EFFECT OF VANADIUM AND TITANIUM SUBSTITUTION OVER AN ANTIMONY-BASED MIXED OXIDE CATALYSTS FOR PROPANE AMMOXIDATION TO ACRYLONITRILE

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Abstract

Antimony (Sb) oxide is known to be the active phase for the ammoxidation of propane to acrylonitrile (ACN). The influenced of V and/or Ti on the physicochemical properties of Sb-based mixed oxide catalysts were studied using catalysts prepared by slurry method. The dried precursor was calcined in air at 350-600 ^oC for a total of 10 h. The active phase in Sb-promoted catalysts were determined using X-ray Diffraction (XRD) while the changes in microstructure of these catalysts were studied using physical adsorption of nitrogen gas. The catalytic activity of these catalysts were tested in a fixed-bed reactor with online GC at 420 ^oC with reaction feed (%v) of 5.8:7:17.4 for propane, ammonia and oxygen, respectively. Results show that promotional of Sb with V and/or Ti has an effect on the chemical environment of the Sb-mixed oxide catalysts, leading to differences in catalytic activity of these catalysts.

Abstrak

Logam Antimoni (Sb) oksida telah dikenali sebagai komponen aktif di dalam mangkin yang digunakan untuk tindak balas pengammoniaan propana bagi penghasilan akrilonitril (ACN). Dalam penyelidikan ini, kesan penambahan logam dopan seperti V dan/atau Ti ke atas sifat fizik dan kimia mangkin oksida campuran logam Antimoni dikaji dengan menggunakan keadah 'slurry'. Precursor mangkin dikeringkan di dalam oven sebelum melalui proses pengkalsinan di dalam udara pada suhu di antara 350-600 ^oC dengan jumlah keseluruhan tempoh pengkalsinan selama 10 jam. Fasa aktif campuran mangkin Sb dicirikan menggunakan teknik Pembelauan Sinar-X (XRD) di samping jumlah luas permukaan mangkin ditentukan melalui teknik Penjerapan Fizik (BET) dengan menggunakan gas nitrogen. Aktiviti mangkin diuji menggunakan reaktor padatan bendalir yang disambung terus kepada kromatografi gas (GC) dengan nisbah kadar suapan iaitu 5.8:7:17.4 (%v) bagi propana, ammonia dan oksigen. Hasil analisis menunjukkan penambahan logam dopan V dan/atau Ti kepada logam Sb menunjukkan kesan kimia pada mangkin oksida campuran logam Antimoni, seterusnya menunjukkan perubahan dalam pengaktifan mangkin.

Introduction

Acrylonitrile (ACN) is a widely used chemical with a production of over five million tons per year principally by catalytic heterogeneous gas phase ammoxidation of propylene. Acrylonitrile (ACN) and other nitriles have been industrially produced as intermediates for the preparation of synthetic resins, synthetic rubbers, fibers and other important products. In recent years, interest has grown in developing an alternative process using propane as feedstock for acrylonitrile production through direct one-step ammoxidation. The main reason for this interest is that propane is considerably more abundant and cheaper than propylene, therefore direct conversion of propane into acrylonitrile is an attractive alternative process [1].

The synthesis of acrylonitrile from propane requires a modification of the catalysts used for propylene ammoxidation, because the latter catalysts are not active enough with the alkane feed. The activity and selectivity of propane ammoxidation are much lower than those of propylene ammoxidation, as the C-H bond strength of the alkane is higher than that of the corresponding alkene. One of the most interesting catalytic systems for the direct ammoxidation of paraffin is antimony-vanadium (Sb-V) mixed oxides [2].

Numerous studies have focused on Sb-V mixed oxides as catalysts for propane ammoxidation [3-4]. Sb-V mixed oxides typically contains several phases. In addition to a $VSbO_4$ rutile phase, Sb_2O_4, V_2O_5, Sb_6O_{13}, amorphous V and Sb oxides can also be formed, depending on the preparation method and the Sb/V ratio [5]. It is accepted that a cation-deficient rutile $VSbO_4$ and a-Sb_2O_4 are the crucial phases for an efficient catalyst [2,4,5]. It is believed that V-O-V pairs are the degradation sites for C_3H_8 to form C_3H_6 and carbon oxides. Therefore, isolation and dispersion of the vanadium site has been recognized as the key factor required for achieving high activity and most importantly, high selectivity to acrylonitrile. Most of the report shows that antimony is mainly in its pentavalent state, so a large amount of vanadium are reduced, with the formation of $V^{III}SbVO_4$ and the possible presence of V^{IV} in substitutional.

