Preparation and Characterization of a New Class of Highly Dispersed Vanadium Oxide Catalysts on Mesoporous Silica

Ja Hun Kwak, Jose E. Herrera, 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 have been extensively studied as heterogeneous catalysts for many industrial applications. In particular, supported vanadium oxide catalysts have attracted much attention because of their unique catalytic properties for various commercial chemical processes. It is well known that vanadium oxide spreads to a monolayer over titania surfaces through a specific support interaction; however, the preparation of highly dispersed vanadium oxide catalysts on other supports still remains a challenge.

In this work, we report the synthesis of highly dispersed vanadium oxide catalysts over mesoporous silica. By means of a carefully grafted deposition of a TiO_2 monolayer over MCM-41, an anchoring phase for VO_x species is created over the mesoporous support material. By this method it is possible to obtain highly dispersed vanadium oxide by using the specific interaction of titania-vanadia; moreover, high loading can be achieved due to the high surface area of the MCM-41. These materials also show excellent thermal stability as the characterization results clearly indicate. Their catalytic performance for partial oxidation is also evaluated.

Materials and Methods

MCM-41 mesoporous silica (BET area ~ 670m^2/g) was obtained from Mobil. The titania precursor solution was prepared by dissolving Ti(i-PrO)$_4$ in toluene. The solution was then refluxed in presence of the MCM-41 support to anchor titania phase on silica. During reflux, N_2 was bubbled through the liquid phase to further limit the presence of water. The suspension was then filtered and dried and the resulting solid calcined in air at 400ºC. This solid was then dispersed with vanadia following the same procedure but using vanadium triethoxide instead of Ti(i-PrO)$_4$. The samples were characterized by XRD, TEM, solid state ^{51}V-NMR, DRS UV-Vis. and Raman spectroscopy. Their catalytic activity was probed via methanol and isopropyl alcohol partial oxidation reactions.

Results and Discussion

Figure 1 show the NMR spectra obtained for V_2O_5, and two different supported vanadia catalysts. A broad peak can be observed for the sample that contains the TiO_2 interfacial phase (Figure 1c), indicating that vanadium is highly dispersed. These highly dispersed species are very sensitive to interaction with the support surface, resulting in a range of isotropic chemical shifts due to the heterogeneity of the surface.[1] By contrast the spectra obtained for the V_2O_5/MCM-41 catalyst (Figure 1b) is dominated by a pattern of spinning side bands which indicates that the V-species are forming polycrystals on the mesoporous silica surface. In fact, this phase shows a similar spectrum to that of bulk V_2O_5 (Figure 1a). These results are consistent with observations obtained by TEM, XRD and N_2 physisorption measurements.

The molecular dispersion of these materials was evaluated using optical absorption spectroscopy. The optical absorption spectra were evaluated using direct allowed transition formalism in Davis and Mott correlation [2]. The energy gap values obtained by this method are shown in Table 2. Here the results are compared to the values for some reference vanadia samples of known domain size obtained by Gao and Wachs [3]. These values support the view of an extremely high dispersion of the sample obtained using TiO_2/MCM-41. Indeed if the correlation developed by the same authors is used to obtain the number of average covalent V-O-V bonds (CVBs), a value of 1.2 is obtained for the VO_x/TiO_2/MCM41 sample. In contrast,

Table 1. Average number of covalent V-O-V bonds (CVB) present on different samples based on the correlation proposed in ref. [3].

Sample	Gap energy	Average CVB number
V_2O_5	2.31	5
$Mg_3V_2O_8$	3.48	0
V_2O_5/MCM-41	2.66	3.5
V_2O_5/TiO_2/MCM-41	3.23	1.2

the energy band gap value obtained for the V_2O_5/MCM-41 corresponds to an average number of CVB of 3.5, which clearly indicates how the dispersion of the VO_x phase is controlled by the existence of the titanium oxide interfacial phase. Moreover, the results from Raman spectroscopy on the VO_x/TiO_2/MCM-41 sample show a band at 1040cm^{-1} which is characteristic of the V-O bond stretching of highly dispersed tetrahedral VO_4^{-3} species. Its presence also demonstrates the high dispersion of the vanadium species in this sample. Moreover, the absence of bands in the V-O-V bending region (200-300cm^{-1}) and the V-O-V stretching region (500-800cm^{-1}) further indicates that the vanadium oxide species are isolated [4,5].

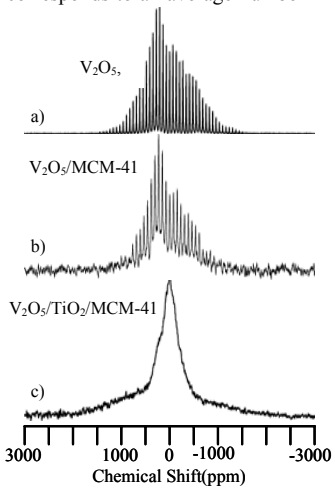

Figure 1. Solid state ^{51}V-NMR of a) V_2O_5, b) V_2O_5/MCM-41, and c) V_2O_5/TiO_2/MCM-41, all taken at a spin rate 10 kHz.

References

1. Miller, J. M., and Lakshmi, L. J. *Appl. Catal. A*: *General* 190, 197 (2000).
2. Davis, E. A., and Mott, N. F. *Philos. Mag.* 22, 903 (1970).
3. Gao, X. and Wachs, I. E. *J. Phys. Chem. B* 104, 1261, (2000).
4. Chua Y.T., Stair P.C., and Wachs I. E. *J. Phys. Chem. B* 105, 8600 (2001).
5. Went G.T., Oyama S.T., and Bell A.T. *J. Phys. Chem.* **94**, 4240(1990).