INFLUENCE OF ORGANIC SPECIES ON THE CHARACTERISTICS OF Mo-V OXIDES

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Abstract

This study investigates on the effect of organic species on the characteristics of molybdenum-vanadium mixed oxide catalysts. The MoV precursors were prepared by homogeneous precipitation method using urea hydrolysis. The oxides were later treated with three organic species namely polyvinyl alcohol (PVA), malic acid (MA) and adipic acid (AA). The solutions were refluxed in a prescribed time. The solid obtained were calcined and subsequently denoted as MoV(PVA), MoV(MA) and MoV(AA). Interesting results in which high surface area values (S_{BET}) were obtained in the range between 10 to 20 $m^2 g^{-1}$. XRD reckoned the samples are in highly crystalline form. H_2-Temperature programmed reduction analysis showed that the total number of oxygen removed are 1.4×10^{22} atoms g^1, 3.3×10^{22} atoms g^1 and 1.8×10^{22} atoms g^1 for MoV(PVA), MoV(MA) and MoV(AA) respectively.

Abstrak

Kajian ini dijalankan untuk memperolehi kesan spesis organik terhadap ciri-ciri mangkin molibdenum-vanadium oksida tercampur. Prekursor MoV telah disediakan melalui kaedah pemendakan homogen menggunakan hidrolis urea. Prekursor MoV ini telah dirawat dengan masing-masing bahan organik polivinil alkohol (PVA), asid malik (MA) dan asid adipik (AA). Kesemua larutan telah direfluks pada masa yang ditetapkan. Pepejal yang diperolehi telah dikalsin dan dilabelkan sebagai MoV(PVA), MoV(MA) dan MoV(AA). Keputusan yang menarik berjaya dicapai di mana nilai luas permukaan yang tinggi (S_{BET}) antara 10 hingga 20 $m^2 g^{-1}$ telah berjaya diperolehi. Pembelauan sinar-X (XRD) menunjukkan bahawa samepl-sampel adalah berhablur. Analisis penurunan berprogram suhu dalam hidrogen (H_2-TPR) menunjukkan jumlah oksigen yang berjaya dikeluarkan adalah masing-masing 4×10^{22}, 3.3×10^{22} dan 1.8×10^{22} atom g^1 bagi sampel MoV(PVA), MoV(MA) dan MoV(AA).

Introduction

The conversion of propane to acrylic acid has been the focus of extensive research worldwide since the early 1990s. In the current commercial process, acrylic acid is produced via two-step selective oxidation process using propylene as the starting materials [1]. Thus, replacing propylene with the much cheaper propane will provide a huge cost saving as the cost of propane feedstock is about 5-6 times less than the cost of propylene [2].

Molybdenum vanadium mixed oxides (Mo-V-O) catalysts have received much attention for its usefulness in the technical production of acrylic acid by partial oxidation of propane [3-5]. The synthesis route commonly used to produce the Mo-V based catalysts is the hydrothermal method [6, 7]. However, this method is very exclusive which involved usage of high pressure and high temperature conditions. From the economic circumstances, it is not a good option. Moreover, the catalysts prepared by laboratory scale hydrothermal synthesis usually have low surface areas (< 10 $m^2 g^{-1}$) [8, 9]. Although these catalysts exhibit a rather good selectivity for small space velocities, the improvement of the catalytic performances by increasing the productivity remains a challenge. A possible way to increase the productivity is to enhance the surface area of these catalysts [10].

Therefore, the aim of this work was to investigate new routes for the preparation of Mo-V mixed oxides with high surface area and to characterize these materials. The strategy was to treat the MoV precursors with 1% wt of additives *i.e.* polyvinyl alcohol (PVA), malic acid (MA) and adipic acid (AA). The properties of precipitates can be strongly influenced by additives. Additives are substances which are not a necessary ingredient of a precipitation reaction [11]. Organic molecules are the most widely used additives in order to control the pore structure. Such organic molecules can later be removed from the precipitate in a calcination step. It is important in this study to look out for the possibility of improved characteristic of the binary oxide when added with additives in the preparation process.

