

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

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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-bonding 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 10 possible thiophene isotopomers in the desorbed gas. Experiments with thiophene coadsorption with CO enable one to associate the sites of thiophene dissociation with those oxygen ions that bound CO giving carbonite CO<sub>2</sub><sup>2−</sup> ions. Three kinds of such sites could be distinguished, which 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 great importance for the search of ways of sulfur 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.<sup>1</sup>

Thiophene adsorption has been studied so far spectroscopically mostly on hydrotreatment (HDT) catalysts (see ref 2 and references cited therein), on acid sites of oxides used as HYT supports, such as alumina,<sup>3–6</sup> silica,<sup>7,8</sup> or of zeolites,<sup>8–11</sup> both pure or modified by transition-metal cations. Interaction of thiophene with basic sites has not been studied much 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,<sup>12</sup> or ozone<sup>13</sup> do not show any tendency to form H-bonds with the adsorbed molecules.<sup>14,15</sup> After activation at about 1000 K, strong basic sites arise at the CaO surface, capable of chemisorbing CO, producing very reactive carbonite CO<sub>2</sub><sup>2−</sup> ions,<sup>16</sup> or of interacting with ozone with the formation of surface ozonides.<sup>13</sup> Ammonia adsorption on such surface results in its dissociation with the formation of OH groups and NH<sub>2</sub><sup>−</sup> ions.<sup>17</sup> This reaction is believed to take place at the same basic oxygen

atoms of the CaO surface. Thus, this oxide is a good model system for studying adsorption on a pure basic surface. Preliminary experiments have shown that thiophene in fact chemisorbs at 300 K on CaO,<sup>18</sup> and here we report, as far as we know, a first detailed study of thiophene interaction with this oxide.

## Experimental Section

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.<sup>16,19</sup> The cell enables sample treatment at 300–1000 K in a vacuum or under controlled atmosphere to be carried out. The pellets were activated at 970 K in a vacuum for 0.5–2 h. To obtain hydroxylated surface, the activated sample was in contact with about 10 Torr of water or D<sub>2</sub>O vapor at 300 K and then evacuated again at 723 K.

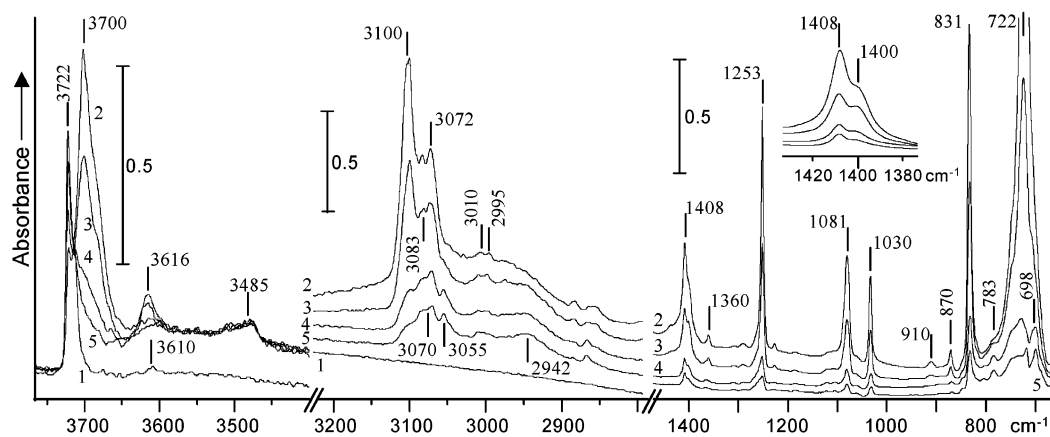
Normally, thiophene was added into the cell cooled by liquid nitrogen, then the temperature was raised until the appearance of the bands of adsorbed species and the following pressure increase indicate thiophene evaporation and adsorption. Then, the spectra were registered with progressively growing 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. To keep the sample always at the desired temperature, the gas probes were taken without complete removal of He from the cell. To do this, the cell was open to an isolated U-trap cooled by liquid nitrogen and gas, desorbed at certain temperature intervals, 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 analyzed gas, as far as possible, was taken the same, close to 0.6 Torr.

