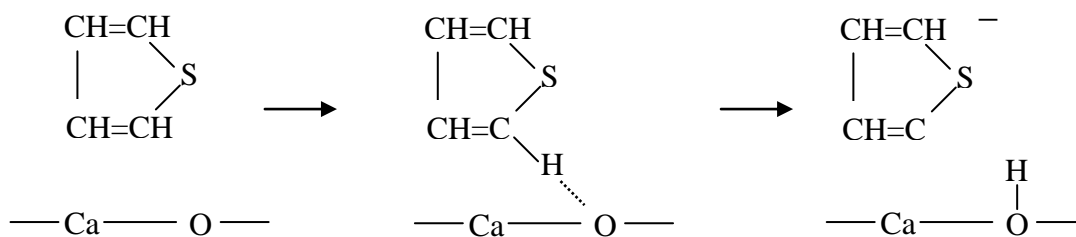
If one thiophene molecule interacts simultaneously as a proton donor with a basic hydroxyl and as an acceptor of proton with more acidic OH group, such chain of H-bonds with the same direction of charge transfer should enhance each other making more favourable perturbation of hydroxyls that act as proton donors.

According to [20] the band at  $2610\text{ cm}^{-1}$  belongs to the groups of type V, that due to the contact with five cations should be more acidic than the type I hydroxyls (band at *c.a.*  $3710\text{ cm}^{-1}$ ) and hence, could be capable of H-bonding. The most remarkable here is the high-frequency shift of the band of OH (OD) groups upon this interaction. However, the blue shifting H-bond is known for certain systems [26] and small frequency increase of CaO surface OH groups perturbed by some weakly adsorbed molecules has been reported [25].

### ***Strong adsorption of thiophene***

Thiophene adsorption on CaO pretreated at 973 K results in simultaneous appearance of bands due to chemisorbed thiophene and new bands in the OH stretching region at 3560, 3485 and  $3430\text{ cm}^{-1}$ . After addition of thiophene- $d_4$  these bands do not appear, and corresponding bands of OD groups arise at 2630, 2580 and  $2535\text{ cm}^{-1}$ . It should be noted that the frequency ratios  $\nu\text{OH}/\nu\text{OD}$  for all the observed kinds of newly formed hydroxyl groups occur within the limits of 1.350-1.357, in a good agreement with the anticipated value. These results provide evidence for thiophene dissociative adsorption with the proton transfer to the basic oxygen atom of the surface. The same OD bands are first to arise after low temperature adsorption of thiophene-2,5- $d_2$ . From this we can conclude that proton-donating ability of thiophene is associated with the CH groups in the nearest positions to the S atom. Apparently, these are the groups that form weak H-bond to the basic hydroxyls and surface oxygen ions of CaO surface when thiophene is adsorbed in molecular form, and if the basicity of oxygen ions is high enough, proton transfer occurs leading to the formation of new OH groups and deprotonated "thiophenide" anion  $\text{SC}_4\text{H}_3^-$ :





The positions of the OH bands that arise as a result of thiophene dissociation is not typical of the hydroxyls of pure CaO surface, that could be explained by their interaction with the adjacent thiophene anion. Band at  $3560\text{ cm}^{-1}$  is close to the  $3580\text{ cm}^{-1}$  band, which appears as a result of ammonia dissociation on oxygen sites of CaO activated at 973 K [17]. In that case OH groups could be influenced by the simultaneously formed  $\text{NH}_2$  groups.

Appearance of three different OH bands as a result of thiophene dissociative adsorption points to the existence of three different kinds of surface oxygen ions capable to attach the proton. Existence of three kinds of basic oxygen sites on thermally activated CaO surface was evidenced by CO adsorption that results in three kinds of surface carbonite ions that have slightly different spectra and formation conditions [27]. Therefore, we shall try to analyse the spectra of chemisorbed thiophene in comparison with those of adsorbed CO paying attention to the coadsorption experiments.

