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Involvement of Redox Sites in Propane Ammoxidation on V-Sb-Oxide Catalysts

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V-Sb-Oxide catalysts were prepared by SS (solid solution) and CP (co-precipitation) methods, and the involvement of redox sites and acid sites in the ammoxidation of propane were investigated by BET, XRD, XPS, NARP (Nitric oxide-Ammonia Rectangular Pulse) and NH3-TPD methods. Both series of catalysts mainly consisted of the SbVO4 phase with minor components of V2O5 and α-Sb2O3 phases. The reaction rate of propane ammoxidation increased linearly with the increase in the number of redox sites measured by NARP technique. There was no significant effect of strength and amount of acid sites on the activity of propane ammoxidation at low conversion levels. The number of redox sites is the determining factor for ammoxidation activity. V-Sb-Oxide catalysts with excess α-Sb2O3 phase exhibited higher turnover frequency.

1. Introduction

There is significant interest in the development of catalytic processes using alkane feedstock. Ammoxidation of propane to acrylonitrile1,2) is an attractive process because commercialization is expected to be possible in a few years. Various metal oxide catalysts have been investigated for propane ammoxidation3,4): (i) Ga-antimonate5), (ii) Bi-V-molybdate6), (iii) vanadyl phosphate6), (iv) Mo-V-Nb-Te mixed oxide7-9) and (v) V-Sb based oxide7-10). V-Sb based oxide is one of the best characterized catalysts with good catalytic performance for propane ammoxidation7-10).

The characteristics of the bulk phase, kinetic studies, and reaction mechanism of the V-Sb-oxide system are well investigated10)-13). Vanadium-antimonate (V2SbO6 or Sb2O3) is essential for propane ammoxidation11,12). XRD studies have shown that the V2SbO6 phase is present as a tetragonal-rutile phase with cell parameters of \( a = b = 4.624 \ \text{Å} \) and \( c = 3.043 \ \text{Å} \). Investigation of the effects of preparation method and Sb/V ratio clarified that excess antimony oxide on the V2SbO6 phase is also important for propane ammoxidation13). Both VSbO5 and SbVO4 have rutile-type structures and often have non-stoichiometric cationic-deficient structures containing cations in various oxidation states10,13-15). XPS and \(^{121}\text{Sb} \) Mössbauer spectroscopy have been used to study the oxidation state of vanadium and antimony in vanadium-antimonate13,15)-16).

The bulk phase of V-Sb-oxide catalyst has been well examined, but the surface structure is less understood. The surface chemical properties or surface functional species, i.e., active sites, are thought to directly interact with the reactants and intermediates and control the reaction pathway17-19), so further investigation on surface structure is required for better understanding of propane ammoxidation on V-Sb-oxide catalyst. Redox sites may be important for the partial oxidation of organic molecules involved in the redox cycle between lattice oxygen and organic molecules, i.e., the Mars-van Krevelen mechanism20). Acid sites may be required for NH3 adsorption and oxygen insertion21). Generally, Lewis acid sites are required for alkane C-H bond activation in selective oxidation22). The activation involves the cleavage of the methylene C-H bond and is likely to be the rate-determining step. Propane is dehydrogenated at the methylene group position to propene via the V=O site which is the rate limiting step for the overall process23,24). The propene product would require activation to \( \pi \)-allyl before reacting with NH3 on antimony oxide or a solid solution containing excess Sb. The importance of surface active sites is clear, but there is little quantitative discussion on the involvement of active sites.

Previously, we used the NARP (Nitric oxide-Ammonia Rectangular Pulse) technique to determine the surface redox sites on V-Sb-oxide catalyst25). We found that the NARP technique can also determine the surface redox sites by selecting optimum conditions of measurement26-28). The number of surface redox species was found to strongly depend on the preparation method and Sb content.

In this study, the relationship between the active sites and propane ammoxidation on V-Sb-oxide catalyst was examined. The NARP technique and NH3-TPD were applied for the characterization of surface active sites.
i.e., redox sites and acid sites. V-Sb-O catalysts with Sb/V ratios from 0.5 to 2.0 were prepared by two different methods, and the effect of bulk structure and chemical composition was investigated.

2. Experimental

2.1. Preparation of Catalysts

V-Sb-Oxide catalysts with Sb/V ratio of 0.5, 1.0, and 2.0 were prepared by the following methods29). Solid state (SS) catalyst preparation was carried out by homogeneous mixing between V$_2$O$_5$ (Kishida Chemical Co., Ltd., 99%) and Sb$_2$O$_3$ (Kishida Chemical Co., Ltd., 99%) in a mortar. The obtained mixture was then calcined in an air flow at 673 K for 6 h and then at 873 K for 3 h. Co-Precipitation (CP) catalyst preparation was carried out by dissolving V$_2$O$_5$ and Sb$_2$O$_3$ aqueous HCl, mixing the solutions and stirring for 3 h. Concentrated NH$_3$ solution was added to pH 9 and the slurry was refluxed for 3 h. After filtration, the obtained precipitate was washed with distilled water several times to remove residual chloride ion. The slurry was dried at 383 K overnight, and calcined in flowing air at 673 K for 6 h, then at 873 K for 3 h. All calcined catalysts were sieved with the particle size in the range of 300-600 µm.

