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FT–IR Spectroscopic Characterization of Oxidized and Reduced Titania

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Fourier transform infrared spectroscopy has been applied to the characterization of titania surface. The bands due to surface OH groups were observed to be more intense in the reduced titania than in the oxidized titania. The IR spectra of CO adsorbed on titania exhibited two C–O stretching bands, namely at 2187 and 2209 cm^{-1}. The intensities were stronger in the oxidized titania. The 2187 cm^{-1}–peak was attributed to CO coordinated to Ti_{5c}^{4+} (subscript indicates the coordination number of the coordinatively unsaturated cation by oxygen ions), while the 2209 cm^{-1}–peak due to the Ti_{4c}^{4+}····CO complex.

Introduction

The surface chemistry of titania has been the subject of considerable research interest in the past[1-10]. The adsorption of carbon monoxide has been used to characterize surface Lewis acidic centers mainly by means of infrared spectroscopy[11]. CO is a soft base and can therefore be used as a highly specific probe for acid sites on oxide surfaces. Nevertheless, the identification of oxidation state and coordination number of cation sites remains still intriguing[9].

A few authors have recently studied the adsorption of CO on reduced titania[1,7-10]. The reduction conditions employed were, however, on the large so severe that all samples became highly opaque in the CO stretching region. To resolve the conflicting views on the surface Lewis acidic centers we have thus investigated the adsorption of CO on slightly reduced titania by the use of a Fourier transform infrared instrument.

Experimetal

A commercial titania sample (Degussa P–25) was used throughout. This was obtained by hydrolysis of the corresponding chloride, and consisted of 84% anatase and 16% rutile. The BET measurement was performed with nitrogen at 77 K, and the surface area was found to be 53 and 47 m^2/g after evacuation overnight at 423 and 773 K, respectively.

Oxygen (99.998%), nitrogen (99.999%), hydrogen (99.999%), and carbon monoxide (99.997%) obtained from Messer Griesheim GmbH (FRG) were used as received. The gas pressure was measured with either 0–100 or 0–1000 Torr (1 Torr = 133.3 Pa) transducer gauge (Datametrics).

Initially, titania powder was spread uniformly on paraffin paper to prevent metal contamination, placed in a 2.5 cm diameter die pellet press, and pressed at 10 kg/cm^2. The self-supporting wafer (~20 mg cm^{-2}) thus obtained was mounted into a specially designed transmission cell with KBr windows[12,13], and pretreated in situ in heating zone of the cell as described below.

Spectra in the hydroxyl stretching (4000–3400 cm^{-1}) and in the carbonyl stretching (2400–1900 cm^{-1}) regions were recorded on a vacuum–purged Bruker 1FS 113v spectrometer at spectral resolution of 2 cm^{-1}. 100 scans with a liquid N_2 cooled MCT (Mercury Cadmium Telluride) detector were used for an individual spectrum. The wave number accuracy read from the spectra is better than ±0.1 cm^{-1}. All spectra taken at the ambient temperature have been corrected by
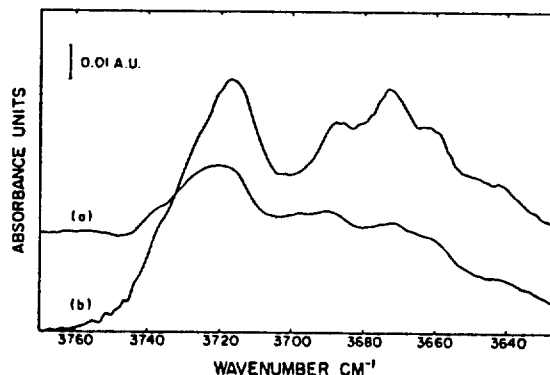

Figure 1. Infrared spectra of (a) "oxidized" and (b) slightly "reduced" titania in the hydroxyl stretching region. See text.

subtraction for absorption of the gas phase and the KBr windows.