Commercial thiophene, as well as thiophene-*d*<sub>4</sub> (99 atom % D) and thiophene-2,5-*d*<sub>2</sub> (98.9 atom % D), produced by

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**Figure 1.** IR spectra of thiophene-*h*<sub>4</sub> adsorbed on CaO pretreated at 723 K. (1) Sample cooled up to 77 K, (2) after addition of thiophene-*h*<sub>4</sub> 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*<sub>4</sub>, Thiophene-2,5-*d*<sub>2</sub>, and Thiophene-*d*<sub>4</sub> in the Gas State<sup>21</sup> and Adsorbed on CaO Pretreated at 973 K**

thiophene- <i>h</i> <sub>4</sub>			thiophene-2,5- <i>d</i> <sub>2</sub>			thiophene- <i>d</i> <sub>4</sub>		
gas <sup>21</sup>	weak ads	strong ads	gas <sup>21</sup>	weak ads	strong ads	gas <sup>21</sup>	weak ads	strong ads
3128	3690 (3616) <sup>a</sup> (OH), 3110(sh), 3100–3090 <sup>b</sup>	3560, 3485, 3430 (OH) 3095, 3084 3054	3101, 3088	2665 (OD) 3088, 3078, 2957	2630, 2580, 2535 (OD) 3081, 3055, 3000	2343	3690, 3616 (OH) 2331	2630, 2580, 2535 (OD) 2314, 2270
3088	3075	3010, 2995	2368, 2336	2316	2314, 2284	2290	2283	2235, 2226
1547		1475	1500			1462	1453	1423
1408,	1408, (1400), 1358 1360		1398, 1310	1393 1304, 1250	1382, 1283	1376, 1248	1373, 1235	
1253	1253	1290	1215	1213, 1182	1227, 1145	1061, 1034	1145, 1112, 1080, 1029	964
1079	1081	1185	1044	1045	1081	896, 846	892, 844	860
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

<sup>a</sup> In parentheses some of the bands observed for the sample outgassed at 723 K are presented. <sup>b</sup> If the band position depends strongly on surface coverage, we give the range of frequency variations, then the first value corresponds to saturating conditions.

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.

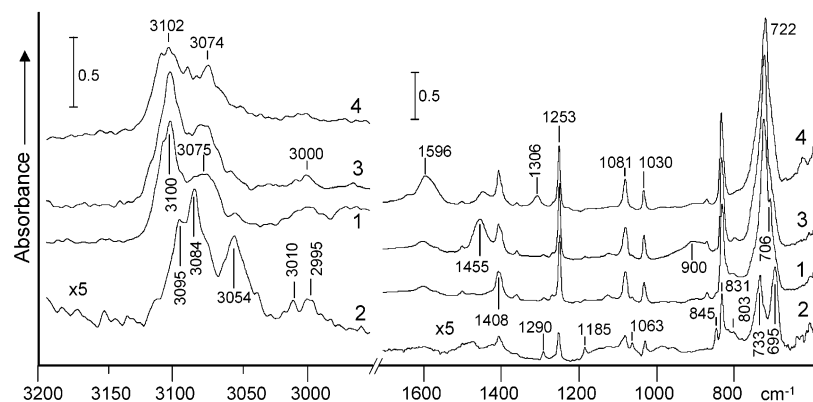
## Results

**Adsorption of Thiophene-*h*<sub>4</sub>.** In the spectrum of CaO, as it was already mentioned in ref 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 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 ref 20 belongs to the OH groups of type V, that is, bound to five 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 Figure 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 a new strong band of perturbed hydroxyls could be seen, which in the spectrum taken 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 the 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 Figure 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 a well-resolved shoulder at 1400 cm<sup>−1</sup>, shown in a special insert in Figure 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 cm<sup>−1</sup> up to about 300 K. These are the bands at 3055, 3010, 2995, 803, 783, and 698 cm<sup>−1</sup>.

Thiophene-*h*<sub>4</sub> adsorption at low temperature on preliminary deuterated surface of CaO pretreated at 723 K, where the double peak at 2746–2740 cm<sup>−1</sup> and a weak maximum at 2661 cm<sup>−1</sup> could be seen instead of corresponding OH bands at 3722–3710 and 3610 cm<sup>−1</sup>, leads to exactly the same spectrum of the adsorbed thiophene. The band of perturbed OD groups arises



**Figure 2.** IR spectra of thiophene- $h_4$  adsorbed on CaO pretreated at 973 K: (1) after addition of thiophene- $h_4$  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.

