Partial Oxidation of Alcohols on TiO_2(110) and $(WO_3)_3/TiO_2$(110) Model Catalysts

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Introduction

Monodispersed clusters with well-defined structure provide an excellent platform for model catalytic studies. Ultimately, they can provide detailed understanding of the site-specific reactivity and yield structure-reactivity relationships that cannot be obtained otherwise. Our work in this area focuses on the catalytic reactions of alcohols on rutile TiO_2(110) and monodispersed cyclic $(WO_3)_3$ clusters supported on TiO_2(110).

Materials and Methods

The experiments were carried out in molecular beam scattering and scanning probe ultra-high vacuum (UHV) systems. A clean rutile TiO_2(110) was prepared by sputtering and annealing in UHV. The $(WO_3)_3$ clusters were prepared using direct evaporation of solid WO_3 and characterized using scanning tunneling microscopy, X-ray photoelectron spectroscopy, and infrared reflection absorption spectroscopy [1]. The products of alcohol dehydration, dehydrogenation, and condensation were analyzed using temperature programmed desorption (TPD). All calculations of the reaction mechanisms employed Density Functional Theory (DFT) with a gradient corrected functional for exchange and correlation.

Results and Discussion

On TiO_2(110), two distinct dehydration channels, one related to reactions on the Ti^{4+} rows and the other on oxygen vacancy sites, were observed [2]. For the $(WO_3)_3/TiO_2$(110) model catalyst, we find a dramatic lowering of the alcohol dehydration barrier as compared to bare TiO_2(110) [3]. The comparison of all C1 to C4 aliphatic alcohols shows that all alcohols readily react with $(WO_3)_3$ clusters by heterolytic cleavage of the RO-H bond to give alkoxy (RO-) bound to W(VI) centers and a proton (H^+) attached to terminal oxygen atom of a tungstyl group (W=O). Two protons adsorbed on the cluster readily react with the doubly-bonded oxygen to from a water molecule which can desorb at 200-300 K. The alkoxy undergoes decomposition at higher temperatures into corresponding alkene, aldehyde, and ether. The trends observed for the alcohol dehydration, dehydrogenation, and condensation barriers for primary, secondary, and tertiary alcohols on $(WO_3)_3$ are determined from TPD (Figure 1) and used to infer the details of the reaction mechanism. The quantitative correlation between the coverage of $(WO_3)_3$ clusters and the product yield indicates that the W=O groups are the primary reaction sites. DFT theory provides reaction mechanisms for all three channels demonstrating that they can occur on W(VI) Lewis acid sites with energy barriers of 30-40 kcal/mol, with dehydration being favored over the others.

Significance

Our results show that the $(WO_3)_3$ clusters provide an extremely efficient dehydration reaction channel for alcohols, which utilizes both strong Lewis acid W(VI) sites and doubly-bonded oxygen tungstyl (W=O) groups. For this specific reaction, the activation energy for the dehydration is practically unaffected by the cluster proximity and/or binding to TiO_2(110). Our results are particularly interesting in that the dominant Lewis acid-based activity of the $(WO_3)_3$ cluster with no support effect contrasts strikingly with the Bronsted acid-based activity of most high surface area WO_x-based supported catalysts which are believed to be strongly affected by the support oxide.

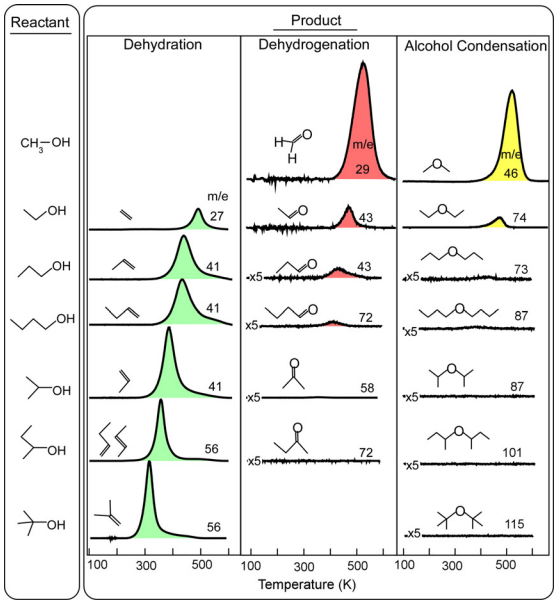

Figure 1. TPD spectra of alkenes, aldehydes, and dialkyl ethers obtained as a result of dehydration, dehydrogenation, and alcohol condensation, respectively, on $(WO_3)_3$ clusters on TiO_2(110).

References

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