

Probing TiO₂ Surface Defect Sites with a Metal Carbonyl Cluster: Characterization by EPR, IR, and EXAFS Spectroscopies

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Introduction

We report a novel approach to the characterization of defect sites on metal oxide surfaces, using a metal carbonyl as a probe molecule. We demonstrate the method with TiO₂, because this oxide has been widely investigated as a photocatalyst, catalyst, and support, and because its unique reactivity is associated in part with its surface defect sites.

Our goals were to investigate the interactions of small, structurally well-defined metal carbonyl clusters with TiO₂ incorporating surface defect sites. Defects on TiO₂ have been investigated with a number of techniques, including EPR spectroscopy, which we have used in the present work. Among the best-defined metal-containing species that have been formed on oxide supports are rhenium carbonyls, and consequently we used H₃Re₃(CO)₁₂ as a probe molecule. Our specific goal was to characterize the species formed from H₃Re₃(CO)₁₂ on TiO₂, especially at the Ti³⁺ surface defect sites, and determine the chemistry of the reactions of the probe molecule with the surface sites.

Materials and Methods

The syntheses and handling were performed with exclusion of air and moisture. The defective TiO₂ was prepared by treatment of anatase powder prepared by a sol-gel procedure from titanium(IV) isopropoxide under vacuum at 450°C. The TiO₂-supported samples containing trinuclear rhenium carbonyls, containing 1 wt% Re, were prepared by bringing H₃Re₃(CO)₁₂ in a slurry with *n*-pentane in contact with defective TiO₂ according to a method used previously.² The supported samples were characterized by IR, EPR, and EXAFS spectroscopies.

Results and Discussion

The EPR spectra of the defective TiO₂ support show that the number of oxygen vacancy sites (Ti³⁺) as well as O₂⁻ and O⁻ (formed by lattice oxygen removal) were created by treatment under vacuum. IR data confirm these results, showing that the intensity of the band characterizing Ti³⁺-bonded OH species ($\nu_{\text{OH}} = 3717 \text{ cm}^{-1}$) increased simultaneously with a decrease in the number of Ti⁴⁺-bonded OH groups and bridging OH groups ($\nu_{\text{OH}} = 3671$ and 3640 cm^{-1} , respectively) (Fig. 1a,b).^{3,4} After adsorption of H₃Re₃(CO)₁₂, a decrease in intensity of the IR peak representing the Ti³⁺-bonded OH groups was observed, with a corresponding increase in intensity of the IR peak representing bridging OH groups, as shown in Fig. 1b,c. Thus, we infer that the OH groups at surface defect sites (Ti³⁺) were the sites for adsorption of the H₃Re₃(CO)₁₂ and formed bridging OH species ($\nu_{\text{OH}} = 3640 \text{ cm}^{-1}$). The EPR results characterizing the sample after adsorption of H₃Re₃(CO)₁₂ show that no paramagnetic species (Ti³⁺, O₂⁻, O⁻) were present in detectable quantities. Combined with the IR results, these data show that the surface-defect oxygen-vacancy sites (Ti³⁺) were fully healed by protonation.

EXAFS data characterizing the clusters on the support after adsorption indicated a Re-Re contribution at 2.97 Å, indicative of deprotonated H₃Re₃(CO)₁₂.⁵ The Re-Re coordination number remained essentially unchanged and approximately equal to 2, consistent with maintenance of the triangular Re₃ cluster frame. Thus, we infer that the protons were supplied to the defect sites on TiO₂ by the H₃Re₃(CO)₁₂. Hence, we infer that the surface reaction with the rhenium carbonyl clusters transformed individual Ti³⁺-bonded OH groups and O⁻ sites into bridging OH sites, simultaneous with the oxidation of Ti³⁺ to Ti⁴⁺ species. The IR data further show that this transformation converted O₂⁻ species into H₂O₂, characterized in the resultant IR spectrum by $\nu_{\text{OH}} = 3610 \text{ cm}^{-1}$.

In summary, rhenium carbonyl clusters are informative probe molecules characterizing the surface species on TiO₂, and identification of the surface species formed in the reaction of the clusters with the TiO₂ surface allows elucidation of the details of the chemistry involving the surface OH groups and defect sites which is important for understanding in catalyst working.

Significance

In this work the knowledge gained from combining several spectroscopic techniques is used to obtain a better understanding of surface defect sites and OH groups on TiO₂ by using an acidic organometallic compound as a probe molecule

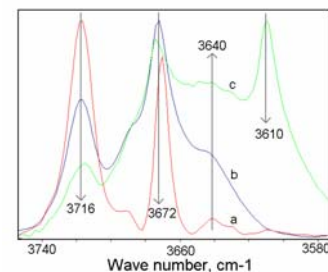


Figure 1. IR spectra in the O-H stretching region characterizing (a) TiO₂, (b) defective TiO₂, and (c) species formed by chemisorption of H₃Re₃(CO)₁₂ on defective TiO₂

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