Although the possible benefit of additive elements during ammoxidation of propane is notorious, only little is known how the various promoter elements influenced the physicochemical and its respective catalytic properties [6]. The patterns reported have shown that an excess of antimony brings about not only a decrease in activity but also a large increase in the selectivity and yields to acrylonitrile. Vanadium ions are the primary active sites for the dehydrogenation of propane, whereas excess antimony is necessary for ammoxidation of the reaction intermediate, propylene to acrylonitrile. It has been found that the substitution of other cations for vanadium can improve the selectivity of a catalyst for acrylonitrile [7-8]. For example, a catalytic test of Sb-V-Al oxides showed much better catalytic properties compared with the Sb-V-O system. The hypothesis is that they contribute to the isolation of the vanadium site in the catalyst, thus improving the selectivity towards acrylonitrile [8]. On the other hand, a study on $VSbFeO_4$ [9] showed that iron helps to stabilize the surface composition, thus limiting the formation of surface antimony oxide during reaction. It was suggested that this effect might lead to more active but less selective catalysts. These results show that the substitution may play several roles, with different effects on catalytic properties. In this case, a study of the relevance of vanadium (V) and titanium (Ti) as a dopant for antimony to become as an active site is interesting since their acidic character may promote a better interaction between ammonia and a catalyst. Therefore, in this paper, three different catalytic systems have been developed in order to study the different roles of V and Ti on the physico-chemical properties of the Sb-based mixed oxide catalysts.

Experimental

Catalyst Preparation

The antimony (Sb) based catalysts were prepared by following the slurry method. Antimony (III) oxide (Sb_2O_3, ACROS, 99+%) was added to an aqueous solution of ammonium metavanadate (NH_4VO_3, R&M, AR) and/or titanylacetonate ($C_{10}H_{14}O_5Ti$, Merck, AR grade). The mixture was stirred at 80 ^{o}C for 3 hours. Viscous slurry was obtained and subsequently dried in a drying oven at 120 ^{o}C for 16 hours. After drying, the sampel was calcined in two calcination steps at temperatures between 350-600 ^{o}C for a total of 10 h in air with a heating rate of 5 ^{o}C min^{-1}.

Characterization

X-ray Diffraction (XRD)

XRD was used to identify the crystal phases exists in the catalysts. This is performed on a Siemens D500 diffractometer equipped with a monochromatic Cu-K_a radiation source. The catalysts were run from 2^o to 80^o with step size of 0.1^o and time step of 1.0 s. XRD phases present in the catalyst samples were identified with the help of ASTM powder data files.

Scanning Electron Microscophy (SEM)

In order to study the surface morphology of the catalyst, a FESEM-LEO 1525 Scanning Electron Microscope (SEM) was utilized. The specimens were covered with a layer of platinum by sputtering to make the sample conductive. The accelerating voltage was 15 kV in 400 second.

Surface Area Measurements

The BET surface areas of Sb-based catalysts were measured by nitrogen adsorption isotherms using a Micromeritics ASAP 2010 surface area instrument. Prior to analysis, 0.5 to 2.0 g of catalysts was degassed at 350^{o}C for 2 h under liquid nitrogen. BET areas were computed from the adsorption isotherm ($0.05<P/Po<0.97$), taking a value of 0.162 nm^2 for the cross-section of the adsorbed N_2 molecule at 77 K. The specific surface area was determined from the linear portion of the BET plot.

Catalytic Performance

The propane ammoxidation reaction was carried out at atmospheric pressure in a quartz microcatalytic fixed-bed reactor in a steady state operating condition. Test was made using 0.5 g samples with particle dimensions in the 212-245 µm range. The reactor temperature was 420 ^{o}C with the composition of the feed expressed as % vol for propane: ammonia: oxygen was 5.8:7:17.4 with a total flow rate of 120 cm^3 min^{-1}. The analyses of propane, ACN, acetonitrile and uncondensable gases were carried out using the gas-chromatograph equipped with a thermal conductivity detector. Yield and selectivity values were determined on the basis of the moles of propane converted.