The most basic oxygen ions detected after pretreatment at 973 K are known to produce the most stable form of carbonite  $\text{CO}_2^{2-}$  ions on adsorption of small amounts of CO at 300 K (bands at  $1485$ ,  $890$  and  $743\text{ cm}^{-1}$ , according to [16, 27]). Experiments with preliminarily adsorbed CO show that the bands of these carbonites, usually stable up to 300 K, disappear after thiophene adsorption at about 200 K that could be explained by the displacement of such chemisorbed CO by strongly adsorbed thiophene. The sites, however, are not destroyed completely, since after evacuation at 300 K, when most of thiophene is gone, the same bands of carbonites could be obtained by the repeated CO addition. Almost complete poisoning of these sites by preliminary CO adsorption could be achieved if the resulting carbonites are oxidised by addition of oxygen. Then, subsequent thiophene adsorption results in the same spectra of adsorbed molecules and thiophenide ions, but does not lead to the band at  $3560\text{ cm}^{-1}$ , while other OH bands could still be observed. Thus, thiophene dissociation leading to the  $3560\text{ cm}^{-1}$  band occurs on the strongest basic sites of CaO, capable to chemisorb CO at 300 K.

The least stable OH band at  $3430\text{ cm}^{-1}$  as well as its OD analogue at  $2535\text{ cm}^{-1}$  resist pumping at 200-220 K, but could be removed by short evacuation at 240- 270 K. However, if

CO is added at 77 K, this band diminishes in intensity and disappears completely after raising the temperature already up to 140 K simultaneously with the appearance of the bands due to dioxoketenes (2065-2040  $\text{cm}^{-1}$  and others) or further complicated products of CO transformations. We can, thus, speak about chemisorbed thiophene displacement by adsorbed CO and associate the sites that account for the OH band at 3430  $\text{cm}^{-1}$  with those oxygen ions of CaO activated at 973 K that reversibly form the low-temperature carbonites at 77 K in the presence of gaseous CO, as evidenced by the bands at 1478, 850 and 717  $\text{cm}^{-1}$  [16, 27]. In the presence of chemisorbed thiophene, the carbonite bands were observed at somewhat different positions, at 1465, 890 and 732  $\text{cm}^{-1}$ , that could be explained by the interaction with coadsorbed molecules.

Third OH band that arise on thiophene adsorption at 3485  $\text{cm}^{-1}$  (OD band at 2580  $\text{cm}^{-1}$ ) corresponds to the basic oxygen ions of intermediate strength, according to the stability of this species. These sites are formed, although are less abundant, after activation already at 723 K. If we try to follow correlation with CO adsorption, we have to note that after such activation only low-temperature carbonites could be formed. After activation at 973 K the bands of the third kind of carbonites that were detected at 77 K and have intermediate thermal stability were detected at 1495, 870 and 733  $\text{cm}^{-1}$  [27, 28].

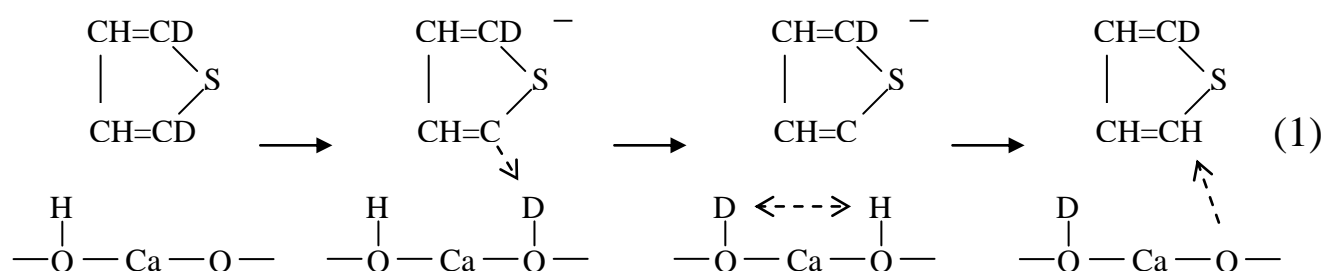
The bands of deprotonated thiophene anion  $\text{SC}_4\text{H}_3^-$  and its deuterated analogues are rather weak in the case of normal or totally substituted thiophene. Like in the case of thiophene itself, more rich is the spectrum of partially deuterated product that arise as a result of thiophene-2,5- $d_2$  adsorption at low temperatures and should have the formula  $\text{SC}_4\text{H}_2\text{D}^-$ . The most intense bands of this compound occur at 1382, 1227, 847 and about 712  $\text{cm}^{-1}$ , close enough to the bands at 1393, 1213, 827 and 749  $\text{cm}^{-1}$  of adsorbed thiophene-2,5- $d_2$  molecules themselves. This could be considered as an evidence for small perturbation of the electronic and geometrical structure of molecule caused by deprotonation. Slightly lowered values of CH stretching vibrations of this compound, as compared with corresponding thiophene isotopomers, reveal a decrease of aromatic character of the ring caused by the loose of proton. Splitting of some CH (CD) bands of adsorbed normal and totally deuterated thiophene (double bands at 3010/2995, 813/803 and 2235/2226  $\text{cm}^{-1}$ ) into two components that disappear not simultaneously on thermoevacuation, could be explained by small difference in the anions formed as a result of dissociation on different surface oxygen sites. It means that anions still keep the connection with hydroxyl group and are affected by difference in the site environment. This is supported by simultaneous disappearance of the components at 2295 and 803  $\text{cm}^{-1}$  with the OH band at 3485  $\text{cm}^{-1}$  that demonstrates the reversibility of thiophene

