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Ammoxidation of propane to acrylonitrile over Mo-V-P-O_y/Al_2O_3 catalysts: Effect of phosphorus content

Minsung Baek [a], Jong Kwon Lee [a], Heung Jung Kang [b], Bum Jin Kwon [b], Ji Hye Lee [b], In Kyu Song [a,*]

[a] School of Chemical and Biological Engineering, Institute of Chemical Processes, Seoul National University, Shinlim-dong, Kwanak-ku, Seoul 151-744, South Korea
[b] S-OIL Corporation, Onsan-eup, Ulju-gun, Ulsan 44995, South Korea

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ABSTRACT

Mo-V-P-O_y/Al_2O_3 (denoted as 18.1Mo1.9VXP/Al: 18.1 wt% Mo, 1.9 wt% V, X wt% P) catalysts with different phosphorus content were prepared by an impregnation method, and they were applied to the acrylonitrile production by ammoxidation of propane. The effect of phosphorus content on the physicochemical properties and catalytic activities was investigated. Conversion of propane and yield for acrylonitrile showed volcano-shaped trends with respect to phosphorus content. Yield for acrylonitrile increased with decreasing binding energy of Mo $3d_{5/2}$. Among the catalysts, 18.1Mo1.9V0.6P/Al with the smallest binding energy of Mo $3d_{5/2}$ showed the best catalytic performance in the ammoxidation of propane to acrylonitrile.

1. Introduction

Acrylonitrile is a useful precursor of various products such as resins, rubbers, and carbon fiber. Currently, acrylonitrile is majorly produced through the ammoxidation of propylene over Bi-Mo mixed oxide catalysts. Although this process is a well-established route for the production of acrylonitrile, ammoxidation of propane to acrylonitrile has attracted much attention as a promising process because propane is more abundant and less expensive than propylene. In this respect, several catalysts for the production of acrylonitrile by ammoxidation of propane have been investigated. These examples include Mo-V-Te-Nb-O_y [1], V-Sb-O_y [2], and V-P-O_y/Al_2O_3 [3]. Among these catalysts, Mo-V-Te-Nb-O_y has been considered as a highly efficient catalyst in the propane ammoxidation [1]. However, it is very difficult to reproduce Mo-V-Te-Nb-O_y catalyst because catalytic activity is highly dependent on the formation of specific orthorhombic phase of the catalyst [1,4]. Furthermore, weak thermal stability of Mo-V-Te-Nb-O_y and volatile property of Te are drawbacks in the long-term operation [4].

Supported metal oxide catalysts have been widely investigated to promote catalytic activity. To enhance the catalytic performance of supported catalysts, addition of second component such as Sb, W, and P has been attempted [2,3,5]. In particular, phosphorus has been widely used to modify physicochemical properties of the catalyst [3,6,7]. Supported molybdenum-vanadium-phosphate catalyst for oxidative dehydrogenation of ethane is an example of using phosphorus as a promotor [7]. In this catalyst, phosphorus remarkably improves the catalytic activity by isolating molybdenum and vanadium components. Therefore, development of a phosphorus-containing efficient catalyst for propane ammoxidation would be worthwhile.

In this work, a series of Mo-V-P-O_y/Al_2O_3 catalysts with different phosphorus content were prepared by an impregnation method for use in the ammoxidation of propane to acrylonitrile. The effect of phosphorus content on the physicochemical properties and catalytic activities was investigated.

