

Formation and Physicochemical and Catalytic Properties of Hydrotreating Catalysts Containing Mo on Various Supports: V. An IR Study of Thiophene Adsorption

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Abstract—Thiophene adsorption on γ - Al_2O_3 , hydrated titanium dioxide, and Mo-containing catalysts on these supports is studied by IR spectroscopy. The form of adsorbed thiophene and the composition of surface species on the catalysts depend on the nature of support.

INTRODUCTION

Correlations of physicochemical and catalytic properties of Mo-containing catalysts for the hydrodesulfurization of raw hydrocarbons supported on traditional γ - Al_2O_3 and other materials, such as TiO_2 whose use is ever growing, has remained a topical problem for a long time [1–5]. Earlier, we considered the interaction of the impregnation solution of ammonium heptamolybdate with γ - Al_2O_3 and hydrated titanium dioxide (HTD), phase compositions and desulfurization activities, and the dispersion of molybdenum of these catalysts [6–8].

The properties of hydrodesulfurization catalysts on various supports are well studied, but no comparative data on the adsorption of sulfur-containing compounds on the catalyst surface were reported. It was only found that the heat of thiophene adsorption and the accompanying change in entropy in the Mo/HTD system are higher than those in the Mo/ Al_2O_3 system [8]. A further study of the adsorption of sulfur-containing model compounds on supports and catalysts at various stages of synthesis would reveal physicochemical features of the catalytic activity of systems with various compositions and clarify the mechanism of desulfurization.

In this paper, we present the results of the IR spectroscopic study of thiophene adsorption on γ - Al_2O_3 , HTD, and catalysts on these supports.

EXPERIMENTAL

We studied the samples of γ - Al_2O_3 (A-64) and HTD, precipitated with ammonium hydroxide from the TiCl_4 solution in HCl at pH 3–6. The support was impregnated to incipient wetness with a solution of ammonium heptamolybdate, dried and calcined in air [8]. Catalysts supported on γ - Al_2O_3 had a specific surface area of 180 m^2/g , and the HTD-based catalysts had an area of 160 m^2/g . The samples contained 0.20–0.25 mg/m^2 of Mo. They were tableted and calcined at 500°C in oxygen and under vacuum for 1 and 3 h, respectively.

The purity of the adsorbate was monitored by spectroscopic and chromatographic techniques. IR spectra were recorded with a Specord 75 JR spectrometer at room temperature in a standard lubricant-free flat optical cell.

RESULTS AND DISCUSSION

Figure 1 shows the IR spectra of the supports and thiophene adsorbed on the supports. The adsorption of thiophene on Al_2O_3 at 25°C (Fig. 1a, spectrum 2) shifts the absorption bands of the OH groups isolated on the surface, which have various acidity (absorption at 3680, 3725, and 3750 cm^{-1}) in the range typical of the hydrogen bond (3550–3650 cm^{-1}). This suggests that a considerable part of OH groups on the Al_2O_3 surface participate in such a binding of thiophene with the surface. We also observed absorption bands at 1250, 1403, 1570, and 3070–3110 cm^{-1} (Fig. 1a, spectrum 2), which are close to the absorption bands in the spectrum of liquid thiophene (Fig. 1c). Besides, some bands caused by the stretching (2920 cm^{-1}) and deformation (1435–1450 cm^{-1}) vibrations of the methylene C–H bonds, and the double bond (1605–1615 and 3025 cm^{-1}) [9] are present in the spectrum. Apparently, under our experimental conditions, thiophene partially interacts with the surface of Al_2O_3 ; the interaction results in the hydrogenation of C=C bond without breaking the ring and leads to the formation of surface species, such as adsorbed dihydrothiophene [10]. The surface OH groups are a possible source of hydrogen [11–13].

If thiophene reacts with the Al_2O_3 surface at 200–350°C, the absorption bands associated with liquid thiophene remain invariable and the absorption bands associated with the surface species of dihydrothiophene (1225, 1440, 1635, 3025, 3045, and 3085 cm^{-1}) [10] become more intense (Fig. 1a, spectrum 3). The absorption bands at 1540–1580 cm^{-1} can be associated with thermostable carboxylate and thio-carboxylate structures [14].

