## Revealing Structure-Activity Relationships in Model Double-Supported WO<sub>3</sub>/TiO<sub>2</sub>/SiO<sub>2</sub> 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  $WO_3/TiO_2/SiO_2$  catalyst system [1]. In this work, a constant 5 wt% loading of  $WO_3$  was deposited via a standard incipient-wetness impregnation technique onto a series of  $TiO_2/SiO_2$  support materials having different  $TiO_2$  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  $\Omega$ -energy filter. The STEM images presented have been low-pass filtered to reduce high frequency background noise.

The microstructure and electronic structure of the  $TiO_2/SiO_2$  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 SiO<sub>2</sub> surface varies with increasing TiO<sub>2</sub> loading from 0.4 nm isolated surface TiO<sub>4</sub> species, to ~1 nm polymeric surface TiO<sub>5</sub> species, to nm scale TiO<sub>2</sub> 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<sub>x</sub> domains as revealed by a gradually decreasing UV-vis absorption edge energy. The microstructure and electronic structure of the TiO<sub>x</sub> domains were found not to be affected by the WO<sub>3</sub> 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 WO<sub>3</sub>/TiO<sub>2</sub>/SiO<sub>2</sub> catalysts. High-angle annular dark-field (HAADF) STEM imaging provided direct information of the structure and distribution of the surface WO<sub>x</sub> species, while bright-field STEM imaging was used to locate the position of crystalline TiO<sub>2</sub> domains. Non-crystalline TiO<sub>x</sub> components on the specimen surface were confirmed by EELS analysis. It was found that WO<sub>x</sub> is preferentially anchored to the TiO<sub>x</sub> domains instead of the amorphous SiO<sub>2</sub> surface, presumably due to the stronger wetting interaction between the WO<sub>x</sub> and the TiO<sub>x</sub> tended to be atomically dispersed on the TiO<sub>x</sub> rafts as mono-tungstate and poly-tungstate species (Fig. 1A). In contrast, at lower TiO<sub>2</sub> loadings (*i.e.* smaller TiO<sub>x</sub> domains with a more localized electron density) ~1 nm WO<sub>x</sub> 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<sub>x</sub> clusters always revealed the co-existence of WO<sub>x</sub> and TiO<sub>x</sub>, suggesting that these ~1 nm WO<sub>x</sub> clusters are strongly associated with surface TiO<sub>x</sub> species and could indeed even be mixed oxide clusters. A nm-scale WO<sub>x</sub> 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.

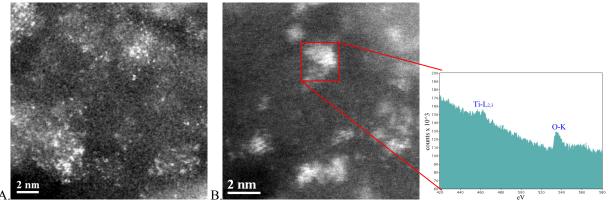
## **References:**

[1] E. I. Ross-Medgaarden et al., J. Am. Chem. Soc. 131 (2009) 680

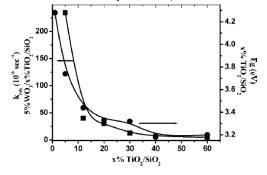
[2] W. Zhou et al., Nat. Chem. 1 (2009) 722

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Support materials	Structure	Domain size	UV-vis $E_g$ value (eV)
5 % TiO <sub>2</sub> /SiO <sub>2</sub>	isolated and polymeric surface $TiO_x$ species	~0.4-1 nm	3.74
12 % TiO <sub>2</sub> /SiO <sub>2</sub>	polymeric surface TiO <sub>5</sub> species	~1 nm	3.43
30 % TiO <sub>2</sub> /SiO <sub>2</sub>	polymeric surface $TiO_5$ species and $TiO_2$ (A)	3-5 nm	3.32
40 % TiO <sub>2</sub> /SiO <sub>2</sub>	polymeric surface $TiO_5$ species and $TiO_2$ (A)	5-9 nm	3.18



**Figure 1.** Representative STEM-HAADF images from (A) 5%WO<sub>3</sub>/30% TiO<sub>2</sub>/SiO<sub>2</sub> (B) 5%WO<sub>3</sub>/5% TiO<sub>2</sub>/SiO<sub>2</sub>. 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<sub>3</sub>O\* intermediates for formation of CH<sub>3</sub>OCH<sub>3</sub> over the supported 5% WO<sub>3</sub>/*x*% TiO<sub>2</sub>/SiO<sub>2</sub> catalysts as determined from methanol TPSR spectroscopy. UV-vis edge energy ( $E_g$ ) as a function of TiO<sub>2</sub> loading is also plotted (adapted from Ref. [1]).