

# Structure and function correlation of supported rhenium oxide catalysts for 2-butanol dehydration and ODH of ethanol

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## Introduction

Supported rhenium oxide catalysts have a wide range of catalytic applications, such as olefin metathesis, hydrosulfurization, hydrogenation and  $\text{NH}_3$ -SCR. Hence, the practical importance of rhenium oxide catalysts has resulted in extensive investigation of the surface structure of supported rhenium oxide catalysts. The molecular structure of supported rhenium oxides has been mainly derived from vibrational [1,2] and X-ray absorption spectroscopic [3] methods. These studies have concluded that surface rhenium oxide species possess monomer structures with  $\text{C}_{3v}$  symmetry, consisting of three equivalent  $\text{Re}=\text{O}$  bond and one inequivalent  $\text{Re}-\text{O}$ -support bond, and that this structure is independent of support type or Re-loading. The existence of a dimer structure is still debated although no direct evidence of  $\text{Re}-\text{O}-\text{Re}$  has been obtained in either Raman or EXAFS measurements. Furthermore, it has been reported that the activity for selective oxidation of methanol [4] or ethanol [5] does not depend on the Re-loading.

We have recently developed a synthetic approach to stabilize highly dispersed  $\text{ReO}_x$  on alumina-modified SBA-15 surface [6], which allows structure and functional characterization of the rhenia catalysts. The acidic and redox chemistry of the supported rhenium oxide catalysts were probed by 2-butanol dehydration and ethanol oxidation, respectively.

## Materials and Methods

$\text{ReO}_x/\text{AlO}_x/\text{SBA-15}$  catalysts were prepared using a serial solution ALD (atomic layer deposition) method. Firstly, a monolayer  $\text{AlO}_x/\text{SBA-15}$  catalyst was prepared by ALD using aluminum isopropoxide as precursor, and calcined at  $400^\circ\text{C}$  in flowing dry air for 1h. Then rhenium was grafted onto  $\text{AlO}_x/\text{SBA-15}$  by ALD, and the loading of rhenium oxide was varied to be  $\sim 1/4$ ,  $1/2$ ,  $3/4$  and 1 monolayer, with a monolayer catalyst corresponding to  $\sim 30\text{wt}\%$   $\text{ReO}_3$ . The catalytic activity measurements were conducted in a quartz flow reactor at atmospheric pressure. Reactants and products were analyzed by a gas chromatography (HP 5890) equipped with a HAYESEP T column and flame ionization and thermal conductivity detectors. The actual Re-content in the calcined catalysts was measured by inductively coupled plasma analysis, and the change in  $\text{ReO}_x$  domain size with Re-loading was monitored by UV-vis diffuse-reflectance spectroscopy (DRS).

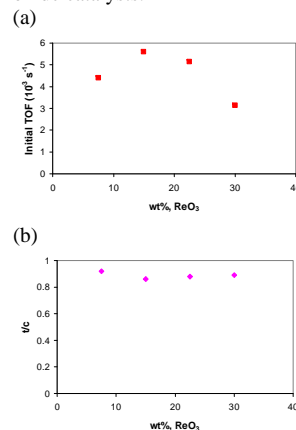
## Results and Discussion

Fig.1 shows the effects of Re loading on the activity (initial TOF) and selectivity ( $t/c$ , trans-2-to cis-2-butene ratio) in 2-butanol dehydration at  $70^\circ\text{C}$ . The TOFs were based on per Re-atom (normal). As can be seen, the optimum activity takes place at intermediate Re-loading,  $1/2$  monolayer, and the TOF decreases with further increase in Re-loading. This

suggests that the number of acid sites responsible for the 2-butanol dehydration maximized at an intermediate loading, which will be further examined by *in situ* titration with pyridine and 2,6-di-tert-butylpyridine [7]. In addition, the  $t/c$  is constant at  $\sim 0.9$  for all catalysts studied here. Besides the acidic properties, supported rhenium oxides also exhibit redox capabilities, which is being probed by the ethanol oxidation reaction over our  $\text{ReO}_x/\text{AlO}_x/\text{SBA-15}$  catalysts with different loadings. The molecular structure and domain size of surface rhenium oxide on different Re-loading catalysts, based on Raman and UV-vis DRS, respectively, will also be discussed. From this study, structure-function correlations are being established for the two types of reactions over supported rhenium oxide catalysts.

## Significance

Structure-function relationships have been investigated for novel single-site type rhenium oxide catalysts.



**Figure 1.** 2-butanol dehydration over  $\text{ReO}_x/\text{AlO}_x/\text{SBA-15}$ . (a) TOF; (b) selectivity,  $t/c$ . Reaction condition: 0.5% 2-butanol-He,  $70^\circ\text{C}$ .

## References

1. Vuurman, M. A., Stufkens, D. J., Oskam, A., Wachs, I. E., *J. Mol. Catal.* 76, 263 (1992).
2. Wachs, I.E., *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 105, 143 (1995).
3. Hardcastle, Franklin D., Wachs, Israel E., Horsley, John A., Via, Grayson H., *J. Mol. Catal.* 46, 15 (1988).
4. Wachs, I. E., Deo, G., Kim, D. S., Vuurman, M. A., Hu, H., L. Guzzi, F. Solymosi and P. Tétényi, *Stud. Surf. Sci. and Catal.* 1993, Elsevier. p. 543-557.
5. Lacheen, H.S., P.J. Cordeiro, and E. Iglesia, *J. Am. Chem. Soc.* 15082 (2006).
6. She, X., Kwak, J. H, Hu, J. Z., Wang, Y., and Peden, C. H.F., *J. Phys. Chem. B* (submitted).
7. Baertsch, Chelsey D., Komala, Kenny T., Chua, Yong-Hwee, Iglesia, Enrique, *J. Catal.* 205, 44 (2002).