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  $3675\text{--}50\text{ cm}^{-1}$ , then with the increasing coverage a 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 easily 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  $3430\text{ cm}^{-1}$ .

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 the 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 the sample activated at 973 K.

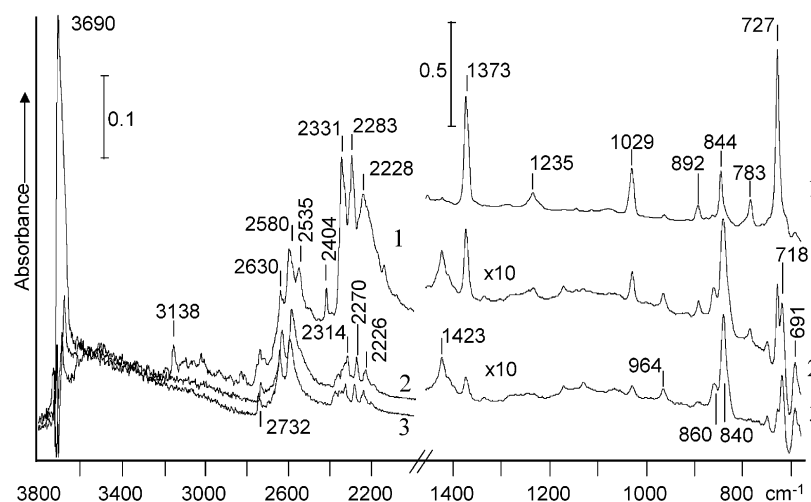
Bands of weakly adsorbed thiophene do not differ much from those of liquid thiophene in their shape, position, and relative intensities. There are few bands, however, that reveal considerable difference in their positions with respect to free molecules. At 200 K, the most intense bands of adsorbed thiophene 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 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 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<sup>21</sup> or  $714\text{ cm}^{-1}$ <sup>22</sup> 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 (Figure 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 demonstrates 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 curve 2 in Figure 2 is 5-fold expanded.

In the CH stretching region, a 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 Figure 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 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  $3084$ ,  $3054$ ,  $3010$ ,  $2995$ ,  $1472$ ,  $1290$ ,  $1185$ ,  $1063$ , and  $845\text{ cm}^{-1}$  could easily be distinguished.

Removal of gaseous thiophene by pumping for several minutes at  $240\text{--}270\text{ K}$  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  $270\text{--}300\text{ K}$  leads to simultaneous decrease of the OH band at  $3485\text{ cm}^{-1}$  and bands at  $2995$  and  $803\text{ cm}^{-1}$ , which disappear completely after evacuation at  $370\text{ K}$ . The bands at  $3095$ ,  $3054$ ,  $3010$ ,  $1290$ ,  $1185$ ,  $1063$ ,  $845$ ,  $813$ , and  $690\text{ cm}^{-1}$  resist evacuation at  $370\text{ K}$ , but could be removed completely together with the OH band at  $3560\text{ cm}^{-1}$  by evacuation at  $420\text{ K}$ . After



**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.

that, only slightly increased absorption below  $3700\text{ cm}^{-1}$  remains in the spectrum; however, treatment of such a thiophene-contacted sample in oxygen at 973 K leads to a dramatic increase of absorption between 1220 and  $1100\text{ cm}^{-1}$  that evidently is due to sulfate ions<sup>23</sup> and testify, thus, for the presence of some quantity of sulfur 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 a CaO sample pretreated at 723 K, intensity diminution of the 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 Figure 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, and  $2535\text{ cm}^{-1}$ . 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 and 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 Figure 3 the absorbance scale for spectra 2 and 3, obtained after evacuation, are 10-fold expanded. In this case the visible intensity of bands of the weak molecular adsorption steadily diminishes from spectrum 1 to 3. The bands of chemisorbed thiophene, on the contrary, are enhanced in curve 2 due to the expanded scale and keep almost the same intensity in spectrum 3. Real band intensity for the strongly held chemisorbed species turns also to diminish notably from spectrum 1 to 2, but to a much smaller extent than the intensities of the bands of weak molecular adsorption.