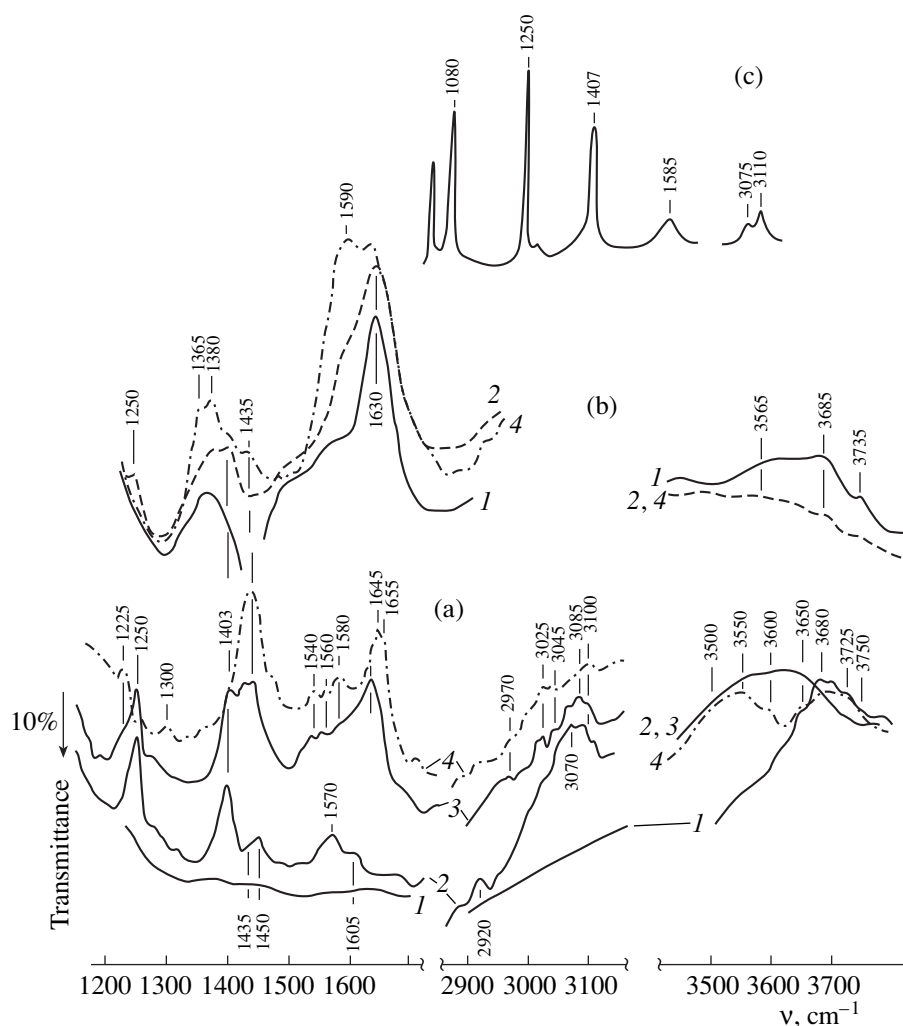


Fig. 1. IR spectra of thiophene on (a) γ - Al_2O_3 and (b) HTD: (1) spectra of the support samples; (2) thiophene is adsorbed at 25°C; (3) thiophene is adsorbed at 200 or 350°C; (4) thiophene is desorbed at 25°C. (c) is the spectrum of liquid thiophene.

Desorption at 25°C removes the absorption bands of weakly bound thiophene at 1250 and 1403 cm^{-1} (Fig. 1a, spectra 4). The hydroxyl cover of Al_2O_3 is partially reduced. The desorption of weakly bound thiophene enables us to detect new surface components of the adsorbate on Al_2O_3 more accurately. Changes in the spectral range typical of the hydroxyl groups on Al_2O_3 (3680–3750 cm^{-1}) suggest that basic OH groups (adsorption at 3750 and 3725 cm^{-1}) are easier to regenerate after thiophene desorption than acidic OH groups (3680 cm^{-1}). Apparently, weakly bound thiophene forms hydrogen bonds with basic OH groups first of all. The interaction of thiophene with acidic hydroxyls is followed by proton transfer and the formation of products that are more strongly bound to Al_2O_3 .