Results and Discussion

A TiO_2 sample was evacuated in the IR cell at 295 K overnight, and then dehydrated at 773 K for 2 hrs. This treatment was followed by calcination with 160 Torr of O_2 at 773 K for 1 hr so as to produce an "oxidized" sample containing excess oxygen. The sample was outgassed at 773 K for 2 min, and then kept under dynamic vacuum (10^{-5} Torr) at 295 K to ensure stoichiometry. After these oxidation/evacuation treatments the sample was a bright white color indicating that the bulk was fully oxidized. At this stage four OH stretching bands at 3719, 3689, 3673, and 3661 cm^{-1} (Figure 1(a)) and a TiO littice vibration around 1000 cm^{-1} were observed.

For rutile two characteristic OH stretching bands near 3690–3700 and 3660–3670 cm^{-1} have been reported[14,15]. Anatase on the other hand appears to be characterized[16-18] by two bands at 3725–3730 and 3665–3670 cm^{-1}. Based on these reported data, the bands at 3719 and 3673 cm^{-1} in Figure 1(a) can be attributed to anatase, and those at 3689 and 3661 cm^{-1} to rutile. It would be appropriate to mention that many authors observed similar OH stretching pattern under oxidation/evacuation treatment like the present work[5]. Moreover, regardless of the purity of the starting material, either anatase or rutile, such a pattern appeared albeit the X–ray diffraction analysis showed no detectable reflections due to the phase different from the starting material.[19]

For a given oxide, the OH stretching frequency and the

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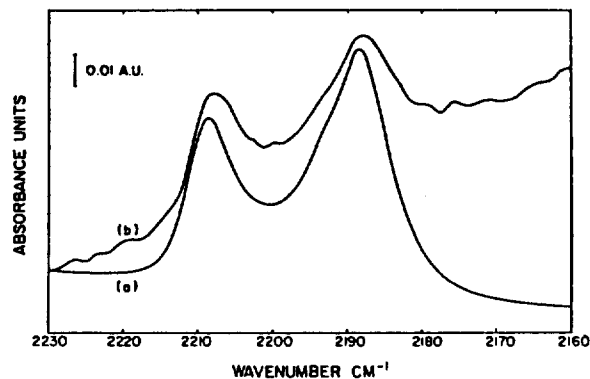*Bull. Korean Chem. Soc., Vol. 11, No. 5, 1990* 397

Figure 2. Infrared spectra of carbon monoxide adsorbed on (a) "oxidized and (b) slightly "reduced" titania. See text.

chemical properties of the group are largely determined by the coordination number of the OH group relative to metal cations. Depending on the oxide structure and the exposed faces which terminate the crystallites, different OH configurations may exist simultaneously. These are usually designated type I, II and III, where the Roman numbers indicate the coordination number[5]. Following the previously reported assignments the type I groups are assumed for the band pair at 3719 and 3689 cm^{-1} to correspond to bonding of the OH group to Ti^{4+} cation. On the other hand, the band pair at 3673 and 3661 cm^{-1} are assigned to the type II groups. Nevertheless, the coordination number of the coordinatively unsaturated (cus) Ti^{4+} cation by oxygen ions can hardly be characterized. Busca *et al.*[3,4] have shown that both 5- and 4-coordinated Ti^{4+} cations are present at the anatase surface. The former are at the flat(011) and (001) planes, and the latter are at the steps, corners and kinks of the above faces, or on rough faces like(110) and (111). Similar cus Ti^{4+} cations have been proposed to exist on powdered rutile surfaces[20].

Figure 1(b) shows hydroxyl spectra of TiO_2 after treating with 8 Torr of H_2 at 773 K for 15 min, followed by evacuation at 773 K for 10 min and kept under dynamic vacuum (10^{-5} Torr) at 295 K. The sample exhibited a faint blue–gray color due to mild reduction. Nevertheless, the hydroxyl groups were sensitive to H_2 exposures. Comparing spectra a and b of Figure 1 shows that the H_2 treatment enhances the intensity of the OH bands and changes the sign of the slope of the background. The latter is attributed to changes in the surface of the titania. The OH stretching bands became more distinct without any peak-shift, however. This may indicate that the sample corresponding to Figure 1(a) was indeed fully oxidized. The exposed H_2 produced the free surface hydroxide (*i.e.* not H-bonded) groups as can be seen in Figure 1(b). Similar observation could be made even after the reduction for less than 1 min. We therefore tend to believe that the coordination site for the hydroxyl group on TiO_2 surface is in fact a Ti^{4+} cation center even for the case of H_2-reduced material. The formation of Ti^{3+}-OH bond seemed not to be favorable under the reducing environment employed in this work.