Detailed analysis of the spectra presented in Figure 3 enables us to separate the 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  $2404\text{ cm}^{-1}$  (Figure 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.

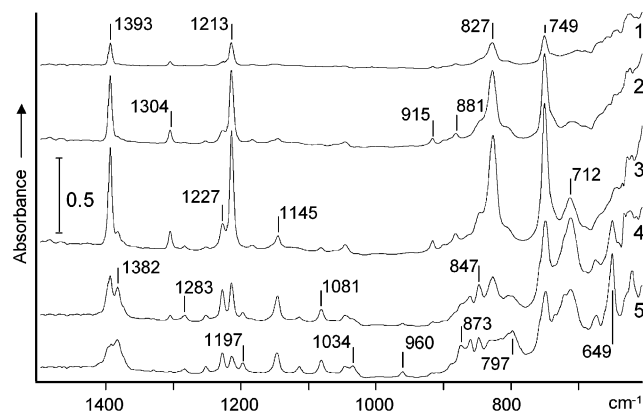
Analysis of gas desorbed from the surface at 200–210 or 250–280 K shows that, in both cases, it is practically pure thiophene- $d_4$  without notable traces of other isotopic compounds.

Adsorption of small doses of thiophene-2,5- $d_2$  on the CaO surface at 300 K, alongside 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.

Data on low-temperature adsorption of thiophene-2,5- $d_2$  on CaO pretreated at 973 K, presented in Figure 4, provide more detailed information and enable one to separate at least three groups of bands. The first to appear at about 180 K are the bands at 1393, 1304, 1213, 827, and  $749\text{ cm}^{-1}$ , and some others (see the table) that are close enough to the values reported for free thiophene-2,5- $d_2$ .<sup>21</sup> 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,

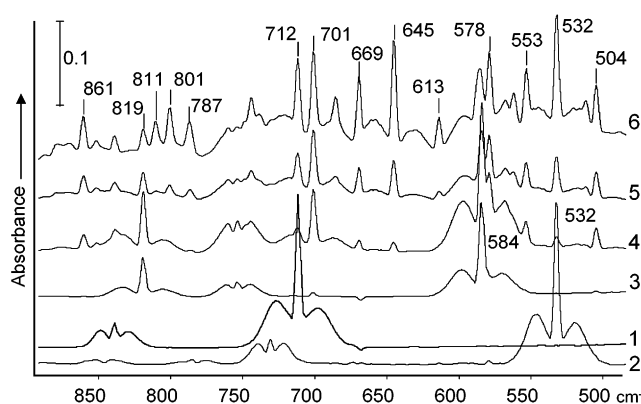




**Figure 4.** IR spectrum of CaO pretreated at 973 K after addition of thiophene-2,5- $d_2$  and raising the temperature up to at 174 (1), 183 (2), 194 (3), 210 (4), and 218 K (5).

grows in the presence of adsorbate up to 210 K, is still intense at 218 K (curve 5), and resists pumping at temperatures up to 230 K. These are the bands at 1382, 1227, 1145, 1081, and 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 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 (Figure 4). 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 300 K. 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  $\mu\text{mol}$  of thiophene-2,5- $d_2$  into the cell at 77 K. 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. The spectrum of gas desorbed at 194–200 K (not shown in the figure) almost does not differ from that of pure thiophene-2,5- $d_2$ . An only slightly increased peak at 701  $\text{cm}^{-1}$  indicates an increased amount of thiophene-2- $d_1$ , which was present as a minor impurity in the spectrum of initial thiophene-2,5- $d_2$ . A temperature increase of less than 10 deg (curve 4) results in a great enhancement of this peak and the 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



**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- $d_2$ .

578  $\text{cm}^{-1}$  turn to be substantially enhanced. According to the literature data<sup>21</sup> these bands should be ascribed to thiophene-3,4- $d_2$ , thiophene-2,5- $d_2$ , thiophene-3- $d_1$ , thiophene-2,3- $d_2$ , thiophene-3,5- $d_2$ , thiophene-2,3,4- $d_3$  and thiophene-2,3,5- $d_3$ , respectively. Thus, spectra of the desorbed gas reveal the presence all 10 different isotopic modifications of thiophene with different deuterium content, testifying for complete isotopic scrambling.