dissociation, at least for this kind of surface oxygen sites. After removal of other kind of thiophene anions at elevated temperatures, the increased overall OH absorption as well as the appearance of strong sulphate absorption after heating such sample in oxygen, indicates of irreversible decomposition of certain part of thiophene with the trapping of sulphur by CaO.

### *Isotopic exchange*

As one could suppose, reversible dissociation of thiophene should result in the H-D isotopic exchange if deuterated thiophene after dissociation is recombined with surface OH group, or if normal thiophene attaches the deuterium from OD groups of deuterated surface. The above results show that such an exchange in fact takes place, and moreover, it leads finally to the formation of up to 10 isotopomers with substitution in all four positions.

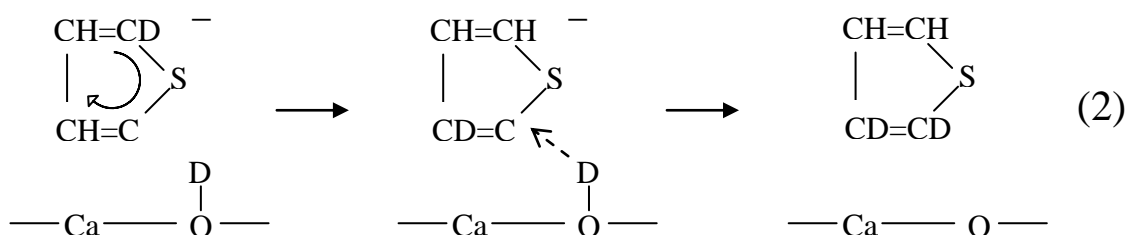
Several mechanisms of the exchange could be proposed. i) The molecule that donates proton to surface oxygen ion remains bound with the formed hydroxyl group, but due to surface proton mobility or to the mobility of the thiophenide ion that jump from one hydroxyl to another, the initial deuterium could be exchanged by proton or *vice versa* (scheme 1).



In this simplest case one could expect that proton will be exchanged at certain position from which the transfer is more favourable, most probably, in the position 2 or 5. In fact, the first evidence for the exchange after adsorption of thiophene-2,5- $d_2$  is the appearance of surface OD groups and thiophene-2- $d_1$  in the gas phase. However, very soon, even at temperatures as low as about 220 K, one could see in the gas other isotopomers, including those with deuterium in the 3 and 4 position. We could suppose that CH groups in 3,4 positions are also capable of H-bonding and proton transfer, but two ways of dissociation occurring at the same conditions seem to be not probable. We have also to take into account that the scrambling is the most rapid on the dehydroxylated surface, where the concentration of surface OH groups is lowered, and type I OH groups that remain at such surface are not exchanged during the reaction, at least, at low temperatures. Thus, the protons of surface OH groups, capable of isotopic exchange with thiophene molecules, should originate from other

