Effects of Thermal Treatment on the Phase Composition and Performance of VMoNbTe(Sb)Ox Catalysts for the Selective Oxidation of Propane to Acrylic Acid

K. Wang[1]*, W. Mortier[2], J. Vartuli[1], R. Nielsen[1], J. Dakka[1], A-J. Bons[3], A. Winesett[4]
[1] *Corporate Strategic Research, ExxonMobil Research and Engineering Company, Annandale, NJ, USA*
[2] *Catalyst Technology, ExxonMobil Process Research, Annandale, NJ, USA*
[3] *European Technology Center, ExxonMobil Chemical Company, Machelen, Belgium*
[4] *Baytown Technology Complex–West, ExxonMobil Chemical Company, Baytown, TX, USA*
*kun.wang@exxonmobil.com

Introduction

Selective oxidation of propane to acrylic acid has attracted much interest due to the potential economic advantages in replacing propylene with propane as the feed-stock [1]. The most effective catalyst known to-date is the VMoNbTe mixed metal oxides [2]. The active phases contain an orthorhombic phase M1 and a hexagonal phase M2; and the role of each phase has been proposed [3]. Optimal M1 and M2 phase distribution has been reported to contain 50-70% M2 phase [4]. Thermal treatment under an inert atmosphere is required for the preparation of VMoNbTeOx catalysts, where the composition and the bulk structure of the mixed oxides are settled [5]. We report here thermal treatment of the catalyst precursors under different gaseous environment and the effects on VMoNbTe(Sb)Ox phase compositions, as well as the catalytic performance for propane oxidation.

Materials and Methods

The VMoNbTe(Sb)Ox catalysts were prepared by modifying the literature method [5]. The dry precursor solid was heated (2 °C/min) at 600 °C for 2 hr under a stream of flowing gas (50 cc/min). Elemental analyses were performed by X-ray florescence spectroscopy. XPS data were collected on an ACD Phi 5600 X-ray photoelectronic spectrometer. Electron microscopy was obtained on a FEI Tecnai G^2 F20ST (200 kV) electron microscope. X-ray diffraction [2θ = 5-60°] was collected on a Scintag powder X-Ray Diffractometer using Cu Kα radiation. Phase assignments were based on literature reports and Rietveld refinement was performed using the GSAS package [6]. Oxidation reactions were carried out with a feed containing propane/O_2/N_2/H_2O = 5/9/69/17 (molar ratio) at 50 psig, 380 °C, and GHSV = 2672 h^{-1}. Products were analyzed by GC.

Results and Discussion

Although it is known that thermal treatment of the mixed metal oxide precursor under air gives inactive materials [5], treatment under different atmospheres or temperature results in significant changes of the phase composition of the mixed oxides (Table 1). Taking advantage of the thermal treatment effects, we obtained a wide range of phase compositions for both the VMoNbTeOx and the VMoNbTeSbOx systems, without significantly changing the elemental compositions. Thus the acrylic acid yield – catalyst phase composition relationship can be established (Fig. 1). For both the VMoNbTeOx and the VMoNbTeSbOx systems, an optimal range of M1 phase fraction exists. The optimal M1 phase fraction is around 0.6 for the VMoNbTeOx system, consistent with that reported by Grasselli et al. [3] for the ammoxidation of propane to acrylonitrile. For the VMoNbTeSbOx system, the optimal M1 phase fraction is around 0.75. The overall yield of acrylic acid from the VMoNbTeSbOx system is also much higher than that for the VMoNbTeOx system, revealing a beneficial effect by incorporating Sb into the catalyst.

Table 1. Phase compositions for thermally treated VMoNbTe(Sb)Ox

Treatment conditions	Composition	M1	M2	$TeMo_5O_{16}$	$Te^{(0)}$	MoO_2
N_2, 600 °C	$V_{0.116}Mo_{0.641}Te_{0.164}Nb_{0.079}$	0.588	0.282	0.097	0.032	
N_2, 500 °C	$V_{0.119}Mo_{0.632}Te_{0.171}Nb_{0.077}$	0.534	0.068		0.047	0.351
N_2, 700 °C	$V_{0.119}Mo_{0.677}Te_{017}Nb_{0.087}$	0.968	0.031			
N_2, 600 °C	$V_{0.132}Mo_{0.653}Te_{0.089}Nb_{0.09}Sb_{0.035}$	0.771	0.158	0.044	0.026	
He, 600 °C	$V_{0.127}Mo_{0.639}Te_{0.116}Nb_{0.089}Sb_{0.029}$	0.79	0.172	0.039	0.027	
CO_2, 600 °C	$V_{0.141}Mo_{0.715}Te_{0.021}Nb_{0.082}Sb_{0.041}$	0.671	0.215	0.041		0.072

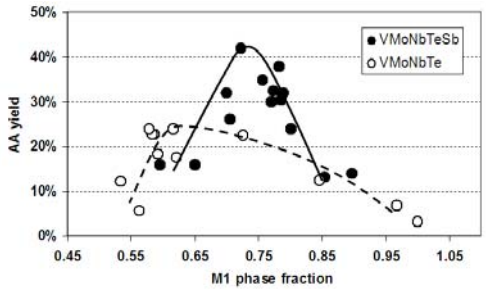

Figure 1. Acrylic acid yield vs. M1 phase fraction for the VMoNbTe(Sb)Ox catalysts.

Significance

A wide range of phase compositions has been achieved by varying the thermal treatment conditions for the mixed metal oxide precursor, which allows determination of the optimal M1 and M2 phase distribution for both the VMoNbTeOx and the VMoNbTeSbOx catalysts.

References

1. J. Vedrine, E. Novakova, E. Derouane, *Catal. Today* 81 (2003), 247.
2. T. Ushikubo, H. Nakamura, Y. Koyasu, S. Wajiki, US Patent 5,380,933 (1995).
3. R. Grasselli, D. Buttrey, P. DeSanto Jr., J. Burrington, C. Lugmair, A. Volpe Jr., T. Weingand, *Catal. Today* 91-92 (2004), 251.
4. M. Baca, M. Aouine, J. Dubois, J. Millet, *J. Catal.* 233 (2005), 234.
5. M. Lin, *Appl. Catal. A: General* 250 (2003), 287.
6. A. Larson, R. Von Dreele, General Structure Analysis System, LANSCE, MS-H805, Los Alamos National Laboratory, Los Alamos, NM 87545 (2000).