The spectra of thiophene adsorbed on HTD (Fig. 1b) are somewhat difficult to interpret. The absorption band at 1370 cm^{-1} and the strong band at 1630 cm^{-1} are still present in the spectrum after multiple thermal treatments of HTD in oxygen and evacuation (Fig. 1b, spec-

trum 1). We can find some common and some individual features of thiophene interaction with Al_2O_3 and HTD. In both cases, the intensity of the absorption bands of the OH groups isolated on the surface (3585–3735 cm^{-1}) lowers (Figs. 1a, 1b, spectrum 2). However, for thiophene adsorbed on HTD, we did not observe a substantial increase in the absorption in the range typical of hydrogen bonds because of the strong self-absorption of HTD. A weak absorption band associated with C–S vibrations of weakly bound thiophene (1250 cm^{-1}) is typical of the spectrum of thiophene adsorbed on HTD at 25°C (Fig. 1b, spectrum 2). The absorption band at 1403 cm^{-1} related to the vibrations of the thiophene ring is not strong either. The absorption bands of thiophene adsorbed on HTD at 1360–1380 and 1590 cm^{-1} become stronger after desorption (Fig. 1b, spectrum 4). The weakening of interaction between adsorbed molecules (in particular, the lateral interaction) after pumping the gas phase out probably causes this effect. Similar effects were observed earlier

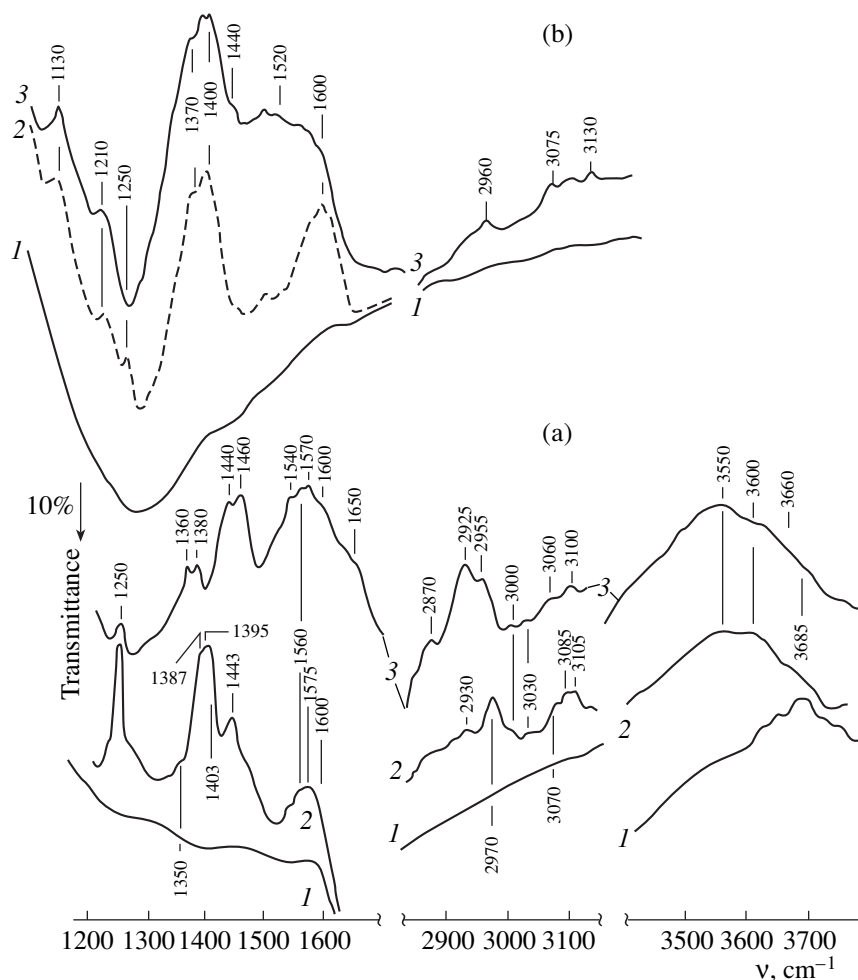


Fig. 2. IR spectra of thiophene on (a) Mo/Al₂O₃ and (b) Mo/HTD catalysts: (1) spectra of the original samples; (2) thiophene is adsorbed at 25°C; (3) thiophene is adsorbed at 200°C.

in the study of strong surface complexes [15, 16]. This suggests that thiophene forms stronger surface compounds with HTD than with Al₂O₃ at 25°C. Possibly, the degree of hydrogenation and the orientation of a ring in the surface species with respect to the surface depend on the nature of support.

The adsorption of thiophene on Mo/Al₂O₃, as well as on Al₂O₃, changes the adsorbent spectrum in the range typical for the absorption of hydroxyl groups and causes absorption bands at 3550–3600 cm⁻¹ typical of the hydrogen bond (Fig. 2a, spectra 1–3). The spectra of thiophene adsorbed at 25°C on the support and on the catalyst (Figs. 1a, 2a, spectra 2) look similar; both spectra contain absorption bands close to those of liquid thiophene (1250, 1403, 1570–1575, and 3070–3100 cm⁻¹) and the absorption bands associated with surface species (1435–1450, 1560–1600, and 3085 cm⁻¹).

