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ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY B · JANUARY 2002

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Effect of Hydrogen Sulfide and Methanethiol Adsorption on Acidic Properties of Metal Oxides: An Infrared Study

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Received: July 11, 2001

Adsorption of H₂S and CH₃SH on SiO₂, Al₂O₃, TiO₂, and ZrO₂ and the resulting changes of surface acidity were studied by means of IR spectroscopy using CO (at 77 K) and 2,6-dimethylpyridine (DMP) (at 300 K) as probe molecules. Both H₂S and CH₃SH form H-bond with surface OH groups of all the adsorbents. For silica it is the only way of adsorption, while coordination as well as dissociative adsorption leading to formation of OH groups and molecular water occur on the three other oxides. Two types of induced Brønsted acidity were established, according to the mechanism of adsorption of the sulfur-containing compound. In the presence of large amount of sulfur-containing molecules, a reversible increase of the OH group acidity occurs, as revealed by the frequency shifts of the bands of H-bonded CO molecules and of perturbed OH groups on increasing H₂S coverage, or by the increased intensity of protonated DMP in the presence of H₂S. This effect is explained by the interaction of molecular H₂S with oxygen atom of the OH group. For Al₂O₃, TiO₂, and ZrO₂, dissociative adsorption of H₂S and CH₃SH results in the appearance of new OH groups that account for an irreversible, at least at 300 K, increase of Brønsted acidity revealed by higher intensity of corresponding bands of H-bonded CO and of protonated 2,6-dimethylpyridine. These new OH groups correspond to the most acidic of those that normally exist at the surface of the considered metal oxides. In no case the S–H groups of adsorbed molecules or surface SH groups formed by dissociation could account for the observed Brønsted acidity increase.

Introduction

Hydrogen sulfide is a compound that is present as a reactant or product in important catalytic processes, such as hydrotreatment or Claus reaction. For hydrotreatment, it has been reported that H₂S can promote or inhibit the activity depending on the H₂S concentration and on the reaction temperature.¹ For the supported hydrotreatment catalysts, H₂S was shown to modify surface properties not only of the sulfide phase but also of the alumina support.^{2,3} Moreover, surface properties of metal oxides, which can be used as Claus catalysts, can be greatly influenced by treatment in H₂S.^{4,5}

Several papers deal with the mechanism of H₂S interaction with alumina.^{6–11} For this oxide, two modes of H₂S adsorption were reported,^{6–8} molecular adsorption or dissociation. The former occurs either on coordinately unsaturated cations with the formation of a coordinate bond or via hydrogen bond to surface OH groups or to previously adsorbed H₂S molecules. Dissociative adsorption takes place on the strong Lewis acid–base pair sites and leads to appearance of acidic OH group and SH[–] species^{6,7} or to S^{2–} ions and either two OH groups or one water molecule^{4,8,11–14} per every dissociated molecule of H₂S. At low H₂S coverage on alumina, dissociative adsorption is generally predominant while non dissociative adsorption mainly occurs at high H₂S coverage.

It should be noted that weak bands observed in the region of stretching S–H vibrations do not enable one to distinguish between molecular and dissociative adsorption of H₂S, while

the bending vibration has even lower intensity and occurs at about 1183 cm^{–1}, where some of the oxides are not transparent to the IR beam. The appearance of bands due to new OH groups or to molecular water is the most direct evidence for the dissociative adsorption of H₂S. An alternative way to obtain information about interaction of sulfur-containing molecules with surface sites of oxides is to study the adsorption of thiols such as methanethiol. Indeed, this compound has chemical properties close to those of H₂S and is much more favorable for infrared study. It possesses a methyl group which gives rise to strong infrared bands and its SH stretching vibration has a much higher molar extinction coefficient than that of H₂S. On alumina, CH₃SH dissociates at low coverage, whereas molecular adsorption occurs at higher coverage, as in the case of H₂S adsorption.⁶

Much less is known about H₂S adsorption on other oxides. On silica, H₂S and CH₃SH only reversibly interact with surface silanol groups.^{11–16} However, CH₃SH adsorption is stronger than H₂S adsorption. On titania, coordination to surface cations is predominant^{17,18} while on zirconia, as on alumina, the first doses of H₂S and CH₃SH dissociate, then molecular adsorption takes place.^{6,19,20}

To obtain additional information about the adsorption sites of H₂S, Desyatov et al.^{11–13} have monitored the occupation of surface sites using CO, CDF₃ and pyridine as probe molecules for Lewis acid sites, basic sites and proton-donating centers, respectively. In most cases, such as Al₂O₃,¹¹ a large amount of Lewis acid and basic sites were blocked by H₂S. This was considered as evidence for dissociative adsorption. For the phosphated silica surface, after H₂S dissociation the authors have detected an increased number of protonic sites that were tentatively associated with the formation of new POH or PSH groups.

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Few attempts were undertaken to establish correlation between catalytic activity induced by H_2S or CH_3SH and their mechanism of adsorption. Ziolk et al.⁴ studied the effect of sulfidation on a series of various metal oxides, such as MgO , TiO_2 , ZrO_2 , CeO_2 , and Al_2O_3 . The authors have shown that sulfidation by treatment in H_2 – H_2S mixture at elevated temperatures modify their activity and selectivity in some acid-catalyzed reactions and have related catalytic properties with the nature of oxides and the ways of H_2S adsorption. Okamoto et al.⁷ observed that isomerization of butene-1 on alumina is poisoned by dissociative adsorption of H_2S .

Hosotsubo et al.⁵ studied the influence of H_2S on the catalytic activity of a wide range of metal ion exchanged Y zeolites, metal ions supported on silica–alumina or on pure silica and alumina, for several acid-catalyzed reactions, such as cumene cracking, toluene disproportionation, and *o*-xylene isomerization or disproportionation. From infrared data, it was concluded that the increase in the catalytic activity observed for zeolites after H_2S treatment is a result of the formation of new OH groups, acting as Brønsted acid sites. For metal ions supported on silica or alumina, the increased activity was associated with the presence of irreversibly adsorbed H_2S . However, for silica–alumina the effect of promoting action of H_2S was associated with H_2S molecules, apparently, coordinated to metal ions. The effect was different, depending on the cations, for all the supports it was the most pronounced for Cd^{2+} , Ag^{2+} , and Cu^{2+} ions and almost negligible for pure oxides used as a support.

However, although H_2S was shown to promote or inhibit the catalytic activity of metal oxides in acid-catalyzed reactions, no clear relationship between the activity and the nature, strength, and concentration of surface acidic sites present after H_2S adsorption has been reported.

The aim of this study was to establish correlation between the ways of H_2S or CH_3SH interaction with the surface of oxides and the resulting changes of surface acidity in order to understand the origin of their influence on the catalytic properties.

Adsorption of H_2S and CH_3SH was studied by means of infrared spectroscopy on four oxides that exhibit quite different acid–base properties: SiO_2 , Al_2O_3 , TiO_2 , and ZrO_2 . To detect the modifications of surface acidic properties caused by adsorption, two probe molecules were used, carbon monoxide and 2,6-dimethylpyridine. At 77 K CO interacts both with Lewis and Brønsted acid sites.^{21–23} Its interaction with free hydroxy groups results both in a downward shift of OH stretching frequency and in the increase of $\nu(\text{CO})$ whose value can be used as a measure of OH group acidity. Nevertheless, for various metal oxides the spectra of adsorbed CO could be rather complex and do not always enable one to detect easily the creation of Brønsted acid sites. Therefore, 2,6-dimethylpyridine (DMP) adsorption was also studied. Due to its higher basicity (proton affinity (PA) = 963.0 kJ/mol²⁴) as compared with pyridine (PA = 930.0 kJ/mol²⁴), DMP is more sensitive to Brønsted acidity than pyridine.²⁵ Application of DMP for the surface acidity studies and band assignment has been considered elsewhere.^{26–28} The 1660–1580 cm^{-1} region is particularly informative, since there occur the bands of ν_{8a} and ν_{8b} vibrations of DMP, the most sensitive to adsorption. Bands between 1655 and 1625 cm^{-1} correspond to protonated DMP (DMPH^+), whereas those between 1618 and 1580 cm^{-1} are due to coordinated DMP or weakly adsorbed DMP.

Thus, in this work CO was used to get information about the nature and strength of acid sites of oxide surfaces before or after contact with H_2S and CH_3SH , while DMP adsorption was

used as a specific probe for creation and poisoning of Brønsted and Lewis acid sites.

Experimental Section

1. Catalysts. SiO_2 (Degussa, 200 $\text{m}^2 \text{g}^{-1}$), $\gamma\text{-Al}_2\text{O}_3$ (GFSC, 223 $\text{m}^2 \text{g}^{-1}$) from Rhone-Poulenc, and TiO_2 (Degussa P25, 58 $\text{m}^2 \text{g}^{-1}$), which contains 0.2% SiO_2 , 0.3% Al_2O_3 , and 0.3% HCl, were used. ZrO_2 was synthesized from zirconium *n*-propylate. It was dried at 383 K and calcined in air at 823 K, and had a specific surface area of 84 $\text{m}^2 \text{g}^{-1}$.

2. Infrared Spectroscopy. Two IR cells were used: (1) a glass cell for room temperature (RT) measurements and (2) a low-temperature stainless steel cell described elsewhere.²⁹ The latter cell is equipped with crystalline ZnSe inner windows that, in combination with the outer KBr windows, enabled us to register spectra at 77–300 K in the region comprised between 4000 and 500 cm^{-1} . All the low-temperature spectra were recorded in the presence of 0.5–1 Torr of He in the inner volume of the cell for better thermal contact of sample with the cooled environment. After removal of liquid nitrogen, the temperature, measured by a thermocouple inserted in the volume for coolant, could be changed by gradual heating of the cell from 77 K up to room temperature.

Samples (about 5 mg cm^{-2}) were pressed into 2 cm^2 disks and first heated under oxygen (10–15 Torr), at 670–1070 K for 30 min to remove organic contaminations and then evacuated at the same temperature for 1 h.