Results and Discussions

X-ray Diffraction (XRD)

The diffraction pattern of Sb based mixed oxide catalysts (Sb-V, Sb-V-Ti and Sb-Ti) calcined at 350-600 ^oC are shown in Figure 1. The figure shows that the diffractogram of Sb-V catalyst consists of three types of crystal phases of tetragonal, orthorhombic and cubic structures. These typical crystalline diffraction peaks of the Sb-V catalyst are identified by the major peak at 2? of about 30^o, 40^o and 50^o, which is in agreement with those reported by Albonetti et al. [10]. Apperently, ˜ $VSbO_4$ phase appeared at 2? = 27.4^o, 35.0^o and 53.5^o which correspond to (110), (101) and (211) planes, respectively, is the principal phase in all samples. However the diffraction lines observed from the XRD patterns found that with the increase of calcination temperature, the peak of crystalline ˜ $VSbO_4$ phase (tetragonal) become reduced a little. Other diffraction line observed are Sb_2O_4 (orthorhombic) at 29^o, 35^o and 39^o, Sb_6O_{13} (cubic) at 31^o and 50^o as well as subphase of a-Sb_2O_4 (orthorhombic) at 38^o and 55^o. According to Centi et al. [5], they reported that the formation of the ˜ $VSbO_4$ phase occurs in the 673-773 K temperature range, with a-Sb_2O_4 reflection is detected when the calcination temperature increases. They also reported that Sb_2O_3 is oxidized directly to a-Sb_2O_4 by imposing heat treatment on the sample at the temperature range 773-873 K. This observation indicates that an increase in calcination temperature promotes the formation of crystalline ˜ $VSbO_4$ and a-Sb_2O_4 phase.

The diffractogram of Sb-V-Ti catalyst, which shown in Figure 1 is found to consist of three types of crystal phases of tetragonal and hexagonal structures. These typical crystalline diffraction peaks of the Sb-V-Ti oxide catalyst are identified by the major x-ray diffractions at 2? values where the hexagonal structures is referred to $(Ti_{0.7}V_{0.3})_2O_3$, which appeared at 24^o, 33^o, 35.7^o, 38.9^o, 49^o and 64^o. While the tetragonal structures are referred to subphase of $VSbO_4$ (27^o and 54^o) and rutile TiO_2 (27.3^o, 35.7^o and 54^o) respectively. It has been shown that $VSbO_4$ phase become reduced drastically compared to peak from Sb-V catalysts as the calcination temperature been increased. However, the predominant peaks of a-Sb_2O_4 are clearly visible in the diffractogram of Sb-V-Ti catalyst at 29^o and 38^o. It is believed that Sb-V-Ti samples either consisted of small crystallites of similar phases or the crystal sites were not properly formed. Wickman et al. [8] reported that with titanium content, the lines froma -Sb_2O_4 is very weak and their intensities decrease as the amount of titanium in the sample is increased.

From the diffractogram of the Sb-Ti catalyst, the presences of some crystal phases with monoclinic, cubic, tetragonal and orthorhombic structures are detected in the catalyst. The monoclinic structure is referred to $SbTiO_6$, which appeared at 11^o, 19^o, 37.2^o, 38^o, 39^o and 40^o while Sb_6O_{13} with cubic structure appeared at 31.9^o and 36^o. The tetragonal and orthorhombic structures are referred to subphases of $SbTi_3$ (12^o, 17^o, 24^o, 42^o, 49^o, 51^o and 59^o) and Sb_3Ti_5 (26.5^o, 29, 38^o and 54^o) respectively. According to Keranen et al. [11], TiO_2 anatase peak should appear at 2? value about 25.3^o in the catalyst system, which contain Ti element. However, in this catalyst system, it is believed that the excess of antimony in the composition shifted the formation of TiO_2 anatase of 25.3^o to 25^o.

The XRD pattern have been clearly show that antimony become a major component in all Sb-based mixed oxide catalyst. According to Nilsson and co-worker, $VSbO_4$ and/or Sb_2O_4 are the important subsystem in the multicomponent catalyst formulations for C_3H_8 ammoxidation [12]. However, these crystal phases were not detected in the Sb-V-Ti and Sb-Ti catalyst.

