Novel Highly Dispersed Tungsten Oxide Catalysts on Mesoporous Silica obtained by Atomic Layer Deposition

Jose E. Herrera, Ja Hun Kwak, Jian Zhi Hu, Yong Wang and Charles H.F. Peden*
Pacific Northwest National Laboratory, P. O. Box 999, MS K8-98, Richland, WA 99352
*chuck.peden@pnl.gov

Introduction

Supported metal oxides are perhaps the most important family of catalysts used in the petroleum industry for acid/base transformations. Their catalytic activity seems to be linked with the formation of strong Brønsted acid sites, which is in turn related to the ability for delocalization of the ionic charge, resulting in the stabilization of the conjugated base of the oxide. Among the transition metals with these characteristics, tungsten has the strongest Brønsted acid sites, either as a bulk oxide or supported [1-3]. However there are very few references in the literature about the use of mesoporous silicates as support for tungsten oxide species. Some research groups have tried to incorporate highly dispersed tungsten oxide into mesoporous materials, obtaining materials with poor thermal/chemical stability [4,5].

We report a novel method for grafting of tungsten oxide species on the surface of a mesoporous (SBA-15) material. This novel method is based on atomic layer deposition of tungsten oxide species. Keeping the system under rigorous dry conditions, we avoid the presence of oligomeric WO_x species which are formed in aqueous solutions. The material thus obtained shows high WO_x dispersions and excellent thermal stability as the characterization results clearly indicate. Their catalytic performance for alcohol dehydration is also compared.

Materials and Methods

SBA-15 mesoporous silica (BET area ~ 860m^2/g) was synthesized using a previously reported protocol [6]. Tungsten precursor solutions were prepared by dissolving WCl_6 in toluene. The solution was then refluxed in presence of the SBA-15 support. During reflux, N_2 was bubbled through the liquid phase to further limit the presence of water. The amount of WCl_6 added to this organic solution was varied in order to obtain different loadings of tungsten oxide on SBA-15. The samples were characterized by XRD, TEM, solid state ^{1}H-NMR, DRS UV-Vis. and FTIR-TPD of adsorbed methanol. The catalytic activity was probed via methanol and isobutanol dehydration reactions.

Results and Discussion

Figures 1a and b show the TEM micrographs obtained for a WO_x/SBA-15 catalyst with a 30wt.% WO_3 loading prepared by atomic layer deposition. We observe virtually a complete absence of tungsten oxide particles on the external surface of SBA-15 samples, revealing that the tungsten oxide could be incorporated into the channels of SBA-15 even at high metal loadings. Figure 1b also illustrates the thermal stability of these samples where even after calcination at 500°C, the sample shows extremely little segregation of tungsten oxide. This together with XRD results demonstrates the stability of these well-dispersed tungsten oxide species to thermal treatment. A contrasting behavior is observed however for the sample obtained using traditional aqueous impregnation, as Figure 1c shows. In this case, tungsten oxide particles can be observed throughout the mesoporous silica structure.

Table 1. Edge energy values obtained for different WOx/SBA-15 catalyst. The values obtained for samples of known domain size are also included for reference.

Sample	Edge energy value (eV)	Sample	Edge energy value (eV)
WO_3	2.4eV	WO_x/SBA-15 0.67 W/nm^2	3.5eV
$(NH_4)_{10}W_{12}O_{41}$	3.0eV	WO_x/SBA-15 1.00W/nm^2	3.5eV
Na_2WO_4	4.6eV	WO_x/SBA-15 1.33 W/nm^2	3.5eV

The molecular dispersion of these materials was evaluated using optical absorption spectroscopy. Table 1 compares the absorption edge values obtained for several WOx species of known domain size together with those of four SBA-15 supported catalysts with different tungsten loadings. The values obtained for these latter samples (3.5eV) suggest that these WOx species are monodispersed, with little, if any, interaction to each other through W-O-W bonds, and that these species exist in a distorted octahedral symmetry [3].

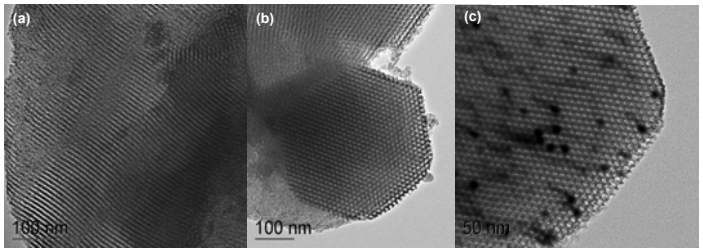

Figure 1. TEM micrographs obtained for a WO_x/SBA-15 sample calcined at 400ºC (a) and at 500ºC (b) and for a (c) WO_x/SBA-15 catalyst prepared by conventional impregnation.

The results of the TPD characterization indicate a different strength of the adsorption sites which is, in turn, dependent on the overall tungsten oxide surface density. Moreover, the positions of the infrared bands for adsorbed MeOH for methoxylated surface species show a shift which is also dependent on the tungsten loading. This seems to confirm that there is dependence of the adsorption site strength on tungsten oxide surface coverage.

References

1. Wachs, I. E. *Catal. Today* 27, 437 (1996).
2. Barton, D. G., Soled, S. L., and Iglesia, E. *Top. Catal.* 6, 87 (1998).
3. Barton, D. G., Shtein, M., Wilson, R. D., Soled, S. L., and Iglesia, E. *J. Phys. Chem. B* 103, 630 (1999).
4. Zhang, Z., Suo, J., Zhang, X., and Li, S. *Appl. Catal., A: General* 179, 11 (1999).
5. Briot, E., Piquemal, J.-Y.; Vennat, M., Bregeault, J.-M., Chottard, G., and Manoli, J.-M. *J. Mater. Chem.* 10, 953 (2000).
6. Zhao, D., Feng, J., Huo, Q., Melosh, N., Fredrickson, G. H., Chmelka, B. F., and Stucky, G. D. *Science* 279, 548 (1998).