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Low temperature infrared study of carbon monoxide adsorption on sulfated titania

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Acidic properties of a TiO_2 sample containing approximately 1 wt% S were examined by low-temperature IR spectroscopy of CO and by coadsorption of CO and NH_3. Due to the almost negligible OH content of the sample, Brønsted acidity could not be detected. However, Lewis acid sites with enhanced acid strengths as compared to sulfate-free titania could clearly be detected. It is inferred that these sites (namely cus Ti^{4+} sites) are located in close proximity to sulfate groups and that CO (and NH_3) coordinated to the Ti^{4+} sites interact with the sulfate groups presumably via electronic inductive effects.

Keywords: CO adsorption; infrared spectroscopy; titania, sulfated; Lewis acidity

1. Introduction

The surface chemistry of anatase attracts great interest due to the material's particular properties as a catalyst support. Thus, vanadia–titania catalysts are used for the selective oxidation of *o*-xylene and other hydrocarbons [1–5]. They have also found application in the catalytic reduction of nitrogen oxides by ammonia [6–10]. Tungsta–titania catalysts are also applied in the industry for the latter reaction [11–13]. However, in most cases the support used is anatase containing sulfate impurities. Recent investigations showed that the surface properties of sulfated titania were significantly different from those of pure anatase. For example, Lewis acidity is characteristic of TiO_2 [14–16], whereas the sulfated oxide has been shown to possess protonic centers and was considered to be among the few known superacid catalysts [17–19]. Therefore, the surface properties of such samples are very interesting from both, practical and

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theoretical points of view. Valuable information on the nature of surface sites can be obtained by studying low temperature CO adsorption by infrared spectroscopy [20,21]. Here, we combine such a study with co-adsorption of ammonia. The blocking of acid sites by the strong base ammonia allows a more detailed description of the CO adsorption states.

2. Experimental

The titania used for the present study was TiO_2–DT51 from Rhone-Poulenc, France, which is pure anatase according to X-ray diffraction analysis. Its N_2 BET surface area was 97 m^2/g. The material contained 1.15 wt% sulfate.

For comparison purposes, a sulfate-free TiO_2 sample was also studied. The material is the Degussa P-25 titania consisting of approximately 80% anatase and 20% rutile, which is prepared by flame hydrolysis from the tetrachloride. The chlorine content of this titania sample is < 0.3 wt% HCl.

The IR spectra were recorded on a Perkin-Elmer 580 B spectrophotometer equipped with a data station. A specially designed transmission cell was used which allowed in situ sample treatments in O_2 at elevated temperatures (720 K) and evacuation ($\leqslant 10^{-5}$ mbar). The spectra could then be recorded at temperatures between 80 and 300 K in static gas atmospheres or in vacuo. Thin self-supporting wafers (15–20 mg/cm^2) were used as samples. The spectral resolution was 2.3–3 cm^{-1} in the carbonyl stretching region (2000–2300 cm^{-1}) and 2.3 cm^{-1} in the sulfate stretching region (1300–1400 cm^{-1}). Linde CO (99.99%) was used for adsorption. O_2 and H_2O contamination levels were further reduced by passing the gas through an Oxisorb cartridge.

3. Results and discussion

The background spectra of the TiO_2 sample gave relatively low transmission ($< 10\%$) in the O–H stretching region due to strong scattering losses. A band at 3670 cm^{-1} was observed after room temperature evacuation and after thermoevacuation at 470 K, which is to be assigned as an O–H stretching vibration of unperturbed surface hydroxyl groups [14–16]. An additional broad band at lower wavenumbers was indicative of H-bonded hydroxyl groups and/or adsorbed water molecules at room temperature. This band was significantly weakened on heating at 470 K. Simultaneously, the deformation band of adsorbed water molecules at 1620 cm^{-1} almost disappeared. When the sample was thermoevacuated at 720 K and when it was treated in 100 mbar O_2 at the same temperature, the intensity of the band at 3670 cm^{-1} of unperturbed hydroxyl groups was reduced to less than 10% of its initial value suggesting a high degree of dehydroxylation after this thermal treatment.