Scanning Electron Microscopy (SEM)

Study on the textural properties of the solids was completed by means of SEM. The images in Figures 2-4 correspond to the Sb-V, Sb-V-Ti, Sb-Ti, respectively. There are 3 types of morphologies and local composition characteristic for the crystallites could be detected; (i) long hexagonal-octagonal type crystallites, sometimes grown (ii) plate-like crystallites, sometimes stacked or assuming a desert rose-like structure and (iii) powdery, like aggregates without a specific morphology [3]. SEM results, showed a non-homogeneous distribution in morphology, texture and particle size for all calcined systems. Surface morphologies of the catalysts are of variable shapes and sizes depending on the dopant used in the catalysts where the images were taken at 10K magnifications. The SEM image of the Sb-V catalyst shows that the powder has microrods cross linking-type structures (Figure 2) oriented in no particular direction with lengths of about 0.3-0.8 µm, which suggest that the solids are in crystalline phase. This result is consistent with that observed in the XRD diffractogram which shows that the catalyst has orthorhombic and tetragonal structures.

* $VSbO_4$ ^ Sb_2O_4 # Sb_6O_{13} + a-Sb_2O_4 ○ $(Ti_{0.7}V_{0.3})_2O_3$
▲TiO_2 ● $SbTiO_6$ ■ $SbTi_3$ □Sb_3Ti_5