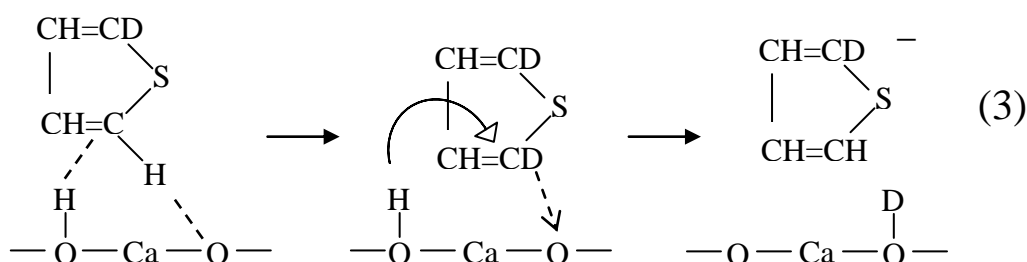
thiophene molecules, and if only positions 2 and 5 are involved in this mechanism of exchange, no visible results should be anticipated.

ii) To explain isotopic substitution in 3,4 position one could suppose that in the formed thiophenide anion proton migration occurs. Then the deuterium that remains in the anion could become bound to carbon atom in the position 3 or 4, and after recombination another isotopomer could arise (scheme 2).

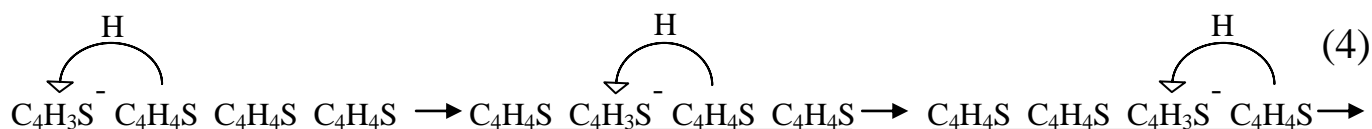


Such mechanism alone, if occurs in the system of one molecule attached to the only surface oxygen site, could explain the appearance of four different isotopomers of thiophene- $d_2$ . All of them indeed could be found in the gas desorbed after thiophene-2,5- $d_2$  adsorption that, however, contains also other products of isotopic scrambling such as pure thiophene- $h_4$  or totally deuterated thiophene- $d_4$ . Their appearance could be accounted for by the combined action of mechanisms i) and ii).

iii) To explain the observed isotopic scrambling by one manifold repeated elementary step, we have to adopt the concerned mechanism that involves, several surface sites. Deuterium transfer from CD group in the position 2 of the molecule to surface oxygen ion can be accompanied by simultaneous transfer of proton of the adjacent OH group that forms H-bond with  $\pi$ -system or S atom. This could lead finally to the fixation of proton in any position, as shown in scheme 3, if the back protonation of thiophenide anion can provoke proton migration over the cycle. However, OH groups capable of H-bonding do not exist initially on CaO surface pretreated at high temperature, and again we have to adopt the migration of protons detached from thiophene molecules over the surface.



iv) One more possibility is to suppose that several thiophene molecules participate in the process, and after deprotonation of one of them, the lack of proton could move in the adsorbed layer from one molecule to another like a hole in semiconductor, and instead of anion mobility, the anionic state will move over the surface due to multiple proton transfers from one molecule to another (scheme 4). Such process, should scarcely be restricted by protons in positions 2 and 5, and for the case of adsorbed thiophene-2,5- $d_2$  can lead to complete isotopic scrambling, as observed in experiment.



Data obtained do not enable us to make a final choice of the mechanism of isotopic exchange. Supplementary experiments including kinetics measurements could clarify this problem. Experiments with hydroxylated samples pre-evacuated at 723 K that display very low ability to chemisorb CO and much slower rate of exchange, show that isotopic scrambling takes place at the same sites that account for carbonite formation. Poisoning of the most basic sites by preliminary adsorption of CO at 300 K with subsequent oxidation of the formed carbonite ions does not stop the scrambling but only slightly lowers its rate. This infers that these are rather less basic sites, which are more abundant and account for reversible carbonite formation at low-temperatures and for the appearance of OH bands at 3485 and 3430  $\text{cm}^{-1}$  after thiophene dissociation, that are responsible for the reaction of isotopic scrambling, at least at lowest temperatures, when only this forms of thiophene dissociative adsorption are reversible. Apparently, each of three kinds of basic sites, capable of thiophene dissociation contribute to the isotopic scrambling, but their share in the total reaction rate is not the same for different temperatures.

