

The mixture was dried over anhydrous magnesium sulfate, filtered and the filtrate concentrated under reduced pressure. Purification of the residue by column chromatography afforded ethyl *a*-methylcinnamate in 67% yield.

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Adsorption of Benzenethiol on $\gamma\text{-Al}_2\text{O}_3$ supported Ni and Mo; Infrared Spectroscopic Study

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For more than two decades infrared absorption spectroscopy has been successfully applied to the analysis of high surface area materials and related adsorption complexes¹⁻³. However, there is still little understanding of the interactions between sulfur compounds and various dispersed metal particles⁴. In this respect, we have previously applied infrared spectroscopy to the benzenethiol molecule adsorbed on the silver surface⁵. We present in this communication further infrared spectroscopic information on the interaction of benzenethiol with the gamma-alumina supported nickel and molybdenum.

The γ -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 maintaining a dynamic vacuum of $\sim 10^{-4}$ Nm⁻². The glass part of the vacuum system was heated with a heating tape. The design of the infrared cell was similar to that of Ramamoorthy *et al.*^{6,7} Infrared spectra were recorded with a Perkin-Elmer model 283 spectrophotometer.

Initially, well-ground γ -alumina was impregnated with aqueous solutions of reagent grade $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$. The samples, dried in air at 378 K for 72 hrs, were ground to a fine powder and pressed into self-supporting discs, 2 cm in diameter and less than 0.05 cm thick. The pellet was reduced in a furnace under the stream of deoxygenated H_2 at 773 K for 15 hrs, and then transferred into the stainless steel holder, which was suspended by a stainless wire in the infrared cell. The pellet was treated further in the cell with the static pressure of 200 Torr H_2 at 773 K for 3 hrs, after which the hydrogen gas was pumped off and the cell was cooled down to ambient temperature. The details of the infrared measurement were already described

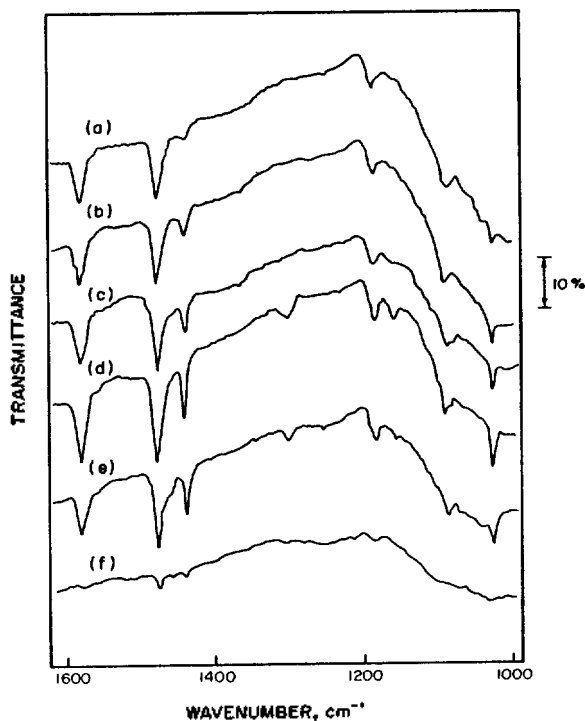


Figure 1. Infrared spectra, in the limited region 1600-1000 cm^{-1} , of benzenethiol adsorbed on 15.0 wt% Ni/ $\gamma\text{-Al}_2\text{O}_3$ at 50(a), 150(b), 500 m Torr(c), and 1 Torr(d), and taken after evacuation for 2 hrs at 298 K(e) and 1 hr at 573 K(f).

in the previous report^{5,7}, and will not be repeated here.

Infrared spectra of benzenethiol adsorbed on 15.0 wt% Ni/ $\gamma\text{-Al}_2\text{O}_3$ (the average particle size of nickel metal

measured from the X-ray diffraction line widths was 120-160 Å) exhibited several bands in the 1600-1000 cm^{-1} region as shown in Figure 1. Spectra (a), (b), (c), and (d) correspond to benzenethiol adsorbed at 50, 150, 500 mTorr, and 1 Torr, respectively. A very distinct surface spectrum was obtained in contact with 50 mTorr of benzenethiol. The most intense bands observed are centered at 1576 and 1475 cm^{-1} both of which can be attributed to aromatic ring-skeletal vibrations (ν_{8a} and ν_{19a}). Bands with moderate intensities appeared at 1438, 1182, 1085, and 1023 cm^{-1} which can be assigned to C-C stretching mode (ν_{19b}), C-H bending mode (ν_{9a}), C-C-C bending mode (ν_1), and C-H bending mode (ν_{18a}), respectively^{8,9}.