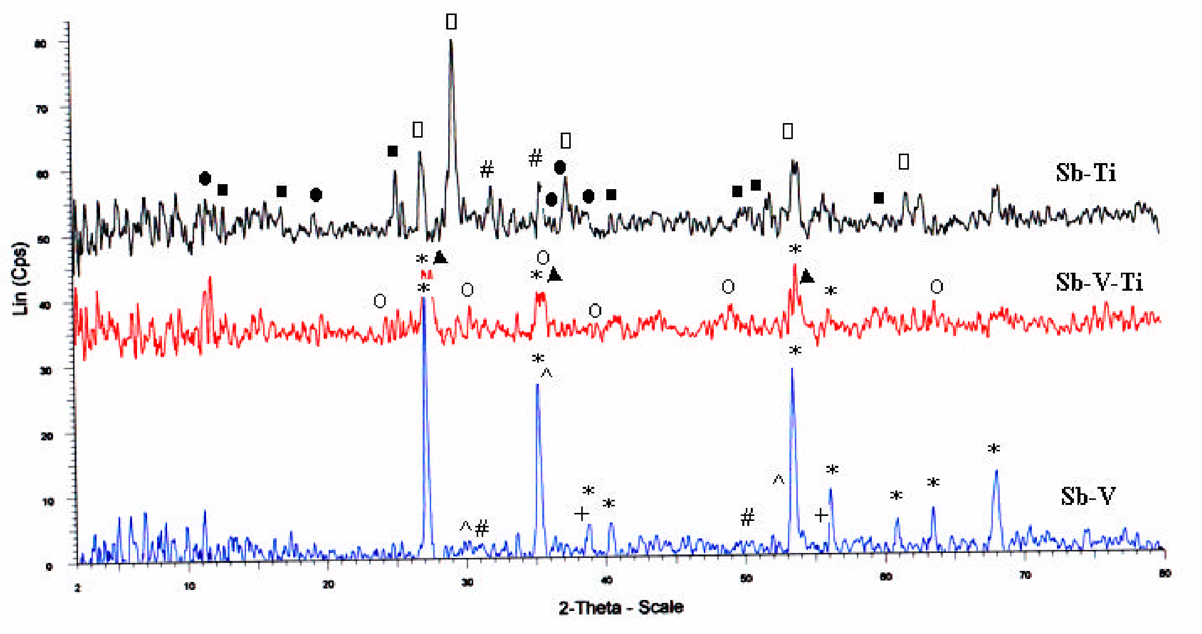

Figure 1: XRD diffractogram of Sb-V, Sb-V-Ti and Sb-Ti catalysts

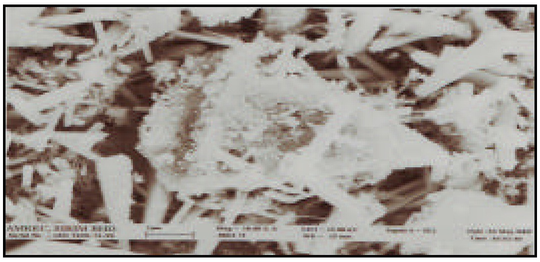

Figure 2: SEM micrograph of Sb-V

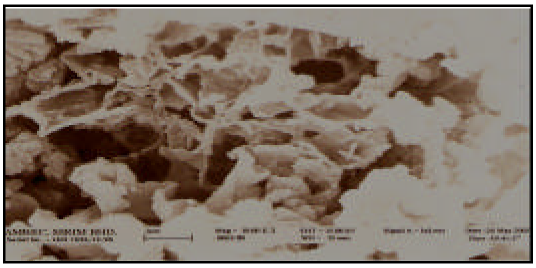

Figure 3: SEM micrograph of Sb-V-Ti

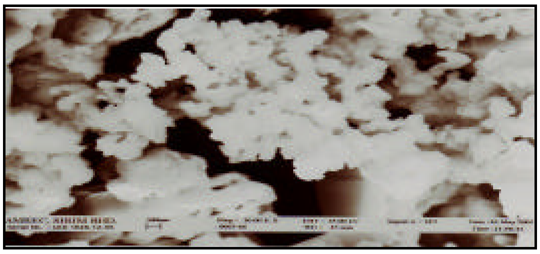

Figure 4: SEM micrograph of Sb-Ti

Figures 3 and 4 show the Sb-V-Ti and Sb-Ti catalysts with length of less than 1 μm diameter and 300-500 nm, respectively, which have the morphology of coral-type structures, formed by aggregates of microgranules. The result is consistent with that observed in the XRD diffractogram which shows that the solids are in crystalline phase with the presence of TiO_2 rutile. The darker areas, which a few nm wide, could possibly be Sb-rich patches, while the lighter areas correspondingly could be less rich in antimony. This result at least shows that the surface can accommodate some variation in antimony content.

Surface Area Measurements

Surface pore analysis is an important tool for characterisation for porous materials, due to the nearly overwhelming contribution of pores to the total surface area. N_2 adsoprtion isotherms are commonly adopted as a concise access to surface pore analysis since it reflects a statistical concept dealing with the probable integral features of surface texture. It is well known that both the activity and the stability of a supported catalyst usually depend on their surface characteristics, which are substantially related to both the intrinsic properties of the catalytic species and the support as well as to the mutual interactions between them.

Nitrogen adsorption-desorption on the Sb based mixed oxide catalysts was carried out to determine the BET surface area (S_{BET}), pore volume (Vp) and average pore radius (?) of the catalysts. The adsorption curves for all catalysts show that these catalysts (Sb-V, Sb-V-Ti and Sb-Ti) are of Type IV mesoporous materials according to IUPAC classification at relative vapour pressure (P/P^0) of 0.65-0.93 [13]. When the catalysts were subjected to desorption, they show a hysteresis loop of type A. This is a characteristic of porous material with open slit-shaped capillary pores where they are formed by two parallel plates [14]. It shows a hysteresis loops because the isotherm does not follow the same path in desorption as it does in adsorption due to evaporation of condensed gas in fine pores does not occur as easily as its condensation [13].

Table 1 shows the BET surface area (S_{BET}), pore volume (Vp) and average pore radius (?) of all the Sb-based catalysts, where the surface area of the Sb-V doped catalysts increases when Ti was used as dopant. However, surface area of the Sb-Ti catalysts is very low, suggesting that only a limited number of pores are available within the Sb-Ti catalyst, contributing to the low surface area and pore volume. Table 1 also shows that the average pore diameters of all the Sb-based catalysts are in the range of 2-4 nm. These catalysts are therefore classified as mesoporous materials with the pore diameters in range between 2-50 nm and in agreement with the hysteresis loop observed in the adsorption-desorption curves. This shows that the porous networks available within the sample are spaced out between the primary particles [15].

Table 1: The specific surface area, pore size and pore volume of catalysts prepared

Catalysts	BET Surface Area (m^2g^{-1})	Pore Volume (cm^3g^{-1})	Average Pore Radius (nm)
Sb-V	25.67	0.0171	3.0285
Sb-V-Ti	42.07	0.0354	4.7504
Sb-Ti	5.57	0.0038	2.6459
TiO_2	10.41	0.0069	4.1703

In general, the smaller the average pore size, the higher the total surface area of the materials. However, even though the average pore size of the Sb-Ti catalyst is smaller than Sb-V and Sb-V-Ti, its pore volume and total surface area are much smaller than that of both catalysts.

Promotional of the Sb-V catalyst with Ti slightly increased both the surface area and the pore radius of the Sb-V-Ti catalyst as compared to those of Sb-V catalyst. It is believed that functional of V which lead to become paraffin activator has take a part to increase the surface area and pore radius since only a very small mole ratio of Ti was added to the Sb-V catalyst, the effect seen in terms of pore radius and surface area are not significant. It is also believed that when Ti atoms were deposited onto the pore openings, the corrosive nature on Ti attacks on the pore openings leading to bigger pore size and deformation of some of the continuous surface into smaller non-continuous surfaces. Besides that, it may showed that Ti helps to stabilize the surface composition, thus limiting the formation of surface antimony oxide during reaction. The substitution of V and Ti into Sb-mixed oxide catalysts was suggested that this effect might lead to more active but less selective catalysts.