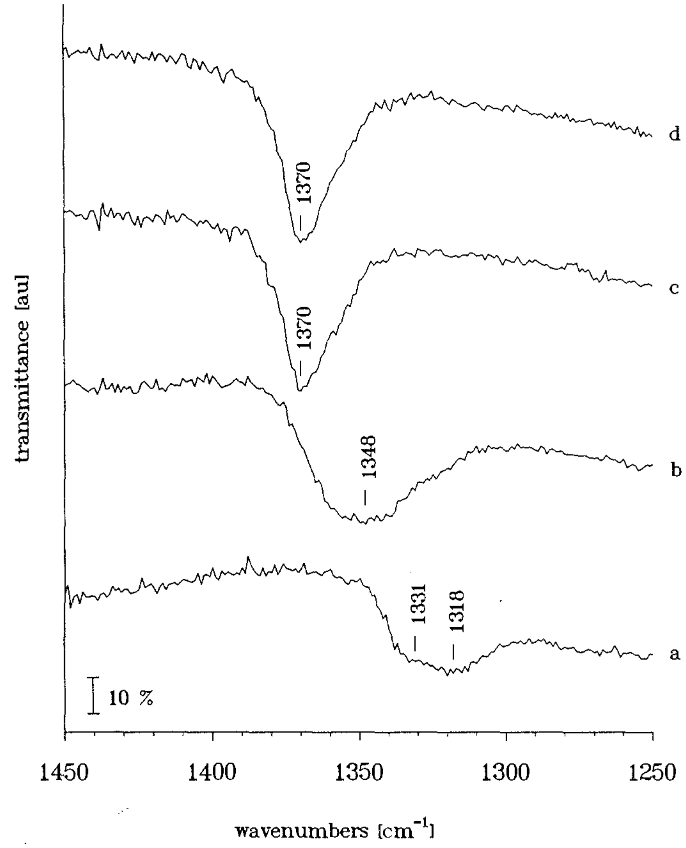


Fig. 1. IR-spectra of sulfated titania in the sulfate region: (a) after evacuation at 298 K, spectrum taken at room temperature; (b) after evacuation at 470 K for 30 min; (c) after evacuation at 720 K for 30 min; (d) after treatment in 100 mbar O_2 at 720 K for 30 min and subsequent evacuation at 720 K for 30 min.

The sulfate groups present on the oxide surface gave rise to bands in the range 1300–1380 cm^{-1} as shown in fig. 1. Bands in this region have been attributed to S–O vibrations of surface groups [17–19]. After room temperature evacuation a band is observed at 1318 cm^{-1} with a prominent shoulder at 1333 cm^{-1}. After thermoevacuation at 470 K the band maximum is observed at 1348 cm^{-1} with a shoulder toward higher wavenumbers and a weak shoulder remaining at 1318 cm^{-1}. Thermoevacuation at 720 K or thermal treatment in 100 mbar O_2 followed by evacuation at the same temperature leads to a band at 1370 cm^{-1}. Similar band positions for surface sulfate groups have been reported in the literature [17–20] and related to varying S–O bond orders. Saur et al. [18] suggested a bridged tri-dentate sulfate structure for the high-wavenumber species which was assumed to interact with H_2O by rupture of one Ti–O bond

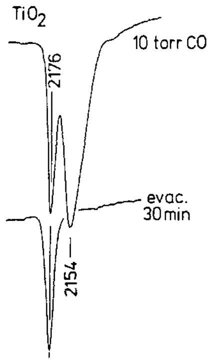
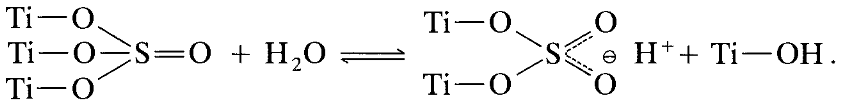


