

FTIR study of low-temperature adsorption and co-adsorption of ^{12}CO and ^{13}CO on a $\text{TiO}_2\text{--SiO}_2$ mixed oxide

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Abstract

Adsorption of ^{12}CO on a $\text{TiO}_2\text{--SiO}_2$ sample prepared via the homogeneous precipitation method (Ti : Si molar ratio 1 : 1) is negligible at ambient temperature. At 85 K, however, different sites are monitored by CO: two kinds of Ti^{4+} cations (ν_{CO} at 2185–2199 and 2173–2177 cm^{-1} , respectively) and CO attached to surface silanol groups (2156 cm^{-1}). Although the higher frequency carbonyls are more stable, all species disappear after evacuation at 85 K. The $\text{Ti}^{4+}\text{--CO}$ band positions are coverage dependent: the first band is shifted from 2199 cm^{-1} at low coverage to 2185 cm^{-1} at high coverage, while the second band shifts from 2177 cm^{-1} at low coverage to 2173 cm^{-1} at high coverage. Co-adsorption of $^{12}\text{CO}\text{--}^{13}\text{CO}$ isotopic mixtures reveals that these shifts are entirely static in character. Some conclusions about the acidity and distribution of the Ti^{4+} cations on the sample surface are drawn. ©1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Titanium dioxide is widely applied as a support for different catalysts used in various reactions [1]. In particular, vanadia/titania materials are the best known catalysts for partial oxidation of *o*-xylene and selective catalytic reduction of nitrogen oxides by ammonia [1–3]. In order to ensure better dispersion of the active phase, some attempts have been made to enhance the specific surface area of the support itself. One of the most promising ways to serve this purpose is supporting titania on silica [4–8] or using mixed titania–silica

oxides [9–11]. Recently, one of us has shown that titania–silica prepared by homogeneous precipitation can be applied as a support for vanadium oxide catalysts [9]. Since it has been demonstrated that, in such catalysts, vanadium is preferentially distributed on the titanium sites [5], it is of interest to study the state of the titanium cations on mixed titania–silica oxides. In the present paper, we report a study of the surface acidity of $\text{TiO}_2\text{--SiO}_2$ sample prepared by homogeneous precipitation. For measuring the surface acidity, analysis of the IR spectra of CO adsorbed at low temperature was performed.

2. Experimental

2.1. Samples and reagents

The $\text{TiO}_2\text{--SiO}_2$ sample (Ti : Si molar ratio 1) was prepared by a homogeneous-precipitation method, as

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described elsewhere [9]. Briefly, a mixed aqueous solution of titanium tetrachloride (Fluka, AR grade), sodium metasilicate (Loba-Chemie, GR grade) and urea (Loba-Chemie) was heated to 368 K with vigorous stirring for about 6 h. Then the precipitate obtained was filtered, washed thoroughly with doubly distilled water and dried for 16 h at 393 K. The product obtained was again washed, first with 5% NH_4NO_3 solution (to remove residual Na^+ cations), and then again with water. Finally, the substance was dried for 16 h at 393 K and calcined for 6 h at 773 K. The composition of the $\text{TiO}_2\text{-SiO}_2$ sample produced was a 1 : 1 mole ratio. This mixed oxide was free from chlorine ions. The product obtained had a BET surface area of $238 \text{ m}^2 \text{ g}^{-1}$ and was found to be X-ray amorphous.

Carbon monoxide (>99.997) was supplied by Linde AG. Labeled carbon monoxide (^{13}CO) was provided by the Aldrich Chemical Company, Inc. and had an isotopic purity of 99.0 at.%. It contained about 10 mol% $^{13}\text{C}^{18}\text{O}$.

2.2. Methods

FTIR spectroscopy studies were carried out with a Bruker IFS-66 apparatus at a spectral resolution of 2 cm^{-1} accumulating 128 scans. The in situ IR cell was connected to a vacuum/sorption system with a residual pressure less than 10^{-3} Pa . The especially constructed cell allowed the IR measurements to be performed at 85 K [12].

Self-supporting pellets were prepared from the sample powder and thermally treated in situ in the IR cell. Prior to the experiments, the sample was activated by heating in an oxygen flow at 673 K for 1 h and evacuation at the same temperature for 1 h. The colour of the activated sample was white, which suggested the absence of Ti^{3+} ions.

