

Effect of Additives on Vanadia-Alumina Composite Aerogels for Propane Ammoxidation

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Introduction

Aerogel is a highly porous nanostructured material that shows catalytically favorable characteristics such as high specific surface area, mesoporosity, high dispersion, and excellent thermal stability [1]. The characteristics of vanadia-based catalysts which are immensely versatile for various selective (amm)oxidations [2] can be varied by additive species. Additives contribute importantly to acidity and electron density [3] leading to changes in adsorption-desorption characteristics, finally resulting in different product selectivity. We here report the effect of additives on vanadia-alumina aerogel catalysts for propane ammoxidation.

Materials and Methods

Vanadia-alumina composite aerogels were prepared by the sol-gel processing of aluminum chloride hexahydrate and vanadium oxychloride with a help of gelation promoter of propylene oxide in ethanol, and subsequently by supercritical drying after solvent exchanges with liquid CO₂. Additional compounds imposed in such aerogels were Sn, Sb and transition metals of Nb, Cr, Mn, Fe, Co, Ni, and Cu. The resultant catalysts were tested for propane ammoxidation at the stoichiometric ratio of 1:1:2 (C₃H₈:NH₃:O₂).

Results and Discussion

Aerogel catalysts were physically and chemically characterized by N₂-sorption, XRD, Raman spectroscopy and NH₃-TPD exhibiting high specific surface area, mesoporosity, no bulk V₂O₅, and mild acidity. Though third elements were added, no significant changes occurred in the resulting characteristics except vanadia reducibility and oxygen bonding energies. Table 1 lists textural properties of the synthesized composite aerogels.

The content of vanadium oxide in aerogel catalyst could be increased up to 40 wt.% without formation of bulk V₂O₅ while 10 wt.% V₂O₅ prepared by impregnation method contained bulk vanadia. Surface vanadates such as monovanadates and polyvanadates play a major role for the oxidation processes. When vanadia exhibits bulk property, it causes not only reduction in the amount of active sites, but also production of unknown byproducts by polymerization, which results from the strong acid sites.

Typical reaction patterns are given in Figure 1 where products are mainly consisted of acrylonitrile and acetonitrile irrespective of other byproducts such as nitrogen and carbon oxides. Product selectivities were changed in the case of addition of Sb, Sn, Nb to vanadia-alumina aerogels, resulting in the changes in acetonitrile selectivity from ca. 10 % to less than

5 %. For transition metal additives, a volcanic relation on the ratio of acrylonitrile to acetonitrile was observed with respect to their acidity.

Differences in product nature of paraffinic (acetonitrile) and olefinic (acrylonitrile) products caused adsorption strength that eventually affected product selectivity. Bulk species of Sb, Sn, and Nb could reduce Lewis acidity by increasing electron density to vanadia sites or could provide desorption sites by neighboring product-adsorbed sites. Decrease in oxygen binding energy (O1s) was also observed by XPS after addition of Sb and Nb species.

Table 1. Specific surface area (S_{BET}), total pore volume (V_p) and average pore size (D_p) of vanadia-alumina aerogel catalysts calcined at 500°C

Type	V ₂ O ₅ (wt %)	Third element (wt %)	S _{BET} (m ² /g)	V _p (cc/g)	D _p (nm)
Aerogel	10	-	753	4.29	22.1
Aerogel	40	-	457	2.21	18.6
Aerogel	15	Sb 5	622	3.10	19.2
Aerogel	15	Co 5	574	2.98	20.0
Aerogel	15	Sn 15	213	1.35	24.3

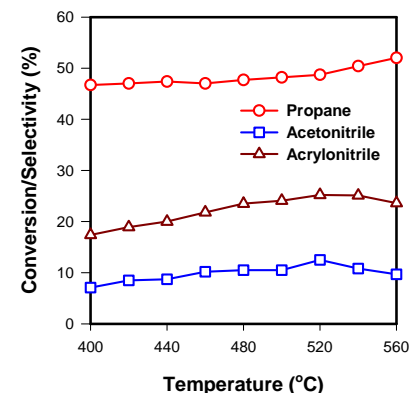


Figure 1. Reaction patterns for the propane ammoxidation over 40 wt.% V₂O₅-Al₂O₃ composite aerogel catalyst.

References

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