Fig. 2. Carbonyl IR-spectra of CO adsorbed at 80 K on sulfate-free titania.

and formation of Ti–OH and S–OH groups:



$$(\mathrm{Ti{-}O})_3\mathrm{S{=}O} + \mathrm{H_2O} \rightleftharpoons (\mathrm{Ti{-}O})_2\mathrm{S}(\mathrm{O})_2^{\ominus}\ \mathrm{H^+} + \mathrm{Ti{-}OH}. \qquad (1)$$

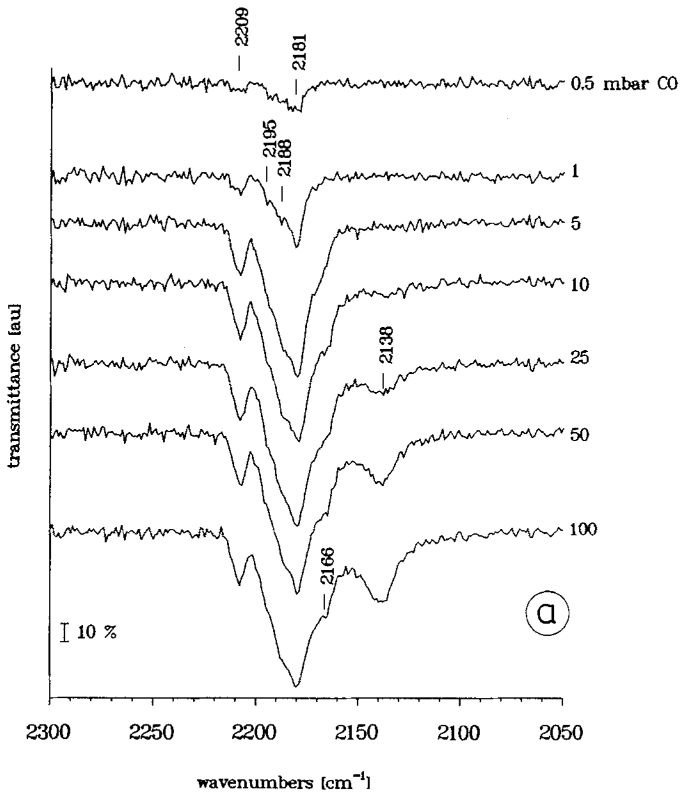


Fig. 3. Carbonyl IR-spectra of CO adsorbed on sulfated titania: (a) pressure dependence at 80 K; (b) evacuation for increasing time periods at dynamic vacuum of $\approx 3\times10^{-5}$ mbar; (c) temperature dependence at 100 mbar CO.

This equilibrium would explain the shift of the S–O vibration to lower wavenumbers in the presence of adsorbed water as seen in fig. 1.

For comparison purposes, carbonyl spectra of adsorbed CO on a sulfate-free TiO_2 sample are shown in fig. 2. Two bands of adsorbed CO are observed in fig. 2, when the sample is exposed to 13 mbar CO at 80 K, namely at 2154 and 2176 cm^{-1}. The former band is due to CO H-bonded to surface hydroxyl groups [21,22], while the band at 2176 cm^{-1} has been assigned to $Ti^{4+} \leftarrow CO$ complexes [21]. It should also be noted, that carbonyl bands were observed in the range 2178–2185 cm^{-1} for CO adsorbed on titania-modified silica [23]. In this case, the silica was modified by reaction with titanium isopropylate, the sample thus certainly being sulfate-free. It is thus concluded that CO coordinated to cus (coordinatively unsaturated) Ti^{4+} sites on pure titania absorbs in the range 2175–2185 cm^{-1}.

