

Oxidation of Ethanol to Acetaldehyde over Na-promoted vanadium oxide catalysts

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Introduction

Catalysts based on supported vanadium oxides are known to be active and selective for a number of industrially important reactions, and it is well known that the support plays an important role in both their activity and selectivity. The spreading of vanadia over a TiO₂ support leads to a modification of its chemical and physical properties and, correspondingly, to an enhancement of its catalytic properties [1]. By contrast to TiO₂, the interaction of vanadia species with SiO₂ is weak and, therefore, the properties of VO_x species supported on SiO₂ are different. On the other hand, the discovery of the family of siliceous mesostructured materials have attracted much attention as catalyst supports since they possess high surface areas and good thermal stability [2]. In spite of these advantages, there are very few references in the literature about the use of mesoporous silicates as supports for vanadium oxide species [3,4]. Alkali metals are observed to enhance the redox properties of oxide-supported metal oxide catalysts. In the present work, we investigate the effect of sodium on the catalytic behavior of vanadia catalysts supported on mesoporous silica (MCM-41) and TiO₂ (anatase) in the partial oxidation of ethanol to acetaldehyde.

Materials and Methods

Materials were prepared by depositing vanadium on the supports (TiO₂ and MCM-41) by incipient wetness impregnation using NaNO₃ and vanadyl oxalate. The resultant solids were dried and then calcined in a muffle furnace at 773 K overnight. Catalysts were prepared with different Na/V molar ratios in the range 0-2, and with a loading of 6 wt.% V₂O₅. Surface areas were obtained using a Micromeritics TriStar 3000 instrument. X-ray diffraction (XRD) measurements were made using a Siemens D5000 diffractometer (CuK_α radiation). Temperature programmed reduction was performed using a Thermo Finnigan instrument TPD/R/O/1100. UV-Vis spectra were recorded on a Varian Cary-5000 spectrometer equipped with a diffuse reflectance accessory. The catalytic activity experiments were carried out at atmospheric pressure in a fixed bed microcatalytic reactor connected to an on-line Agilent 3000 micro GC. All samples (40mg) were treated in flowing dry air (0.8 cm³ s⁻¹) at 673K for 1 hr before catalytic measurements. TPO analysis of the spent catalyst was performed using a methanator and a FID detector connected in series using a ramp of 10K/min.

Results and Discussion

The presence of Na influences the catalytic activity on both MCM-41- and TiO₂-supported materials; however, the extent of the modification of the catalytic materials seems to depend on

both on the Na loading and the support itself. First, from the XRD results it is clear that in both supports highly dispersed surface VO_x species were present. Based on the XRD and BET results it is clear that the mesoporous structure was preserved in all samples after introduction of vanadium and sodium species and that the VO_x is located inside the mesopores. Indeed, these results are supported by the optical absorption experiments which indicated the presence of relatively high dispersed vanadia species on the catalyst. Initial catalytic rates observed for the V-TiO₂ samples decreased with the Na content (Figure 1a); while the UV-DRS and TPR results clearly indicated that when the sodium loading increased the vanadium species formed highly dispersed but very refractory sodium vanadate. This decrease in the number of active vanadium species was followed by a decrease in the reducibility observed for the doped VO_x/TiO₂ catalysts. Contrasting behavior was displayed by the V-MCM-41 catalysts. In this case, a steady increase on the catalytic activity is observed when Na content increases up to a Na/V = 0.5 molar ratio; beyond this limit the activity decreased progressively as the Na amount

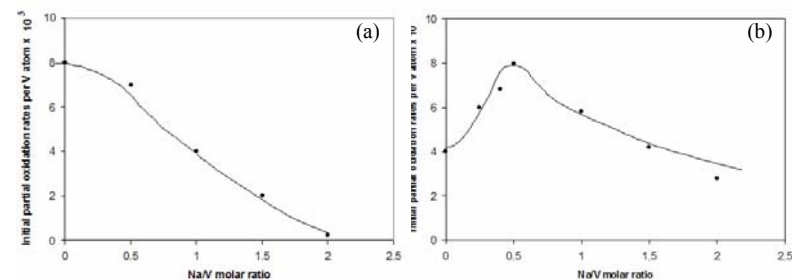


Figure 1. Initial partial oxidation rates normalized by the amount of vanadium present in the catalyst as a function of the Na content for: (a) V₂O₅/TiO₂; and (b) V₂O₅/MCM-41 samples.

in the catalyst increases (Figure 1b). However, for the case of the MCM-41 supported catalyst an enhancement in the selectivity to acetaldehyde was observed as the amount of Na increased. These changes in activity are also intimately correlated with the changes in the edge energies and the reducibility observed in the DRS-UV Vis and TPR experiments, respectively.

Significance

The effect of Na addition on vanadia dispersion and its catalytic performance was evaluated leading to relevant structure-function relationships for the investigated catalytic system in the oxidative dehydrogenation (ODH) reaction of alcohols into aldehydes.

References

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