H_2S (or CH_3SH) was adsorbed either at room temperature or at about 120 K, to increase the amount of adsorbed molecules and to prevent their dissociation that could be activated at 300 K. In the latter case, a small amount of the studied gas was introduced into the cooled cell, which already contained helium. The cell temperature was then increased from 77 K up to about 120 K in order to evaporate the sulfur-containing molecules, which had condensed on the cooled walls of the cell. When the increase of pressure and the changes in the IR spectrum indicated H_2S (or CH_3SH) adsorption on the sample, the cell was cooled again up to 77 K before CO admitting. In some cases, two sharp bands at 2544 and 2526 cm^{-1} due to the film of solid H_2S on the cold cell windows could be distinguished, then these were subtracted to obtain the spectra of pure adsorbed H_2S . As a next step, the cell was evacuated at about 120 K to decrease the amount of adsorbed H_2S (or CH_3SH), and again the surface was characterized by CO adsorption at 77 K. Then the same procedure was repeated after raising the temperature and evacuation at 300 K.

To characterize the samples by CO adsorption before or after contact with sulfur-containing molecules, about 8 Torr of CO at equilibrium pressure were admitted into the cell. Then, evacuations during increasing times were performed to study the spectrum dependence on the CO coverage.

Experiments on the catalyst acidity monitored with DMP as a probe molecule were carried out at room temperature. In this case, to study the effect of H_2S or CH_3SH adsorption, two different procedures were used. In the first case, small calibrated H_2S doses were successively introduced up to saturation. Then, after evacuation at room temperature, 1 Torr of DMP was let into the cell that was again evacuated up to about 2×10^{-5} Torr. In the second case, DMP was first adsorbed until a pressure of 2×10^{-5} Torr was reached, then doses of hydrogen sulfide were introduced as above, and spectra were recorded in the presence of H_2S gas and after its removal. The latter procedure was used for the quantitative measurements. Typically, the intensity of DMPH^+ bands increased rapidly with the first doses

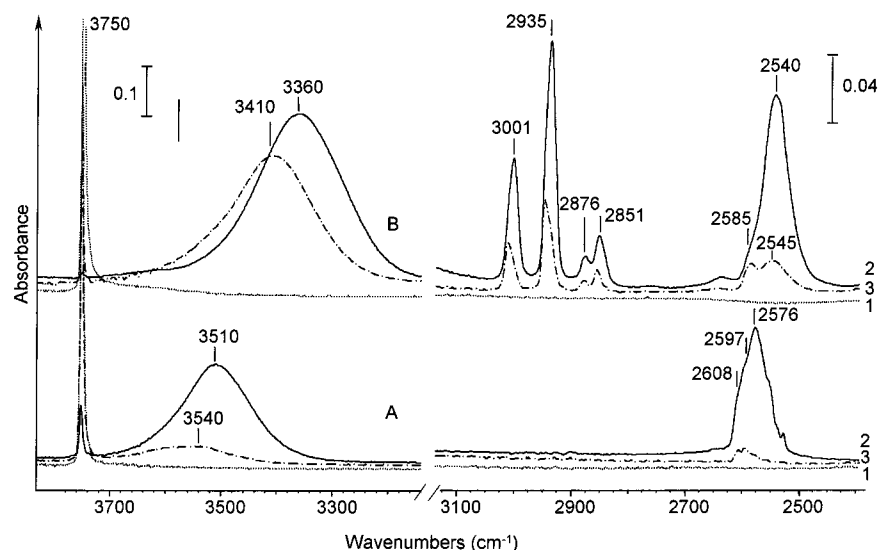


Figure 1. IR spectra of H₂S (A) and CH₃SH (B) adsorbed on silica pretreated at 970 K. 1: Before adsorption. 2: After adsorbate addition at 120 K. 3: After pumping off the excess of adsorbate at the same temperatures. All the spectra are recorded at 77 K.

of introduced H₂S (up to about 300 $\mu\text{mol g}^{-1}$), and then saturation took place, when the pressure of H₂S was several Torr.

The concentration of Brønsted sites (site number per nm²) induced by H₂S or CH₃SH adsorption on the studied metal oxides was estimated from the spectra of adsorbed DMP, taking into account the surface area of the oxide disk and assuming that the integrated absorption coefficient for the complex band of two ν_8 DMPH⁺ vibrations of protonated form does not depend on the adsorbent. Its value was determined in a special experiment with adsorption of small calibrated doses of DMP onto the surface of HY zeolite. On this sample, in the conditions of experiment, all the introduced DMP was adsorbed and protonated, and the integrated absorption was related to the quantity of adsorbate admitted into the cell. The measured value of ϵ for ν_{8a} and ν_{8b} vibrations of DMPH⁺ was found to be $17 \pm 3 \text{ cm mmol}^{-1}$.³⁰

Commercial oxygen, helium, and carbon monoxide were purified by passing through a trap cooled by liquid nitrogen. Helium and DMP were also purified by contacting with preliminary outgassed zeolite at 77 K or room temperature, respectively.

Spectra were recorded on a Nicolet FT-IR 710 spectrometer with 4 cm⁻¹ resolution.

Results

1. Silica. 1.1. H₂S and CH₃SH Adsorption. After activation at 970 K, silica spectrum exhibits a single hydroxy band at 3750 cm⁻¹ due to isolated silanol groups (Figure 1A,B, spectra 1).³¹ When excess H₂S is added at about 120 K, the intensity of this band decreases and a broad band of perturbed OH groups appears at 3510 cm⁻¹ (Figure 1A, spectrum 2). In the $\nu(\text{SH})$ vibration region, an intense band at 2576 cm⁻¹ develops with shoulders at 2608 and 2597 cm⁻¹. When excess H₂S is removed by evacuation at 120 K, the intensity of the band at 2576 cm⁻¹ decreases, whereas those bands at 2608 and 2597 cm⁻¹ remain almost unaffected (Figure 1A, spectrum 3). The intensity of the band of perturbed OH groups at 3510 cm⁻¹ also diminishes, whereas its maximum shifts toward higher values, up to about 3540 cm⁻¹.

Adsorption of CH₃SH on silica in excess leads to the appearance of perturbed $\nu(\text{OH})$ band at 3360 cm⁻¹ (Figure 1B,

spectrum 2). As in the case of H₂S, upon evacuation at 120 K, it decreases in intensity and shifts toward higher wavenumbers, up to 3410 cm⁻¹. Most of the bands of adsorbed CH₃SH appear as doublets. In particular, the band of $\nu(\text{SH})$ vibration presents two components at 2585 and 2540 cm⁻¹. Evacuation at 120 K mainly diminishes the intensities of the lower wavenumber components of the C—H and S—H bands (Figure 1B, spectrum 3). This points to the existence of at least two different forms of molecular adsorption.

1.2. CO Adsorption. In accordance with the earlier studies,^{21,23,32} CO adsorption at 77 K on SiO₂ shifts the band of free silanol groups to 3670 cm⁻¹ and results in the appearance of bands of H-bonded and physisorbed CO species at 2157 and 2140 cm⁻¹, respectively (Table 1).

After H₂S or CH₃SH preadsorption at 120 K, the $\nu(\text{CO})$ band at 2157 cm⁻¹ presents a lower intensity, as could be expected from the smaller amount of remaining free silanols capable of hydrogen bonding. The magnitude of the $\nu(\text{OH})$ shift, however, is the same as without preadsorbed species.

1.3. DMP Adsorption. Admission of 1 Torr of DMP at 300 K results in a complete disappearance of the band of free silanol groups, while a broad band due to perturbed OH groups appears at ca. 2900 cm⁻¹. The changes are essentially reversible since most part of adsorbed DMP could be removed by prolonged evacuation at 300 K. The ν_8 bands of adsorbed DMP occur at 1602 and 1580 cm⁻¹ and do not shift with surface coverage. These data show that H-bonding with silanol groups is the only adsorption mode of DMP.

Introduction of H₂S or CH₃SH at 300 K before or after DMP adsorption does not affect the spectrum of the latter. When most part of DMP is removed, one could observe weak manifestations of H₂S or CH₃SH adsorption on silanol groups and a very slight decrease of the remaining DMP bands.² Subsequent H₂S addition at 120 K to the sample, with preadsorbed DMP, leads to a slight shift of the band of perturbed OH groups toward lower frequencies.

2. Al₂O₃. 2.1. H₂S and CH₃SH Adsorption. After activation at 770 K, the spectrum of Al₂O₃ presents $\nu(\text{OH})$ bands at 3795, 3775, 3730, and 3680 cm⁻¹ (Figure 2A, spectrum 1). H₂S addition at 120 K (Figure 2A, spectrum 2) leads to the decrease or complete disappearance of the free OH bands. In parallel, appearance of a broad band due to perturbed OH groups at about

TABLE 1: Band Positions (in cm^{-1}) of H-Bonded CO and of the Corresponding Bands of Perturbed OH Groups (in Parentheses) for the Studied Oxides at Different Surface Coverages by CO Adsorbed at 77 K, before and after Treatment by H_2S

oxide	activation temperature/K	after activation	H_2S adsorbed at 120 K	H_2S and evacuation at 120 K	H_2S and evacuation at 300 K
SiO_2	970	2157 (3670)	2157 (3670)		
Al_2O_3	770	2155 –2160 ^a (3610 –3560) ^a		2158 –2163 (3540 –3510)	
Al_2O_3	1070	~ 2155 –2160 (3600 –3560)	2157 –2163 (3520 –3505)	2160 –2165 (3515 –3500)	2155 –2158 (3550 –3530)
TiO_2	770	2156 –2158, 2149 –2151 (3575 –3555)		2156 –2160 (3545 –3530)	2153 –2159 (3570 –3550)
ZrO_2	770	2152 –2156 (3610 –3600)	2152 –2156 (3560 –3550)	2155 –2162 (3560 –3540)	2152 –2158 (3580 –3555)

^a The two values represent the band shift when the CO coverage decreases from saturation (in bold) down to the lowest intensities that enable band position measurements to be made.