Fig. 3 shows carbonyl spectra as they develop on adsorption of CO on the sulfated TiO_2 sample which was thermoevacuated at 720 K. The development of carbonyl bands with pressure at constant temperature of 80 K is shown in fig. 3a. At the lowest pressures of 0.5 and 1 mbar CO two bands at 2181 and 2209 cm^{-1} and a shoulder at 2192 cm^{-1} are observed. The high frequency band at 2209 cm^{-1} saturates at 5 mbar CO while the band at 2181 cm^{-1} continues

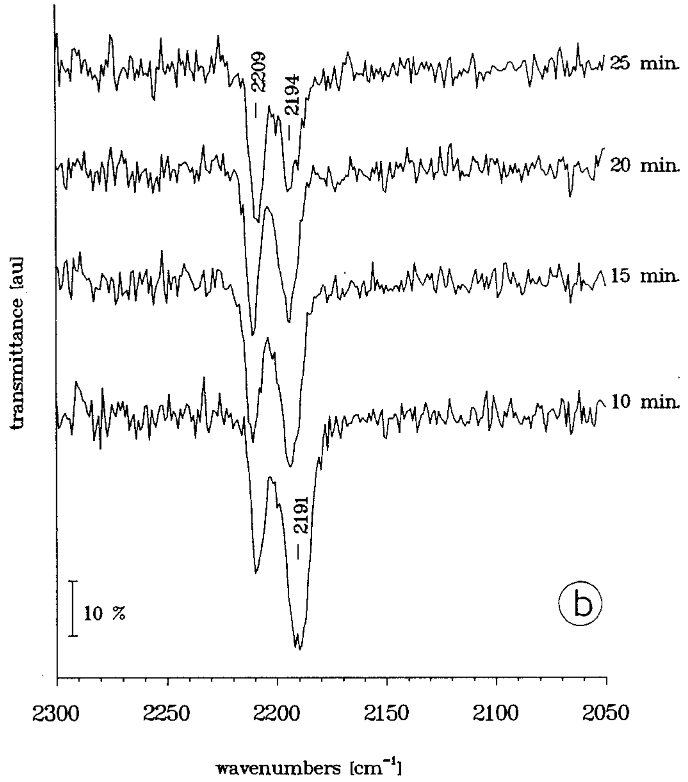


Fig. 3 (continued).

growing and strongly superimposes the shoulder at 2192 cm^{-1}. A shoulder at 2166 cm^{-1} and an additional band at 2138 cm^{-1} grow in at increasing pressures. These two bands belong to weakly adsorbed CO species, namely H-bonded and physically adsorbed [21,22], which immediately desorb on evacuation (fig. 3b) or temperature increase at constant pressure (fig. 3c). The other bands at 2181, 2192 and 2209 cm^{-1} are in the region of CO coordinated to Ti^{4+} sites. There might be an additional weak shoulder at about 2188 cm^{-1}. Still another very weak band at 2176 cm^{-1} can possibly be identified in difference spectra.

The position of the strongest band at 2181 cm^{-1} coincides closely with that observed on sulfate-free materials. With the low sulfate concentration of the sample, the surface density of these species should be low and Ti^{4+} sites unaffected by SO_4^{2-} species should be abundant. CO coordinated to these sites is the most weakly adsorbed among the three observed $Ti^{4+} \leftarrow CO$ surface complexes as indicated by its disappearance on evacuation at 80 K (fig. 3b). The evacuation series in fig. 3b also shows that the high frequency species (2209 cm^{-1}) is the most stable, since its band intensity remains unchanged during evacuation while that of the 2193 cm^{-1} species slowly decreases. The same stability sequence for the three coordinated CO species can be seen in fig. 3c,