The exposure of CO (see below) to either oxidized or reduced samples has not accompanied any noticeable change in the OH stretching region. This would certainly indicate that the heat of formation of the surface complex $TiOH^{\delta+}\cdots$

CO is very low as one may expect. Zaki and Knözinger[5] reported that adsorption of CO perturbed all OH groups of TiO_2 at lower temperature (*e.g.* 77 K). Based on the frequency shifts, the heat of adsorption was estimated by these authors to be ~20 kJ/mol.

Figure 2 shows the spectra of CO adsorbed on the TiO_2 sample investigated. The spectra have been taken at 295 K and 10 Torr. When CO is adsorbed on the oxidized titania (Figure 2(a)), two intense bands appeared at 2209 and 2187 cm^{-1}. As H-bonding does not occur at the ambient temperature, these bands must be due to $Ti^{x+}\cdots$ CO complexes. However, those species disappeared immediately upon moderate evacuation. It is interesting to note that the carbonyl bands of CO adsorbed on H_2-reduced TiO_2 occurred at very similar frequencies (Figure 2(b)). Nevertheless, the band intensities were observed to be substantially less intense by about a factor of 3 compared with those measured on the oxidized titania.

Tanaka and white[1] reported that two carbonyl bands appeared at 2185 (strong) and 2115 cm^{-1} (weak) when 22 Torr of CO was exposed to anatase oxidized at 673 K. When the pressure was decreased to 10 Torr, the 2185-cm^{-1} peak dropped steadily to zero while the 2115-cm^{-1} peak remained constant. Evacuation at room temperature removed all of the adsorbed CO. These CO stretching vibrations were accompanied by small peaks at 1420 cm^{-1} and near 1600 cm^{-1} indicative of the formation of surface bicarbonate species. On the other hand, exposure of CO to a sample reduced at 673 K gave only the 2185-cm^{-1} peak, which was also completely removed by evacuation. No carbonate type species were observed when CO was exposed to the reduced anatase. The nature of $Ti^{x+}\cdots$ CO complexes has not been referred by these authors.

Morterra *et al.*[6] investigated also the adsorption of CO on pure anatase. They observed only one weak band centered at ~2185 cm^{-1} when the sample was oxidized at $T\leq423$ K. After the O_2-treatment at temperatures in the 423-873 K range, the overall intensity of the spectra increased and there were two resolved CO species, centered at ~2207 and ~2187 cm^{-1} respectively, that moved somewhat with coverage (2208.5-2206; 2192-2186 cm^{-1}).

Infrared spectra of CO adsorbed on oxidized (at 670 K) and reduced (at 770 K) rutile samples were reported by Zaki and Knözinger[7]. CO adsorption at 80 K on TiO_2 gave rise to carbonyl bands at 2133, 2150 and 2174 cm^{-1}. The bands at 2133 and 2150 cm^{-1} corresponded to weakly adsorbed species as indicated by their low thermal stability. They were respectively attributed to physically adsorbed and H-bonded CO. At room temperature the band at 2178 cm^{-1}, shifted by 4 cm^{-1} from the above 2174-cm^{-1} peak, was only observed. The carbonyl band of CO adsorbed on H_2-reduced TiO_2 occurred at a very similar position, namely at 2182 cm^{-1}. Based on these observation, the authors made a conclusion that the oxidation states of Ti^{x+} coordination sites were the same most probably +3, on both the O_2 and H_2 treated samples. In a later study on TiO_2/SiO_2 system, Knözinger *et al.*[8] made a similar conclusion. It has to be pointed out that this view is in contrast with the proposition of Busca *et al.*[3] who have assigned a band at 2120-2110 cm^{-1} to $Ti^{3+}\cdots$ CO.

Recently Bolis *et al.*[10] have shown that two types of CO adsorb on pure anatase: one absorbing at 2184-2188 cm^{-1}, the

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other at $2203-2208$ cm^{-1}. The two CO species were ascribed to Ti$^{4+}\cdots$ CO complexes, differing in the polarizing power of the cation, according to Busca *et al.*[3,4].