It can be seen from Figure 1(a), 1(b), and 1(c) that the infrared bands grow as the admitted benzenethiol pressure increases. However, the increase of the band intensities is far behind the pressure increment. Furthermore, band positions hardly changed upon the pressure increase. These may indicate that 50 mTorr is enough for the full monolayer coverage of benzenethiol on the nickel surface. It is somewhat interesting to observe that new bands began to appear at 1298 and 1154 cm^{-1} when the benzenethiol pressure was increased to 1 Torr (133.3 Nm^{-2}), as can be seen in Figure 1(d). As described below, this may be related with changes in the orientation of adsorbed molecule on the nickel surface.

In our previous work, it was found that benzenethiol is chemisorbed dissociatively on the silver surface by rupture of S-H bond and the benzenethiolate formed upon adsorption is bound to silver via its sulfur atom^{5,10}. Similar instance seems to occur when the benzenethiol molecule adsorbs on the nickel surface. The fact that the band at 2567 cm^{-1} in the neat liquid infrared spectrum which can be assigned to the stretching vibration of S-H bond^{8,9} is no longer detected in the adsorbed spectrum supports the cleavage of S-H bond upon adsorption to the nickel surface. According to numerous thermodesorption and LEED investigations¹¹⁻¹³, sulfur compounds are, in general, chemisorbed dissociatively on the nickel surface by rupture of S-H and S-S bonds, and the sulfur atoms occupy sites of high coordination on the non-reconstructed adsorbent at a spacing of ca 1 Å above the underlying nickel layer. These results provide indirect support for our conclusion about the adsorption of benzenethiol on a nickel surface. This conclusion is further supported by the fact that the band frequencies in the adsorption spectrum of benzenethiol are closer to those of nickel benzenethiolate salt than to those of neat benzenethiol. For example, the three prominent bands, ν_{8a} , ν_{19a} , and ν_{19b} ^{8,9}, appeared, respectively, at 1576, 1475, and 1438 cm^{-1} in the adsorbed spectrum, at 1575, 1473, and 1435 cm^{-1} in the salt spectrum, and at 1584, 1479, and 1443 cm^{-1} in the neat liquid spectrum. Hence, it is very likely that benzenethiolate formed upon adsorption is attached to the nickel surface via its sulfur atom.

Benzenethiol adsorbed was not removed by evacuation at the ambient temperature (see Figure 1(e)), which is indicative of strong nickel-sulfur interaction¹⁴. Evacuation at 573 K, however, resulted in the disappearance of adsorbed species (see Figure 1(f)). Readmission of benzenethiol to the sample after the thermal desorption at 573 K did not exhibit any absorption band. This would indicate that sulfur atoms remain on the nickel surface blocking the active sites for the adsorption of benzenethiol. It has already been shown from the thermal desorption experiment¹² that sulfur atoms remain on

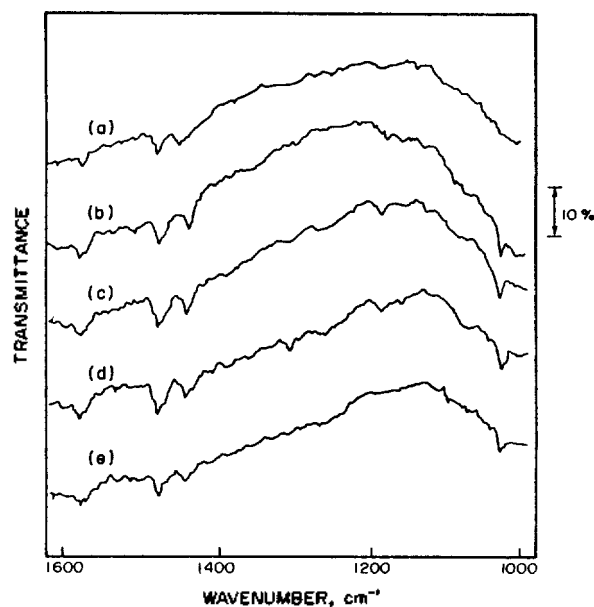


Figure 2. Infrared spectra, in the limited region 1600-1000 cm^{-1} , of benzenethiol adsorbed on Ni-Mo/ γ - Al_2O_3 (atomic ratio: Ni/Al = 0.127 and Mo/Al = 0.025) at 50(a), 150(b), 500 mTorr(c), and 1 Torr(d), followed by evacuation for 1 hr at 300 K(e).

the silica supported nickel while hydrocarbon residues are desorbed following the decomposition reaction into various chemical species at the temperature above 550 K.