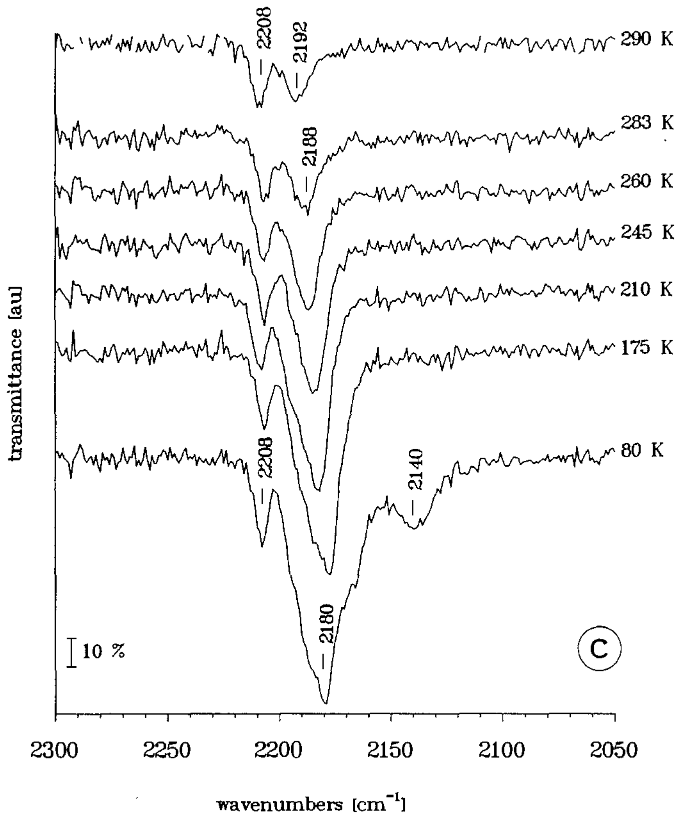


Fig. 3 (continued).

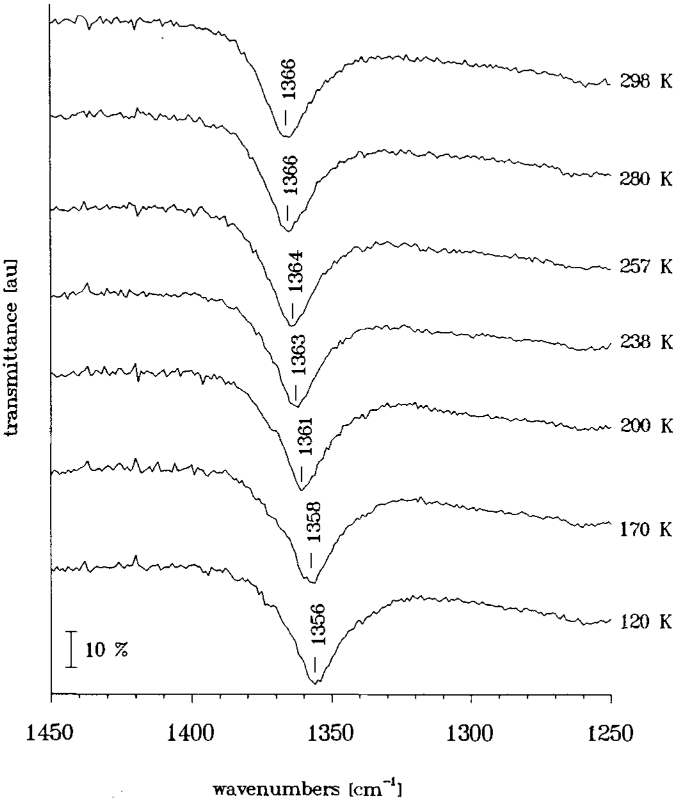


Fig. 4. IR-spectra of the sulfate region of sulfated titania at increasing temperatures in the presence of 100 mbar CO.

where the effect of increasing temperature at constant CO pressure is demonstrated. Hence, the presence of sulfate surface groups induces new coordination (Lewis acid) sites which provide acidities higher than that of cus Ti^{4+} sites on sulfate-free titania.

