

Revealing Structure-Activity Relationships in Model Double-Supported WO₃/TiO₂/SiO₂ Solid Acid Catalysts by Atomic Scale Characterization

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Supported tungsten oxide catalysts offer a promising alternative for many practical industrial applications involving acidic catalytic reactions. In the past two decades, significant progress has been made in this field and a better understanding of these materials is now developing. However, revealing the structure-activity relationships in supported tungsten oxide catalyst systems is still a great challenge. Previous studies suggest that the catalytic performance is directly related to the charge transfer that occurs during catalytic reaction, including that (i) between the metal oxide active component and the underlying oxide support material, and (ii) between the reactant molecules and the catalytically active tungstate sites.

In order to investigate the influence of the dimension of the oxide support (in the critical 0.5-10 nm range) on the resultant catalytic properties, we have performed a fundamental systematic study on a double-supported WO₃/TiO₂/SiO₂ catalyst system [1]. In this work, a constant 5 wt% loading of WO₃ was deposited via a standard incipient-wetness impregnation technique onto a series of TiO₂/SiO₂ support materials having different TiO₂ loadings. Aberration-corrected analytical electron microscopy and a variety of optical spectroscopy techniques were then applied to characterize the structure and composition of this set of materials at the atomic scale. The catalytic performance of these materials was also assessed with methanol temperature programmed surface reaction (TPSR) spectroscopy and the steady-state methanol dehydration reaction. High resolution transmission electron microscopy (HRTEM) imaging and aberration-corrected scanning transmission electron microscopy (STEM) imaging and microanalysis were performed on a 200 kV JEOL 2200FS (S)TEM equipped with a CEOS probe corrector and an Ω -energy filter. The STEM images presented have been low-pass filtered to reduce high frequency background noise.

The microstructure and electronic structure of the TiO₂/SiO₂ support materials was studied using HRTEM imaging and UV-vis spectroscopy. It was found that the domain size of the titania species (or *nano-ligands*) dispersed on the SiO₂ surface varies with increasing TiO₂ loading from 0.4 nm isolated surface TiO₄ species, to ~1 nm polymeric surface TiO₅ species, to nm scale TiO₂ rafts, and finally to 5-9 nm anatase nanoparticles (see Table 1). This trend accordingly results in progressively more delocalization of the electron density in the TiO_x domains as revealed by a gradually decreasing UV-vis absorption edge energy. The microstructure and electronic structure of the TiO_x domains were found not to be affected by the WO₃ loading.

Aberration-corrected STEM imaging and electron energy-loss spectroscopy (EELS) analysis were applied to study the surface structure and relative distribution of all the metal oxide components in the double-supported WO₃/TiO₂/SiO₂ catalysts. High-angle annular dark-field (HAADF) STEM imaging provided direct information of the structure and distribution of the surface WO_x species, while bright-field STEM imaging was used to locate the position of crystalline TiO₂ domains. Non-crystalline TiO_x components on the specimen surface were confirmed by EELS analysis. It was found that WO_x is preferentially anchored to the TiO_x domains instead of the amorphous SiO₂ surface, presumably due to the stronger wetting interaction between the WO_x and the TiO_x species. At higher TiO₂ loadings (*i.e.* larger TiO_x domains with a more delocalized electronic structure) the WO_x tended to be atomically dispersed on the TiO_x rafts as mono-tungstate and poly-tungstate species (Fig. 1A). In contrast, at lower TiO₂ loadings (*i.e.* smaller TiO_x domains with a more localized electron density) ~1 nm WO_x clusters were found to be the dominant tungstate structure (Fig. 1B). X-ray energy dispersive spectrometry (XEDS) and EELS chemical analysis from these latter WO_x clusters always revealed the co-existence of WO_x and TiO_x, suggesting that these ~1 nm WO_x clusters are strongly associated with surface TiO_x species and could indeed even be mixed oxide clusters. A nm-scale WO_x cluster (especially when mixed with other cationic

species) has recently been found to be highly beneficial for catalyzing some acidic catalytic reactions [2]. The STEM observations are in good agreement with Raman spectroscopy results from this set of materials. Further *ex-situ* and *in-situ* analysis revealed that the structural evolution of the surface WO_x species mainly occurred during the calcination step of catalyst preparation.