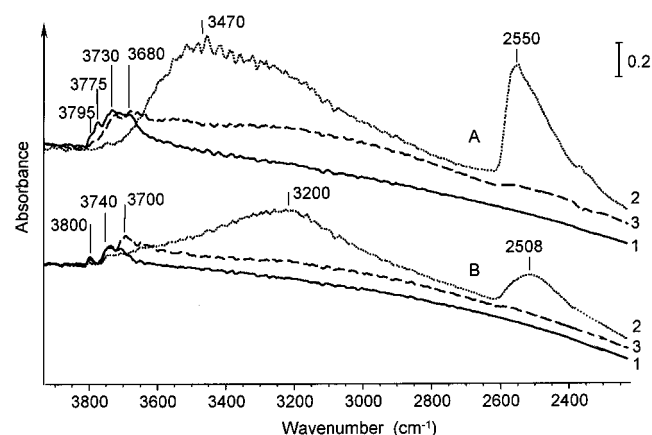


Figure 2. A. IR spectra of H_2S adsorbed on alumina pretreated at 770 K (A) or 1070 K (B). 1: Before adsorption. 2: After H_2S addition at 120 K. 3: After pumping off the excess of H_2S at 120 K. All the spectra are recorded at 77 K.

3470 cm^{-1} , a $\nu(\text{SH})$ band at about 2550 cm^{-1} with a tailing on the low-frequency side and a weak $\delta(\text{HSH})$ band at 1177 cm^{-1} are observed. Removal of the excess of H_2S at 120 K (Figure 2A, spectrum 3) restores the bands of free OH groups at 3730 and 3680 cm^{-1} , whereas the high frequency $\nu(\text{OH})$ bands at 3795 and 3775 cm^{-1} are still perturbed. Evacuation also results in the decrease and broadening of the bands at 3470 and 2550 cm^{-1} , whose maxima are shifted to 3240 and 2520 cm^{-1} , respectively. The band of the $\delta(\text{HSH})$ mode can no longer be detected.

Heating the sample up to 300 K in the presence of H_2S followed by cooling to 77 K lead to an increase in the intensities of the SH band at 2520 cm^{-1} and of the broad perturbed OH band at about 3400 cm^{-1} . A $\delta(\text{HOH})$ band at 1620 cm^{-1} , characteristic of molecular water, also arises. It could not be removed by evacuation at 300 K. The bands of free OH groups completely disappear and could not be restored by pumping at 120 K.

After raising the pretreatment temperature up to 1070 K (Figure 2B, spectrum 1) three bands of isolated OH groups remain at 3800 , 3740 , and 3700 cm^{-1} . Subsequent H_2S addition at 120 K (Figure 2B, spectrum 2) leads to the appearance of a broad band at 3200 cm^{-1} of perturbed OH groups and $\nu(\text{SH})$ band at 2508 cm^{-1} . Removal of the excess of H_2S by evacuation at 120 K decreases their intensities (Figure 2B, spectrum 3). Heating at 300 K followed by evacuating at the same temperature lead to the disappearance of these bands. This is accompanied by an increase in the intensity of the OH bands at

3740 and 3700 cm^{-1} which become more intense than before H_2S adsorption.

CH_3SH addition at 120 K to the sample pretreated at 770 K leads to a decrease of the bands of free OH groups, mainly of that at 3775 cm^{-1} and to the appearance of broad bands of OH and SH vibrations at about 3150 and 2450 cm^{-1} . The C–H bands of adsorbed CH_3SH appear at 2990 , 2932 , 2855 , 1442 , and 1321 cm^{-1} for both the samples treated at 770 and 1070 K.

2.2. CO Adsorption. CO adsorption at 77 K on alumina pretreated at 770 K results in the decrease of free OH bands and appearance of the band of perturbed OH groups at 3610 cm^{-1} (Figure 3, spectrum 1). Bands of adsorbed CO arise at 2235 , 2180 , 2155 , and 2145 (sh) cm^{-1} and are assigned to coordination on strong and weak Lewis sites, H-bonding, and physisorption, respectively.²¹ With decreasing amount of adsorbed CO, the band at 2145 cm^{-1} is the first to disappear, while that at 2155 cm^{-1} strongly diminishes and shifts up to 2160 cm^{-1} (Table 1). Finally, after removal of the most part of adsorbed CO, only the bands first detected at 2235 and 2180 cm^{-1} remain in the spectrum with their maxima shifted up to 2245 and 2200 cm^{-1} , respectively. On evacuation, the maximum of the band of perturbed OH groups shifts to lower wavenumbers, to ca. 3560 cm^{-1} (Table 1) and ultimately disappears together with the CO band at 2160 cm^{-1} assigned to H-bonded CO molecules.

Raising the pretreatment temperature up to 1070 K (Figure 4, spectrum 1) results in several changes in the spectrum of adsorbed CO. The bands of H-bonded CO and of perturbed OH groups occur at almost the same positions as those for the sample activated at 770 K but present a much weaker intensity, as expected from the reduced number of surface OH groups. On the contrary, the bands of coordinated CO species at about 2235 and 2180 cm^{-1} are more intense, and are observed in the presence of gas phase even at 300 K.

H_2S preadsorption at 120 K on the sample pretreated at 770 K (Figure 3, spectrum 2) results in noticeable changes in the spectrum of adsorbed CO. The intensity of the band at 2180 cm^{-1} decreases significantly, indicating the occupation of surface cations by H_2S . The band of H-bonded CO species appears at 2158 cm^{-1} accompanied by the band of perturbed OH groups at 3540 cm^{-1} . Lowering CO coverage leads to a shift of the CO/OH band up to 2163 cm^{-1} while the perturbed OH band shifts further up to 3510 cm^{-1} (Table 1). Comparison of the spectra recorded at low CO coverage in the absence and in the presence of adsorbed H_2S clearly indicates a stronger acidity of surface OH groups in the latter situation since the $\nu(\text{CO})$ increases by 3 cm^{-1} , while the maximum of the

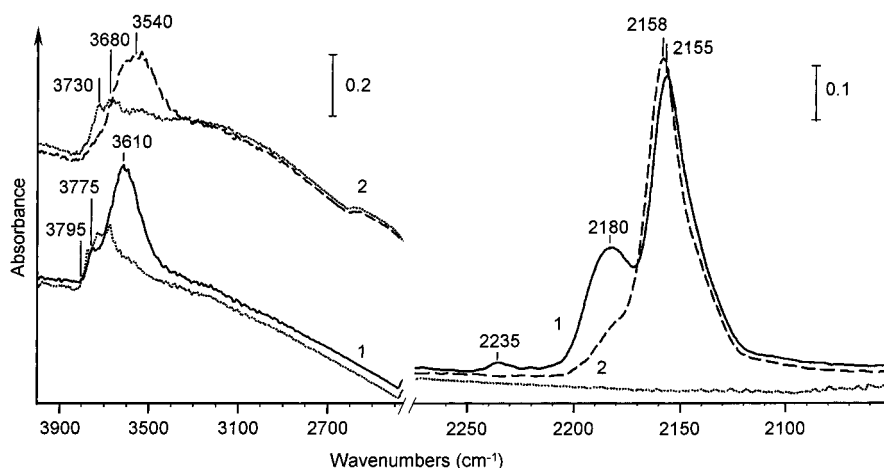


Figure 3. IR spectra of CO (8 Torr) adsorbed at 77 K on alumina pretreated at 770 K. 1: On pure alumina. 2: On alumina with preadsorbed H₂S after removing the excess of H₂S by pumping at 120 K. Dotted line: spectra before CO adsorption.

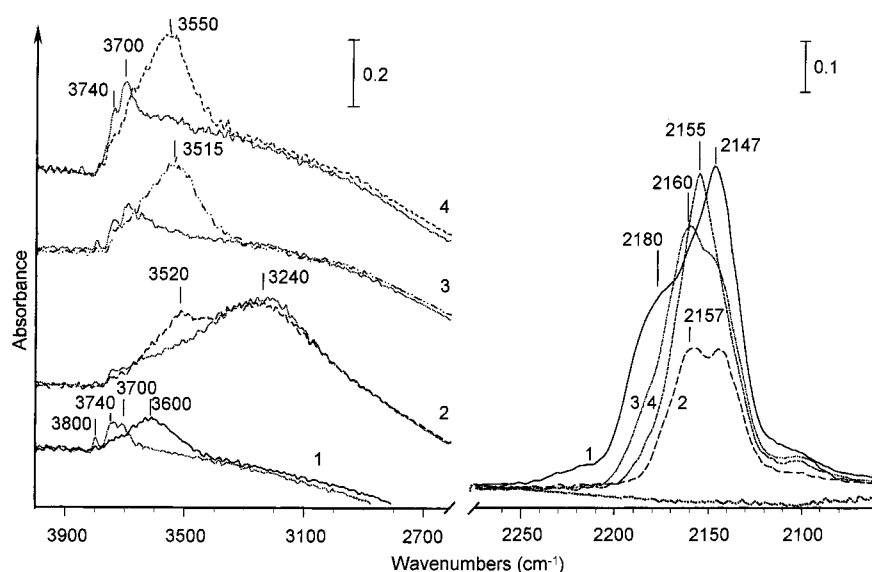


Figure 4. IR spectra of CO (8 Torr) adsorbed at 77 K on alumina pretreated at 1070 K. 1: on pure alumina. 2: After preadsorption of H₂S at 120 K. 3: After subsequent evacuation at 120 K. 4: After evacuation at 300 K. Dotted line: spectra before CO adsorption.

corresponding band of perturbed OH groups is shifted by 50 cm⁻¹ toward lower frequencies.

CH₃SH preadsorption also leads to a decrease in the intensity of the bands of CO adsorbed on Lewis acid sites and hydroxy groups of the sample pretreated at 770 K, although no frequency shifts that could point to acidity changes were observed.

Exposing the sample pretreated at 1070 K to a large dose of H₂S followed by subsequent adsorption of CO leads to the appearance of two $\nu(\text{CO})$ bands at 2157 and 2144 cm⁻¹ (Figure 4, spectrum 2). Their intensities are lower than in the absence of preadsorbed H₂S. The perturbed OH band appears in this case at 3520 cm⁻¹. Removing the excess of H₂S at 120 K (Figure 4, spectrum 3) leads to an increase of the intensity of the band at 2157 cm⁻¹, while its maximum shifts to 2160 cm⁻¹ and even to 2165 cm⁻¹ with decreasing the CO coverage (Table 1). Simultaneously, the band of perturbed OH groups shifts down to ca. 3500 cm⁻¹, the lowest observed position for alumina. The intensity of this band, as well as that of the corresponding band of H-bonded CO, become noticeably higher than before H₂S adsorption, if the latter is removed at 300 K (Figure 4, spectrum 4). Same features occur when H₂S is adsorbed at 300 K with subsequent evacuation at the same temperature. The increased amount of H-bonded CO is expected,

because the above-mentioned growth of the OH bands after contact with H₂S at RT reveals the creation of new OH groups as a result of dissociative adsorption. However, the band position of CO adsorbed on such hydroxyls (2155 cm⁻¹) is not as high as after H₂S removal at 120 K (Table 1).