Experimental

Preparation of precursor Mo-V

The precursors, Mo-V oxides with a molar ratio of 1:0.3 were prepared by homogeneous precipitation method using urea hydrolysis. Ammonium heptamolybdate, $(NH_4)_6Mo_7O_{24}$ (12.36 g from Merck) was dissolved in 50 mL of hot distilled water (100 °C). Separately, urea, NH_2CONH_2 (6.31 g from Hmb G) was added together with vanadium (IV) oxisulphate hydrate, $VOSO_4$ (3.42 g from Riedel-de Haën) in 50 mL of distilled water. This solution mixture was slowly heated until 90 °C where the urea was slowly hydrolyzed to generate hydroxyl ions. Both of the solutions (Mo and V-solutions) were mixed together in a round bottom flask. After 5 minutes of N_2 gas bubbling to replace the residual air, the mixture was reflux for 1 h to ensure it homogeneously mixed. The dark purplish gel that formed was filtered and washed sparingly with distilled water. Precipitates were dried overnight in desicator to give the Mo-V oxides precursor. Organic species was then added to the precursor and mixtures were reflux for 1 h. The organic species used were polyvinyl alcohol (PVA), malic acid (MA) and adipic acid (AA). All of the samples were calcined in flow of nitrogen gas for 2 h at 773 K.

Samples characterization

The precursor samples as well as the catalyst after heat treatment were characterized using X-ray diffraction analysis (Shimadzu diffractometer model XRD-6000 diffractometer) employing CuK_a radiation generated by Philips glass diffraction X-ray tube broad focus 2.7 kW type on the catalyst at ambient temperature and was scanned at the 2? range of 2°-60° with scanning rate of $0.02^o s^{-1}$.

The BET (Brunauer-Emmet-Teller) total surface area of the catalysts was measured by nitrogen adsorption with Sorptomatic 1990 Series ThermoFinnigan at 77 K.

The bulk chemical composition was determined using a sequential scanning inductively coupled plasma-atomic emission spectrometer (ICP-AES) Perkin-Elmer Emission Spectrometer model Plasma 1000.

H_2-Temperature Programmed Reduction (H_2-TPR) was performed using ThermoFinnigan 1100 Series TPD/R/O. The samples were pre-treated by heating it to 393 K in a nitrogen flow (1 bar, 20 cm^3 min^{-1}) before cooling to ambient temperature prior to H_2-TPR analysis. Samples were heated from room temperature to 1273 K at a heating rate of 10 K min^{-1} in a flow of 5% H_2/Ar (25 cm^3 min^{-1}).

Results and Discussion

X-ray diffraction

X-ray diffractograms of precursors are shown in Figure 1. In this complex patterns, phases that have been identified are Mo-V-O orthorhombic (W. Ueda *et. al*., 2004) [6], $V_{0.95}Mo_{0.97}O_5$ –anorthic (JCPDS File No. 01-077-0649), V_2MoO_8 (JCPDS File No. 01-074-1510) and VO_2 –tetragonal (JCPDS File No. 42-0876). For untreated precursor, small diffraction lines were observed indicating the amorphosity of the sample. On the other hand, treated precursor samples showed sharp and intense peaks which are present in all samples at 2? = 9.0, 16.2 and 27.6°. This is to suggest that crystalline structure of the orthorhombic, anorthic and tetragonal phases are achievable when treated with organic species.

In Figure 2, the diffractograms show different patterns as compared to Fig. 1. All of the samples transformed into Mo-V-O orthorhombic phase [6] with the appearance of peaks at 2? = 22° and 45° and $(V_{0.07}Mo_{0.93})_5O_{14}$-tetragonal (JCPDS File No. 31-1437). Well developed orthorhombic phase is successfully achieved when using MA and PVA in the synthesis process. Meanwhile AA gives mixture of orthorhombic and tetragonal phases which is identical to untreated sample. One significant observation is the highly intense and sharp diffractograms displayed by MoV(MA) and MoV(PVA) samples suggesting the existence of a well formed crystals within these samples.