The degree of electron delocalization in the TiO_x domains and the different surface WO_x structures present were both found to have a significant effect on the catalytic activity of surface acidic WO_x sites (Fig. 2). A progressively more highly localized electron density in the TiO_x domains and an increasing surface WO_x domain size anchored to the TiO_x rafts, both correlated well with increasing acidic activity of the surface WO_x species. This study clearly demonstrates that the electronic structure and catalytic activity of the active surface WO_x component can be tuned by modifying the size and nature of the underlying metal oxide nano-domain support. Furthermore, the degree of catalytic activity shows a combined dependence on the different level of charge transfer between the WO_x and TiO_x domains and the change of electronic structure in the WO_x species itself.

References:

- [1] E. I. Ross-Medgaarden *et al.*, *J. Am. Chem. Soc.* **131** (2009) 680
 [2] W. Zhou *et al.*, *Nat. Chem.* **1** (2009) 722
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Table 1. Surface TiO_2 domain size and UV-vis absorption edge energy (E_g) for the $\text{TiO}_2/\text{SiO}_2$ materials [1]

Support materials	Structure	Domain size	UV-vis E_g value (eV)
5 % $\text{TiO}_2/\text{SiO}_2$	isolated and polymeric surface TiO_x species	~0.4-1 nm	3.74
12 % $\text{TiO}_2/\text{SiO}_2$	polymeric surface TiO_5 species	~1 nm	3.43
30 % $\text{TiO}_2/\text{SiO}_2$	polymeric surface TiO_5 species and TiO_2 (A)	3-5 nm	3.32
40 % $\text{TiO}_2/\text{SiO}_2$	polymeric surface TiO_5 species and TiO_2 (A)	5-9 nm	3.18

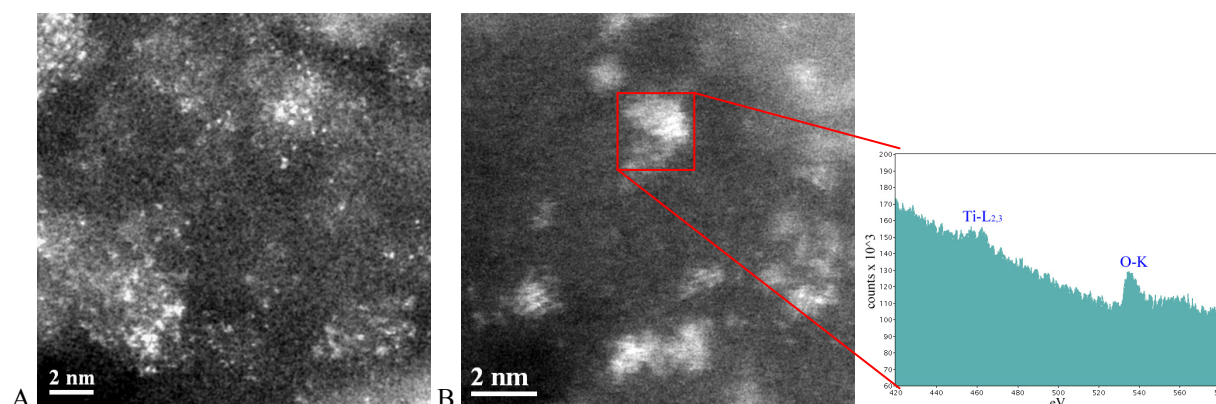


Figure 1. Representative STEM-HAADF images from (A) 5% $\text{WO}_3/30\%$ $\text{TiO}_2/\text{SiO}_2$ (B) 5% $\text{WO}_3/5\%$ $\text{TiO}_2/\text{SiO}_2$. Insert: STEM-EELS spectrum (collected from the square area in (B)) showing a weak, but distinct, Ti signal.

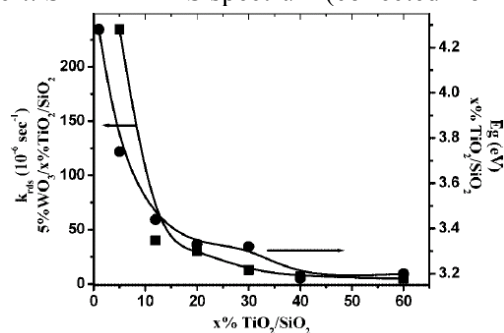


Figure 2. First-order rate constants (k_{rds}) for breaking the C-O bond of surface CH_3O^* intermediates for formation of CH_3OCH_3 over the supported 5% $\text{WO}_3/x\%$ $\text{TiO}_2/\text{SiO}_2$ catalysts as determined from methanol TPSR spectroscopy. UV-vis edge energy (E_g) as a function of TiO_2 loading is also plotted (adapted from Ref. [1]).