3. Results

3.1. Background spectrum and CO adsorption at ambient temperature

The IR spectrum of the activated sample is similar to the published IR spectra of activated silica. In the $\nu(\text{OH})$ region, there is an intense and narrow band

at 3740 cm^{-1} which is assigned to terminal silanol (Si-OH) groups. No evidence for any Ti-OH hydroxyls was found. Below 1300 cm^{-1} , the bulk absorption of the solid catalyst begins, which determines the so-called sample ‘cut-off’ at this wavenumber. Three bands of medium intensity were also detected, their maxima being at 1964, 1867 and 1638 cm^{-1} . These bands characterize overtones and combination modes of the skeletal vibrations of silica.

Adsorption of CO on the sample at ambient temperature and under 6.4 kPa equilibrium pressure leads to the appearance of one band with very weak intensity and the maximum at ca. 2194 cm^{-1} . This band declines very fast with decreasing equilibrium pressure and is not observable at pressures below 1 kPa.

3.2. Low-temperature CO adsorption

Adsorption of carbon monoxide on our sample at 85 K (100 Pa equilibrium pressure) results in the appearance of three principal bands in the carbonyl stretching region, their maxima being located at 2180.5, 2156 and 2139 cm^{-1} (Fig. 1, spectrum a). In addition, a weak band is also visible at 2108 cm^{-1} . In the $\nu(\text{OH})$ region, the 3740 cm^{-1} band is converted into another, broader and coverage-independent band,

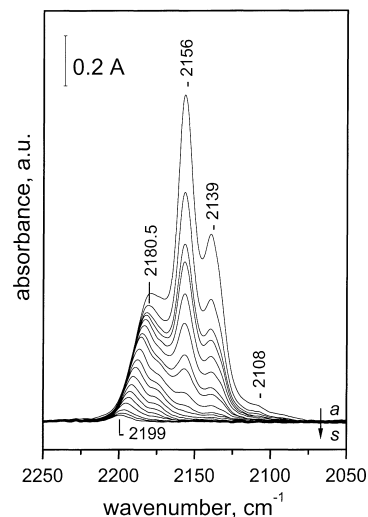


Fig. 1. FTIR spectra of CO adsorbed at 85 K on a $\text{TiO}_2\text{-SiO}_2$ sample. Equilibrium CO pressure of 100 Pa (a), 30 Pa (b), 20 Pa (c) and 10 Pa (d) CO, after short evacuations (e–g), and under dynamic vacuum (h–s).

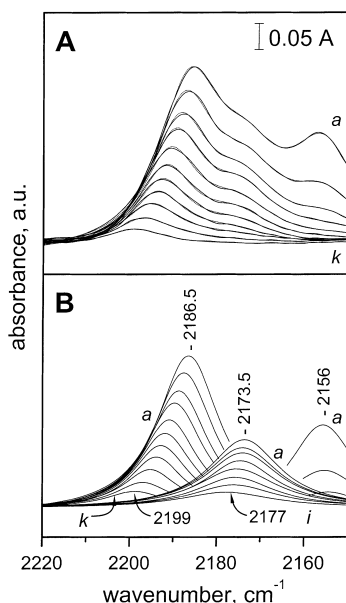


Fig. 2. FTIR spectra of CO adsorbed at 85 K on a $\text{TiO}_2\text{-SiO}_2$ sample. Initial equilibrium pressure of 100 Pa CO, followed by evacuation at different times (panel A, spectra a–k, full lines). Computer deconvoluted spectra are presented on panel B, whereas the fitting curves are shown by dotted lines in panel A.

with the maximum at 3662 cm^{-1} . Decrease in the equilibrium pressure and evacuation lead to fast disappearance of the bands at 2139 cm^{-1} and then at 2156 cm^{-1} and the original spectrum in the O–H stretching region is restored. The band at 2180.5 cm^{-1} splits into two bands at lower coverages (Figs. 1 and 2). The first, more intense band, is shifted from 2181 to 2199 cm^{-1} with decreasing coverage, whereas the second band shifts from 2173 to ca. 2177 cm^{-1} . Despite having a comparable stability, it is the band at $2181\text{--}2199\text{ cm}^{-1}$ that is more resistant towards evacuation.

