Synthesis and Catalytic Behavior of Mo-V-(Te-Nb)-O Catalysts Possessing M1 and M2 Phase Structures

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Introduction

Recently discovered Mo-V-Ox catalysts containing so-called M1 and M2 phases have been reported to be active in lower alkanes oxidation or ammoxidation reactions [1,2]. Different additives, such as Te, Sb, Nb, Bi, Cr, Ta, etc., have been used to improve the structural stability and catalytic activity of these phases. Several groups have reported improvement in the acrylonitrile (ACN) yield due to a cooperation of the M1 and M2 phases in the Mo-V-Te-Nb-O system [3]. However, the effect of different additives on M1 and M2 phase formation, structural stability and catalytic activity has not been examined. In order to study the roles of Te and Nb on the M1 and M2 phase formation, structural stability and catalytic activity we performed the hydrothermal synthesis of Mo-V, Mo-V-Te and Mo-V-Te-Nb systems with different Mo/V ratios.

Materials and Methods

The hydrothermal synthesis of mixed Mo-V-(Te-Nb) oxides was conducted in a static autoclaves according to a reported procedure [2]. $(NH_4)_6Mo_7O_{24}$, hydrated $VOSO_4$, H_6TeO_6 and $Nb(HC_2O_4)_5{\cdot}6H_2O$ were used as precursors for Mo, V, Te and Nb. The Mo/V ratio was varied in the 0.25-4 range for the 2- and 3-component systems. After hydrothermal treatment, the uniform slurry was filtered, washed with H_2O and dried overnight in air at 363 K. This catalyst precursor was calcined in a tubular furnace under ultra pure N_2 at 773 K - 873 K for 2h. The phase compositions and microstructures were characterized by XRD and TEM. The bulk and local chemical elemental compositions were determined by ICP-AAS and EDS, respectively. The BET surface areas were measured using the N2 adsorption/desorption method. The surface morphology was characterized with SEM technique. The catalytic behavior of these model Mo-V based catalysts was studied in propane ammoxidation.

Results and Discussion

In the Te-free Mo-V-O_x catalytic system, the Mo_8-V_2-O_x M1 phase obtained for C_Σ=1.0 mol/l was particularly thermally stable. This solution concentration was employed to explore the formation of the M1 and M2 phases at synthesis Mo/V = 0.25 – 4. The M2 phase was not observed in any as-synthesized and activated Te-free catalysts indicating that Te is an important structural component for the formation and stability of the M2 phase. The pure M1 phase was obtained after thermal treatment at 673-773K for $Mo_6V_3Te_1$, $Mo_5V_4Te_1$, $Mo_4V_5Te_1$ and $Mo_3V_6Te_1$ compositions, whereas the pure M2 phases were obtained after thermal treatment at 873K. The yield of these phases was proportional to the amount of Mo in synthesis solutions indicating that the Mo source was the limiting reagent for the formation of the M1 and M2 phases. Moreover, the bulk chemical composition of the M1 phase in the Mo-V-Te-O system was relatively independent of the synthesis composition centering around $Mo_{30.0}V_{10.0}Te_{8.0}$ which is in excellent agreement with the theoretical M1 unit cell composition of $M_{40}Te_8$ (M=Mo, V and Nb) for fully occupied Te locations in the hexagonal and heptagonal channels of the M1 phase. A 4-component Mo_1-$V_{0.3}$-$Te_{0.17}$-$Nb_{0.12}$-O_x catalyst heated in ultra pure N_2 at 873K consisted from ~ 75% M1 and ~25% M2. Pure M1 was obtained by treatment with H_2O_2 (15%) according to the procedure reported by M. Baca et all. [3].

Despite close similarities in the bulk crystal structure and chemical composition, the Mo-V-(Te-Nb)-O catalysts displayed significant differences in catalytic performance in propane ammoxidation to ACN. The M2 phases were inactive in propane ammoxidation in agreement with previous observations [4]. The $Mo_8V_2O_x$ M1 phase displayed the highest activity among all M1 phases studied, but modest selectivity to ACN. It was capable of activating propane selectively into propylene (60-80 mol. % selectivity) at low temperatures (<653K) and low propane conversions (<10%). The propylene intermediate was increasingly converted into ACN above 653K and the performance of this catalyst was similar to that of the $Mo_6V_3Te_1$ M1 catalyst. The presence of Te resulted in a moderate reduction of activity in propane consumption and improvement in the selectivity to ACN. The $Mo_6V_3Te_1$, $Mo_5V_4Te_1$, $Mo_4V_5Te_1$ and $Mo_3V_6Te_1$ catalysts containing pure M1 phase displayed 47, 66, 37 and 35 mol. % selectivity to ACN, respectively, at 6-22 % propane conversion at 713K. The presence of Nb *together* with Te in the M1 phase resulted in a dramatic drop in the activity in propane and propylene ammoxidation accompanied by significant enhancement in the selectivity to ACN.

Significance

Acrylonitrile is one of the most important bulk chemicals and more than 5 billion kg/year of acrylonitrile are produced world wide using the SOHIO/BP process [1]. Replacing the olefin feed (propylene) with the more abundant and less expensive propane would provide a significant economic advantage for the production of acrylonitrile. Our work addresses the urgent need to develop suitable catalysts that possess high activity, selectivity and stability for this transformation.

References

1. E. M. Thorsteinson, T. P. Wilson, F. G. Young and P. H. Kasai, Journal of Catalysis, 52(1) (1978) 116-132; Guliants VV, Bhandari R, Swaminathan B, Vasudevan VK, Brongersma HH, Knoester A, Gaffney AM, Han S., J Phys Chem B Condens Matter Mater Surf Interfaces Biophys., 109 (50) (2005) 24046-55; P. Concepción, P. Botella and J.M. López Nieto, Appl. Catalysis A: General, 278 (1) (2004) 4;
2. Wataru Ueda, Damien Vitry, Tomokazu Katou, Cat. Today, 99 (2005) 43; Cat. Today 96 (2004) 235;
3. T. Ushikubo, Catalysis Today, 57, 331-338, 2000; R.K. Grasselli, D.J. Buttrey, P. DeSanto, Jr., J.D. Burrington, C.G. Lugmair, A.F. Volpe, Jr., T. Weingand, Catalysis Today, 91-92, 251-258, 2004; M. Baca, A. Pigamo, J.L. Dubois, J.M.M. Millet, Topics in Catalysis, 23, 39-46, 2003; M. Baca, M. Aouine, J.L. Dubois, J.M.M. Millet, Journal of Catalysis, 233, 234-241, 2005; R.K. Grasselli, D.J. Buttrey, J.D. Burrington, A. Andersson, J. Holmberg, W. Ueda, J. Kubo, C.G. Lugmair, A.F. Volpe, Jr., Topics in Catalysis, 38, 7-16, 2006; R.K. Grasselli, Catalysis Today, 99, 23-31, 2005;
4. D. Vitry, Y. Morikawa, J. L. Dubois, W. Ueda, Topics in Catalysis, 23(1-4), 47-53, 2003; J. Holmberg, R.K. Grasselli, and A. Andersson, Topics in Catalysis, 23, 55-63, 2003; P. Botella, E. García-González, J.M. López Nieto, J.M. González-Calbet, Solid State Sciences, 7, 507-519, 2005.