601f Novel Wox Catalysts Grafted on Mesoporous Silica by Atomic Layer Deposition: Role of Tungstates Morphology in Methanol Dehydration

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Introduction Supported metal oxides are perhaps the most important family of catalyst 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 is 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 on 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 WOx species which are formed in aqueous solutions. The material thus obtained shows high WOx dispersions and excellent thermal stability as the characterization results clearly indicate. Studies on catalytic activity were performed using methanol TPD, 2-butanol and methanol dehydration reactions. The results indicate an intrinsic relationship between acid site strength, acid site distribution and dispersion of the tungsten oxide species.

Materials and Methods SBA-15 mesoporous silica (BET area ~ 860m2/g) was synthesized using a previously reported protocol [6]. Tungsten precursor solutions were prepared by dissolving WCl6 in toluene. The solution was then refluxed in presence of the SBA-15 support. During reflux N2 was bubbled trough the liquid phase to avoid the presence of water. The amount of WCl6 added to this organic solution was varied in order to obtain different loadings of tungsten oxide on SBA-15. Samples at 25% (ALD 7.5% wt. WO3), 50% (ALD 15% wt. WO3), 75% (ALD 22.5% wt. WO3), 100% (ALD 30% wt. WO3) and 200% (ALD 60% wt. WO3) monolayer coverage were prepared. Two additional samples of SBA-15 impregnated (IWI) with an aqueous solution of ammonium metatungstate at incipient wetness point were also prepared for comparison. The samples were characterized by XRD, TEM, solid state 1H-NMR, DRS UV-Vis. and FTIR-TPD of adsorbed methanol. The catalytic activity was probed trough methanol and 2-butanol dehydration reactions.

Results and Discussion The TEM micrographs obtained for a WOx/SBA-15 catalyst with a 30wt.% WO3 loading prepared by atomic layer deposition (ALD), showed that tungsten oxide particles on the extra surface of SBA-15 are not present in the samples. This certainly reveals that the tungsten oxide could be only incorporated into the channels of SBA-15 even at high metal loadings. This high dispersion was maintained even after severe thermal treatment. This together with the XRD results shows the stability of these well-dispersed tungsten oxide species to thermal treatment. A contrasting behavior was observed however for the sample obtained using regular aqueous impregnation; in this case deposits of tungsten oxide were clearly observed through the mesoporous silica structure.

Figure 1 shows the values obtained for dehydration rates obtained at zero reactant conversion as a function of the WO3 loading on the catalyst. As reported previously by Baertsch et al. 2-butanol dehydration rates depend on the WOx surface density [7]. Low 2-butanol dehydration rates (per W-atom) are observed in our case for samples with low surface densities, which probably contain monotungstate species, as the results obtained by UV-Vis DRS indicate. As isolated WOx species condense into polytungstate species as the loading increases, 2-butanol dehydration rates increase; and then again at higher surface densities (60% wt. WO3), dehydration rates decrease as three-dimensional WO3 crystallites form. The dependence on surface density is also observed for the case of methanol dehydration, which should have initial mechanistic steps similar to 2-butanol dehydration (i.e. protonation of an OH moiety by a surface Brønsted site). Additionally, it was observed that for the case of methanol dehydration the catalyst shows a stronger deactivation. The reason for deactivation should be linked to the reaction conditions, in the case of methanol dehydration the reaction temperature is 573K compared to 373K used in the case of 2-butanol. This deactivation might be linked to sintering of the tungsten oxide species or carbon deposition on the catalyst surface as the stronger acid sites generate dehydrogenation products during the initial steps of the reaction which are in turn linked to the reduction of tungsten oxide species [7]. This phenomenon might explain the different activities observed for methanol dehydration (Fig. 12) in the case of samples obtained by different preparation methods but with same tungsten loading. The reason for this difference in catalytic behavior and the origin of the deactivation will be discussed based on characterization results obtained on the spent catalyst.

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). 7. C. D. Baertsch, K. T. Komala, Y-H Chua, E. Iglesia, J. Catal. 205 (2002) 44.

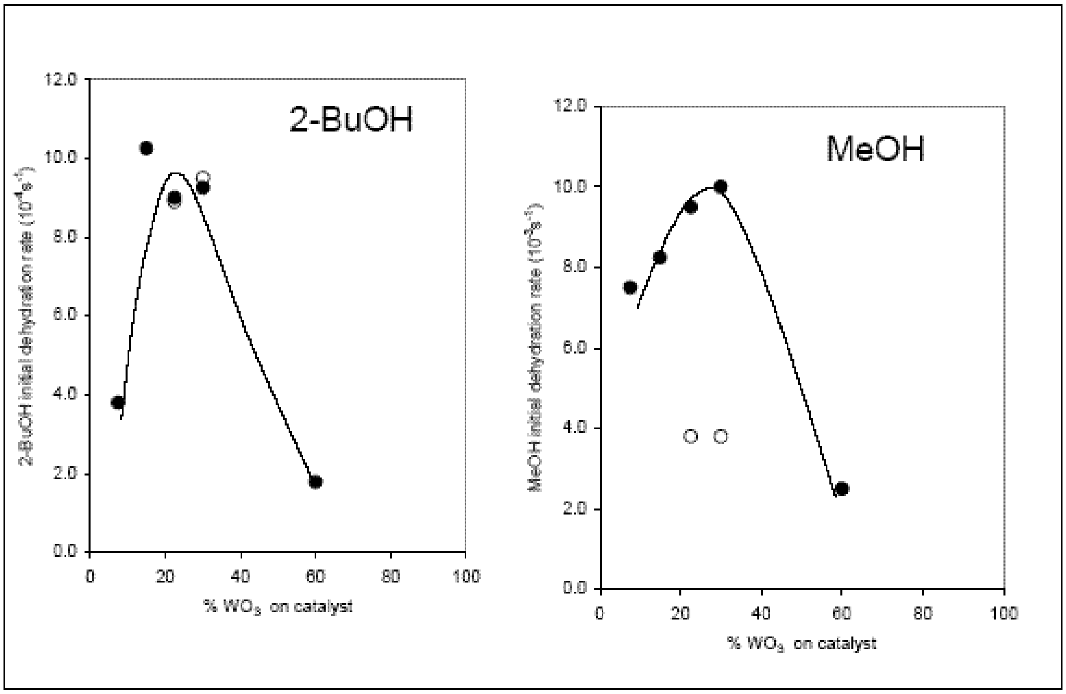

Figure 1. Left: Initial 2-butanol dehydration rates (per W-atom) at 373 K as a function of tungsten oxide loading in the catalyst. Right: Initial methanol dehydration rates (per W-atom) at 573 K as a function of tungsten oxide loading in the catalyst. The filled circles correspond to catalyst obtained by ALD and the open ones to regular impregnated samples.