### Conclusions

Spectra of thiophene and its deuterated derivatives adsorbed at 170-300 K on thermally activated surface of CaO enable us do distinguish several surface species formed mostly on basic sites.

Molecular adsorption of thiophene occurs on surface oxygen ions and basic OH groups by weak H-bond of CH groups with the lone electron pairs of oxygen. Interaction with basic hydroxyls results in OH stretching frequency lowering by about 22  $\text{cm}^{-1}$ , for deuterated surface the same effect leads to OD frequency shift by 17  $\text{cm}^{-1}$ . Spectrum of thiophene

adsorbed in such a form has asymmetric CH band lowered up to  $2100\text{ cm}^{-1}$  and out-of-plane CH bending increased from  $712\text{ cm}^{-1}$  up to  $722\text{ cm}^{-1}$ . Bands of the same vibrations are shifted up to  $3090$  and  $733\text{ cm}^{-1}$  if H-bond is formed with surface oxygen atoms.

If the temperature of pretreatment does not exceed  $723\text{ K}$ , one more band of more acidic OH groups occurs at  $3610\text{ cm}^{-1}$  that reveal blue shift up to  $3616\text{ cm}^{-1}$  and intensity increase on thiophene adsorption. Despite the anomalous effect of frequency increase, we believe this effect to be due to the formation of H-bond with thiophene molecules, that could be either bound by this bond only, or form simultaneously other H-bond via CH group with oxygen atom of surface or of basic OH group. A shoulder of C=C band at  $1400\text{ cm}^{-1}$ , observed in the spectrum of thiophene adsorbed on such samples, is typical of H-bond with the  $\pi$ -electron system. This confirms that the OH perturbation is caused in fact by H-bond. As far as we know, this is the first indication of the blue-shifting H-bond in heterogeneous systems.

Low temperature thiophene adsorption on CaO pretreated at  $973\text{ K}$  results in the appearance of three new bands in the OH stretching region at  $3560$ ,  $3485$  and  $3430\text{ cm}^{-1}$ . simultaneously with the bands due to chemisorbed thiophene. Appearance of corresponding OD bands at  $2630$ ,  $2580$  and  $2535\text{ cm}^{-1}$  after adsorption of thiophene- $d_4$  proves that the new hydroxyl groups arise as a result of dissociative adsorption on three different kinds of surface oxygen ions. Experiments with coadsorbed CO provide evidence that these are the same oxygen sites that account for the appearance of surface carbonite  $\text{CO}_2^{2-}$  ions on CO interaction with thermally activated CaO. Three kinds of thiophenide  $\text{SC}_4\text{H}_3^-$  anions formed as a result of dissociative adsorption of thiophene on the three kinds of basic sites only slightly differ in the positions of some bands, but have rather different thermal stability. Those which arise together with the OH band at  $3430\text{ cm}^{-1}$  could be removed by pumping at  $240\text{--}270\text{ K}$ , while the most stable products with the OH band at  $3560\text{ cm}^{-1}$  resist pumping at  $300\text{ K}$  and disappear completely after evacuation at elevated temperature. Thiophene adsorption on CaO is mostly reversible and the main product detected in the desorbed gas is thiophene. However, heating of the sample in oxygen after thiophene adsorption leads to the appearance of sulphate ions, thus demonstrating that certain part of sulphur remains in the sample, apparently, in the form of sulphide  $\text{S}^{2-}$  ions.

