Title: Synthesis of Mo and V-based Mixed Oxide Catalysts with Metastable Structure: Easy Access to the MoVNbTe(Sb)O_x Catalytically Active Structure Using Reductant and Oxoacid

Hideto TSUJI, Kazunori OSHIMA, and Yukio KOYASU

Mitsubishi Chemical Corporation, Science & Technology Research Center

Supporting Information

Catalyst Examination

The black powder samples after calcination were used without any grinding, pelletizing and sieving for the catalyst examinations. The catalytic reactions for the (amm)oxidation of propane were carried out at atmospheric pressure in a conventional plug flow fixed bed reactor with a quartz tube (i.d. 6 mm ϕ) in a electric furnace. The temperature was raised to the reaction temperature in a stream of the feed gas in both cases. The products and the unreacted substrates were analyzed with an on-line GC using a TCD detector, and calculated with an internal standard that was analyzed together. Reported conversion and yield values are based on the feed propane.

Figure s1 illustrates a variation in the catalytic performance of $\text{Mo}_1\text{V}_{0.3}\text{Nb}_{0.07}\text{Sb}_{0.17}\text{O}_x$ with the amount of sulfuric acid added to the preparative aqueous mixture. The catalytic performance strongly depended on the H_2SO_4 content in the aqueous mixture.

Figure s1 Variation in the catalytic performance with sulfuric acid content in the preparative mixture. Square, conversion of propane; circle, yield of acrylonitrile. The catalysts are $\text{Mo}_1\text{V}_{0.3}\text{Nb}_{0.07}\text{Sb}_{0.17}\text{O}_x$ prepared using hydrazine hydrate (0.077 mol / mol-Mo) and calcined at 625 °C for 2 h in a stream of N_2 . The reaction conditions are: catalyst, 550 mg; feed gas, 500 NmL; $\text{C}_3\text{H}_8/\text{NH}_3/\text{Air} = 1/1.2/15$; reaction temperature, 430 °C.

Catalyst Analysis

Elemental analyses of the materials were performed by energy dispersive XRF using a Shimadzu EDX-700 instrument with standard samples and the fundamental parameter technique. X-ray diffraction (XRD) measurements were carried out by the continuous scanning ($3^\circ / \text{min}$) powder method using a phillips PW 1700 diffractometer with Cu $K\alpha$ radiation. The released gas from the dried gel during the heating process were analyzed by mass spectrometry using a LEDA-MASS Microvision 100D quadrupole mass spectrometer which was connected to the outlet of sample tube for calcination through a needle valve.

Figure s2 shows the XRD patterns for the calcined MoVNbTeO_x prepared with and without acidification. The catalyst prepared from the aqueous mixture without the addition of H_2SO_4 showed a pattern of the Mo_5O_{14} structure significantly.

Figure s2 X-ray diffraction patterns of $\text{Mo}_1\text{V}_{0.30}\text{Nb}_{0.12}\text{Te}_{0.17}\text{O}_x$ prepared using hydrazine hydrate (0.134 mol/mol-Mo) and calcined at 600 °C for 2 h in a stream of N_2 . (a) from the aqueous mixture acidified with H_2SO_4 (0.134 mol/mol-Mo); (b) from the aqueous mixture without acidification.