

A Combined Experimental and Theoretical Investigation of the Structure and Reactivity of $\text{VO}_x/\text{TiO}_2/\text{SiO}_2$

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Introduction

Supported vanadium oxides have been the subject of much research for the oxidation of alcohols to aldehydes. Recent studies have shown that the specific activity of vanadium in such catalysts is a strong function of the support composition. For example, in methanol oxidation to formaldehyde, isolated vanadate groups supported on titania exhibit nearly 10^3 times the activity when supported on silica [1, 2]. The aim of the present study was to examine the structure and performance of catalysts comprised of a high surface area, mesoporous silica support containing a fractional monolayer of titania (up to one monolayer, 4 Ti nm^{-2}), and isolated vanadate sites ($< 0.7 \text{ V nm}^{-2}$). In this investigation, experimental and theoretical techniques have been applied to study the role of Ti in $\text{VO}_x/\text{TiO}_2/\text{SiO}_2$ catalysts and the ability of the oxide to form and stabilize oxygen vacancies.

Materials and Methods

MCM-48, the mesoporous support used for these studies, was prepared following the procedures reported in Ref. [1]. TiO_2 and isolated vanadate species were grafted onto the MCM-48 support in an inert atmosphere using a solution of $\text{Ti}(\text{O}^i\text{PR})_4$ and $\text{OV}(\text{O}^i\text{PR})_3$ (Sigma-Aldrich) in anhydrous toluene, respectively. The BET surface area of all samples was determined using N_2 adsorption (Autosorb, Quantachrome). The structural characterization of the catalysts was performed with X-ray diffraction (XRD), X-ray absorption spectroscopy (XAS), infrared (IR) and Raman spectroscopy, ^{51}V nuclear magnetic resonance (NMR) and electron paramagnetic resonance (EPR). Temperature programmed desorption (TPD) and temperature programmed reaction (TPR_x) measurements were performed on the catalyst to determine the kinetic data for the reaction.

Density functional theory (DFT) calculations were performed using cluster models of the active site, in a manner similar to that used in our earlier studies of VO_x/SiO_2 [3] and VO_x/TiO_2 [4]. Geometry optimizations and frequency calculations were carried out using the B3LYP functional and the 6-31G* basis set within Gaussian 03. The transition metals V and Ti were treated using the LANL2DZ effective core potential. Final energy calculations were performed using the expanded 6-311++G** basis sets. The growing string method [5] was used to determine all transition state estimates, which were later optimized within Gaussian 03.

Results and Discussion

The surface area of the MCM-48 support was determined to be $1550 \text{ m}^2 \text{ g}^{-1}$ with a hydroxyl concentration of 1.7 OH nm^{-2} . Three samples were synthesized with 0.7 V nm^{-2} and Ti surface concentrations of 0.2, 0.9, and 1.4 Ti nm^{-2} . In addition, a reference sample without Ti was synthesized for comparison with literature. The Raman spectroscopy indicated that Ti and V are atomically dispersed with no evidence of V_2O_5 or anatase on the sample. The results

of XANES characterization showed that V is predominantly in the 5+ oxidation state and analysis of the EXAFS signal indicated that the V atoms were present as isolated vanadate species containing one $\text{V}=\text{O}$ and three V-O-support bonds. On average, one of these bonds is a V-O-Ti bond, for Ti loadings of 0.9 and 1.4 Ti nm^{-2} . EPR spectroscopy revealed the presence of Ti^{3+} on silica supported Ti samples, suggesting the presence of surface O-vacancies.

TPR_x measurements indicated a decrease in the temperature for the onset of formaldehyde from 700 K to 580 K with the addition of small quantities of Ti. The activation energy for methanol oxidation decreases from 23 kcal mol^{-1} for isolated V on SiO_2 to 18 kcal mol^{-1} for submonolayer coverages of Ti. The reaction rate increased one to two orders of magnitude over that for V/SiO_2 , depending on the Ti surface coverage, although the rates were still slower than that for isolated vanadate species supported on TiO_2 .

A theoretical model of the active site, similar to previous studies [3, 4] was used to determine the apparent activation energy and first-order rate constant for active sites with 0 to 3 V-O-Ti support bonds. These two parameters were determined for active sites with and without an O-vacancy. Sites containing an O-vacancy were shown to be much more active than sites without one, similar to previous results on VO_x/TiO_2 [4]. The distribution of active sites on the surface was determined as a function of the Ti support coverage and a Boltzmann distribution describing the energetic preference of V to have 3 V-O-Ti support bonds. The theoretically determined average number of V-O-Ti supports is one, consistent with experiment. Finally, the number of sites with a defect was determined by assuming an equilibrium number of surface defect sites. Using the distribution of active sites, the theoretical reaction rates were calculated as a function of Ti surface coverage for an assumed percentage of surface O-vacancies (1-10%), and were found to be in good agreement with experiment. These results indicate that O-vacancies in the support play an important role when TiO_x is present. Experiments are currently being carried out based on reduction-oxidation measurements and EPR spectroscopy to study the formation and loss of O-vacancies from the dispersed TiO_x layer.

Significance

The results of this study demonstrate that very large enhancements in the rate of methanol oxidation to formaldehyde on isolated vanadate species can be achieved by dispersing these species on silica containing a submonolayer dispersion of titania. Theoretical analysis suggests that the vanadate species bond preferentially with multiple V-O-Ti bonds and that the most active form of the supported vanadate species have an oxygen vacancy located adjacent to the vanadate species.

References

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