2. Experimental

2.1. Catalyst preparation

Molybdenum-vanadium-phosphorus mixed oxide catalysts supported on alumina were prepared by an impregnation method with a variation of phosphorus content. In short, 1.66 g of ammonium heptamolybdate (Sigma-Aldrich), 0.22 g of ammonium metavanadate (Sigma-Aldrich), and 2.85 g of oxalic acid (Sigma-Aldrich) were dissolved in 25 g of distilled water with stirring for 1 h at 85 °C. Phosphoric acid (Sigma-Aldrich) was then added into the solution as a structural modifier. During this process, Mo:V:P weight percentage was adjusted to be 18.1:1.9:X (X = 0, 0.6, 1.2, 2.3, and 3.5). Subsequently, γ-alumina (Alfa Aesar, S_{BET}: 220 m^2/g) support was added into the homogeneous solution. After stirring the mixture for 1 h, it was dried using a rotary evaporator at 85 °C. The resultant was calcined using a tube-type furnace in a nitrogen flow at 550 °C for 2 h. The prepared catalysts were denoted as 18.1Mo1.9VXP/Al (X = 0, 0.6, 1.2, 2.3, and 3.5), where X represented the phosphorus weight percentage. The sum of molybdenum and vanadium loading was fixed at 20 wt% in all catalysts.

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[*] Corresponding author.
E-mail address: inksong@snu.ac.kr (I.K. Song).

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2.2. Catalysts characterization

Textural properties of 18.1Mo1.9VXP/Al catalysts were obtained by nitrogen adsorption-desorption measurements (BELSORP-mini II, BEL Japan). Atomic compositions of the catalysts were measured by ICP-AES (inductively coupled plasma atomic emission spectroscopy) analyses (ICPS-7500, Shimadzu). Crystalline structures of the catalysts were investigated by XRD (X-ray diffraction) measurements (D-Max2500-PC, Rigaku). In order to confirm the dispersion of constituent elements, TEM-EELS mapping analyses (Technai F20) were conducted. Binding energies and surface atomic ratios of the catalysts were determined by XPS (X-ray photoelectron spectroscopy) analyses (ThermoVG, Sigma Probe). TPR (Temperature-programmed reduction) measurements were conducted using a U-shaped quartz reactor. For the TPR measurement, 50 mg of each catalyst was reduced with a mixed stream H_2 (2 ml/min) and N_2 (20 ml/min). TPR profile was obtained using a thermal conductivity detector (TCD) at a heating rate of 10 °C/min from room temperature to 950 °C.

2.3. Ammoxidation of propane to acrylonitrile

Acrylonitrile production by ammoxidation of propane was carried out in a continuous flow fixed-bed quartz reactor at 480 °C under atmosphere pressure. Prior to the reaction, each calcined catalyst (200 mg) was loaded into the reactor and it was treated with a mixed stream of NH_3 (6 ml/min) and N_2 (48 ml/min) at 480 °C for 2 h as a pre-activation step. After the activation, the reactant stream comprising C_3H_8 (4 ml/min), O_2 (12 ml/min), NH_3 (6 ml/min), and N_2 (48 ml/min) was introduced for the reaction. Catalytic reaction was carried out at 480 °C for 6 h. Reaction products were analyzed using gas chromatographs equipped with a thermal conductivity detector and a flame ionization detector. The carbon balance was in the range of 94–100% in all the reaction tests.

3. Results and discussion

3.1. Characterization of Mo-V-P-O_y/A_2O_3 catalysts

Detailed physicochemical properties of 18.1Mo1.9VXP/Al (X = 0, 0.6, 1.2, 2.3, and 3.5) catalysts are summarized in Table 1. Actual phosphorus content (wt%) was similar to the designed value. All the catalysts showed high surface area (>187 m^2/g), large pore volume (>0.31 cm^3/g), and large pore diameter (>6.4 nm), indicating the existence of well-developed mesopores. It is interesting to note that pore volume and pore diameter of the catalysts decreased with increasing phosphorus content. This result might be attributed to the pore blockage by phosphorus.