Preadsorption of CH₃SH affects the spectrum of adsorbed CO in a similar way. Bands of coordinated CO disappear. Removing the excess of CH₃SH at RT from the sample pretreated at 1070 K leads to the appearance of a new OH band with a maximum at 3700 cm⁻¹. CO adsorption at 77 K results in a band of perturbed OH groups at 3540 cm⁻¹ and a band of adsorbed CO at 2159 cm⁻¹ that slightly shifts to higher wavenumbers with decreasing coverage.

It should be noticed that in no case CO adsorption gives rise to any perturbation of stretching SH bands or displaces adsorbed H₂S or CH₃SH.

2.3. DMP Adsorption. When DMP is adsorbed on alumina activated at 670 K, the hydroxy groups are perturbed, leading to the appearance of a strong band centered at 2960 cm⁻¹. A large number of bands assigned to adsorbed DMP also arise. The most sensitive to adsorption are those that correspond to the ν_{8a} and ν_{8b} modes observed in the 1650–1550 cm⁻¹ region (Figure 5, spectra 1 and 2). The intense band at 1594 cm⁻¹

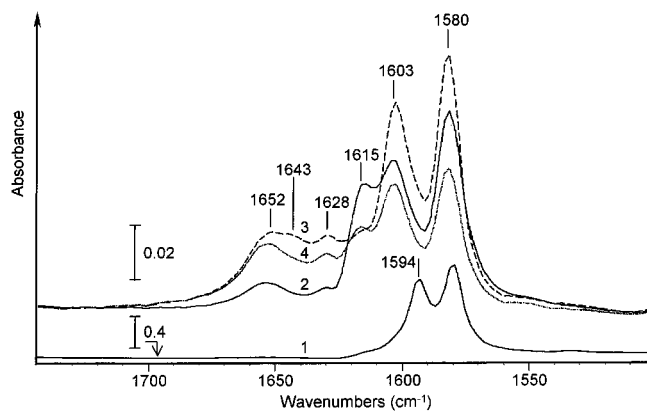


Figure 5. Effect of H₂S on the spectrum of DMP adsorbed on alumina pretreated at 670 K in the ν_8 vibration region. 1: After addition of DMP (1 Torr). 2: After evacuation at 300 K. 3: After subsequent addition of H₂S (1 Torr). 4: After evacuation at 300 K.

TABLE 2: Effect of H₂S on Surface Concentration of Brønsted Acid Sites (Number of Sites per 100 nm²) Determined from IR Spectra of Adsorbed DMP

oxide	before H ₂ S addition	in the presence of H ₂ S (5 Torr) Al ₂ O ₃	after evacuation at 300 K
Al ₂ O ₃	0.4	5.8	5.3
TiO ₂	5.9	29.8	21.9
ZrO ₂	0.2	12.6	7.1

disappears following a short evacuation at 300 K, indicating that it is associated with the physisorbed DMP molecules. The intensity of the bands at 1603 and 1580 cm⁻¹ decreases simultaneously with that of perturbed OH groups. This enables one to assign these two bands to the ν_{8a} and ν_{8b} modes of DMP molecules that form H-bond with surface hydroxy groups, in agreement with previous studies.² A pair of weak bands at 1615 and 1580 cm⁻¹ that resist to evacuation at 300 K are assigned to ν_{8a} and ν_{8b} vibration modes of DMP coordinated to surface cations. These bands could be removed by evacuation at 370 K together with two others at 1652 and 1628 cm⁻¹ (weak) that correspond to ν_{8a} and ν_{8b} modes of protonated DMPH⁺.²

Subsequent introduction of H₂S after preadsorption of DMP at 300 K and removal of weakly bound molecules by evacuation at the same temperature, results in the disappearance of bands due to free OH groups and to the concomitant growth of the bands of perturbed hydroxyls. As in the case of H₂S adsorbed alone at 300 K, the band of ν (SH) vibrations could be seen at 2585 cm⁻¹. In the spectrum of adsorbed DMP (Figure 5,

spectrum 3), H₂S addition leads to a decrease in the intensity of the band of coordinated species (1615 cm⁻¹) and an increase of those corresponding to the protonated (1652 and 1628 cm⁻¹) and H-bonded (1603 cm⁻¹) species. A shoulder also appears at 1643 cm⁻¹ and could be removed on evacuation at 300 K (spectrum 4). From the comparison with the spectral features of the δ (HOH) band which characterizes H₂O formation when H₂S is added, one can exclude that this shoulder is due to water. It evidently characterizes specific DMPH⁺ species.

When DMP is added after H₂S preadsorption, the increase in the intensity of the bands of protonated form at the expense of those due to coordination also occurs. However, in this case the band intensity of protonated molecules is lower than when H₂S is added to preadsorbed DMP. It should be noted that, in the presence of H₂S in the gas phase, the bands of protonated species present a higher intensity than after evacuation (spectra 3 and 4 in Figure 5). Quantitative estimation of the number of Brønsted acid sites (see Table 2 below) shows that it increases from 0.4×10^{-2} nm⁻² on pure alumina to 5.8×10^{-2} nm⁻² when H₂S is added. This amount decreases to 5.3×10^{-2} nm⁻² when weakly adsorbed H₂S is removed on evacuation.

Adsorption of CH₃SH also affects the spectrum of adsorbed DMP. It leads to the complete elimination of the band of coordinated DMP species and to an increase in the intensity of DMPH⁺. However the amount of protonated DMP is lower than that observed after H₂S addition.

3. TiO₂. 3.1. H₂S and CH₃SH Adsorption. After treatment at 770 K, the spectrum of titania sample displays a sharp ν (OH) band at 3742 cm⁻¹ and a broader one at about 3675 cm⁻¹ (Figure 6A, spectrum 1). H₂S adsorption at 120 K perturbs all the OH groups giving rise to a broad band near 3300 cm⁻¹ (Figure 6A, spectrum 2) and to the intense ν (SH) band with a complex contour and a maximum at 2544 cm⁻¹. A weak band of the bending mode of H₂S could also be distinguished at 1174 cm⁻¹. Evacuation at 120 K results in a decrease of the intensity of the S–H band, especially from the high-frequency side, allowing one to distinguish maxima at 2544, 2535, and 2526 cm⁻¹. The band of perturbed OH groups also diminishes and shifts to 3270 cm⁻¹ (Figure 6A, spectrum 3), while the OH band at 3742 cm⁻¹ recovers its intensity almost completely and the band at 3675 cm⁻¹ becomes much more intense than before H₂S addition, evidently, as a result of H₂S dissociation.

H₂S adsorption at 300 K, leads to the appearance of a ν (SH) band at 2530 cm⁻¹ and perturbation of free OH groups. A strong broad band near 3400 cm⁻¹ also appears and is accompanied

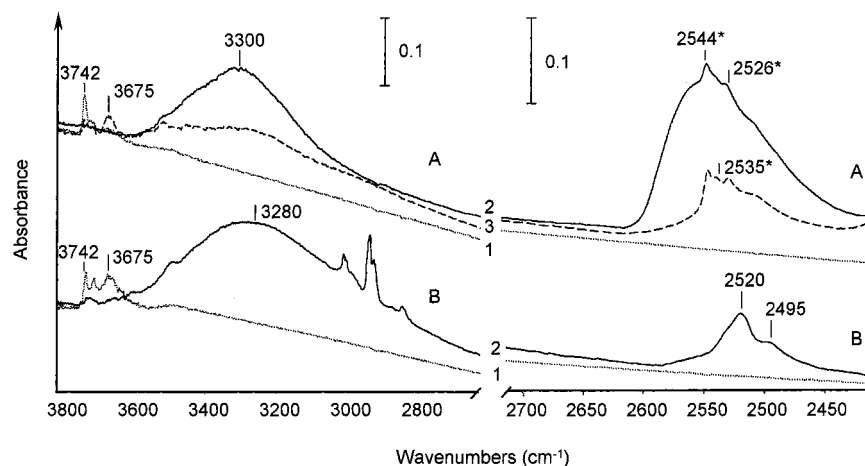


Figure 6. IR spectra of H₂S (A) and CH₃SH (B) adsorbed on titania pretreated at 770 K. 1: Before adsorption. 2: After addition of adsorbate at 120 K. 3: After evacuation at 120 K. All the spectra are recorded at 77 K. [*]: Solid H₂S bands.]

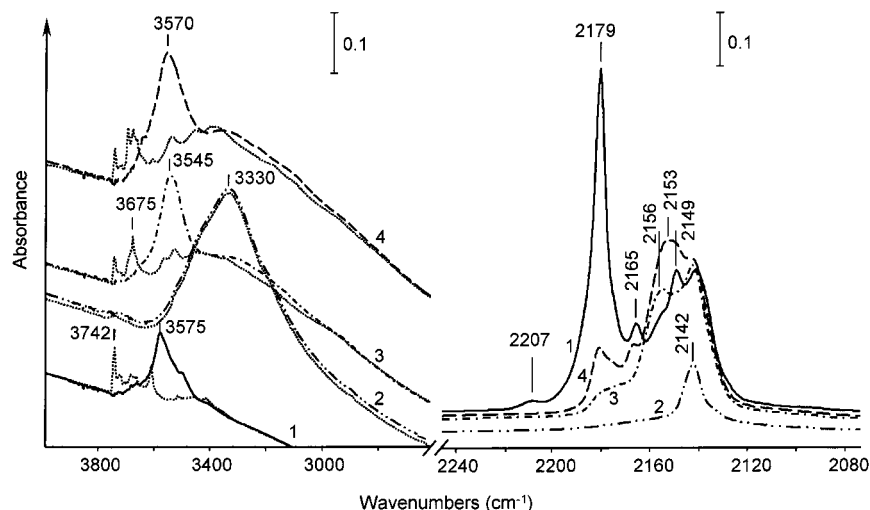


Figure 7. IR spectra of CO adsorbed at 77 K on titania pretreated at 770 K. 1: On pure titania. 2: After H₂S adsorption at 120 K. 3: After evacuation of H₂S at 120 K. 4: After evacuation of H₂S at 300 K. Dotted line: spectra taken before CO adsorption.

by a $\delta(\text{HOH})$ band at 1614 cm^{-1} , characteristic of molecular water, that could not be completely removed by evacuation at 300 K.