Bulk composition

Table 1 shows the bulk composition of the calcined samples. ICP analysis revealed that all of the samples had a composition of $Mo_1V_{0.29}O_x$, which is almost identical with the theoretical stoichiometry. A slight deviation of composition is observed for samples treated with organic species.
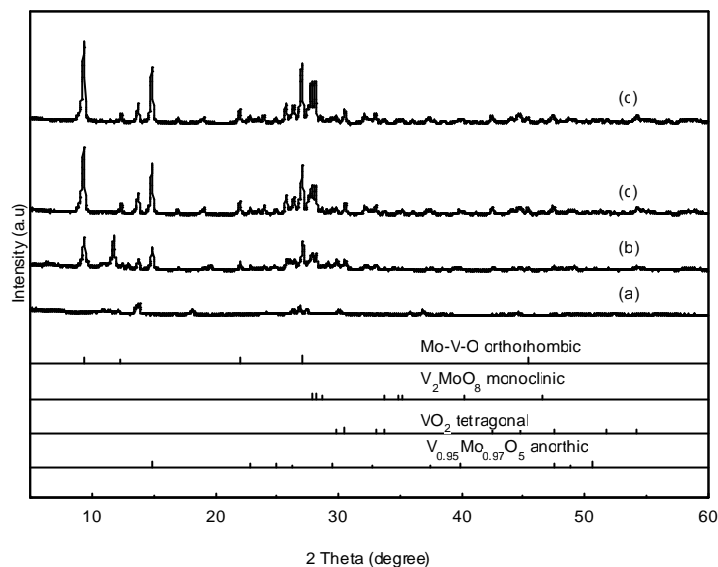
Figure 1: XRD diffractograms of precursors a) MoV(control), b) MoV(AA), c) MoV(MA) and d) MoV(PVA).
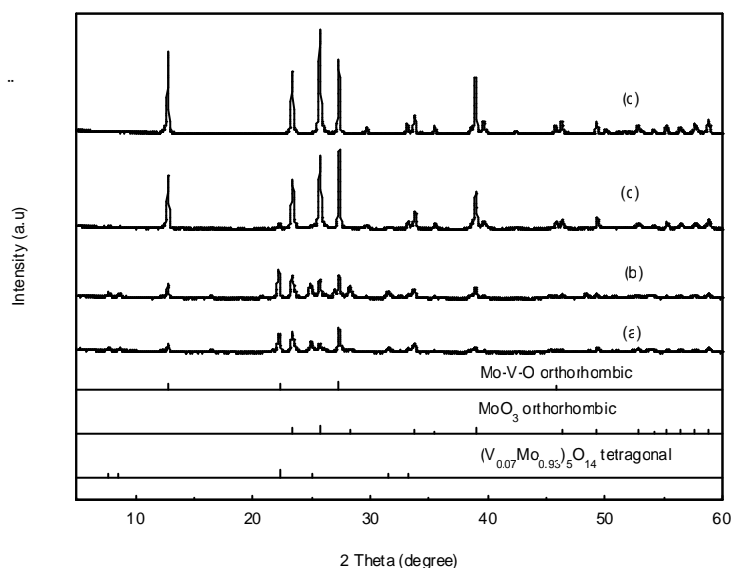

Figure 2: XRD diffractograms of calcined samples a) MoV(control), b) MoV(AA), c) MoV(MA) and d) MoV(PVA).

BET surface area measurements

BET surface area results are also listed in Table 1 with MoV(PVA) shows the highest surface area. The samples treated with MA and AA also have surface areas higher than what had been previously reported by other researchers. According to Le *et al*. [12], when a precursor contains any substance which can be burned during calcinations, the surface area of the final product can be increased. The statement is found true in this case as the calcinations were done at temperature 773 K while the melting point for PVA, MA and AA is 473 K, 403 K and 363 K, respectively. The MoV(control) also gives high surface area which is found higher than MoV(MA). This is to suggest that when MA was heated during calcinations, it not only leaves spaces but also induced the particles to aggregate. Whereas other organic species, AA and PVA left voids or spaces which contributed to higher surface area value of the samples. The removal of organic species from precursor can be represented by the following Diagram 1.
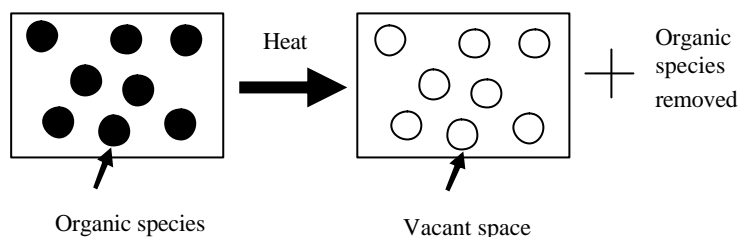
(Diagram 1)

Table 1: S_{BET} and bulk composition for the calcined samples.

Samples	S_{BET} (m^2 g^{-1})	Bulk composition[a] (Mo/V)
MoV(control)	13.2	1/0.29
MoV(AA)	15.5	1/0.27
MoV(MA)	10.6	1/0.27
MoV(PVA)	20.8	1/0.26

[a] Bulk composition was determined by ICP analysis.

H$_2$-Temperature Programmed Reduction

Figure 3 shows the temperature programmed reduction profile obtained by flowing 5% H$_2$/Ar (1 bar, 25 cm^3 min^{-1}) continuously over the pre-treated samples. The reaction temperature was increased linearly at 10 K min^{-1}. The onset of reaction is ~700 K. All four samples display similar profile with only one distinct peak maxima is observed. The interaction of hydrogen with the catalyst surface can be represented by the following equation:

$$H_2(g) + O(a) \rightarrow H_2O(g) + \ ?\ ?$$

(1)
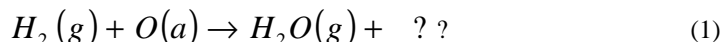
where (a), (g) is adsorbed and gaseous species respectively, while $?$ is a vacant site.

