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Influence of alumina precursor on the physico-chemical properties of V–Sb–P–W/Al_2O_3 catalyst studied for the ammoxidation of propane

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ABSTRACT

Influence of alumina precursor on active phase formation in $V_{1.0}$–$Sb_{3.5}$–$P_{0.5}$–$W_{1.0}$/50% Al_2O_3 catalyst was studied for the ammoxidation of propane in the temperature range of 490–530 °C at W/F = 2.8 g_{cat} s ml^{-1}. Three different alumina precursors such as, aluminum chloride (AlC), aluminum hydroxide (AlH) and aluminum nitrate (AlN) were employed in the study. The physico-chemical characterisitics of the synthesized catalysts were investigated by BET surface area-pore size method, XRD, FTIR, HAADF/EDS, NH_3 TPD-mass and XPS techniques. XRD result demonstrates $AlPO_4$ phase for all the three catalysts which was likely due to P interaction with alumina precursor. Formation of propylene and acrylonitrile (ACN) in this study was influenced by the nature of the active surface on Al_2O_3 synthesized from different precursors. Among the catalysts, AlC exhibited greater propane conversion (76%) and ACN selectivity (28%) at 530 °C. The higher activity of AlC was associated with (i) active surface enriched in V–Sb–W phase as established by XPS and HAADF/EDS results (ii) higher adsorption ability for NH_3 in the presence of residual chloride (coming from $AlCl_3$) followed by efficient nitrogen insertion in the intermediate molecule of propane to yield ACN. The surface with Sb–W–O related phase in AlN and AlH possibly contributes to the degradation of adsorbed propane/propylene and NH_3 to yield methane, ethane, ethylene, CO_x and NO_x. To our knowledge, this is the first report for the influence of alumina precursor on the active phase formation in V–Sb–P–W/Al_2O_3 catalyst studied for the propane ammoxidation.

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1. Introduction

Acrylonitrile is industrially produced by the catalytic ammoxidation of propylene also known as SOHIO process [1]. In 2013, worldwide production of acrylonitrile reported as 6 million tons from propylene/propane [2]. Poly acrylonitrile is the major component of several industrial textile fibers synthesized from acrylonitrile monomers. It is also copolymerized with vinyl chloride to produce a wool like fibers which are used for blankets and sweaters. The future global demand-supply gap cannot be fulfilled by acrylonitrile-propylene based process alone due to the price increase of propylene feed-stock. Alternative feed stock based acrylonitrile synthesis can help to accomplish the upcoming demands for acrylonitrile fiber. Propane is more abundant and less expensive feed-stock compared to propylene, which can be directly converted into acrylonitrile by catalytic ammoxidation process [3–6]. An efficient catalyst composition is necessary to achieve acrylonitrile in useful yields from propane. Principally, two types of catalyst compositions are reported in the literature on propane ammoxidation (i) Mo–V–Nb–Te–O (ii) V–Sb–W/Al_2O_3. In the present study, our focus is on complex V–Sb–W/Al_2O_3 catalyst for propane ammoxidation. Further, the propane ammoxidation performance of V–Sb catalyst was improved by using excess amount of antimony oxide which, exists as Sb_2O_4 in the final catalyst [7].

Nilsson et al. [8,9] extensively studied V–Sb, V–Sb–Al and V–Sb–W/Al_2O_3 catalysts for propane ammoxidation reaction. According to the authors, propane adsorption followed by dehydrogenation to propylene and subsequent nitrogen insertion step to form acrylonitrile takes place on V-sites. Addition of Al and Sb primarily isolate V-sites to a suitable degree to avoid degradation of propane, propylene and ammonia. And incorporation of W tunes the V-sites in a direction that helps to improve the acrylonitrile formation. These authors [8] further reported rutile type of Sb(V,W)O_4 active phase for $V_{1.0}$–$Sb_{5.0}$–$W_{1.0}$/50%Al_2O_3 catalyst in propane ammoxidation. Recently, Mamedov studied the propane ammoxidation on W doped V–Sb/Al catalyst. According

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to the author the improved ACN selectivity was due to the higher adsorption ability for NH_3 on W–V–Sb/Al surface compared to V–Sb/Al [10]. Centi et al. [11] have studied the propane ammoxidation on $VO_2P_2O_7$, V–Ti mixed oxide, V–Sb and Fe–Sb catalysts. They found high activity and ACN selectivity on vanadium phosphate and vanadium antimonite catalysts. Mikolajska et al. [12] have studied the vanadium phosphorus mixed oxides supported on Al_2O_3 for propane ammoxidation. The authors attributed the high activity of VPO to V^{+5} site stability and tuned acid-base properties on Al_2O_3 support. Bilde et al. [13] described the catalytic behavior of thermally induced Sb_2O_3 spread on V/Al catalyst in the propane ammoxidation and the greater acrylonitrile selectivity was endorsed to V–Al–SbO_4 rutile phase. Therefore, all the above studied catalysts in the propane ammoxidation showed the significant role of Al as an element in the active phase and/or as a support. Accordingly, catalysts of different performance can be obtained depending on the type of alumina precursor used. Thus, it is essential to study the characteristics and performance of V–Sb–W/Al_2O_3 catalyst obtained through different alumina precursors for propane ammoxidation.