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 needs more time and a higher temperature to obtain spectra comparable with that presented in curves 5 and 6, Figure 5.

**Influence of Co-adsorbed 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 a concentration of about 0.3  $\text{nm}^{-2}$  could easily be saturated by adsorption of small quantities of CO at 300 K.<sup>16</sup> For that, about 10  $\mu\text{mol/g}$  of CO was adsorbed, which leads 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 three OD bands simultaneously with the disappearance of carbonite bands already at about 190 K. However, after removal of the most of the thiophene by prolonged evacuation at 300 K, repeated CO addition results in the appearance of the same, although less intense, bands of carbonites.

To avoid a possible displacement of CO from basic sites by stronger adsorbed thiophene, in another experiment after addition of a small portion of CO the resulting carbonites were oxidized 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  $\text{cm}^{-1}$ , does not appear at all or has very low intensity even after raising the temperature up to 300 K; however, bands at 3485 and 3430  $\text{cm}^{-1}$  appear as

usual. 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 a CaO sample pretreated at 973 K shows that after poisoning by CO with subsequent oxidation scrambling also occurs; however, comparison of the spectra taken under 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 chemisorbed thiophene 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 spectra very close to those obtained for pure CaO.<sup>16</sup> The strong band of molecular CO at  $2153\text{ cm}^{-1}$  disappears after heating 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  $2032\text{ cm}^{-1}$  and other bands of dioxoketenes ( $1340$  and  $992\text{ cm}^{-1}$ ) arise, grow, and reach maximum intensities at 160–200 K and then diminish but still are visible at 273 K. Bands of further CO chemisorption products at about  $1600$ ,  $1306$ ,  $1175$ , and  $1110\text{ cm}^{-1}$  increase constantly 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 resists pumping at 205 K starts to diminish in the presence of CO already at 77 K and disappears 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.** The 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 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  $21\text{ cm}^{-1}$ , which is well above the values typical of physisorption.

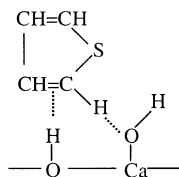
Another important spectral manifestation of molecular adsorption is the reversible perturbation of surface hydroxyl groups by weakly bound thiophene. Appearance of new bands of perturbed OH groups at  $3700$ – $3675\text{ cm}^{-1}$  is accompanied by simultaneous reversible diminution of the bands of unperturbed hydroxyls and could be observed on addition of both usual or

deuterated thiophene. 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<sup>14,15</sup> or acetone<sup>12</sup> nor adsorption of more inert molecules such as  $\text{CCl}_4$ ,<sup>12</sup>  $\text{CO}$ ,<sup>24</sup> benzene, *n*-hexane, nitrogen, and oxygen<sup>25</sup> produce any remarkable shift of these bands. This result could be elucidated if we take into account the 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 a weak H-bond by the C–H group with the oxygen atom of hydroxyl, leading to a slight lowering of the OH stretching frequency. Such an 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 the out-of-plane bending mode of adsorbed thiophene from  $712$  up to  $723\text{ cm}^{-1}$ , observed for samples dehydrated at 723 K. The even lower position of CH stretching (up to  $3090\text{ cm}^{-1}$ ) and an upward shift of the bending vibration band (up to  $733\text{ cm}^{-1}$ ) observed for the samples activated at 973 K at low surface coverages could naturally be explained by the same mechanism of thiophene interaction with the basic oxygen atoms formed on a CaO surface upon dehydroxylation.

Somewhat unexpected is the different ability of the surface hydroxyl groups (bands at  $3722$ – $3710\text{ cm}^{-1}$ ) 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 the 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 under the same conditions. To our mind, the reason is the formation of a 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.

