

Conversion of Methanol over Solid Acidic WO₃/ZrO₂ Catalysts: Molecular/Electronic Structure-Activity Relationships

E.L. Ross¹, T. Kim¹, W.V. Knowles², M.S. Wong² and J.E. Wachs^{1*}
¹*Operando* Molecular Spectroscopy & Catalysis Laboratory,

Department of Chemical Engineering, Lehigh University, Bethlehem, PA 18015 USA

²Departments of Biological & Chemical Engineering and Chemistry,

Rice University, Houston, TX, USA

*lew0@lehigh.edu

Introduction

Several different models have been proposed in the recent catalysis literature to explain the nature of the acidic catalytic active sites in supported tungsten oxide catalysts. The molecular level relationships between the different tungsten oxide structures present in these catalytic materials and their surface acidic characteristics, however, are not fully understood at present because of conflicting tungsten oxide structural assignments in the literature. In order to address these unresolved issues and determine the nature of the surface acidic sites present in both model supported WO₃ catalysts as well as the super-active WO₃/ZrO₂ catalysts, the relationships between the tungsten oxide molecular and electronic structures and the corresponding acidic catalytic activity for methanol dehydration to dimethyl ether were investigated.

Materials and Methods

Both “model” well-defined supported WO₃/ZrO₂ and calcined supported WO₃/ZrO(OH)₂ catalysts were synthesized by incipient wetness impregnation of preformed ZrO₂ and ZrO(OH)₂, respectively, and calcined in the 450-900 °C range. The molecular nature of the different supported tungsten oxide phases, two-dimensional surface and bulk crystalline phases was determined with *in situ* Raman spectroscopy because of the ability of Raman to readily discriminate among the different tungsten oxide structures. The corresponding electronic structures of the different tungsten oxide species were determined with *in situ* UV-vis DRS spectroscopy where the UV-vis DRS spectra were converted to edge energy, Eg, values. The catalytic surface chemistry of the supported tungsten oxide phases was chemically probed both by CH₃OH-Temperature Programmed Surface Reaction (TPSR) spectroscopy and steady-state CH₃OH dehydration studies. Methanol was found exclusively to dehydrate to dimethyl ether (DME) with 100% selectivity over the acidic supported WO₃ catalysts. Fundamental information about the catalytic dehydration of CH₃OH to DME (k_{RDS} , K_{ADS} , TOF, reaction order and product selectivity) was obtained for the different catalysts from both the CH₃OH-TPSR and steady-state CH₃OH dehydration studies.

Results and Discussion

Monolayer surface WO_x coverage was determined to occur at 4.5-5 W/nm² for both sets of supported WO₃/ZrO₂ catalysts from Raman and XPS surface analysis. Although the UV-vis DRS Eg values are essentially the same below monolayer surface coverage, the corresponding Raman signals are not identical. The “model” WO₃/ZrO₂ catalysts exhibit the conventional dehydrated surface WO_x band at 1000-1020 cm⁻¹, but the WO₃/ZrO(OH)₂ catalysts possess this band as well as several others in the ~820-920 cm⁻¹ range. The additional Raman bands present

in the WO₃/ZrO(OH)₂ catalysts arise from highly distorted WO₃ nanoparticles (NPs). This suggests that the ZrO(OH)₂ precursor interacts with the WO₃ component during the synthesis and retards its crystallization. Above monolayer coverage, WO₃ NPs are present for both catalytic systems, but the WO₃ NPs present are not the same. For the “model” supported WO₃/ZrO₂ catalysts, the WO₃ NPs exhibit a Raman band at ~805 cm⁻¹ characteristic of bulk-like WO₃. For the supported WO₃/ZrO(OH)₂ catalysts, the Raman bands of the WO₃ NPs are very broad and shifted to higher wavenumber values, 820-850 cm⁻¹, reflecting the distortion of these WO₃ NPs. Further, the corresponding UV-vis DRS Eg values are higher for the WO₃/ZrO(OH)₂ catalysts than the WO₃/ZrO₂ catalysts above monolayer coverage, which reflects the smaller WO₃ NP domain size of the WO₃/ZrO(OH)₂ catalysts at the same surface W/nm² density. Thus, the nature of the tungsten oxide species present in the supported WO₃/ZrO(OH)₂ catalysts are very different than found in conventional “model” supported WO₃ catalysts because of the interaction of the ZrO(OH)₂ precursor with the tungsten oxide component during calcination.

The surface chemistry of the zirconia supported tungsten oxide catalysts was chemically probed with both CH₃OH-TPSR and steady-state CH₃OH dehydration to DME. The number of catalytic active sites was obtained from the CH₃OH-TPSR for the production of DME and the steady-state catalytic reaction rates were determined in a fixed-bed plug flow reactor. The catalytic TOF values for dehydration of CH₃OH to DME are significantly larger for the supported WO₃/ZrO(OH)₂ catalysts, sometimes > 10², compared to the corresponding supported WO₃/ZrO₂ catalysts at the same surface W/nm² density. This catalytic enhancement is observed at all surface W/nm² density values and exhibits a maximum in TOF at ~6 W/nm². This enhancement is related to the stabilization of the poorly ordered and distorted WO₃ NPs caused by their interaction with ZrO_x “impurities” that retard the crystallization of WO₃. Above 6 W/nm² ordered WO₃ NPs are also present and the corresponding TOF values decrease. Thus, the dramatic enhancement in surface acidity and CH₃OH dehydration to DME specific reaction rate is related to poorly ordered and distorted WO₃ NPs caused by ZrO_x impurities that are only present in the supported WO₃/ZrO(OH)₂ catalytic system. In the model supported WO₃/ZrO₂ catalyst system, the ZrO₂ support is encapsulated by the surface WO_x monolayer and can't interact with the WO₃ NPs during synthesis.

Significance

The current electronic and molecular structural information generated in this investigation are providing new insights into the nature of solid acidity for the supported WO₃/ZrO₂ catalysts that have led to the development of a new solid acidity model. The design of improved solid acid catalysts requires a fundamental molecular level understanding of the origin of the acidity.