It may be very informative that all the bands appeared in the surface infrared spectra (Figure 1) can be attributed to the in-plane vibrational modes. This is conjectured to be related with the orientation of the adsorbed benzenethiol molecule. There have been several suggestions that selection rules exist in infrared reflection-absorption spectroscopy for molecules adsorbed on metal surfaces¹⁵. Physical arguments were used to demonstrate that only those molecular vibrations having nonzero dipole moment derivative components perpendicular to the surface would be infrared active¹⁶. According to this rule, it seems likely that flat orientation is less plausible than perpendicular (or inclined) one for the adsorbed benzenethiol species. Both two bands which began to grow at 1298 and 1154 cm^{-1} when the exposed benzenethiol pressure is 1 Torr (see Figure 1(d)) correspond to the in-plane C-H bending modes^{8,9}. Hence, it appears that the benzene ring gets more perpendicular orientation as the exposed pressure of benzenethiol increases.

The observations made for the 15 wt% Ni/ γ - Al_2O_3 are hardly different from those for the 6.8 wt% sample. In order to get further information on the strength of interaction between the benzenethiol molecule and the transition metal surface we have also studied the bimetallic Ni-Mo system. Figure 2 exhibits the adsorption spectrum of benzenethiol on Ni-Mo/ γ - Al_2O_3 (atomic ratio, Ni/Al = 0.127 and Mo/Al = 0.025). Peak positions were comparable to those in Figure 1. However, the band intensities are considerably weak compared with the previous nickel sample. In addition, peaks were substantially diminished after evacuation for 1 hr at the ambient temperature.

For the molybdenum rich Ni-Mo/ γ - Al_2O_3 (Ni/Al = 0.025 and Mo/Al = 0.127) sample, adsorption bands of benzenethiol did not appear until the exposure of 1 Torr. After 30

min exposure at 1 Torr, very small bands at 1576, 1475, 1438, and 1023 cm^{-1} appeared. However, those peaks disappeared completely after evacuation at room temperature. For the 22.3 wt% Mo/ γ - Al_2O_3 sample, any characteristic adsorption band was not observed even at higher pressure of benzenethiol.

Earlier studies of the reduction mechanism of Mo/ γ - Al_2O_3 catalyst postulated that the Mo monolayer structure is not affected by reduction¹⁷. Later studies which viewed the calcined catalysts as formed by Mo clusters bonded to the Al_2O_3 surface suggest that, on reduction, the polymolybdate structure undergoes certain rearrangements to form MoO_2 -like cluster of similar dimension¹⁸. Although the X-ray diffraction pattern does not provide the exclusive information on the surface layer, the X-ray analysis of the molybdenum containing sample in this work exhibited the co-existence of Mo, MoO, and MoO_2 clusters. Hence, we conclude tentatively that the benzenethiol molecule adsorbs hardly on these clusters.

For the bimetallic Ni-Mo/ γ - Al_2O_3 samples, the X-ray diffraction pattern evidenced that nickel is present as completely reduced state while molybdenum is composite of Mo, MoO, and MoO_2 clusters. The fact that, for the nickel-rich Ni-Mo/ γ - Al_2O_3 sample, the adsorbed benzenethiol peaks appeared at the same positions as observed on the Ni/ γ - Al_2O_3 surface suggests that the adsorption sites of benzenethiol to give the peaks in Figure 2 can be assigned to the nickel atoms. On the other hand, the relatively weak band intensities may indicate that, for the bimetallic Ni-Mo sample, the various Mo clusters are enriched at the surface layer inhibiting the exposure of bare nickel particles. The X-ray diffracted intensity of Ni(111) peak was observed to be substantially diminished by the incorporation of molybdenum to Ni/ γ - Al_2O_3 . This would support the above argument.

In summary, it is concluded that benzenethiol is chemisorbed dissociatively on the nickel surface by rupture of its S-H bond and the benzenethiolate formed upon adsorption is bound to the surface via its sulfur atom as on the silver surface. Infrared desorption study suggests that sulfur atoms remain on the nickel surface even after the prolonged evacuation at 573 K. Benzenethiol appears hardly to adsorb on the molybdenum (Mo, MoO, and MoO_2) clusters. For the bimetallic Ni-Mo/ γ - Al_2O_3 sample, the molybdenum clusters

seem to be enriched at the surface layer.

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Glycolipid from the Korean Marine Red Alga *Gracilaria verrucosa*

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In 1969, Weinheimer and Spraggins reported the first high yield isolation of nonmammalian-type prostaglandins from the Caribbean gorgonian *Plexaura homomalla*.¹ This finding stimulated a world wide survey of prostaglandins in marine life. Especially, marine red alga *Gracilaria verrucosa* is one of the marine organism which metabolize the pro-

staglandins A_2 and E_2 ,² and biological significance for the metabolites of this red alga is of interest.

From the red alga *G. verrucosa* collected at Chungmu, Kyung-Nam Prefecture in May 1987, I have isolated a mixture of fatty acids designated as GV-4 [palmitic acid, oleic acid and arachidonic acid (in a ratio of 2:1:6)] and a galac-