Elucidation the Roles of CeO$_2$ for Selective Oxidation of Methanol in Supported Vanadia Catalysts

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Introduction

Supported vanadia catalysts have received much attention due to their good activity and selectivity in a number of reactions. The catalytic performance of supported vanadium oxide depends strongly on the catalyst supports [1,2]. However, the origin of support effect is still not clear. In previous research, due to the structural and chemical complexity of oxide-based heterogeneous catalysts, experimental assessment can seldom be interpreted with atomic-level precision. In this work, we prepared VO$_x$/CeO$_2$ catalysts with well-defined CeO$_2$ morphologies and exposed facets as promising model catalysts with specific care being taken in order to eliminate the effect by Na impurity [3,4]. The effects of CeO$_2$ facets on the surface structures and dispersion of VO$_x$ species and its activity in selective oxidation (ODH) of methanol were further investigated. This well-defined model catalyst system not only reduces the complexity of this class of catalyst materials to the levels addressable and controllable at the atomic level, but also directly bridges the gap with the practical catalytic materials.

Materials and Methods

CeO$_2$ supported monolayer VO$_x$ catalysts were prepared by incipient wetness impregnation methods. The nature of the VO$_x$ species, namely surface structures and dispersion, were investigated by a variety of microscopic and spectroscopic techniques including TEM, FTIR, H$_2$-TPR and Raman. The effects of exposed facets of CeO$_2$ supports on the catalytic performance of VO$_x$ catalysts were further investigated using oxidative dehydrogenation (ODH) of methanol as a probe reaction.

Results and Discussion

In the present work, CeO$_2$ supports including nanocubes (C), nanorods (R) and nanopolyhedras (PL) with dominating facets, i.e., low index (100), (110) and (111) facets, are prepared [5]. As evidenced by TEM imaging, the CeO$_2$-C is predominantly enclosed with (100) facets, CeO$_2$-R with almost equal numbers of (100) and (110) facets, while for CeO$_2$-PL (111) facets are dominant with minor quantities of (100) facets. The effect of sodium on the structure and catalytic performance of 5V-VO$_x$/CeO$_2$ for methanol ODH can be minimized if Na/V ratios are controlled at <0.25 [3]. With the safe exclusion of sodium interference, the facet effects on the structure and catalytic performance of supported vanadium oxide catalysts are investigated using oxidative dehydrogenation (ODH) of methanol as a model reaction. In the presence of mixed facets, Infrared and Raman spectroscopic measurements demonstrate that surface vanadia species preferentially deposit on the (100) facet of CeO$_2$, presumably because of its higher surface energy. At the same surface vanadium densities, VO$_x$ species on (100) facets show better dispersion, followed by (110) and (111) facets. The VO$_x$ species on CeO$_2$ nanorods with approximately equal amount of (110) and (100) facets display higher ODH activity and lower apparent reaction activation energies compared to VO$_x$ species on CeO$_2$ nanopolyhedras with dominating (111) facets and CeO$_2$ nanocubes with dominating (100) facets. The higher activity for VO$_x$/CeO$_2$(110) might be related to the more abundant oxygen vacancies present on the (110) facets, evidenced from Raman spectroscopic measurements.

Significance

In this work, we demonstrate that the well-defined VO$_x$/CeO$_2$ catalyst system not only allows atomic-level characterization of catalytically active centers, but also provides meaningful kinetic measurements, leading to better understanding of the role of the support for the important class of selective oxidation catalysts.

References