The band at 2139 cm^{-1} is due to physically adsorbed CO. The band at 2156 cm^{-1} changes in intensity simultaneously with the 3662 cm^{-1} band and its decrease is accompanied by restoration of the original spectrum in the $\nu(\text{OH})$ region. For this reason, and in agreement with the literature data [13,14], this band is assigned to CO attached to surface OH groups. The respective ^{13}CO satellite, arising from the ^{13}CO natural abundance, was detected at 2108 cm^{-1} . Both bands, at $2181\text{--}2199$ and $2173\text{--}2177\text{ cm}^{-1}$, have not been observed on pure silica. The position of their maxima

suggests that they are due to CO adsorbed on Lewis acid sites. It is known that the number of Ti^{3+} ions formed on titania even after reduction with hydrogen at 400°C is negligible, less than the number of the CO adsorption sites [15]. Therefore, no measurable amount of Ti^{3+} is expected on our sample, which is also supported by its white colour. For these reasons, we attribute the bands at $2181\text{--}2199$ and $2173\text{--}2177\text{ cm}^{-1}$ to two kinds of $\text{Ti}^{4+}\text{-CO}$ species, differing in the electrophilic properties of the respective Ti^{4+} cations.

3.3. Low-temperature $^{12}\text{CO}\text{-}^{13}\text{CO}$ co-adsorption

Adsorption of ^{13}CO at 85 K (30 Pa equilibrium pressure) on the sample results in the appearance of three principle bands in the spectrum, their maxima being located at 2131, 2109 and 2092 cm^{-1} (Fig. 3, spectrum a). They correspond to the three main bands observed after ^{12}CO adsorption, namely CO on Ti^{4+} cations, CO on Si–OH groups and physically adsorbed CO, respectively. The experimental shifts coincide very well with the theoretically calculated values. In addition, two weak bands at 2057 and 2040 cm^{-1} originate from $^{13}\text{C}^{18}\text{O}$ contaminants in ^{13}CO and are assigned to H-bonded and physisorbed $^{13}\text{C}^{18}\text{O}$, respectively. The band due to $^{13}\text{C}^{18}\text{O}$ adsorbed on Ti^{4+} ions is not observable because it is superimposed by the strong band at 2092 cm^{-1} .

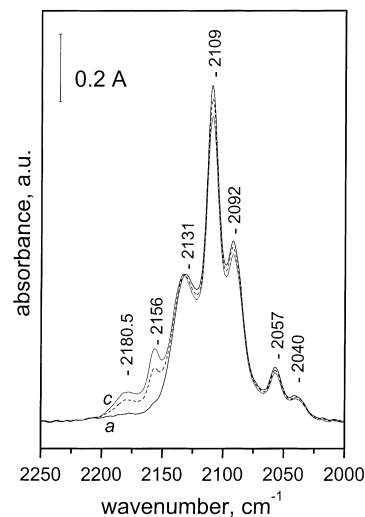


Fig. 3. FTIR spectra of ^{13}CO (30 Pa) adsorbed at 85 K on a $\text{TiO}_2\text{-SiO}_2$ sample (a) and after introduction of small amounts of ^{12}CO (b, c).

Small portions of ^{12}CO were then successively introduced into the IR cell (Fig. 3, spectra b and c). This leads to the appearance and rise in intensity of two bands with maxima at 2180.5 and 2156 cm^{-1} (already assigned to $\text{Ti}^{4+}\text{-}^{12}\text{CO}$ and $\text{SiOH-}^{12}\text{CO}$ species, respectively). Simultaneously, the bands at 2109, 2092, 2057 and 2040 cm^{-1} decrease slightly in intensity, whereas the band at 2131 cm^{-1} is shifted to 2133 cm^{-1} . The latter effect is attributed to the superimposition of this band with the band due to physically adsorbed ^{12}CO . A decrease in the equilibrium pressure/evacuation results in a decrease in intensity and the disappearance of all bands, consistent with the stability of the different species, as described above, for ^{12}CO adsorption.

4. Discussion

4.1. Acid sites on the surface of the $\text{TiO}_2\text{-SiO}_2$ sample

Adsorption of CO clearly revealed that, on the surface of the $\text{TiO}_2\text{-SiO}_2$ sample, there are two types of Ti^{4+} sites. The first kind of sites is characterized by a CO band at 2199 cm^{-1} at low coverages which shifts to 2181 cm^{-1} at saturation. The respective values for the second band are 2177 and 2173 cm^{-1} .

