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IDENTIFICATION OF DIFFERENT HYDROGEN-REDUCED TITANIA CRYSTALLOGRAPHIC FORMS BY ^{1}H NMR SPECTROSCOPY

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^{1}H NMR spectra are presented as a function of temperature where hydrogen associated with both crystal modifications of hydrogen-reduced titania can be resolved. In addition, further fine-structure can be resolved as a doublet on both of the two main signals. These doublets are of low intensity and may correspond to hydrogen in two different isolated and dynamically static interstitial sites in each crystal lattice.

1. Introduction and review

Titania is of great interest as it exhibits the Strong Metal Support Interaction (SMSI) effect when group VIII metals are dispersed on it and is reduced with hydrogen at elevated temperatures [1]. This study attempts to explain the ^{1}H NMR observations of hydrogen-reduced titania. Titania has two non-cubic crystallographic forms, anatase and rutile [2,3]. The titanium lattice is identical in both crystallographic forms, the difference arising from the arrangement of the oxygen ions [2,3]. Their tetragonal unit cells have cell dimensions $c \neq a = b$ [2,3].

Munoz et al. [4] and Conessa et al. [5,6] have investigated hydrogen-reduced Rh/TiO_2 by NMR, ESR and other analytical techniques. In their investigations, they claim that the SMSI effect arises from the following sequence of events: (a) oxygen vacancies are caused by hydrogen-reduction, the charge being balanced by Ti^{3+}, which produces a characteristic ESR signal; (b) at higher temperatures, atomic hydrogen forms a $(TiH)^{3+}$ species, this being diamagnetic and provides no ESR signal; (c) $(TiH)O_x$ species migrate and encapsulate the dispersed metal particles. If such a mechanism is appropriate for the description of the formation of the SMSI state, then such parameters as the quantity of hydrogen adsorbed in the oxide lattice and its diffusion rate is of extreme importance. Lambert et al. have also investigated Ni/TiO_2 and Pt/TiO_2 catalysts and claim that there are three distinguishable types of hydrogen present on Ni/TiO_2 [7].

In an earlier study, Jonsen investigated the ^{1}H NMR (100 MHz) spectroscopy of titania, hydrogen-reduced at 523 and 773 K [8]. The two samples gave similar series of spectra as a function of temperature but with a shift of temperature scale. This implied that the hydrogen species in the two titania samples were closely similar but that the higher hydrogen-reduction temperature increased the dynamic exchange rates. Gajardo et al. have studied titania by ^{1}H NMR under 3 and 510 Torr of hydrogen [9]. The ^{1}H NMR spectra they obtained are broad and featureless and appear identical to each other and are very different to those presented here.

2. Experimental

2.1. PREPARATION OF THE HYDROGEN-REDUCED TITANIA

Degussa P25 TiO_2 was reduced in flowing hydrogen at 773 K for 2 hrs. The sample was sealed in a 5 mm OD glass tube under 50 Torr of hydrogen (without exposure to air) immediately following reduction.

2.2. VARIABLE-TEMPERATURE ^{1}H NMR SPECTROSCOPY

The ^{1}H NMR spectra were obtained on a Bruker MSL 300 NMR spectrometer. The standard 300 MHz 5 mm ID Bruker high-power proton probe was used. 90° pulse times of 2.5 μs with 200 W of radio frequency power were achieved and the deadtime was determined to be ca. 6 μs. Temperature control was achieved with the Bruker BVT 1000 temperature controller, the accuracy of the temperature control is ± 1 K. The spectra are the result of sixty four acquisitions with full quadrature phase detection and with a spectral width of 100 kHz. Recycle delay times used were of 10 s duration. The applied magnetic field was shimmed to 15 Hz (full width at half-height of the ^{1}H NMR resonances from a static sample of 3-(Trimethylsilyl)-1-propane sulphonic acid, sodium salt and the residual protonated component of the D_2O solvent) over the sample area.

3. Results

Figure 1 depicts the single pulse excitation ^{1}H NMR spectra of the hydrogen-reduced titania recorded at temperatures from $T = 250$ to 385 K. The spectra are similar to those obtained from the same sample at 100 MHz in the previous study [8]. However, the greater dispersion of chemical shifts obtained at the higher B_0 field, leads to greater resolution of the fine structure. The linewidths indicate that the residual broadening is not dominated by homonuclear ^{1}H dipolar coupling. This is in agreement with ^{1}H multipulse NMR studies performed elsewhere [10].

The ^{1}H NMR spectra at $T = 250$ K consist of three sharp lines superimposed on a broad base. As the sample temperature is raised, the broad signal narrows. At 280 K, another sharp peak appears and is fully developed by $T = 295$ K. This