CH₃SH adsorption at 120 K gives rise to a stronger perturbation of OH groups than that observed following H₂S adsorption under the same conditions (Figure 6B, spectrum 2). The appearance of a $\nu(\text{SH})$ band at 2520 cm^{-1} with a shoulder at 2495 cm^{-1} indicates the presence of nondissociated CH₃SH.

3.2. CO Adsorption. On TiO₂, CO adsorption at 77 K results in the decrease of the intensity of the free OH band at 3742 cm^{-1} and in the appearance of perturbed hydroxy band at 3575 cm^{-1} (Figure 7, spectrum 1; Table 1). In the region of CO stretching vibrations, an intense band appears at 2179 cm^{-1} accompanied by weaker bands at 2207 , 2165 , 2156 (sh), 2149 , and 2141 cm^{-1} . Evacuation at increasing temperatures indicates that the thermal stability of CO surface species increases with increasing $\nu(\text{CO})$ frequency. The band of physisorbed CO at 2141 cm^{-1} disappears upon evacuation. The bands at 2156 and 2149 cm^{-1} could be removed by short evacuation at 77 K together with the OH perturbation, and could be assigned to H-bonded CO species. The weak band at 2165 cm^{-1} disappears after prolonged evacuation and is assigned to CO adsorption on weak Lewis acid sites.²¹ The 2207 and 2179 cm^{-1} bands, shifted to higher wavenumbers, can be observed in the presence of CO gas even at 300 K and are due to CO coordinated to two types of Lewis acid sites.³³

The effect of H₂S preadsorption on the spectra of adsorbed CO depends on the amount of adsorbed H₂S. After exposure to H₂S at 120 K (Figure 7, spectrum 2), CO does not induce any changes, either in $\nu(\text{OH})$ or in $\nu(\text{SH})$ region. It only gives rise to weak band of physisorbed CO at 2142 cm^{-1} . This indicates a complete coverage of titania surface by H₂S which hinders CO adsorption both on the cationic sites and on the acidic OH groups.

Removal of excess H₂S at 120 K followed by CO adsorption (Figure 7, spectrum 3) leads to the appearance of the band of perturbed hydroxyls at 3545 cm^{-1} , while the corresponding $\nu(\text{CO})$ band appears at 2156 cm^{-1} . These bands are more intense than on pure titania, evidently due to the creation of new acidic OH groups. On lowering the CO coverage, the latter band moves to 2160 cm^{-1} and the band of perturbed OH groups reaches ca. 3530 cm^{-1} (Table 1). When CO adsorption is performed on CH₃SH precovered sample, the $\nu(\text{CO})$ band and $\nu(\text{OH})$ band perturbed by CO appears at wavenumbers similar to those obtained for pure titania.

When H₂S is adsorbed at 300 K and pumped off at the same temperature, the above-mentioned formation of new OH groups and water leads to the increased intensity of the band of H-bonded CO (Figure 7, spectrum 4). However, these new OH groups do not exhibit stronger acidity than the initial OH groups of pure oxide, even at small CO coverage. As seen from the Table 1, the differences in the band positions of perturbed OH groups and corresponding $\nu(\text{CO})$ bands are within the limits of experimental error.

As observed in the case of alumina, the bands in the $\nu(\text{SH})$ region are never affected by CO addition.

3.3. DMP Adsorption. DMP adsorption at 300 K on TiO₂ pretreated at 670 K leads to the perturbation of free OH groups with the appearance of a broad band with two maxima at about 2800 and 2000 cm^{-1} and to the numerous bands assigned to adsorbed DMP. After evacuation at 300 K, the decrease in intensity of the perturbed $\nu(\text{OH})$ band is accompanied by the decrease in intensity of intense band at 1600 cm^{-1} that is due to the elimination of H-bonded DMP species. The bands characteristic of protonated species remain at 1645 and 1625 cm^{-1} . A shoulder at 1607 cm^{-1} could also be distinguished, which is due to DMP molecules coordinated to Lewis acid sites.

When H₂S is introduced after DMP evacuation at 300 K, the intensity of the bands of protonated DMP at 1645 and 1625 cm^{-1} increases while a new DMPH⁺ band appears at 1634 cm^{-1} . Simultaneously, a decrease in the intensity of the band assigned to DMP coordinated to Lewis acid sites (1607 cm^{-1}) is observed. Quantitative estimations (see Table 2) show that H₂S addition leads to ca. a 5-fold increase of the number of detected Brønsted acid sites, their total concentration being ca. 0.3 nm^{-2} . About one-third of these newly formed sites disappear after removal of gaseous H₂S. Adsorbing H₂S before DMP also results in the appearance of supplementary DMPH⁺ species, the amount of which is increased at the expense of the coordinated species.

Introduction of CH₃SH after DMP adsorption leads to similar features. But, as observed in the case of alumina, the increase in intensity of the bands of DMPH⁺ species to the detriment of those of coordinated DMP is less pronounced as compared to the case of H₂S adsorption.

4. ZrO₂. **4.1. H₂S and CH₃SH Adsorption.** After activation at 770 K, ZrO₂ presents two $\nu(\text{OH})$ bands at about 3780 and 3670 cm^{-1} . As seen from the spectrum 2 in Figure 8A, H₂S adsorption at 120 K leads to disappearance of the high-frequency

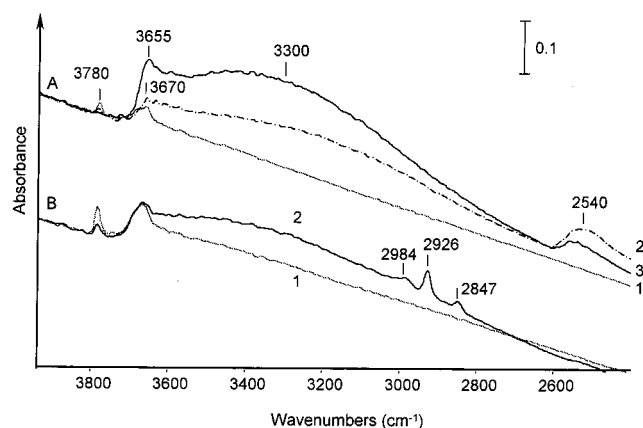


Figure 8. IR spectra of H₂S (A) and CH₃SH (B) adsorbed on zirconia pretreated at 770 K. 1: Before adsorbate adsorption. 2: After adsorbate addition at 120 K. 3: After adsorbate evacuation at 120 K. All the spectra are recorded at 77 K.

band, while a broad $\nu(\text{OH})$ band centered at c.a. 3300 cm^{-1} arises, accompanied by a $\delta(\text{HOH})$ band at 1590 cm^{-1} , a broad band $\nu(\text{SH})$ at 2540 cm^{-1} , and a weak $\delta(\text{HSH})$ band at 1173 cm^{-1} . Subsequent evacuation diminishes the intensity of the last two bands, whereas the band at 3670 cm^{-1} increases considerably in intensity and shifts to 3655 cm^{-1} (Figure 8A, spectrum 3).

H₂S adsorption at RT or at 120 K followed by an increase of the temperature up to 300 K in the presence of H₂S leads to further increase in the intensity of bands at 3655, 3300 and 1590 cm^{-1} corresponding respectively to the $\nu(\text{OH})$ modes of the surface hydroxyls and to the stretching and bending mode of molecularly adsorbed water. In the $\nu(\text{SH})$ region, a weak and broad band with two maxima at 2570 and 2540 cm^{-1} are observed together with a weak $\delta(\text{HSH})$ band at 1163 cm^{-1} . After evacuation at 300 K, the $\nu(\text{SH})$ and $\delta(\text{HSH})$ bands disappear together with the bands of water at 3300 and 1590 cm^{-1} .

CH₃SH adsorption at low temperature (Figure 8B, spectrum 2) also perturbs mainly the high-frequency OH groups and gives rise to a broad $\nu(\text{OH})$ band at ca. 3300 cm^{-1} , a very weak SH stretching band at 2500 cm^{-1} , and CH stretching bands at 2984, 2926, and 2847 cm^{-1} .

4.2. CO Adsorption. CO adsorption at 77 K on zirconia results in the decrease in intensity of both free OH bands at 3780 and

3670 cm^{-1} and the appearance of a band of perturbed hydroxyls at 3610 cm^{-1} (Figure 9, spectrum 1; Table 1). CO bands appear at 2183 (sh), 2171, 2152, and 2141 cm^{-1} . The last two bands, assigned to H-bonded and physisorbed CO, disappear after removal of gaseous CO at 77 K, whereas the initial spectrum in the OH region is restored. With the decreasing CO coverage, the two other $\nu(\text{CO})$ bands corresponding to coordinated CO shift to higher wavenumbers (up to 2207 cm^{-1}), in agreement with earlier studies.

The IR spectrum obtained for the sample with preadsorbed H₂S indicates that CO adsorption shifts the OH band from 3665 to 3560 cm^{-1} (Figure 9, spectrum 2). The intensity of the $\nu(\text{CO})$ band at 2152 cm^{-1} becomes higher than in the initial spectrum, indicating hydroxy groups creation. On the other hand, the $\nu(\text{CO})$ band at 2171 cm^{-1} and the shoulder at 2183 cm^{-1} strongly decrease, indicating the poisoning of Lewis acid sites. On CO desorption, the band of perturbed OH groups diminishes and moves to 3550 cm^{-1} , while the band at 2152 cm^{-1} shifts to 2156 cm^{-1} (Table 1). After evacuation at 120 K, the $\nu(\text{OH})$ band of the hydroxy groups perturbed by CO is slightly shifted toward low wavenumbers whereas the frequency of the corresponding $\nu(\text{CO})$ increases up to 2162 cm^{-1} (Table 1).