We mentioned already that the carbonyl bands of CO adsorbed on H$_2$-reduced titania appeared at nearly the same frequencies as those on the oxidized sample (see Figure 2). The oxidation states of the coordination cation sites are thus supposed to be same on both the oxidized and reudced samples. Although surface Ti^{3+} ions could be formed upon reduction, the amount would be assumed far below than that of Ti^{4+} ions, at least under the present expeimental environment. It has been reported that the formation of Ti^{3+} could not be detected[8] by XPS on pure TiO$_2$ (Degussa, P-25) when treated under flowing H$_2$ at 773 K. Hence we tend to believe that the coordination site for CO on the present TiO$_2$ surfaces is in fact a Ti^{4+} cation center. That is, the bands at 2209 and 2187 cm^{-1} in Figure 2 are both supposed to occur from coordination of CO to cus Ti^{4+} on surfaces.

The surface area of reduced titania was hardly different from that of oxidized titania. The relatively less intense carbonyl bands observed on the H$_2$-treated sample (compare b with a of Figure 2) may then be attributed to the decrease in the number of cus Ti^{4+} ions on surfaces. Such a phenomenon may take place by the formation of surface hydroxyl groups and/or surface Ti^{3+} ions upon the H$_2$ treatment. As already discussed above, the hydroxyl bands, probably due to OH groups bonded to cus Ti^{4+} ions, increased noticeably in their intensity upon reduction (see Figure 1(b)). Hence the spectral pattern in the CO stretching region seems to be consonant with that in the OH stretching region.

The explanation made here is in contrast with that of Fernandez *et al.*[8]. Even though they observed only one carbonyl band at 2178 cm^{-1}, the intensity was, like the present work, always much greater in the thermo-evacuated sample than in the samples reduced at the same temperature with H$_2$. Assigning a band near 2180 cm^{-1} to the Ti$^{3+}\cdots$ CO complex, the authors suggested a certain mechanism that incorporated hydrogen into the oxygen vacancies near the Ti^{3+} species leading to a removal of exposed Ti^{3+} ions.

It may be necessary to discuss further the origin of the two carbonyl bands in Figure 2. Both bands have been assigned already to CO coordinated to Ti^{4+}. But the nature of Ti^{4+} sites can hardly be clarified. One may attribute the appearance of two carbonyl bands to the co-existence of anatase and rutile. Although such a possibility can not be completely ruled out, a more plausible interpretation would be to explain the doublet in terms of the coordination number of the CO-bound Ti^{4+} cation by oxygen ions.

Zaki and Knözinger[9] applied an empirical procedure to determine the oxidation state and coordination number of the cus surface sites. This procedure was based on a correlation between C-O stretching frequency and electric field strength exerted by the cation. Although the authors assigned the ~ 2180 cm^{-1} peak to the Ti$^{3+}\cdots$ CO complex, the possibility due to a Ti$^{4+}\cdots$CO complex was not excluded. According to their empirical correlation the carbonyl frequency of CO adsorbed on TiO$_2$ appeared to be same for both cases of 4-coordinated Ti^{3+} and 5-coordinated Ti^{4+} centers. Hence, we tend to attributed the 2187-cm^{-1} peak in Figure 2 to CO coordinated to Ti$_{5c}^{4+}$ (subscript indicates the coordination number of the cus cation by oxygen ions), while the 2209-cm^{-1} peak

due to the Ti$_{4c}^{4+}\cdots$ CO complex.

According to Busca *et al.*[3], the CO stretching mode for Ti$^{3+}\cdots$ CO species should appear at 2110 cm^{-1}. Even though it is not evident from Figure 2(b), we could observe a distinct band at 2130 cm^{-1} after the H$_2$ treatment of TiO$_2$ at 773 K for 1 min. The peak at ~ 2130 cm^{-1} is believed to arise from a Ti$_{5c}^{3+}\cdots$ CO species. Nonetheless, we insist that the present carbonyl band assignment is in better agreement with Busca *et al.* and Bolis *et al.* As referred already, Busca *et al.*[3] have shown that both 5- and 4-coordinated Ti^{4+} cations are present at the anatase surface. More recently, Bolis *et al.*[10] reported that the band at ~ 2208 cm^{-1} appears after pretreatment around 540 K, and then to increase steadily up to 900 K. We may certainly expect that 4-coordinated Ti^{4+} ions are more favorable at higher thermal treatment.