On the other hand, without using vanadium as promoter on the Sb-Ti catalyst compared to Sb-V-Ti catalyst, which has been reduced both the surface area and the pore radius of the Sb-Ti catalyst by about 8-fold and 2-fold, respectively. This suggests that not only the Ti were deposited onto the openings of the pores but such deposition also leads to closing some of the pore opening resulting in the reduction of the surface area. In addition, the corrosive nature of Ti also attacks on the pore openings. Without vanadium atoms, which have been suggested as paraffin activator and primary active sites, the propane ammoxidation process is thought to be activating unless Ti could replace the function of vanadium in the Sb-based catalyst. These suggest that only a limited number of pores available in the Sb-Ti catalyst, contributing the low surface area and pore volume

Catalytic Properties

The catalytic performances by all the Sb-based mixed oxide catalysts (Sb-V, Sb-V-Ti and Sb-Ti) were tested for the ammoxidation of propane to ACN. Figure 5 shows the performance of both Sb-V and Sb-V-Ti catalyst give higher conversion of propane than Sb-Ti catalysts. However, although the Sb-V-Ti catalyst has higher surface area as compared to Sb-V and Sb-Ti catalyst, a much lower selectivity to ACN was observed. This could be due to the absence of Sb_6O_{13} phase and insufficient existence of a-Sb_2O_4 phases within the catalyst system. The relationship observed suggests that Sb is the nitrogen-inserting component. This inference can be perceived considering that the V^{3+} species is the propane activator and if Sb^{5+} performs the nitrogen insertion, then an increase in the Sb^{5+}:V^{3+} ratio of the active material should increase the probability of nitrogen insertion and formation of acrylonitrile. On the other hand, higher selectivity to ACN observed from the Sb-Ti catalyst could be resulted by the lower surface area available within the catalyst, thus restricting the reaction from taking place, even though it shows good existence of crystalline phases of Sb_6O_{13} phase. This also could be due to the fact that TiO_2 has been found to be an efficient catalyst for NH_3 activation and/or the NH insertion step in the ammoxidation reaction, which favoured in the selectivity to ACN. This shows that the Sb-V is the best catalyst formulation for the production of ACN under reaction condition used in this work.

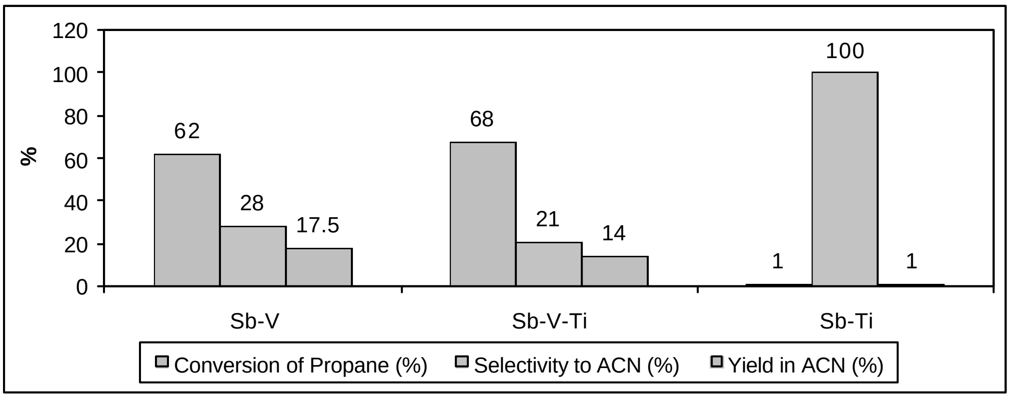

Figure 5: Catalytic performance (conversion and selectivities) of the Sb-based mixed oxide catalysts in the ammoxidation of propane.

Conclusion

Antimony and Vanadium (Sb-V-Ti and Sb-V) had given better performance in antimony-based mixed oxide catalyst by producing better catalytic activity in propane ammoxidation as compared to titanium (Ti). Various physicochemical characterizations used in this study show that Ti could not replace the function of V in Sb-based catalyst for propane ammoxidation reaction to ACN.

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