When molecular H₂S is removed by evacuation at 300 K (Figure 9, spectrum 3), the bands of coordinatively bonded CO species disappear almost completely. On the other hand, the band of H-bonded CO is much more intense than in the case of CO adsorption on pure zirconia. Spectra recorded at low CO coverage show that band positions of the perturbed OH groups and H-bonded CO are only slightly different from those observed on the pure oxide, indicating a small increase of OH acidity with respect to initial zirconia sample (Table 1). When CH₃SH is adsorbed at 120 K, no increase of OH acidity is detected by CO adsorption after removal the excess of adsorbate, neither at 120 K nor at 300 K.

As in the case of other oxides, CO adsorption caused no perturbation in the SH stretching region.

4.3. DMP Adsorption. DMP adsorption on zirconia leads to the complete disappearance of the high-frequency band at 3780 cm^{-1} and a decrease in of the intensity of the band at 3670 cm^{-1} whereas a broad band of perturbed hydroxy groups appears at ca. 3150 cm^{-1} . Strong bands of adsorbed DMP arise at 1610 and 1580 cm^{-1} with a shoulder at 1603 cm^{-1} . Weak bands at 1652 and 1627 cm^{-1} corresponding to protonated species are also observed.

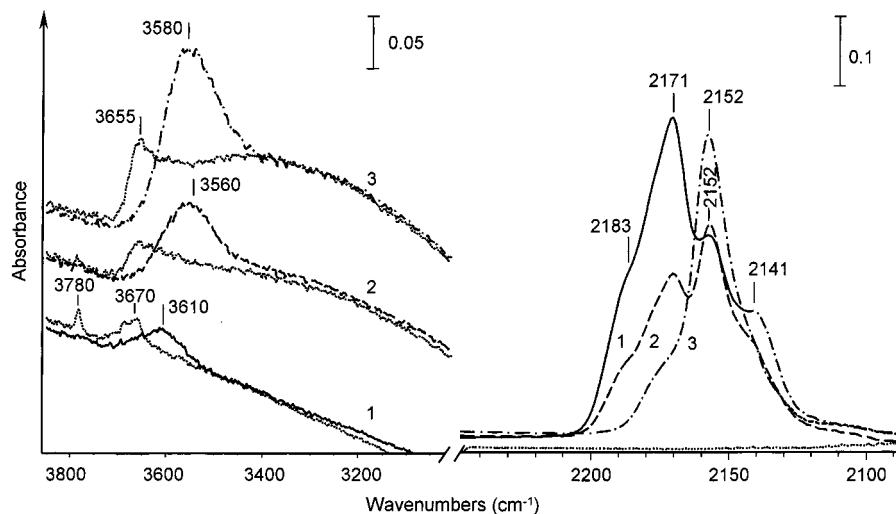


Figure 9. IR spectra of CO adsorbed at 77 K on zirconia pretreated at 770 K. 1: On pure sample. 2: After H₂S adsorption at 120 K. 3: After heating in H₂S up to 300 K. Dotted line: spectra taken before CO adsorption.

Evacuation at 370 K restores the OH bands at 3780 and 3670 cm^{-1} , although the former one presents a lower intensity than before adsorption. Evacuation also dramatically decreases the intensity of the band assigned to perturbed OH groups. In the ν_8 vibrations region, a shoulder at 1603 cm^{-1} , which corresponds to H-bonded DMP, disappears. The pair of bands at 1610 and 1580 cm^{-1} that is assigned to coordinately bound DMP species is still present and resists to an evacuation at 423 K.

Addition of H_2S at 300 K to the sample with preadsorbed DMP results in a further decrease of the intensity of the band at 3670 cm^{-1} and the appearance of a broad absorption centered at 3000 cm^{-1} . In the ν_8 region, the band of coordinated DMP at 1610 cm^{-1} disappears, and bands of DMPH^+ species increase in intensity at 1652 (weak), 1636, and 1627 cm^{-1} . Evacuation at 300 K leads to a decrease of the intensity of the latter bands, as well as of those due to H-bonded DMP and of absorption around 3000 cm^{-1} , whereas a partial restoration of the band of free OH groups and coordinately bound species is observed. The concentration of Brønsted acid sites detected in the presence of H_2S , about 0.12 nm^{-2} is twice greater than that for alumina, but still much lower than that for titania (Table 2). Almost one-half of these sites are due to reversible adsorption of H_2S and disappear after evacuation.

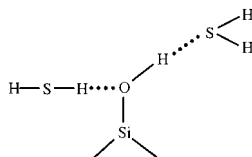
When the sample is first contacted with H_2S at 300 K, subsequent DMP addition does not reveal any remaining Lewis acid site whereas the bands of protonated DMP species appear with a lower intensity than that observed when H_2S is adsorbed after DMP.

Adsorption of CH_3SH after DMP introduction also leads to the decrease of the bands of coordinated DMP and to the appearance of very weak bands of protonated species.

Discussion

1. H_2S and CH_3SH Adsorption on Silica. Our results on H_2S interaction with silica are in agreement with those of Mayer and Bastick,^{15,16} who show that the only adsorption mode of H_2S is hydrogen bonding. No evidence for H_2S dissociation or for creation of new acid sites was found in the present study. Two bands at 2608 and 2597 cm^{-1} , not reported in ref 16, that arise simultaneously with the OH perturbation by small doses of H_2S , can be assigned, respectively, to the symmetric and antisymmetric S–H stretching vibrations of hydrogen bonded molecules. Because H_2S is a rather strong base, it shifts the silanol $\nu(\text{OH})$ band by 210–240 cm^{-1} , twice more than CO (80 cm^{-1} ²¹) or ozone (about 100 cm^{-1} ^{34,35}) and more than ethylene (152 cm^{-1} ³⁶). As for CH_3SH , it shifts the silanol OH band by 330–400 cm^{-1} in agreement with its stronger basicity: the proton affinity (PA) of CH_3SH is 773.4 kJ/mol as compared with 705.0 kJ/mol for H_2S .²⁴

It is noticeable that after H_2S and CH_3SH adsorption, the $\nu(\text{OH})$ frequency shift increases with the amount of adsorbate. The same effect was earlier observed for ozone adsorbed on silica.³⁴ The stronger perturbation of OH groups at increased coverage can be explained by interaction of a second molecule with the oxygen atom of the silanol group:³²



This process should finally lead to polymeric chains or two-dimensional film of H_2S and silanol groups. Thus, lowering of

the $\nu(\text{OH})$ wavenumbers at increased coverage is expected for such a structure. The increase in the $\nu(\text{OH})$ frequency shift of silanol groups upon H-bond is caused by an additional H_2S interaction with their oxygen atoms. This leads to an increase of the OH group acidity induced by its interaction with H_2S acting as an acid. The same process is proposed for CH_3SH adsorption. This phenomenon was well demonstrated in a recent study³⁷ which has shown that coadsorption of acidic and basic molecules on silica could even lead to the protonation of the bases by the silanol group.³⁷

This explanation is also in agreement with the lowering of $\nu(\text{SH})$ frequency observed at high CH_3SH or H_2S coverages. Indeed, Saur et al.⁶ have reported that CH_3SH molecule linked via its sulfur atom to the surface has higher CH and SH stretching vibration frequencies as compared to CH_3SH molecule bound via its hydrogen atom. Accordingly, at low coverage, CH_3SH is H-bonded through its sulfur atom and presents a high $\nu(\text{SH})$ maximum at 2585 cm^{-1} and high-frequency components of the CH bands. At higher coverages, supplementary CH_3SH molecules interact by H-bond via their protons with oxygen atoms of silanol groups, which would account for the $\nu(\text{SH})$ band at 2545 cm^{-1} and low-frequency CH components.

2. H_2S and CH_3SH Adsorption on Alumina, Titania, and Zirconia. On alumina, titania, and zirconia, the presence of Lewis acid sites and of OH groups with various acidities gives rise to several adsorption modes of H_2S and CH_3SH . Perturbation of surface OH groups by weakly adsorbed H_2S could also be observed for these metal oxides. Such reversible adsorption leads to perturbed $\nu(\text{OH})$ bands, which, contrary to the case of silica, shift to lower wavenumbers when H_2S coverage decreases.

Pumping at about 120 K removes at least a part of H-bonded H_2S . However, the spectra of initial OH groups of metal oxides are only partially recovered. The low-frequency $\nu(\text{OH})$ bands are totally restored or become more intense than before H_2S adsorption, whereas the high-frequency OH bands are either not observed or have lower intensity. The latter are shifted and present reduced intensities when H_2S is adsorbed at 300 K.

Both H_2S and CH_3SH molecules could be adsorbed by coordination via their sulfur atom to the coordinately unsaturated surface cations. This form of adsorption should remain at the surface after removal of physisorbed and H-bonded molecules. In fact, after pumping at about 120–140 K, weak $\nu(\text{SH})$ bands could still be observed at wavenumbers rather different from those of weakly bound molecules. The spectra of CO adsorbed on the samples with preadsorbed H_2S show that most of the Lewis acid sites are still inaccessible for CO. However, it is difficult to determine whether these sites are occupied by molecular H_2S or by the products of its dissociation. Observation of the $\delta(\text{HSH})$ bending vibration mode of molecular H_2S at about 1183 cm^{-1} ³⁸ could be helpful for identification of molecular adsorption. However, its extinction coefficient is very low, and the corresponding band was observed at 1175–1163 cm^{-1} only at highest coverages, i.e., in the presence of weakly bound H_2S . The adsorption mode of CH_3SH is easier to determine. Simultaneous observation of the bands of SH and CH vibrations in the spectra of CH_3SH adsorbed on titania or alumina at low temperatures enables one to conclude that in these conditions some molecules are not dissociated. It is assumed that, under the same conditions, coordination of H_2S also occurs at low temperature on the three metal oxides. Then, the higher intensity of $\nu(\text{OH})$ bands and the absence of S–H stretching bands that was observed after heating to 300 K point to H_2S dissociation at higher temperatures.