Reversible dissociation accounts for the catalytic reaction of isotopic scrambling, established for thiophene- $2,5\text{-}d_2$  by means of FTIR spectroscopy of desorbed gas. The reaction starts at  $200\text{--}220\text{ K}$  and leads to the appearance of up to ten different thiophene isotopomers in the desorbed gas with substitution in all four hydrogen positions of the molecule. Experiments with site poisoning by preadsorbed CO, variation of pre-treatment

conditions and comparison of the spectra of gas desorbed at different temperatures with simultaneously observed spectra of surface species ensures us that isotopic scrambling is catalysed by the same three kinds of sites that account for dissociative thiophene adsorption. The share of each kind of sites in the total reaction rate could be not the same at different temperatures.

Table 1 Band positions of thiophene-h<sub>4</sub>, thiophene-2,5-d<sub>2</sub> and thiophene-d<sub>4</sub> in in the gas state [21] and adsorbed on CaO pretreated at 973 K.

| Thiophene-h <sub>4</sub> |                             |                              | Thiophene-2,5-d <sub>2</sub> |                      |                              | Thiophene -d <sub>4</sub> |                              |                              |
|--------------------------|-----------------------------|------------------------------|------------------------------|----------------------|------------------------------|---------------------------|------------------------------|------------------------------|
| Gas [21]                 | Weak ads.                   | Strong ads.                  | Gas [21]                     | Weak ads.            | Strong ads.                  | Gas [21]                  | Weak ads.                    | Strong ads.                  |
|                          | 3690<br>(3616)*<br>(OH)     | 3560<br>3485<br>3430<br>(OH) |                              | 2665<br>(OD)         | 2630<br>2580<br>2535<br>(OD) |                           | 3690<br>3616<br>(OH)         | 2630<br>2580<br>2535<br>(OD) |
| 3128                     | 3110(sh)<br>3100-<br>3090** | 3095<br>3084<br>3054         | 3101<br>3088                 | 3088<br>3078<br>2957 | 3081<br>3055<br>3000         | 2343                      | 2331                         | 2314<br>2270                 |
| 3088                     | 3075                        | 3010<br>2995                 | 2368<br>2336                 | 2316                 | 2314<br>2284                 | 2290                      | 2283                         | 2235<br>2226                 |
| 1547                     |                             | 1475                         | 1500                         |                      |                              | 1462                      | 1453                         | 1423                         |
| 1408<br>1358             | 1408<br>(1400)<br>1360      |                              | 1398<br>1310                 | 1393<br>1304<br>1250 | 1382<br>1283                 | 1376<br>1248              | 1373<br>1235                 |                              |
| 1253                     | 1253                        | 1290                         | 1215                         | 1213<br>1182         | 1227<br>1145                 | 1061<br><br>1034          | 1145<br>1112<br>1080<br>1029 | 964                          |
| 1079                     | 1081                        | 1185                         | 1044                         | 1045                 | 1081                         | 896<br>846                | 892<br>844                   | 860                          |
| 1032                     | 1030                        | 1063                         | 918                          | 915                  |                              | 785                       | 783                          | 840                          |
| 838                      | 831                         | 845<br>813<br>803            | 884<br>818                   | 881<br>827           | 847                          | 731                       | 727<br>710(sh.)              | 718                          |
| 712                      | 733-<br>722                 | 706-<br>690<br>640           | 754<br>584                   | 749                  | 717-<br>695<br>652           | 531                       |                              | 691                          |

\* in brackets some of the bands observed for the sample outgassed at 723 K are presented.

\*\* if the band position depend strongly on surface coverage, we give the range of frequency variations, then the first value corresponds to saturating conditions.