Finally we will mention briefly about the formation of surface carbon dioxide and carbonate species. When 10 Torr of CO was exposed to an oxidized sample, an asymmetric peak centered at ~ 2352 cm^{-1} was also observed. This species is supposed to be formed by the reaction of CO with the "excess" oxygen of TiO$_2$. On the reduced TiO$_2$ sample, no surface CO$_2$ species was observed. Bands due to carbonate and bicarbonate species appeared only for the oxidized sample (at ~ 1580, 1450, and ~ 1320 cm^{-1}). This observation is also consonant with our conclusion that the adsorption (and subsequent reaction) site of CO is the Ti^{4+} ion.

In summary, we have applied FT-IR spectroscopy to the characterization of titania surface. The bands due to surface OH groups were observed to be more intense in the reduced titania than in the oxidized titania. The IR spectra of CO adsorbed on titania exhibited two C-O stretching bands, namely at 2187 and 2209 cm^{-1}. The intensities were stronger in the oxidized titania. The 2187 cm^{-1} peak was attributed to CO coordinated to Ti$_{5c}^{4+}$, while the 2209 cm^{-1}-peak due to the Ti$_{4c}^{4+}$.... CO complex.

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^{13}C NMR Studies of the Chelate Ring Opening–Closing Process in (Nitrilotriacetato)vanadate(V)dioxovandate(V) Ion

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Activation parameters of the exchange between two types of glycinate groups in (nitrilotriacetato)dioxovanadate(V) ion, $[VO_2(NTA)]^{2-}$, have been determined as the results of ^{13}C NMR measurements over a range of temperatures between 277 and 306 °K. The exchange mechanism is proposed on the basis of the chelate ring opening–closing process, assuming rupture of the metal–oxygen (glycinate) bond *trans* to V = O bond to give a five–coordinated intermediate.

Introduction

Vanadium is widely recognized as a biologically important element.[1,2] The first two naturally occurring vanadium–proteins, V(V)–bromoperoxidase[3,4] and V–nitrogenase,[5] have been discovered recently.

The chemistry of vanadium(V) in aqueous solution is very complex, with the formation of various oligomeric forms as a function both of pH and of concentration.[6] Vanadium(V) forms stable complexes with a few ligands such as oxalate,[7-10] ethylenediaminetetraacetate (EDTA),[11,12] etc. The equilibrium and kinetic studies of some V(V)–aminopolycarboxylate complexes are reported.[13-19] The rarity of vanadium(V) complexes is mainly due to its strong oxidizing power, with most ligands being oxidized by the metal center.

NMR spectroscopy has been used extensively in the study of certain types of rapid equilibria. These must be processes involving the exchange of nuclei between different magnetic sites with first order rate constants falling in the range of approximately 1 to 10^3s, in the temperature range (103 to 473 °K) available within the probe of spectrometers. The associated free energies of activation for these processes may therefore range from 5 to 25 kcal/mol, and most of the studies which have been made deal with examples of two

general types of unimolecular processes.[20,21]

The first type involves changes of molecular geometry without major changes in bonding while the second type involves rapid bond reorganization in so–called fluxional molecules. The first type of process is for the most part restricted to conformational changes in organic molecules associated with rotation about single and double bonds, inversion of the conformation of cyclic compounds and of the configuration of certain tricovalent atoms. The fluxional molecules have been particularly widely recognized in inorganic chemistry and organometallic chemistry, in addition quite a large number of organic compounds undergo electrocyclic bond reorganizations which are sufficiently fast to be studied by NMR lineshape methods.

In the previous study[22] we studied the solution structure of V(V)–nitrilotriacetate (NTA) complex ion, $[VO_2(NTA)]^{2-}$, by ^{13}C NMR spectroscopy. The glycinates in the complex ion fall into two groups depending on whether or not they are *trans* to V = O bond but showed averaged signal at ambient temperature, indicating the occurrence of rapid exchange between two types of glycinate groups on NMR time scale. In this paper we have studied the exchange between two types of glycinate groups in (nitrilotriacetato)dioxovanadate(V) ion, $[VO_2(NTA)]^{2-}$. From the ^{13}C NMR spectra over a range of temperatures we have obtained the kinetic data for the exchange by the total lineshape method.[23] And we have cal-

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