Unlike Al₂O₃, additional surface species are formed on Mo/Al₂O₃; they are characterized by strong adsorption at 1387–1395 cm⁻¹ with an intensity comparable with that of the band at 1403 cm⁻¹, and weaker bands at

1443 and 2970 cm⁻¹ (Fig. 2a, spectrum 2). The intensity of the latter increases with an increase in temperature to 100°C and with the reaction time. This is typical of weakly activated adsorption. We analyzed the behavior of these adsorption bands under various conditions together with the published data in [17, 18] and assigned the absorption bands at 1385–1395, 1440, and 2970 cm⁻¹, to a surface species formed by the interaction of the α -carbon of a coordinated thiophene molecule with hydrogen of the surface OH groups without C–S bond breaking. Weak bands at 3000, 3030, and 3085 cm⁻¹ show that a nonaromatic C=C fragment exists in the surface species. It was shown that thiophene complexes with reduced Cu⁰ and Cu¹⁺ sites (absorption bands at 1372 and 1191 cm⁻¹) are more stable than complexes with unreduced Cu²⁺ sites (1397, 1312, and 1218 cm⁻¹) in the Cu/Al₂O₃ system [18]. In our case, the absorption bands at 1385–1395 cm⁻¹ may demonstrate the existence of coordination bonding of thiophene with the Mo ions in various oxidation states. The absorption band at 3085 cm⁻¹ may correspond to

the terminal adsorption of thiophene via a sulfur atom [17]; the bands at 3000–3030 cm^{-1} correspond to edge adsorption [17, 19], and the band at 2970 cm^{-1} corresponds to the plane orientation of the adsorbed thiophene molecules with respect to the surface [17].

If the adsorption of thiophene on $\text{Mo}/\text{Al}_2\text{O}_3$ occurs at 200°C (Fig. 2a, spectrum 3), the absorption bands of weakly bound thiophene (1250 cm^{-1}) becomes weak. The absorption bands at 1360–1380, 1440–1460, 2870, 2925, and 2955 cm^{-1} assigned to CH_2 - and CH_3 -groups and 1540–1600 cm^{-1} assigned to conjugated $\text{C}=\text{C}$ bonds [9] are very pronounced in this case. The absorption at 1540–1560 cm^{-1} may also indicate the presence of thiocarboxylate structures [14]. The latter cannot be desorbed in a vacuum at 450–500°C, and have a spectrum similar to that of butadiene adsorbed on the catalyst [10]. The spectrum indicates that polymer compounds may exist. The addition of hydrogen atoms of the surface OH groups to the α -carbon atoms of thiophene can form the surface species of butadiene on $\text{Mo}/\text{Al}_2\text{O}_3$ at temperatures higher than $\geq 200^\circ\text{C}$, when hydrogen atoms of OH groups become more mobile [10].

The spectrum of thiophene on Mo/HTD (Fig. 2b, spectrum 2) at 25°C contains the same bands in the ranges 1370–1400 and 1580–1600 cm^{-1} as that of thiophene on $\text{Mo}/\text{Al}_2\text{O}_3$. The intensities of the absorption bands also increase with the duration of adsorption. However, unlike $\text{Mo}/\text{Al}_2\text{O}_3$, the intensity of the weakly bound thiophene absorption at 1250 cm^{-1} decreases considerably. Simultaneously with an increase in the intensity at 1370–1400 and 1580–1600 cm^{-1} , the absorption bands at 1210 and 1130 cm^{-1} become visible. Comparison with the published data [18] permits us to assign these absorption bands to the surface species of thiophene coordinately bound to the Mo ions on HTD, which are reduced by thermal treatment under vacuum. This strongly bound surface species can only desorb at high temperatures ($>200^\circ\text{C}$). Therefore, it is converted to a different surface species. Partial reduction of Mo by thermal treatment in a vacuum may cause the strength of the coordinately bound thiophene in the Mo/HTD system. It is easier to reduce Mo in Mo/HTD than in $\text{Mo}/\text{Al}_2\text{O}_3$ [20].

Thus, the character of surface species formed in the adsorption of thiophene on Mo-containing catalysts and the mechanism of adsorption strongly depend on the nature of the support. The difference in the catalytic properties of $\text{Mo}/\text{Al}_2\text{O}_3$ and Mo/HTD , in particular more intensive formation of *n*-butane in the hydrogenolysis of thiophene on Ti-containing system, were reported earlier [20]. They may be related to the fea-

tures of thiophene adsorption on these catalysts and supports described in this paper.

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