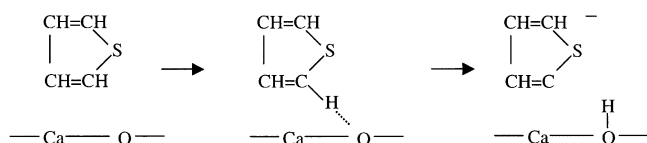
The band at  $3616\text{ cm}^{-1}$  which appears after thiophene adsorption on samples pretreated at 723 K should also be due to the perturbed OH groups, since it arises after adsorption of both usual or deuterated thiophene. It does not appear in the spectra of samples activated at 973 K where the 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  $2661\text{ cm}^{-1}$  which 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 the C=C stretching band to lower wavenumbers is characteristic of a 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, H-bonds in such a chain with the same direction of charge transfer should enhance each other making more favorable perturbation of hydroxyls that act as proton donors.

According to ref 20 the band at  $3610\text{ cm}^{-1}$  belongs to the groups of type V, which due to contact with five cations should be more acidic than the type I hydroxyls (band at ca.  $3710\text{ cm}^{-1}$ ) 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<sup>26</sup> and a small frequency increase of CaO surface OH groups perturbed by some weakly adsorbed molecules has been reported.<sup>25</sup>

**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 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 the first to arise after low-temperature adsorption of thiophene-2,5- $d_2$ . From this we can conclude that the 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 the 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” anions  $\text{SC}_4\text{H}_3^-$ :



The positions of the OH bands that arise as a result of thiophene dissociation are not typical of the hydroxyls of a pure CaO surface, which could be explained by their interaction with the adjacent thiophene anions. The 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.<sup>17</sup> 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 the 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.<sup>27</sup>

Therefore, we shall try to analyze 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 refs 16 and 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, which 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 repeated CO addition. Almost complete poisoning of these sites by preliminary CO adsorption could be achieved if the resulting carbonites are oxidized 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.

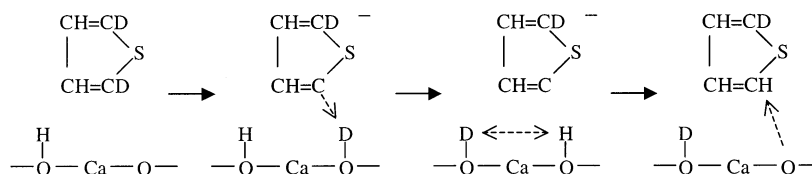
The least stable OH band at  $3430\text{ cm}^{-1}$  as well as its OD analogue at  $2535\text{ cm}^{-1}$  resist pumping at 200–220 K but could be removed by short evacuation at 240–270 K. However, if CO is added at 77 K, this band diminishes in intensity and disappears completely after raising the temperature up to 140 K simultaneously with the appearance of the bands due to dioxoketenes ( $2065\text{--}2040\text{ cm}^{-1}$  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  $717\text{ cm}^{-1}$ .<sup>16,27</sup> 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.

The third OH band that arises 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  $733\text{ cm}^{-1}$ .<sup>27,28</sup>

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 arises 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 evidence for a weak 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 those of the corresponding thiophene isotopomers, reveal a decrease of



## SCHEME 1



aromatic character of the ring caused by the loss 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 a small difference in the anions formed as a result of dissociation on different surface oxygen sites. This means that anions still keep the connection with the hydroxyl group and are affected by differences 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 site. After removal of other kinds of thiophene anions at elevated temperatures, the increased overall OH absorption, as well as the appearance of strong sulfate absorption after heating such a sample in oxygen, indicates irreversible decomposition of a certain part of thiophene with the trapping of sulfur by CaO.

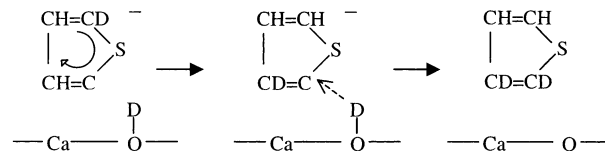
**Isotopic Exchange.** As one could suppose, reversible dissociation of thiophene should result in H–D isotopic exchange, if deuterated thiophene after dissociation is recombined with the proton of surface OH group or if normal thiophene attaches the deuterium from OD groups of the deuterated surface. 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 a proton to the 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 a proton or vice versa (Scheme 1).

