

Tantalum Clusters Supported on Silica-Alumina and on γ -Al₂O₃: Influence of Support Composition and Chemistry on Cluster Structure

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Introduction

Reports of clusters of early transition metals on supports are still rare, although there is an extensive literature of the synthesis and chemistry of such clusters in solution [1]. Our earlier work demonstrated that tantalum clusters could be prepared on SiO₂ supports by treatment of the physisorbed precursor pentabenzyltantalum in H₂, and the materials catalyze the conversion of alkanes, including ethane, albeit only at low rates [2]. To understand the surface chemistry of these catalysts better, we have now extended the work to a family of supports with systematically varied compositions, including silica-aluminas of various compositions and γ -Al₂O₃. The surface species have been characterized by infrared (IR) spectroscopy, extended X-ray absorption fine structure (EXAFS) spectroscopy, and transmission electron microscopy, and the products evolved during the formation of tantalum clusters were monitored by mass spectrometry. The data demonstrate a significant effect of the support surface composition on the conversion of physisorbed pentabenzyltantalum, leading to the formation of clusters

Materials and Methods

γ -Al₂O₃ (Degussa) was used as received. Silica-alumina samples were synthesized by a reported procedure [3]. Before addition of the tantalum-containing precursor to any of the supports to prepare the supported tantalum samples, each of the supports was partially dehydroxylated by treatment *in vacuo* at 773 K for 20 h. Addition of pentabenzyltantalum to each of the supports was done as before [3]. IR experiments were done with samples in a cell that served as a flow reactor; it had CaF₂ windows and was mounted in a Bruker IFS 66v spectrometer. X-ray absorption spectra of the samples were recorded at beam line X-18B of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory and at beam line 3-2 of the Stanford Synchrotron Radiation Laboratory (SSRL). Details of the spectroscopy experiments and data analysis are described elsewhere [3].

Results and Discussion

The decomposition of physisorbed pentabenzyltantalum on a series of supports ranging from SiO₂ to silica-aluminas with various Si:Al ratios to γ -Al₂O₃ was investigated. A qualitative result from IR spectroscopy of the solids and analysis by gas chromatography and mass spectrometry of the gas-phase products resulting from the treatments in H₂ demonstrate a significant support composition effect on the tantalum chemistry. On SiO₂, the coordination of surface bridging oxygen atoms to the tantalum precursors facilitated a reaction, possibly proceeding via free-radicals, leading to the formation of mainly bibenzyl, with a low yield of toluene—in contrast to the intermolecular hydrogen transfer reactions of pentabenzyltantalum that the literature indicates to occur in C₆D₆ [4], whereby toluene is the main product. The incorporation and increasing fraction of Al in the support resulted in an increased electron-donor tendency of support surface oxygen atoms, as a result of which the Ta–C bond strength

increased and the activation of C–C bonds linking the carbon atoms of methyl groups to the aromatics rings was facilitated; further, Brønsted acid sites may also have been involved in the C–C bond breaking. Products such as diphenyl methane, triphenyl methane, benzene, ethylene, methane, and C₄ hydrocarbons were observed with the Al-containing supports. EXAFS and XANES data indicated that very small cationic tantalum clusters (Ta–Ta coordination number approximately 3) were prepared by treating the physisorbed pentabenzyltantalum at 523 K for 24 h in flowing H₂. Figure 1 gives typical EXAFS results characterizing the tantalum clusters, which are inferred to have been anchored to the support via bridging oxygen atoms. The significant contrast in amplitude between k^1 - and k^3 -weighted Ta–Ta contributions confirms that a high-Z backscatterer (identified as Ta) was necessary to fit the EXAFS data satisfactorily. The tantalum clusters were also observed by STEM (images not shown). The influence of the support surface composition on the structure of the supported clusters (e.g., the Ta–Ta bond distance and coordination sphere around tantalum) was found to be slight. The Ta L_{III} edge data characterizing the supported tantalum clusters show that the edge energy decreased gradually as the support was changed from SiO₂ to silica-aluminas to γ -Al₂O₃; the difference in the values characterizing the clusters on SiO₂ and on γ -Al₂O₃ was approximately 0.4 eV, corresponding to a range of approximately 2.6–3.0 in the formal Ta oxidation state. The results indicate the different electron-donor abilities of the supports affect the chemistry of the tantalum clusters, and, by inference, their catalytic properties.

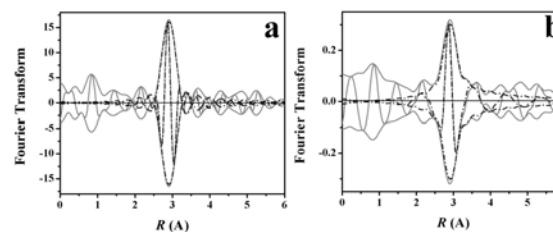


Figure 1. a) k^3 - and b) k^1 -Weighted phase- and amplitude-corrected Fourier transforms of the Ta–Ta contribution to the EXAFS spectra characterizing tantalum clusters supported on silica-alumina with a Si:Al atomic ratio of 30.

Significance

Pentabenzyl tantalum was used as a precursor to form small cationic tantalum clusters on a family of supports including γ -Al₂O₃ and silica-aluminas. The support composition had little influence on the cluster structure, but it influenced the charge on the tantalum and offers the opportunity to influence the catalytic properties for alkane conversion.

References

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