

## COMMUNICATIONS TO THE EDITOR

Vibrational Spectroscopic Study of Benzenethiol Adsorbed on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>

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Formation of alkoxide as well as carboxylate species from alcohols on alumina has already been reported by various workers<sup>1-4</sup>. However, there is no detailed information on the interaction between the thiol molecules and the alumina surface. Nevertheless,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is of great use as a support-material in the industrial hydrodesulfurization process<sup>5,6</sup>. Following the above implications, we present in this communication the vibrational spectroscopic study of benzenethiol adsorbed on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

The  $\gamma$ -alumina was supplied by Morton Thiokol Corporation. Benzenethiol purchased from Aldrich Chemical Company was dried under vacuum at the dry-ice temperature and stored in a vacuum bulb which was connected to the conventional vacuum apparatus. The design of the infrared cell used in this work is similar to that of Ramamoorthy *et al.*<sup>7</sup>  $\gamma$ -Alumina, dried in air at 378K for 72 hr, was ground to a fine powder and pressed into a self-supporting disc, 2 cm in diameter and less than 0.05 cm thick. The pellet was pretreated with the method which is to be discussed later. The pellet was eventually placed in a stainless steel holder, which was suspended by a stainless steel wire in the infrared cell. After preparing the sample, a background spectrum was recorded using the Perkin-Elmer model 283 spectrophotometer. The cell was subsequently returned to the vacuum system, and benzenethiol was added to the cell and then the cell was isolated from the vacuum system. The pressure of benzenethiol gas was monitored using a thermocouple vacuum gauge (Sargent-Welch model 1515). All observable changes were complete within 10 min when using this procedure. Before taking the spectrum, the cell was evacuated for 10 min to remove any remaining gas. After recording the spectrum, the cell was returned to the vacuum system. Then, additional benzenethiol of a higher pressure was admitted to the cell and the process was repeated. The vacuum system was capable of maintaining a dynamic vacuum of 10<sup>-4</sup> Nm<sup>-2</sup>. The glass part of the system was heated with a heating tape.

Without any pretreatment of  $\gamma$ -alumina pellet, no spectra of adsorbed benzenethiol species appeared when the added gas pressure was 50, 150, or 500 mTorr. When 1 Torr of benzenethiol was exposed to the pellet, weak peaks appeared in the infrared spectrum. However, those peaks disappeared completely after evacuation for 30 min at the ambient temperature. Similar observation was made as well in the case when the  $\gamma$ -alumina pellet, calcined at 673K overnight, was exposed to air for a while. Hence, it appears that the benzenethiol molecule is physisorbed on the  $\gamma$ -alumina surface with-

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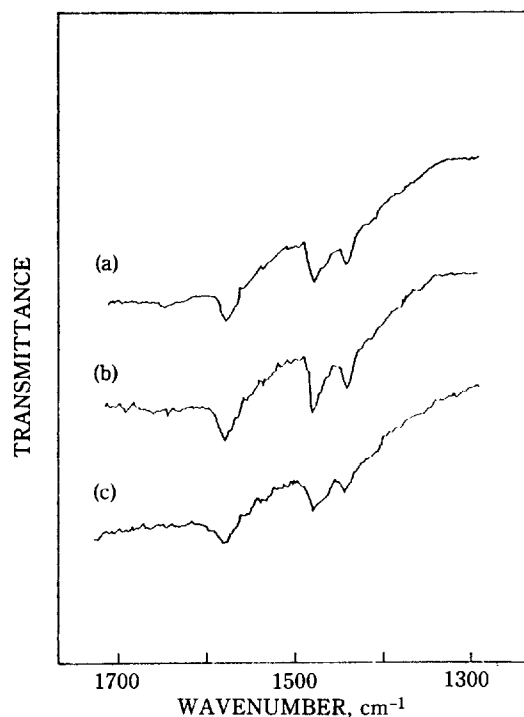
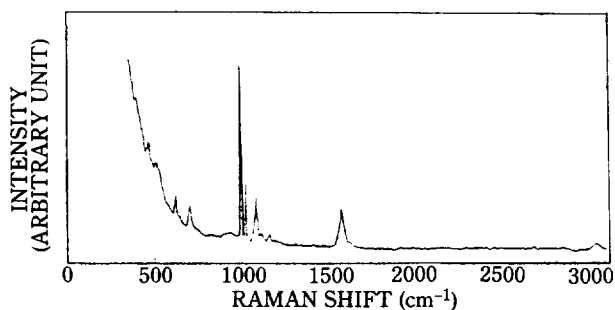


Figure 1. Infrared spectra, in the limited region 1700-1300 cm<sup>-1</sup>, of benzenethiol adsorbed at 200 mTorr(a) and 1 Torr(b), and taken after pumping for 30 min at the ambient temperature(c).

out proper pretreatment of the pellet in situ.

After the above observation, the pellet was treated in the cell under the static pressure of 200 Torr deoxygenated H<sub>2</sub> at 673K for 2 hrs. After pumping off the hydrogen gas, benzenethiol was admitted to the cell. Figure 1(a) and 1(b) show the infrared spectra, in the limited region 1700-1300 cm<sup>-1</sup>, of benzenethiol adsorbed at 200 mTorr and 1 Torr (133.3 Nm<sup>-2</sup>), respectively. The band centered at 1582 cm<sup>-1</sup> may correspond to the benzene ring stretching mode,  $\nu_{8a}$ <sup>8-10</sup>. The bands at 1480 and 1444 cm<sup>-1</sup> can be assigned to the ring stretch plus deformation modes,  $\nu_{19a}$  and  $\nu_{19b}$ , respectively. It was observed that the band intensities were not strongly dependent on the pressure of benzenethiol in the range studied here. This indicates that 200 mTorr is enough for the full monolayer coverage of benzenethiol on the  $\gamma$ -alumina surface.