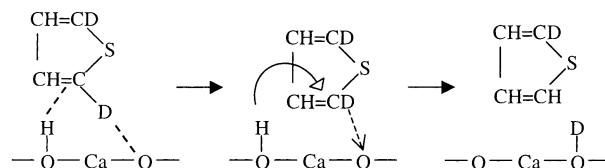
In this simplest case one could expect that a proton will be exchanged at a certain position from which the transfer is more favorable, most probably in position 2 or 5. In fact, the first evidence for the exchange after adsorption of thiophene-2,5- $d_2$  is the appearance of surface OD groups and thiophene-2- $d_1$  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 positions 3 and 4. We could suppose that CH groups in these positions are also capable of H-bonding and proton transfer, but two ways of dissociation occurring under the same conditions seems 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 a 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 positions 3 and 4, one could suppose that in the formed thiophenide anion proton migration occurs. Then the deuterium that remains in the anion

## SCHEME 2



## SCHEME 3



could become bound to a carbon atom in the position 3 or 4, and after recombination another isotopomer could arise (Scheme 2).

Such a mechanism alone, if it 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.

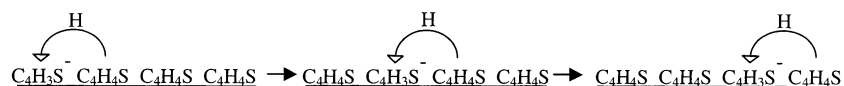
(iii) To explain the observed isotopic scrambling by one manifold repeated elementary step, we can consider also the concerned mechanism that involves several surface sites. Deuterium transfer from the CD group in position 2 of the molecule to a surface oxygen ion can be accompanied by simultaneous transfer of a proton of the adjacent OH group to the molecule. This could lead finally to the fixation of a 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 a 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 like a hole in a semiconductor, due to multiple proton transfers from one molecule to another (Scheme 4). Such a process should scarcely be restricted by protons in positions 2 and 5 and for the case of adsorbed thiophene-2,5- $d_2$  could lead to complete isotopic scrambling, as observed in the 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 preevacuated at 723 K that display very low ability to chemisorb CO and a 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



## SCHEME 4



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, which are responsible for the reaction of isotopic scrambling, at least at lowest temperatures, when only these forms of thiophene dissociative adsorption are reversible. Apparently, each of the 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 a thermally activated surface of CaO enable us to distinguish several surface species formed mostly on basic sites.

Molecular adsorption of thiophene occurs on surface oxygen ions and basic OH groups by a weak H-bond of CH groups with the lone electron pairs of oxygen. Interaction with basic hydroxyls results in the OH stretching frequency lowering by about 22  $\text{cm}^{-1}$ , for a deuterated surface the same effect leads to an OD frequency shift by 17  $\text{cm}^{-1}$ . Spectrum of thiophene adsorbed in such a form has an asymmetric CH band lowered up to 2100  $\text{cm}^{-1}$  and an out-of-plane CH bending increased from 712 up to 722  $\text{cm}^{-1}$ . Bands of the same vibrations are shifted up to 3090 and 733  $\text{cm}^{-1}$  if the H-bond is formed with surface oxygen atoms.

If the temperature of pretreatment does not exceed 723 K, a band of more acidic OH groups occurs at 3610  $\text{cm}^{-1}$  that reveals a blue shift up to 3616  $\text{cm}^{-1}$  and an intensity increase on thiophene adsorption. Despite the anomalous effect of frequency increase, we believe this effect to be due to the formation of H-bonds with thiophene molecules, which could be bound either by this bond only or simultaneously by another H-bond via a CH group with an oxygen atom of the surface or of the basic OH group. A shoulder of the C=C band at 1400  $\text{cm}^{-1}$ , observed in the spectrum of thiophene adsorbed on such samples, is typical of an H-bond with the  $\pi$ -electron system. This confirms that the OH perturbation is caused in fact by an 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 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 240–270 K, while the most stable products with the OH band at

3560  $\text{cm}^{-1}$  resist pumping at 300 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 sulfate ions, thus demonstrating that a certain part of sulfur remains in the sample, apparently, in the form of sulfide  $\text{S}^{2-}$  ions.

Reversible dissociation accounts for the catalytic reaction of isotopic scrambling, established for thiophene-2,5- $d_2$  by means of FTIR spectroscopy of desorbed gas. The reaction starts at 200–220 K and leads to the appearance of up to 10 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 pretreatment 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 catalyzed 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.

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