Appearance of $\nu(\text{OH})$ bands with enhanced intensities could be regarded as the most direct evidence for H_2S dissociation. It was established for Al_2O_3 pretreated at 1070 K and for ZrO_2 and TiO_2 pretreated at 770 K, when adsorption of H_2S at low temperature was followed by an evacuation at 120 K. For TiO_2 , this was also observed after CH_3SH adsorption at 300 K. For the three metal oxides, the $\nu(\text{OH})$ bands that are due to dissociation present the same spectral features than the lowest frequency $\nu(\text{OH})$ bands that are observed in the spectra of pure oxides. According to current models of oxide surfaces,^{39–41} these bands correspond to the hydroxy groups bound to the highest possible number of metal atoms. Hence, one can consider that the supplementary OH groups formed upon dissociation result from a proton transfer from the adsorbed molecules to coordinately unsaturated surface oxygen atoms.

When H_2S is adsorbed at 300 K, a band appeared at about 1620 cm^{-1} for Al_2O_3 , 1614 cm^{-1} for TiO_2 , and 1590 cm^{-1} for ZrO_2 . It is always accompanied by a strong broad absorption band of OH stretching vibrations and is assignable to the bending mode of adsorbed H_2O . For zirconia, these changes already occur at 120 K indicating that at this temperature proton mobility is sufficiently high for OH groups recombination. Until water is formed, H_2S adsorption at 120 K is essentially reversible since one can readily recover most of the initial spectrum of surface OH groups on evacuation. However, once water is formed, the restoration of the high-frequency OH bands is not possible upon subsequent evacuation. This could be explained taking into account the basic character of these OH groups that are bound to one metal atom.⁴¹ Presumably, proton transfer from H_2S to these OH groups leads to the formation of a surface SH group and a water molecule:



3. Acidic Properties of Pure Oxides. Spectra of adsorbed CO and DMP provide detailed information about the nature and concentration of acid sites of oxides. CO adsorption on OH group results in frequency shift of the OH stretching vibration toward lower wavenumbers and in the increase of the adsorbed CO frequency. Both shifts could be used as a measure of proton acidity of surface hydroxy groups. Coordination to Lewis acid sites results in more important $\nu(\text{CO})$ shifts to higher wavenumbers. The extinction coefficient of CO adsorbed on oxides does not differ too much from that of a free molecule.⁴² Thus the intensities of the bands of chemisorbed CO at saturating conditions could be used for a rough comparison of the concentrations of various adsorption sites.

The position of the ν_{8a} band of adsorbed DMP could also characterize the strength of hydrogen bond or coordination. However the observed shifts values are rather small, and the bands are not always resolved. Because of steric hindrance, the molecule cannot interact with all the Lewis acid sites, but it is a good probe for Brønsted acidity, since the spectrum of DMPH^+ ion presents characteristic ν_{8a} and ν_{8b} vibration bands in the $1670\text{--}1620\text{ cm}^{-1}$ region.^{25–28}

Our spectra of CO and DMP adsorbed on metal oxides prior H_2S or CH_3SH addition are in agreement with the earlier data.^{21,23,25,44} For silica, H-bond is the only adsorption mode of carbon monoxide. It shifts the frequencies of silanol groups and CO molecules to 3670 and 2157 cm^{-1} , respectively. These values are not dependent on coverage, thus indicating a high degree of homogeneity of the acid strength of OH groups. DMP adsorption on silica leads to only one ν_{8a} band at 1602 cm^{-1} . This indicates that silanol acidity is not sufficient for the proton transfer, and the only adsorption mode of DMP on silica is also

H-bonding. This H-bond gives rise to a large displacement of the OH frequency, up to 2900 cm^{-1} , in agreement with the high basicity of DMP ($\text{PA} = 963.0\text{ kJ/mol}$).^{24,28}

Alumina, titania, and zirconia exhibit a much wider variety of surface sites than silica. H-bond with surface OH groups results in perturbed $\nu(\text{OH})$ bands and $\nu(\text{CO})$ bands which positions depend on the coverage of adsorbed molecules. Thus, for alumina the perturbed $\nu(\text{OH})$ and $\nu(\text{CO})$ bands move on desorption from 3610 and 2155 cm^{-1} to 3560 and 2160 cm^{-1} , respectively (Table 1). This phenomenon can be accounted for the presence of several types of OH groups with different acid strengths. On average, the Brønsted acidity characterized at high CO coverage by the band at 2155 cm^{-1} is weaker than that for silica. However, the hydroxy groups that are probed at low CO coverage are considerably more acidic ($\nu(\text{CO})$ at 2160 cm^{-1} , Table 1). For titania, the presence of two well resolved bands at 2156 and 2149 cm^{-1} in the spectrum of CO could be assigned to adsorbed CO on hydroxy groups presenting different acid strengths. After evacuation at 120 K, the perturbed OH band shifts from 3575 to 3555 cm^{-1} while the two $\nu(\text{CO})$ bands are observed at 2158 and 2151 cm^{-1} . For zirconia, the spectra show $\nu(\text{CO})$ band at $2152\text{--}2156\text{ cm}^{-1}$, depending on CO coverage, and thus, do not reveal Brønsted acidity stronger than silica. The spectra of DMP reveal the presence of Brønsted sites on the surface of alumina, titania, and zirconia, thus showing that some of their hydroxy groups are acidic enough for protonation.

Coordinated DMP species reveal stronger Lewis acidity of Al_2O_3 (ν_{8a} at ca. 1615 cm^{-1}) as compared with TiO_2 and ZrO_2 (ca. 1610 cm^{-1}), in agreement with the results reported with pyridine as a probe molecule.²⁵ CO adsorption provides more detailed information about Lewis acidity. On alumina, two types of Lewis sites could be distinguished, leading to $\nu(\text{CO})$ bands at $2230\text{--}2220$ and $2200\text{--}2180\text{ cm}^{-1}$, depending on CO coverage, and are associated with CUS (coordinately unsaturated sites) corresponding to tetrahedrally and octahedrally coordinated cations, respectively.^{21,22} The dependence of the position of both $\nu(\text{CO})$ bands on the coverage is caused by lateral interactions between adsorbed CO molecules.⁴⁵ On titania, three types of Lewis acid sites are observed, leading to $\nu(\text{CO})$ bands at $2213\text{--}2207$, $2195\text{--}2179$, and 2165 cm^{-1} .²¹ For zirconia, the band of CO molecules bound to Lewis acid sites occurs at $2207\text{--}2171\text{ cm}^{-1}$.^{43,44}

4. Modification of Acidic Properties by H_2S and CH_3SH Adsorption. Adsorption of H_2S and CH_3SH leads to strong modifications of surface acidic properties, revealed in the spectra of adsorbed CO and DMP. Few changes are observed for silica. For Al_2O_3 , TiO_2 , and ZrO_2 , a decrease in Lewis acid sites concentration is observed, which is accounted for their occupation by adsorbed sulfur-containing molecules or by the products of their dissociation. Simultaneously, an increase of the number of Brønsted acid sites as well as modification of their strength take place. This accounts for the increased intensities of the bands of protonated DMP, of H-bonded CO, and of the corresponding bands of perturbed OH groups, as well as of the shifts of the band positions of CO and perturbed OH groups.

One could anticipate that hydrogen bonding of an SH group with an adsorbed molecule, such as CO, should result in a downward shift of the $\nu(\text{SH})$ band and in the appearance of a corresponding $\nu(\text{CO})$ band. However, such a phenomenon was never observed. We can thus conclude that the acidity of SH group is too low to be the source of proton acidity. Hence, the increased number of Brønsted acid sites is not associated with the presence of SH groups themselves.

One can distinguish at least two different effects of sulfur compounds on the Brønsted acidity, depending on the adsorption

mode of the sulfur-containing molecule. The first effect that we shall discuss below is the acidity enhancement caused by molecular H_2S or CH_3SH . The second effect could be detected after removal of the adsorbed sulfur-containing molecules and is caused by the products of their dissociation. It will be discussed later (section 4.2)

4.1. Acidity Induced by Molecular Adsorption of H_2S and CH_3SH . On silica, the additional shift to lower frequencies of perturbed $\nu(\text{OH})$ bands on increasing coverage in H_2S or CH_3SH is attributed to the interaction of a second molecule with the oxygen atom of the silanol group. This phenomenon can be interpreted as an increase of the OH group acidity induced by the adsorption of the second molecule acting as an acid.³⁷ However, this effect cannot be detected by coadsorption of CO, because sulfur-containing molecules which are more basic than CO preferentially form H-bond with silanol groups. Hence, CO can only adsorb on the remaining free OH groups.

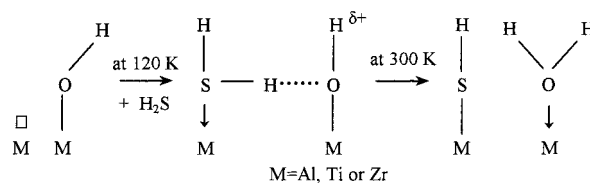
Coadsorption of H_2S or CH_3SH with DMP at 300 K also indicates competitive adsorption on silanol groups. At 120 K addition of H_2S to silica with preadsorbed DMP does not lead to protonation, but to a slight increase in the $\nu(\text{OH})$ frequency shift upon H-bonding with DMP. This reveals an increase of OH groups acidity due to H_2S . Addition of a more acidic compound like SO_2 under the same conditions results in an almost complete transformation of H-bonded DMP to the protonated form.³⁷ Clearly, the acidity of H_2S molecules is not strong enough to enhance that of silanol groups to afford DMP protonation.

For the other metal oxides, the effect of molecular adsorption is observed following exposure to a large amount of H_2S and outgassing at 120 K. On alumina, titania and zirconia, coadsorption of H_2S and CO at 120 K leads to lower intensity of H-bonded CO, indicating a lower accessibility of hydroxy groups to CO. This is to be expected at high coverage. However, spectra recorded for small CO coverage clearly reveal the enhancement of OH group acidity, as compared to that of pure oxides. In fact, under these conditions, the lowest positions of perturbed $\nu(\text{OH})$ bands and the highest frequencies of H-bonded CO were detected (Table 1). For example, in the case of alumina, after contact with H_2S at 120 K and for low CO coverage, the band of perturbed OH groups appears at 3500 cm^{-1} while the corresponding $\nu(\text{CO})$ band increases up to 2165 cm^{-1} , whereas on pure alumina, these bands occur at 3560 and 2160 cm^{-1} , respectively. After removal of molecular H_2S by pumping at 300 K, these bands appear at 3530 and 2158 cm^{-1} , i.e., at values close to those for pure Al_2O_3 surface.