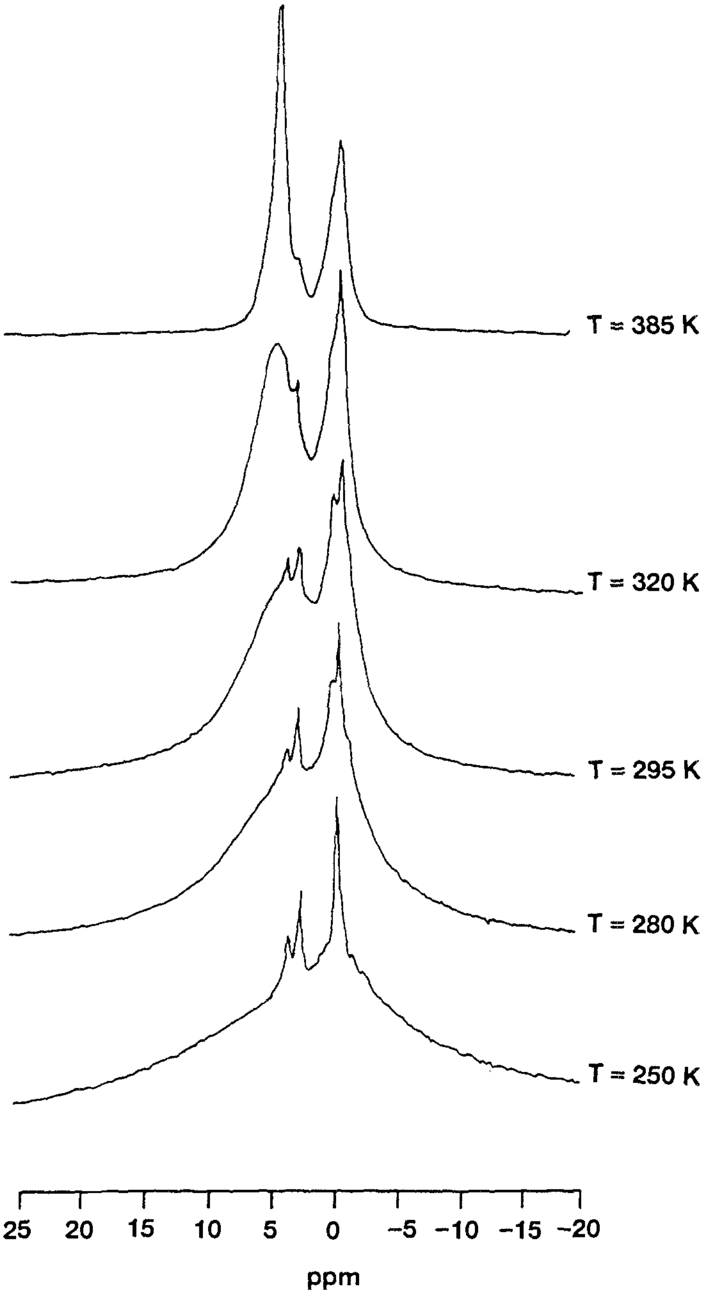

Fig. 1. ^{1}H NMR spectra recorded between $T = 250$ K and $T = 385$ K at 300 MHz. The depicted spectral widths are expanded from the original data sets. Peak heights (not areas) are normalised.

fourth sharp peak then disappears and the sharp feature to high frequency appears to begin to lose intensity and has disappeared at $T = 320$ K. The broad resonance continues to narrow into two resonances with a sharp component on each of the two resonances into ca. 73 : 27 doublet (high frequency : low frequency). At $T = 385$ K, there is a sharp component on the side of the high frequency signal and a sharp component superimposed on the low frequency resonance.

4. Discussion

The change in the appearance of the ^{1}H NMR spectra in fig. 1 as a function of temperature indicates the extent of the dynamics occurring with the hydrogen species in this system. The ca. 73 : 27 doublet components observed at 385 K are assigned to hydrogen associated with the two crystallographic forms, anatase and rutile. The ratio of these two crystallographic forms was determined by XRD on the starting material as 75 : 25 (anatase : rutile). On the same basis, it is suggested that the six components observed at $T = 295$ K (two broad signals and four sharp peaks) correspond to three hydrogen species on each crystallographic form.

The quantity of hydrogen present as the sharp components is very small when compared to the amount of hydrogen responsible for the main resonances. The narrow linewidth of the low intensity components implies that these hydrogen species are magnetically and dynamically isolated. A possibility is that these sharp components correspond to hydrogen situated in dynamically static and isolated interstitial sites within the oxide lattice, two such interstitial sites on each crystallographic form. The possibility of organic impurities with two labile proton species being present is thought unlikely.

The broad resonances, probably involving hydroxyl protons and labile interstitial protons (surface and/or bulk) for both crystallographic modifications, experience extensive dynamic averaging. The correlation time, τ_c, required to average the lines must be greater than the inverse linewidth, $\Delta\omega^{-1}$. Therefore, the timescale required to average the linewidth for the titania is $\tau_c \geqslant 10^{-4}$ s. At most temperatures, the rutile resonance is narrower than the anatase resonance. The broader anatase ^{1}H NMR signal narrows with a simultaneous shift to high frequency as the temperature (and the pressure) is increased. The sharp resonances seem to disappear as the temperature is increased. However, there is evidence from the high temperature spectra and other observations [11] that these resonances may still exist as separate signals at high temperatures but the chemical shift differences between them and the dominant resonances is less than the spectral resolution. Shoulders for both the sharp resonances can be seen at the higher temperatures. It is possible, therefore, that these sharp signals arise from hydrogen species which are not in rapid dynamic exchange with each other or with the main signal.

A more detailed study of hydrogen-reduced titania and Ru/TiO_2 is currently being pursued [11].

5. Conclusion

The use of ^{1}H NMR spectroscopy to distinguish the two crystallographic forms of a hydrogen-reduced titania sample has been successfully demonstrated. In addition, two low-intensity sharp resonances superimposed on each of the signals from rutile and anastase are assigned to two isolated, dynamically static sites. The dominant resonances are shown to experience extensive dynamic processes on the NMR timescale. These dynamic processes are observed to be in the line-narrowing limit above room temperature with the sample studied here ($\tau_c \geqslant 10^{-4}$ s). The residual line width at room temperature does not arise from homonuclear ^{1}H dipolar coupling [10]. This investigation emphasizes the use of variable-temperature ^{1}H NMR to study solid nonstoichiometric binary metal-oxides, especially in "high-resolution" obtained from a highly shimmed external magnetic field. It also demonstrates the value of using higher values of B_0.

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