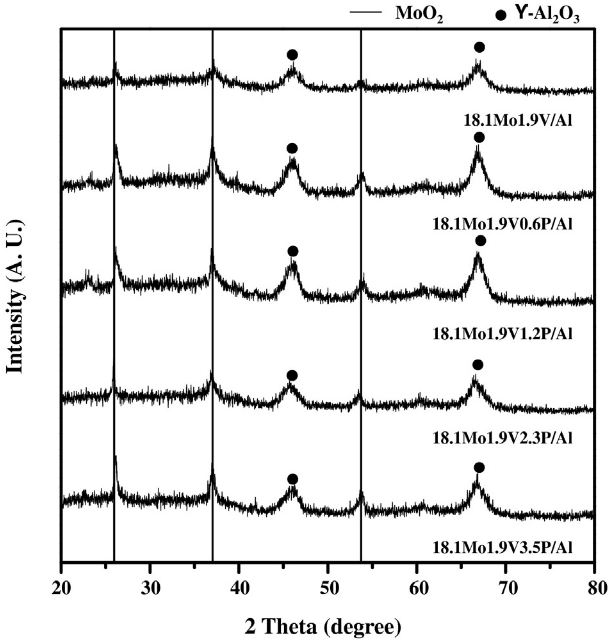

Fig. 1. XRD patterns of 18.1Mo1.9VXP/Al (X = 0, 0.6, 1.2, 2.3, and 3.5) catalysts.

Crystalline structures of 18.1Mo1.9VXP/Al (X = 0, 0.6, 1.2, 2.3, and 3.5) catalysts were confirmed by XRD measurements as shown in Fig. 1. All the catalysts showed the diffraction peaks of γ-alumina and MoO_2. It has been reported that small amount of MoO_2 structure is formed when supported molybdenum oxide is thermally decomposed under inert gas [7]. Characteristic diffraction peaks related to vanadium and phosphorus species were not observed. To confirm the distribution of molybdenum, vanadium, phosphorus, and aluminum species in the 18.1Mo1.9V0.6P/Al catalyst, TEM-EELS analyses were conducted (Fig. S1 of Supporting Information). Each species was finely dispersed in the catalyst. From this result, it can be inferred that amorphous molybdenum-vanadium-phosphorus oxide was successfully dispersed on the surface of alumina.

X-ray photoelectron spectroscopy analyses were conducted to measure binding energies and surface atomic ratios of the catalysts. The measured binding energies of Mo $3d_{5/2}$ and surface atomic ratios are summarized in Table 1. Deconvolution of XPS spectra was performed by the Gaussian curve-fitting method. Surface atomic ratios were calculated from XPS peak area of individual component. As listed Table 1, P/Al surface atomic ratio increased with increasing phosphorus content. (Mo + V)/Al surface atomic ratio of 18.1Mo1.9VXP/Al (X = 0.6, 1.2, 2.3, and 3.5) was higher than that of 18.1Mo1.9V/Al. This result implies that phosphorus assisted the migration of molybdenum and vanadium to alumina surface by weakening the interaction between molybdenum-vanadium oxide and alumina [7].

Fig. 2 shows the XPS spectra of Mo 3d level. Compared to 18.1Mo1.9V/Al, the phosphorus-containing catalysts showed negligible Mo^{4+}. In addition, majority of molybdenum in the phosphorus-containing catalysts existed in the state of Mo^{6+}. The presence of Mo^{4+} is

Table 1
Physicochemical properties and XPS results of 18.1Mo1.9VXP/Al (X = 0, 0.6, 1.2, 2.3, and 3.5) catalysts.

Sample	Phosphorus content (wt%)[a]	Surface area (m^2/g)[b]	Pore volume (cm^3/g)[c]	Pore diameter (nm)[d]	Binding energy of Mo $3d_{5/2}$ (eV)	Surface atomic ratio[e]	
						(Mo + V)/Al	P/Al
18.1Mo1.9V/Al	0	192	0.36	7.5	232.75	0.14	–
18.1Mo1.9V0.6P/Al	0.6	193	0.36	7.4	232.54	0.17	0.07
18.1Mo1.9V1.2P/Al	1.1	197	0.35	7.2	232.63	0.18	0.14
18.1Mo1.9V2.3P/Al	2.2	187	0.32	6.8	232.90	0.16	0.18
18.1Mo1.9V3.5P/Al	3.2	192	0.31	6.4	233.02	0.18	0.20

[a] Determined by ICP-AES measurement.
[b] Calculated by the BET equation.
[c] Total pore volume at $P/P_0 = 0.99$.
[d] Average pore diameter.
[e] Determined by XPS analysis.