The involvement of sulfate species in the creation of the new sites can also be demonstrated by the effect of CO adsorption on the S–O vibration at 1370 cm^{-1}. Even small doses of CO which particularly saturate the strongest coordination sites at 80 K (2209 cm^{-1}, see fig. 3) lead to a shift of the S–O band from 1370 cm^{-1} to 1355 cm^{-1}. Increasing equilibrium pressures do not induce any further changes, presumably because CO adsorption then occurs on sites sufficiently remote from sulfate groups. The sulfate band gradually shifts back to its original position when the sample temperature is increased to room temperature at constant pressure (100 mbar CO) as shown in fig. 4. This effect cannot be due to decreasing population by CO of coordination sites in close proximity to the sulfate group, since the intensity of the band at 2209 cm^{-1} remains practically unchanged. The origin of this temperature effect is not clear yet. We

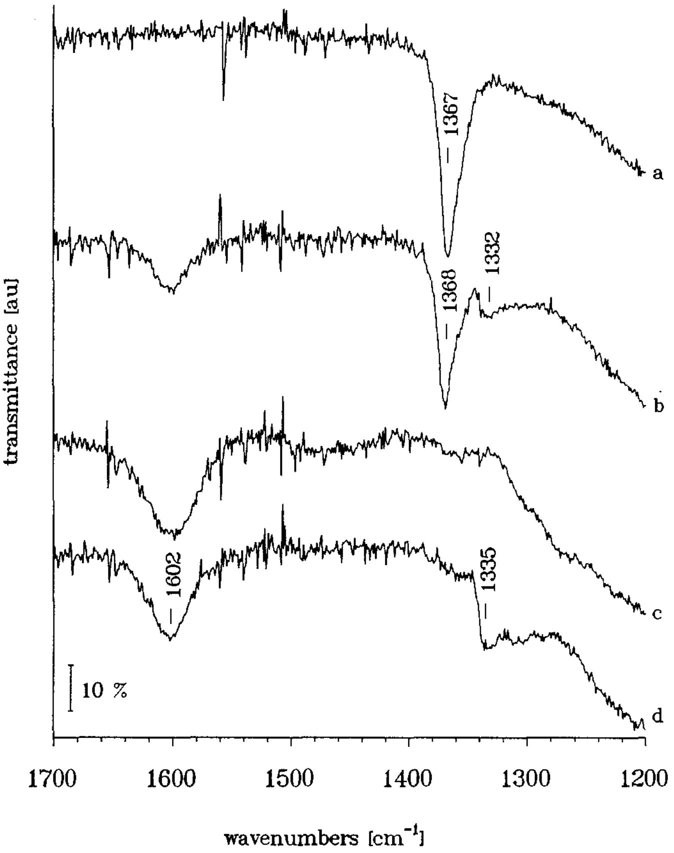


Fig. 5. IR-spectra of sulfated titania after adsorption of NH_3 at room temperature: (a) background spectrum after standard pretreatment and evacuation at 298 K; (b) exposure to 50 mbar NH_3 for 15 min; (c) exposure to 100 mbar NH_3 for 15 min; (d) after evacuation for 60 min.

infer that the wavenumber shift observed for the S–O vibration on adsorption of CO is probably caused by electronic inductive effects.

Adsorption of ammonia at room temperature on the sulfated titania after thermoevacuation at 720 K gave rise to N–H stretching bands ($\nu_{as} = 3390$ and 3350 cm^{-1}, $\nu_s = 3240$ cm^{-1}) and a Fermi resonance component ($2\delta_{as} + \nu_s$) at 3150 cm^{-1}. As shown in fig. 5, the antisymmetric deformation mode develops at 1600 cm^{-1} while the symmetric deformation mode remains buried in the cut-off region near 1200 cm^{-1}. There is no clear evidence for the formation of NH_4^+ species although a broad and ill-defined absorption between 1400 and 1450 cm^{-1} possibly due to the asymmetric deformation mode of NH_4^+ can be detected in the presence of 100 mbar NH_3. The low or even vanishing concentration of NH_4^+ species (which would be indicative of the presence of protonic acidity) is likely related to the severe dehydroxylation of the titania after thermoevacuation at 720 K (vide supra).