2.2. Characterizations

X-Ray powder diffraction (XRD) analysis was carried out using a Rigaku Corp./RINT-1200 with Cu Kα radiation. X-Ray photoelectron spectra (XPS) were measured with a Shimadzu Corp./KRATOS AXIS-HS using Mg Kα radiation at 1253.6 eV. Surface composition expressed as the Sb/V ratio was determined from the intensities of V 2p$_{3/2}$ and Sb 3d$_{3/2}$ on XPS spectra using the theoretical sensitivity factor30).

NARP (Nitric oxide-Ammonia Rectangular Pulse) measurements were carried out with the equipment reported previously31). After oxidation of catalyst (0.1 g) in flowing oxygen at 773 K for 30 min, the sample was cooled down to a predetermined temperature (450-600 K). NO-NH$_3$ mixture (NO/NH$_3$ = 1/4) gas was injected as a rectangular pulse with a width of 60 sec. The number of surface redox sites was determined according to the analysis of nitrogen produced31). NH$_3$-TPD spectra were measured by a conventional apparatus32). The sample (1.0 g) was pretreated under vacuum at 773 K and then calcined under 100 Torr oxygen at 773 K for 30 min. After cooling to room temperature followed by evacuation, the sample was exposed to 100 Torr NH$_3$ for 30 min followed by evacuation at room temperature to remove physisorbed NH$_3$. The NH$_3$-TPD profile was recorded in a helium stream with a heating rate of 5 K/min from room temperature to 773 K.

2.3. Catalytic Reaction Test

Propane ammoxidation was carried out in a packed-bed reactor (Pyrex glass) with an outer diameter of 12 mm. The reactor was heated in a fluidized sand bed. The catalyst weight was 0.20 g, and 1.0 g of quartz powder was added as a diluent. The composition of the feed gas was C$_3$H$_8$/O$_2$/NH$_3$/N$_2$ in the ratio of 1/2/1/2.5 and the total flow rate was 5 dm$^3$/h$^{-1}$. The product gas was analyzed by online-gas chromatography. Organic products, i.e., acrylonitrile, acetonitrile, acrylic acid, and light hydrocarbons, were separated with a Porapak QS (4 m long) column and detected by FID. Gaseous products, CO, CO$_2$, N$_2$, and O$_2$, were separated with a PorapakQ column (3 m) and a MS-13X column (5 m) and detected by TCD.

3. Results and Discussion

3.1. Characterization of Catalysts

Figure 1 shows the XRD patterns of SS and CP catalysts with various Sb/V ratios. All V-Sb oxide catalysts mainly consisted of the SbVO$_4$ phase with diffraction lines in agreement with JCPDS16-600. The compositions of the bulk phase were also confirmed by FT-IR spectra30).

Fig. 1 XRD Patterns of V-Sb-Oxide Catalysts

Fig. 2 shows the NH$_3$-TPD spectra of SS and CP catalysts with various Sb/V ratios. All V-Sb oxide catalysts mainly consisted of the SbVO$_4$ phase with diffraction lines in agreement with JCPDS16-600. SS catalysts had higher intensity diffraction lines of SbVO$_4$ compared to CP catalysts. Weak diffraction lines of V$_2$O$_5$ were also observed in catalysts with Sb/V ratios of 0.5 and 1.0. α-Sb$_2$O$_3$ phase was present in SS 1.0, SS 2.0, and CP 2.0. The compositions of the bulk phase were also confirmed by FT-IR spectra30).

Figure 2 shows the NH$_3$-TPD spectra of SS and CP. In the case of V$_2$O$_5$, the maximum desorption rate of NH$_3$ was observed at 350 K, and NH$_3$ desorption was terminated at 460 K. Integration of the peak showed that the surface concentration of acid sites on V$_2$O$_5$ was $4.4 \times 10^{15}$ mol/m$^2$. NH$_3$ desorption shifted to higher
temperature after the addition of antimony oxide. A broad desorption peak for SS catalyst was newly observed at 450-640 K. The second peak increased as Sb/V ratio increased. The second peak was more clearly observed in CP catalyst after addition of antimony oxide. The peak became sharper and occurred at higher temperature as Sb/V ratio increased.