A few remarkable spectral changes occurred following



**Figure 2.** Raman spectrum of benzenethiol adsorbed on  $\gamma$ - $\text{Al}_2\text{O}_3$  (514.5 nm excitation at 100 mW,  $10\text{ cm}^{-1}$  bandpass).

the adsorption of benzenethiol to  $\gamma$ - $\text{Al}_2\text{O}_3$ . Most prominently, the bands at  $2567$  and  $917\text{ cm}^{-1}$  in the neat liquid infrared spectrum which can be assigned to the stretching and bending vibrations of S-H bond<sup>8-10</sup>, respectively, were no longer detected in the adsorbed spectrum. This observation indicates that benzenethiol is chemisorbed dissociatively on the  $\gamma$ -alumina surface by rupture of its S-H bond. In this respect, infrared spectra of thiols on  $\gamma$ - $\text{Al}_2\text{O}_3$  appears to resemble those for alcohols on  $\gamma$ - $\text{Al}_2\text{O}_3$ <sup>1-4</sup>.

The dissociative chemisorption of benzenethiol on  $\gamma$ - $\text{Al}_2\text{O}_3$  is also confirmed from the Raman spectroscopic study. The  $\gamma$ -alumina pellet exposed to 1 Torr of benzenethiol was taken out of the cell, and then Raman measurement was made. In order to insure that there is no laser-induced change, the pellet was spun during the Raman spectral measurements at 3000 rpm using an AC motor as used in the previous work<sup>11</sup>. Details of Raman measurement have been described elsewhere<sup>12</sup> and will not be repeated here. The Raman spectrum obtained is shown in Figure 2. The band corresponding to the stretching vibration of S-H bond is clearly absent in the Raman spectrum as well. Hence, it appears indeed that the benzenethiol molecule is dissociatively chemisorbed on the  $\gamma$ -alumina surface by rupture of its S-H bond.

The infrared spectrum of the adsorbed benzenethiol hardly changed on evacuation at the ambient temperature (see Figure 1(c)). The benzenethiol on the  $\gamma$ - $\text{Al}_2\text{O}_3$  surface could be completely removed after evacuation at 573K for 1 hr. This would indicate that benzenethiol is rather strongly chemisorbed to  $\gamma$ - $\text{Al}_2\text{O}_3$ .

It is a well-known experimental fact that in mono-substituted benzene the frequencies of  $\nu_1$ ,  $\nu_{6a}$ ,  $\nu_{7a}$  and  $\nu_{16b}$  modes are more sensitive to the mass of the substituent than other ring modes<sup>9</sup>. In the Raman spectrum of the adsorbed benzenethiol, the bands associated with the above vibrational modes appeared at  $1077$ ,  $696$ ,  $407$ , and  $472\text{ cm}^{-1}$ , respectively. The corresponding peaks appeared in the Raman spectrum of neat benzenethiol at  $1093$ ,  $700$ ,  $414$ , and  $464\text{ cm}^{-1}$ , respectively. Hence, it can be noticed that the substituent sensitive modes are more or less shifted from their positions in the neat Raman spectrum. In specific, the  $\nu_1$  band which is particularly sensitive to the substituent has shifted  $16\text{ cm}^{-1}$  downwards. On the other hand, smaller shifts were seen for the substituent insensitive modes such as  $\nu_{8a}$ ,  $\nu_{12}$ ,  $\nu_{15}$ , and  $\nu_{18a}$ .

For example, the  $\nu_{8a}$ ,  $\nu_{12}$ ,  $\nu_{15}$  and  $\nu_{18a}$  bands appeared in the surface spectrum at  $1580$ ,  $1000$ ,  $1159$ , and  $1026\text{ cm}^{-1}$ , respectively, and in the neat spectrum at  $1584$ ,  $1002$ ,  $1158$ , and  $1026\text{ cm}^{-1}$ , respectively. Together with the observation that benzenethiol is chemisorbed dissociatively on  $\gamma$ - $\text{Al}_2\text{O}_3$  by rupture of the S-H bond, it now appears that the benzenethiolate anion formed on adsorption is bound to the  $\gamma$ -alumina surface via the sulfur atom.

It is not evident what the active site of  $\gamma$ - $\text{Al}_2\text{O}_3$  is for the adsorption of the benzenethiol molecule. Nevertheless, it seems that the surface hydroxyl group of  $\gamma$ - $\text{Al}_2\text{O}_3$  is not the active site, for no spectra of adsorbed species appear without any in situ heat pretreatment of the  $\gamma$ - $\text{Al}_2\text{O}_3$  pellet. For the case of pyridine, Parry<sup>13</sup> reported that the molecule adsorbed exclusively to the  $\text{Al}^{3+}$  cation of  $\gamma$ - $\text{Al}_2\text{O}_3$  via the nitrogen lone pair electrons. Along with the assumption that benzenethiolate anion is formed upon adsorption to the  $\gamma$ -alumina surface, the most plausible active site of  $\gamma$ - $\text{Al}_2\text{O}_3$  is supposed to be the  $\text{Al}^{3+}$  cation for the adsorption of the benzenethiol molecule.

In summary, the results of infrared and Raman spectral studies have led to the conclusion that benzenethiol is chemisorbed dissociatively on the  $\gamma$ -alumina surface by rupture of its S-H bond and the benzenethiolate formed upon adsorption is bound to the surface via its sulfur atom. Although we could not present decisive evidence, it seemed likely that the active site of  $\gamma$ - $\text{Al}_2\text{O}_3$  is the  $\text{Al}^{3+}$  cation for the adsorption of the benzenethiol molecule. In order to understand the exact nature of adsorbed species, more detailed experimental information will, of course, be needed.

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