It is known that the shift of the CO bands with the coverage is due to lateral (adsorbate–adsorbate) interactions. There are two mechanisms of lateral interaction, namely (i) dynamic and (ii) static interactions [16,17]. The dynamic interaction is due to the dipole–dipole coupling between the adsorbed CO molecules and leads to an increase in the CO frequency. For dynamic interactions to occur, the adsorbed molecules must (i) be oriented parallel to each other, (ii) be located in close proximity, and (iii) vibrate with the same intrinsic frequency. The third condition allows the elimination (and thus the calculation) of the dynamic interaction using $^{12}\text{CO}\text{-}^{13}\text{CO}$ isotopic mixtures. Comparison of the results of ^{12}CO adsorption and $^{12}\text{CO}\text{-}^{13}\text{CO}$ co-adsorption on the present sample shows that the ^{12}CO stretching frequency remains constant, within the limits of the experimental error, for comparable total coverages (see Fig. 4). Hence, the dynamic interaction between

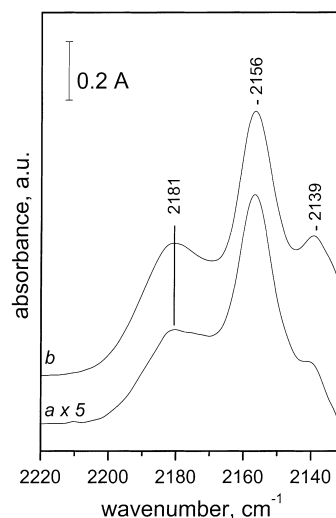


Fig. 4. Changes in the IR spectrum of ^{13}CO adsorbed at 85 K on $\text{TiO}_2\text{-SiO}_2$ sample (30 Pa equilibrium pressure) after the introduction of a small amount of ^{12}CO (a) and IR spectrum of ^{12}CO (30 Pa equilibrium pressure) adsorbed on a $\text{TiO}_2\text{-SiO}_2$ sample (b).

the adsorbed CO molecules on the sample, if any, is negligible.

The static shift (also called chemical shift) occurs through the solid and is a measure of the ability of the adsorbed molecules to transmit negative charge to the neighboring adsorption sites. Let us first consider the 2199–2185 cm^{-1} band. In this case, the static shift is relatively large as compared to other oxide systems. This means that the adsorption sites can not be described as isolated Ti^{4+} cations. We assign these sites to titanium cations having at least one c.u.s. Ti^{4+} cation in their second coordination sphere. The lack of a dynamic shift in this case suggests that the adsorbed CO oscillators are not oriented parallel to each other. For the second type of sites, the chemical shift is very small, which suggests that they represent isolated titanium cations. This is consistent with the small chemical shift for CO adsorbed on silica–titania systems with a low concentration of titanium cations [4,18].

It has been reported [19] that, when calcined at high temperature, e.g. 1073 K, there were two titania phases in our sample: an amorphous phase containing Ti^{4+} sites coordinated tetrahedrally by Si–O and OH groups and a segregated paracrystalline TiO_2 (anatase and rutile). We infer that the associated Ti^{4+} ions on the 773 K calcined sample are precursors for the formation of the TiO_2 phases.

The Brønsted acidity of the sample is determined by the surface silanol groups. Many data in the literature point out that the shift of $\nu(\text{OH})$ for surface silanols, observed upon CO adsorption, is -90 cm^{-1} [13,14]. However, we measured a smaller shift, namely -78 cm^{-1} . This does not necessarily mean that the original acidity of the silanols on our sample is smaller than the acidity of Si–OH groups of silica. However, CO adsorbed on the Ti^{4+} sites may change the acidity of the Si–OH groups located nearby. Indeed, the Ti^{4+} sites are occupied by CO at pressures lower than the pressures at which CO is adsorbed on the Si–OH groups, and the ability of CO adsorbed on the Lewis acid sites to transmit negative charge through the solid was evidenced by the relatively large chemical shift of the $2199\text{--}2185\text{ cm}^{-1}$ band. Similar effects of probe-molecules adsorbed on Lewis acid sites on the acidity of titania hydroxyls have been reported earlier [20,21].