Table 1 summarizes the results of various measurements. Surface Sb/V ratio determined by XPS was basically higher than that in the bulk catalyst. Surface Sb/V ratio on SS 1.0, SS 2.0 and CP 2.0 was higher than the stoichiometric ratio of SbVO4. In these catalysts, the α-Sb2O3 phase was also observed in XRD patterns, suggesting the presence of excess α-Sb2O3 phase on the surface. CP catalysts had a higher surface area than SS catalysts for any ratio of Sb/V. The surface areas obtained in this study were in the same range as those previously reported. The concentration of surface redox sites was higher on the SS catalyst than on V2O5, but was lower on the CP catalysts. The increased number of redox sites caused by the addition of antimony indicates that the surface V=O species is not only the redox site on V-Sb-oxide catalysts but the V-O-Sb bond in the rutile structure of SbVO4 probably also acts as a redox site. The surface concentration of acid sites increased with the addition of antimony oxide. There was no significant difference in the surface concentration between the two methods at the same Sb/V ratio. The number and strength of the acid sites measured in this study agreed fairly well with those reported previously.

3.2. Ammoxidation of Propane

Table 2 shows typical results of propane ammoxidation over the V-Sb-O catalysts. The catalytic reaction was carried out at a low conversion of propane, i.e., 1.8-24%, and oxygen conversion was also below 30%.
under the present reaction conditions. Effectiveness of conversion was in the order CP 2.0 > SS 1.0 > SS 2.0 = SS 0.5 > CP 1.0 > CP 0.5, which is different from the order of surface area. SS catalysts generally provided higher specific reaction rate than CP catalysts, and catalysts with higher Sb/V ratio had higher reaction rate. Catalysts with low Sb/V ratio showed higher acrylonitrile and carbon oxide selectivity and lower propene selectivity than catalysts with high Sb/V ratio. Acrylonitrile selectivity over V-Sb-O catalyst usually increases with Sb/V ratio34), but the catalysts examined in this study showed the opposite trend, which may be due to the lower conversion of propane observed. Propane ammoxidation is a consecutive reaction that proceeds as C3H8 → C3H6 → C2H3CN → COx19). The higher selectivity for C3H6 on the catalysts with higher Sb/V ratio may suggest less over-oxidation. However, since the product distribution changes as a function of propane conversion, the effect of the preparation method and Sb/V ratio on the selectivity is not clear in Table 2 due to the differences in the conversion level.

3.3. Relationship between Ammoxidation Activity and Surface Sites

Figure 3 shows the correlation between the number of surface redox sites and the specific reaction rate at 713 K. The reaction rate per surface area increased linearly with the increase in the surface concentration of redox sites. Similar results were obtained at the other temperatures. These results clearly indicate that the redox sites are the key factor for catalytic activity in propane ammoxidation. Centi et al. pointed out that propane ammoxidation involves redox mechanisms including the dehydrogenation of propane to propene and oxygenation of propene35,36). Since oxydehydrogenation of propane to propene is thought to be the rate-determining step for propane ammoxidation, the number of surface redox sites measured by the NARP technique may correlate with the dehydrogenation step in propane ammoxidation.

However, the catalysts could be classified into two groups, SS 1.0, SS 2.0 and CP 2.0 (Group A) and CP 0.5, CP 1.0, and SS 0.5 (Group B). This suggests that there is an intrinsic difference in the quality of the redox sites. Examination of the acid strength (Fig. 2) and acid amount (Table 1) showed no correlation with the groups in Fig. 3. The XRD results in Fig. 1 show that Group A includes α-Sb2O3 phase whereas Group B does not. Table 1 shows that the surface Sb/V ratio of Group A catalysts was >1 and that of Group B was <1. These results suggest that the excess α-Sb2O3 phase is stabilized on the SbVO4 surface of Group A catalysts. Therefore, the excess α-Sb2O3 phase enhances the active sites of V-Sb-oxide catalysts in propane ammoxidation.

There was no significant difference in the acid amount and acid strength between the two groups, so the enhanced activity may be due to the change in the redox properties of the active sites. The redox properties of antimony oxide were already reported for other catalytic oxidation systems. It is suggested that, in Mg–V–Sb catalysts, selective oxydehydrogenation of propane may occur on isolated (Sb–O–V–O–Sb) sites37). As Burrington et al. suggested, antimonate sites may be involved in the selective ammoxidation and oxidation of propene over antimonates38). Sb5+-O sites catalyse the chemisorption of propene, and bridging oxygens of Sb5+-O polyhedra perform H-abstraction from intermediates in the pathway of acrylonitrile formation. Therefore, excess α-Sb2O3 may act as a promoter for the redox sites on SbVO4.

4. Conclusion

The structure-activity relationships in propane ammoxidation over V-Sb-oxide catalysts were investigated by the measurement of surface redox sites and acid sites. The number of redox sites is the determining factor for the catalytic activity of propane ammoxidation. The qualitative change in the redox sites was correlated to the presence of excess surface α-Sb2O3.

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References


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Active site, Oxide catalyst, Vanadium antimonate, Ammoxidation, Propane