This source of Brønsted acidity cannot be attributed to adsorbed H_2S , since the $\nu(\text{SH})$ bands are not perturbed by CO. Furthermore, this acidity is inhibited in the presence of excess H_2S . Similarly, one cannot relate this Brønsted acidity to H_2O molecules since for Al_2O_3 and TiO_2 an increase in acidity is observed at 120 K, whereas water formation does not occur at this temperature. Thus, acidity enhancement is more likely induced by the presence of reversibly adsorbed H_2S molecules, which modifies OH group acidity.

Another evidence for Brønsted acidity induced by molecular H_2S is in the reversible increase of the intensity of DMPH^+ in the presence of the excess of H_2S . Data obtained from DMPH^+ intensity measurements after exposure to H_2S are summarized in the Table 2. For all the three oxides, the concentration of the Brønsted acid sites increases after H_2S addition. Subsequent evacuation at 300 K shows that these changes are partially reversible. The amount of protonated DMP decreases after removal of gaseous H_2S , but the final Brønsted acid site

SCHEME 1



concentration is always much greater than that measured for initial samples. The above spectral data on CO adsorption enable one to associate a part of the Brønsted acidity which is eliminated by pumping at 300 K to the acidity induced by molecular adsorption of H_2S , while the dissociative adsorption, evidently, accounts for irreversible generation of Brønsted sites, at least at 300 K.

For alumina, CO adsorption shows that, after elimination of molecular H_2S by pumping at 300 K, Brønsted acid sites present the same strength than those initially present (Table 1). On zirconia, after evacuation at 300 K, some Brønsted acid sites still present an increased acid strength, but weaker than after H_2S addition at low temperature (Table 1). On titania, complexity of CO spectra does not allow any conclusion to be drawn with respect to the variation of OH acid strength after H_2S removal at 300 K.

It is believed that the mechanism of acidity enhancement in the presence of molecular H_2S slightly differs from that observed for silanol groups. Indeed on silica, H_2S (or CH_3SH) interaction with oxygen atom of the silanol group is only possible if a first H_2S molecule already interacts as a base with hydrogen of the OH groups, whereas on alumina, titania, and zirconia the OH groups presenting an enhanced acidity still remain accessible for H-bond, since CO is able to detect the acidity increase. This means that molecular H_2S that account for acidity enhancement is more strongly bonded on these oxides than on silica. On metal oxides, the H_2S molecules that are coordinated to surface cations can simultaneously interact with oxygen of an adjacent OH group, leading to an increase in its acidity. At 300 K, a proton transfer should occur since water formation is observed for all three oxides. Scheme 1 is therefore proposed. Such a scheme can also explain the large width and low frequency position generally observed for the SH band as well as the comparatively high energy of H_2S adsorption. This interaction increases the acidity of the OH group, which is reflected in the large $\nu(\text{OH})$ frequency lowering on CO adsorption and high position of the $\nu(\text{CO})$ band.

Conversely, no clear enhancement of acidic strength can be detected when coadsorption of CH_3SH and CO are performed at low temperature. This can be related to the weaker acidity of CH_3SH compared to H_2S , leading to a weaker interaction with the oxygen atom of OH group.

When the sample is heated in the presence of H_2S up to 300 K, proton transfer from coordinated H_2S to the OH group could be activated, leading to the formation of coordinated water molecules and surface SH group. The water formed, which resists to evacuation at 300 K, could remain coordinated to the cation. Water, like H_2S in the previous scheme, could also interact with OH groups, increasing their acidity. Compared to H_2S , however, the enhancement of the OH acidity by H_2O should be limited by the partial consumption of basic OH groups and by the weaker acidity of water compared to that of H_2S .

Water formation may also explain the irreversible perturbation of high-frequency OH band at ca. 3795 cm^{-1} observed on alumina even after evacuation of adsorbed H_2S at 300 K. According to current models of oxide surfaces,⁴¹ these OH

groups are bound to one aluminum cation (type I OH groups) and present a higher basicity than other types of OH groups. Hence, type I OH groups could play the role of proton-acceptors in H-bond. These groups are less acidic than type III groups that absorb at ca. 3700 cm^{-1} and which can form stronger H-bond, but only as proton donors. The fact that after removal of H-bonded H_2S , the type III OH groups are recovered while the type I OH groups are still perturbed is not surprising if one assumes that these groups interact with coordinated H_2S molecules via their oxygen atoms at low temperature and react with H_2S at higher temperature to form water. On alumina surface, this happens at about 300 K, while on zirconia water formation occurs already at 120 K, evidently, because of the more basic character of the type I OH groups bound to zirconium.

On silica, the silanol groups are sufficiently acidic for the proposed mechanism of strong Brønsted acidity enhancement by molecular H_2S , but unlike alumina, there are no other sites to fix H_2S molecules close to the hydroxy groups. It should be noted that acidity increases caused by adsorbed molecular H_2S was reported by Hosotsubo⁵ for silica, alumina, and silica–alumina modified by transition metal cations. Such cations were shown to be the sites of H_2S adsorption, then interaction of adsorbed molecules with the adjacent silanol groups or type I hydroxyls of alumina could account for the acidity increase observed under conditions allowing molecular adsorption of H_2S on the cations to take place.

4.2. Modification of Acidic Properties after Dissociation of H_2S and CH_3SH . Another mechanism of Brønsted acidity generation was evidenced after H_2S adsorption and subsequent evacuation at 300 K on Al_2O_3 , TiO_2 , and ZrO_2 . The increased intensity of OH bands is indicative for H_2S dissociative adsorption. The absence of any bands in the S–H stretching region could be due to their very low extinction coefficient. Spectra of adsorbed CO reveal an increased amount of H-bonded CO molecules and a decreased number of Lewis acid sites that, evidently, are occupied by the products of the reaction of H_2S with the surface (SH, OH, S^{2-} , and H_2O).

On alumina, titania, and zirconia, DMP adsorption after H_2S interaction at 300 K reveals a significant increase of the number of Brønsted acid sites. Protonated species are also formed, even in a lower abundance than after H_2S addition to the sample with preadsorbed DMP. In both cases, most part of the protonated form cannot be removed by evacuation and, hence, should be associated with the formation of acidic OH groups produced by H_2S dissociation.

For Al_2O_3 , TiO_2 , and ZrO_2 , the spectral features of the new hydroxy groups and their behavior toward CO are similar to those of the most acidic hydroxy groups present on the pure oxide. Indeed, the newly created OH groups are formed, according to recent models of oxide surfaces,^{39,40,41} by proton attachment to coordinatively unsaturated surface oxide ions that are bound to the maximum number of metal ions possible for the crystal lattice: three for Al_2O_3 and ZrO_2 and two for TiO_2 . The positions of the bands assigned to these hydroxyls are comparable to those observed following H_2S adsorption.

Conclusions

Adsorption of H_2S and CH_3SH on SiO_2 , Al_2O_3 , TiO_2 , and ZrO_2 and the resulting changes of surface acidity were studied by means of IR spectroscopy. Spectra of CO adsorbed at 77 K as well as the shifts of $\nu(\text{OH})$ bands caused by CO adsorption were used to characterize Lewis acidity of surface cations and proton-donating ability of surface hydroxy groups. The positions

of ν_{8a} and ν_{8b} bands of adsorbed 2,6-dimethylpyridine were used to distinguish molecules protonated on Brønsted sites, coordinatively bound to Lewis acid sites, and H-bonded to surface hydroxyls.

Both H_2S and CH_3SH form H-bond with surface OH groups of all the adsorbents at least, at low temperatures. These molecules are rather strong bases, and shift the silanol OH band by 210–240 and 330–400 cm^{-1} , respectively. For silica, H-bond is the only mode of adsorption but it is not restricted to the formation of 1:1 complexes. At high coverage, additional frequency shifts of the OH and SH bands reveal the interaction of two molecules with one silanol group or the formation of polymeric chains at the surface.

For the three other metal oxides, spectra of adsorbed H_2S or CH_3SH with coadsorbed CO or DMP provide evidence for the occupation of surface Lewis acid sites by coordinatively bound molecules if adsorbed at low temperatures. At 300 K or higher temperatures, the increased intensity of $\nu(\text{OH})$ and $\delta(\text{HOH})$ is accounted for the dissociative adsorption of the sulfur-containing molecule, leading to the formation of surface OH groups and molecular water. The formation of SH^- or S^{2-} ions is not detected by IR, but it could account for the occupation of Lewis acid sites when molecular H_2S or CH_3SH are no more detectable in the spectra. Water molecules are formed as a result of the protonation of basic type I OH groups by H_2S or CH_3SH . This takes place below 120 K on ZrO_2 and 300 K on Al_2O_3 and TiO_2 .

Two types of induced Brønsted acidity were established. In the presence of an excess of adsorbed sulfur-containing molecules, a reversible increase of OH groups acid strengths was observed for all the four oxides. It was shown to be induced by molecular H_2S H-bonded to the oxygen atom of surface OH groups. For silica, this interaction leads to an increase of the $\nu(\text{OH})$ frequency shift with increasing coverage of H_2S or CH_3SH . In the case of alumina, titania, and zirconia, the enhanced OH acidity results in additional frequency shifts of $\nu(\text{CO})$ and perturbed $\nu(\text{OH})$ bands observed on CO adsorption at 77 K.

For Al_2O_3 , TiO_2 , and ZrO_2 , dissociative adsorption of H_2S and CH_3SH results in the appearance of new OH groups that account for the irreversible, at least at 300 K, increase of Brønsted acidity revealed by the higher number of H-bonded CO and of protonated DMP. These new OH groups are the most acidic among those that normally exist at the surface of the considered metal oxides. In no case the S–H groups of adsorbed molecules or surface SH groups reveal any proton-donating ability that could account for the increase in Brønsted acidity.

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