Interestingly the S–O vibration at 1370 cm^{-1} is strongly perturbed on adsorption of NH_3 as shown in fig. 5. On exposure of the sample to 50 mbar NH_3, the intensity of the 1370 cm^{-1} decreases and a new band develops at 1332 cm^{-1}. These bands almost entirely disappear when the NH_3 pressure is increased to 100 mbar, while several weak bands seem to be superimposed on the cut-off background between 1200 and 1300 cm^{-1}. After evacuation at room temperature the band at 1370 cm^{-1} remains shifted to lower wavenumbers. Similar shifts of the band at 1370 cm^{-1} on adsorption of NH_3 on sulfated titania have also been reported by Dines et al. [20]. It can clearly be inferred from these observations that ammonia strongly interacts with the surface sulfate groups. Unless the full vibrational spectrum of the surface sulfates with and without coadsorbed ammonia becomes available, only speculative interpretations can be given. In analogy to the interaction with water (see eq. (1) above), ammonia might also dissociatively chemisorb with formation of S–OH and Ti–NH_2 groups. Alternatively, the strong base NH_3 will coordinate to Lewis acid sites and thus exhibit an inductive effect on nearby sulfate groups. Evidence for the expected occupation of Lewis acid sites by NH_3 comes from the position of the antisymmetric deformation mode at 1600 cm^{-1} [16,20,24] and from the fact that CO cannot be coordinated to cus Ti^{4+} sites when the sample was precovered by

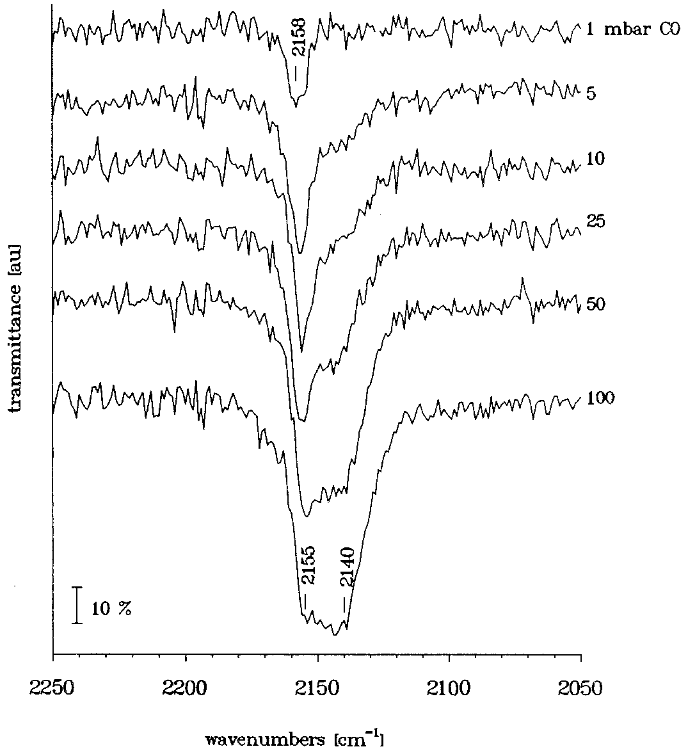


Fig. 6. Carbonyl IR-spectra of CO adsorbed on NH_3-precovered sulfated titania at 80 K.

NH_3. This becomes clearly evident from the spectra shown in fig. 6, where the high-wavenumber bands (2180–2210 cm^{-1}) are entirely absent. Hence, the strong base NH_3 blocks the Lewis sites for the weak base CO.

4. Conclusions

The present results suggest that sulfate groups anchored to the titania surface induce cus Ti^{x+} (probably Ti^{4+}) sites having enhanced Lewis acidity in close proximity to the sulfate group. CO adsorbed on these sites interact with the sulfate group by inductive effects. Stronger bases, such as NH_3, exhibit a significantly stronger effect. Some of these conclusions may relate to the induction of superacidity on sulfation of certain oxide surfaces. The mechanistic details of the described phenomena, however, can only be elucidated when the complete vibrational spectra of the surface sulfates become available and unequivocal structure assignments can be made.

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