Vanadium and molybdenum sites can be isolated to a certain extent by incorporation of phosphorous (P) and P also improves the acidity moderately which intern minimizes the complete oxidation of propane using VPO and V–Mo–P–O [10–12,14] catalysts. Keeping this in mind, in the present work, the influence of phosphorous addition and Al_2O_3 prepared from different alumina precursor on V–Sb–W phase was examined with the catalyst composition of $V_{1.0}$–$Sb_{3.5}$–$P_{0.5}$–$W_{1.0}$/50% Al_2O_3. The preparation method and the V–P–Sb–W atomic composition was adopted from the US patent obtained by Brazdil and Guttmann [7]. The physico-chemical characteristics of these catalysts was analyzed by BET-pore size method, XRD, NH_3-TPD-mass, XPS and HAADF-EDS techniques and correlated to propane ammoxidation activity and acrylonitrile selectivity.

2. Experimental

2.1. Reagents

Ammonium metavanadate (NH_4VO_3, assay ≥ 98%), antimony oxide (Sb_2O_3, assay ≥ 99%), Aluminum hydroxide dried gel ($Al(OH)_3$), ammonium tungstate ($(NH_4)_2WO_4$, assay ≥ 99.99%), di ammonium hydrogen phosphate ($(NH_4)_2HPO_4$, assay ≥ 99%), Aluminum chloride ($AlCl_3{\cdot}6H_2O$, assay ≥ 99%), ammonia solution (NH_4OH, 30 wt.%) and Nitric acid (HNO_3 60%) were purchased from ACROS chemical suppliers and used without further purification. The preparation method and the V–P–Sb–W atomic composition was adopted from the US patent obtained by Brazdil and Guttmann [7].

2.2. Catalyst preparation A

V–Sb–P–W (1:3.5:0.5:1 atomic ratio) containing 50% Al_2O_3 produced from aluminum hydroxide dry gel precursor (this considered as a base catalyst).

Step-1: 3.81 g of ammonium metavanadate was dissolved in 90.0 cm^3 of hot (80 °C) deionized water and followed by the addition of 16.6 g of Sb_2O_3 to this solution. The resulting slurry was refluxed for 17 h under continuous stirring. The color of the mixture turned to gray-green.

Step-2: 47.88 g of aluminum hydroxide (dried gel) was added to 140.0 cm^3 of 10% acetic acid and stirred for 3 h to form a homogeneous suspension. The suspension was kept under continuous stirring for 3 h. No gelling was observed. The pH of the slurry recorded as 6.0.

Step-3: 9.23 g of ammonium tungstate was dissolved partially in 20 cm^3 of deionized water and to this 5 cm^3 of di ammonium hydrogen phosphate (2.15 g) solution was added.

The slurry obtained from step-1 was slowly added to step-3 solution under continuous stirring. Later, the step-2 suspension was added to this solution quickly under continuous stirring. The excess water was evaporated under continuous stirring on a preheated oil bath at 120 °C. The resultant solid was dried in a preheated oven at 120 °C overnight in static air.

2.3. Preparation B

V–Sb–P–W (1:3.5:0.5:1 atomic ratio) containing 50% Al_2O_3 produced from aluminum chloride precursor.

Aluminum chloride was used instead of aluminum hydroxide (dry gel) in step-2 and reaming procedure was identical to preparation A.

Step-2: 47.8 g of $AlCl_3{\cdot}6H_2O$ was dissolved in 2.5 m^3 of deionized water. In another beaker 77.0 cm^3 of 12N ammonia solution was diluted with deionized water to 500 cm^3 and quickly added to the $AlCl_3$ solution under continuous stirring. As formed white gelatinous precipitate (pH 8.0) was aged for overnight. The resultant precipitate was separated by means of filtration and washed thoroughly with deionized water to remove the Cl^- ions. Further, 47.0 cm^3 of 10% acetic acid solution was added to the gel and the remaining steps were identical to preparation A.

2.4. Preparation C

V–Sb–P–W (1:3.5:0.5:1 atomic ratio) containing 50% Al_2O_3 produced from aluminum nitrate (aluminum hydroxide dry gel + HNO_3) precursor.

Synthesized, aluminum nitrate was used instead of aluminum hydroxide (dry gel) in step-2 and reaming procedure was identical to preparation A.

One hundred and forty cubic centimeter of 60% HNO_3 was added to 48 g aluminum hydroxide (dried gel) and the resulting solution temperature was maintained at 80 °C under continues stirring until the color of the solution turns to clear yellow which, is indicative of aluminum nitrate formation. Here, the resultant solution was weakly acidic (pH 5.0) due to the presence of excess HNO_3. The remaining steps were identical to preparation A.

Further, the powder samples were pelletized and sieved to 0.5–2.0 mm size and calcined at 350 °C, 5 h followed by 610 °C for 3 h under static air conditions.

For example, V–Sb–P–W (1:3.5:0.5:1 atomic ratio) containing 50% Al_2O_3 catalyst produced from aluminum hydroxide (dry gel) precursor denoted as AlH, likewise, for aluminum chloride precursor as AlC and aluminum nitrate precursor as AlN.

2.5. Catalyst characterization

The BET surface area and pore size distribution of calcined samples used in the present study were determined by using Quantachrome Nova Station adsorption equipment at liquid nitrogen temperature after out gassing the samples at 200 °C under the flow of N_2 for 2 h.

The X-ray patterns of the samples used in the present study were obtained on a EQUINOX 1000 inel XRD instrument using Co $K\alpha = 1.7902$ Å with X-ray source generator settings at 40 kV and 30 mA and real time acquisition for $2\theta = 110°$. The FTIR analysis of calcined AlN, AlH and AlC samples were performed on a Bruker Vertex 70/70 v FTIR spectrometer using a KBr pellet method.

High angle angular dark field (HAADF)-scanning transmission microscopy (STEM) and energy dispersive X-ray (EDS) analysis with focused/parallel beam results of calcined samples were collected on

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