- 
1. Travert, A.; Manoilova, O.V.; Tsyganenko, A.A.; Maugé, F.; Lavalley, J.C. *J.Phys.Chem. B* **2002**, *106*, 1350-1362.
  2. Tarbuck, T.L.; McCrea, K.R.; Logan, J.W.; Heiser, J.L.; Bussel, M.E. *J.Phys.Chem.B* **1998**, *102*, 7845.
  3. Sultanov, A.S.; Khakimov, U.B.; Talipov, G.Sh.; Shchekochihin, J.M. *React. Kinet. Catal. Lett.* **1975**, *2*, 243-250.
  4. Lyapina, N.K.; Lygin, V.I.; Ulendeeva, A.D. *Russian Chemical Reviews.* **1980**, *49*, 526-535.
  5. Padley, M.B.; Rochester, C.H.; Hutchings, G.J.; King, F. *J.Catal.* **1994**, *148*, 438-452.
  6. Quigley, W.W.C.; Yamamoto, H.D.; Aegerter, P.A.; Simpson, G.J.; Bussell, M.E. *Langmuir.* **1996**, *12*, 1500-1510.
  7. Tam Nguyen The; Cooney, R. P.; Curthoys, G. *J. Colloid Interface Sci.* **1975**, *51*, 340-344
  8. Garcia, C.L.; Lercher, J.A. *J.Phys.Chem.* **1992**, *62*, 2669-2675
  9. De Angelis, B.A.; Appierto, G. *J. Colloid Interface Sci.* **1975**, *53*, 14-19.
  10. Geobaldo, F.; Turnes Palomino, G.; Bordiga, S.; Zecchina, A.; Otero Arean, C. *Phys. Chem. Chem. Phys.* **1999**, *1*, 561-569.
  11. Sugioka, M.; Aomura, K. *Bull. Fac. Eng. Hokkaido University.* **1980** no.99, p. 79-88.
  12. Low, M.J.D.; Takezawa, N.; Goodsel, A.J. *J. Colloid Interface Sci.* **1971**, *37*, 422-429.
  13. Bulanin, K.M.; Lavalley, J.C.; Tsyganenko, A.A. *J. Phys.Chem. B* **1997**, *101*, 2917-2922.
  14. Tretyakov, N.E.; Filimonov, V.N. *Kinetics and Catalysis.* **1970**, *11*, 815-821.
  15. Tret'yakov, N.E.; Filimonov, V.N. *Kinetics and Catalysis.* **1972**, *13*, 735-737.
  16. Babaeva, M.A.; Bystrov, D.S.; Kovalgin, A. Yu.; Tsyganenko, A.A. *J.Catal.* **1990**, *123*, 396-416.
  17. Tsyganenko, A.A.; Pozdnyakov, D.V.; Filimonov, V.N. *J. Molecular Structure.* **1975**, *29*, 299-318.
  18. Manoilova, O.V.; Travert, A.; Bazin, P.; Tsyganenko, A.A.; Gilson, J.-P.; Maugé, F. *5th Eur. Congr. Catal., EuropaCat-5. Limerick, Ireland 2001, Abstr. Book 1.* *20*, P.32.
  19. Otero Areán, C.; Manoilova, O.V.; Tsyganenko, A.A.; Turnes Palomino, G.; Peñarroya Mentrut, M.; Geobaldo, F.; Garrone, E. *European J. Inorg. Chem.* **2001**, 1739-1743.
  20. Tsyganenko, A.A.; Filimonov, V.N. *J. Molecular Structure* **1973**, *19*, 579-589.
  21. Sverdlov, L.M.; Kovner, M.A.; Krainov, E.P. Vibrational spectra of polyatomic molecules. *Moscow, "Nauka" 1970* (Russ.).
  22. Rico M.; Orza, J.M.; Morcillo, J. *Spectrochim. Acta.* **1965**, *21*, 689-719.
  23. Nakamoto, K. *Infrared and Raman spectra of inorganic and coordination compounds, 4-th edition.* *Wiley-intersci., N.Y.- Chichester, 1986.*
  24. Rodionova, T.A.; Tsyganenko, A.A.; Filimonov, V.N. *Adsorbtsiya i adsorbenty No 10, Kiev, 1982*, p.33. (Russ).
  25. Tsyganenko, A.A.; Khomenya, A.V.; Filimonov, V.N. *Adsorbtsiya i adsorbenty No 4, Kiev, 1976*, p.86. (Russ).
  26. Hermansson, K. *J. Phys. Chem. A* **2002**, *106*, 4695-4702.
  27. Babaeva, M.A.; Tsyganenko, A.A. *Reaction Kinetics Catal.Lett.* **1987**, *34*, 9.
  28. Babaeva, M.A.; Bystrov, D.S.; Tsyganenko, A.A. *IR spectroscopy in Studies of Surface (Uspekhi Fotoniki, No 9) Leningrad 1987*, 69. (Russ.).