It might be possible that the frequency of isolated Ti–OH groups on the sample coincides with the frequency of silanol groups, and thus, the 3740 cm^{-1} band might be a superposition of Ti–OH and Si–OH bands. Although this possibility cannot be ruled out totally, we believe that the observed OH bands correspond to Si–OH groups because only one shifted band was detected after low-temperature CO adsorption.

4.2. Comparison of the surface properties of $\text{TiO}_2\text{--SiO}_2$ with the surface properties of related materials

The results of the present study show that the surface properties of the present sample differ strongly from the properties of the pure oxides. Many investigations show that CO adsorption on both anatase and rutile TiO_2 modifications results in the appearance of Ti^{4+} carbonyls that are well visible at ambient temperature and under CO equilibrium pressure [15,22,23]. Two Ti^{4+} sites have been reported for anatase [15,22]. The maxima of the respective bands are located at 2208 (α sites) and 2192 (β' sites) cm^{-1} at low coverages and a shift to 2206 and 2186 cm^{-1} , respectively, at higher pressures/coverages [15]. For rutile, one band is reported at 2191 cm^{-1} [23]. On the present $\text{TiO}_2\text{--SiO}_2$ sample, the CO adsorption at ambient temperature was negligible, which evidences that, in general, it

is characterized by weaker Lewis acidity than TiO_2 itself.

However, on the surface of both anatase and rutile, there are also large fractions of Ti^{4+} sites that are not acidic enough to be detected by CO at ambient temperature [20,22,23]. Thus, in addition to the sites monitored by CO at ambient temperature, two more types of sites can be detected at low temperature on anatase [20]. First, these are the so-called β'' sites, which produce, together with the β' sites, a common band with a maximum at 2179 cm^{-1} at higher coverage. These sites are believed to be located on the (101) and (100) anatase planes [1,20]. Secondly, a family of very weak acid sites (γ sites) is monitored by a CO band at 2165 cm^{-1} . They have been assigned to Ti^{4+} cations on the (001) basal anatase plane [1,20]. For CO on the β sites ($\beta' + \beta''$), a static shift of -17 cm^{-1} has been measured, whereas the dynamic shift has been found to be $+4\text{ cm}^{-1}$ [16,20]. The static shift for the $2199\text{--}2185\text{ cm}^{-1}$ CO band on our sample is -14 cm^{-1} which is very similar to the shift of CO on the β sites of anatase. Although both samples have different structures, the results support the assignment of the sites to ‘associated’ Ti^{4+} cations.

The absence of strong Lewis acid sites on the present $\text{TiO}_2\text{--SiO}_2$ sample is the main difference when compared to pure titanias. However, Lewis acidity appears to be similar to both the acidity of silica-supported titania [4] and the acidity of titanium silicalite [18,24]. Thus, one coverage-independent CO band at 2182 cm^{-1} was observed at low temperature on TS-1 [18]. No CO adsorption has been observed on a $\text{TiO}_2/\text{SiO}_2$ sample at room temperature, whereas one band, shifting from 2184 to 2180 cm^{-1} with increasing coverage, has been reported at low temperature [4].

5. Conclusions

Adsorption of ^{12}CO on a $\text{TiO}_2\text{--SiO}_2$ sample prepared via a homogeneous precipitation method (Ti : Si mole ratio 1) is negligible at ambient temperature.

CO adsorption at 85 K reveals the existence of (i) two kinds of Ti^{4+} cations (ν_{CO} at $2185\text{--}2199$ and $2174\text{--}2177\text{ cm}^{-1}$, respectively) and (ii) CO bonded to Brønsted acid sites, namely silanol groups (2156 cm^{-1}).

The Ti^{4+} -CO bands are coverage dependent: the first band is shifted from 2199 cm^{-1} at low coverage to 2185 cm^{-1} at maximum coverage, whereas the second is shifted from 2177 cm^{-1} at low coverage to 2173 cm^{-1} at maximum coverage. Co-adsorption of ^{12}CO - ^{13}CO isotopic mixtures reveals that the shifts are entirely static in character. The 2199 – 2185 cm^{-1} band is assigned to CO adsorbed on associated Ti^{4+} cations, whereas the band at 2177 – 2173 cm^{-1} is attributed to CO on isolated Ti^{4+} sites.

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