A rough estimation on the amount of oxygen removed was made by deconvoluting the area under the peak. The total amounts of oxygen are 7.3 x 10^{21}, 1.8 x 10^{22}, 3.3 x 10^{22} and 1.4 x 10^{22} atoms g^{-1} for MoV(control), MoV(AA), MoV(MA) and MoV(PVA), respectively. These are listed in Table 2. All samples treated with organic species displayed lower reduction activation energy, E_r which derives from the need to remove oxygen from the lattice. These reduction activation energies for the interaction of chemisorbed H$_2$ with surface and bulk oxygen pre-treated catalysts to form H$_2$O can be obtained from a modified version of the Redhead equation:

$$\frac{E_r}{RT_m^2} = (\frac{Ar}{\beta})[H_2]_m \exp(\frac{E_r}{RT_m})$$

(2)

where T_m is the peak maximum temperature (K), E_r is the reduction activation energy (kJ mol^{-1}), A is the reduction pre-exponential term (cm^3 mol^{-1} s^{-1}) that is given the value of a standard collision number of 10^{13} cm^3 mol^{-1} s^{-1} and [H$_2$]$_m$ is the gas phase concentration of hydrogen (mol cm^{-3}) at the maximum peak.

The reduction activation energies for MoV(control), MoV(AA), MoV(MA) and MoV(PVA) are 177 kJ mol^{-1}, 162 kJ mol^{-1}, 172 kJ mol^{-1} and 171 kJ mol^{-1}. These high reduction activation energies were resulted from the need to remove strongly bonded oxygen species. Therefore, these oxygen are surface lattice and lattice oxygen species. Confirmation of the origin of these species can be made by determining the total amount of removal oxygen species which give value of more than 1.0 x 10^{15} atom g^{-1}. According to Arrhenius, surface oxygen species is accounted of roughly 1.0 x 10^{15} atom g^{-1} over a 1 cm^2 surface area. The value displays as evidenced in Table 2 is more than surface species, therefore more than a monolayer of oxygen was removed, hence the oxygen species are lattice ones. Thus, H$_2$-TPR analysis gives an initial indication of the possible high activity and selectivity of the oxide, which may display in the selective oxidation of hydrocarbon (propane).

The reaction for removal oxygen from the lattice could occur according to the Rideal–Eley reaction (Diagram 2) [13], with the H_2 molecules removing the surface oxygen upon collision. The oxygen species become available as a result of a migration from the lattice to the surface.
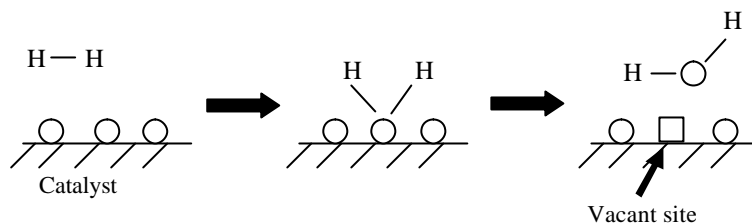
(Diagram 2)

Table 2: Total number of oxygen atoms removed from the samples obtained by H_2-TPR

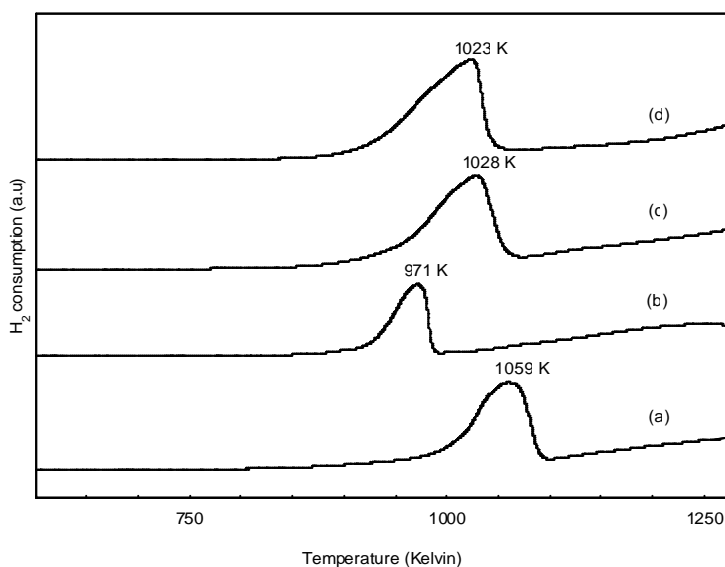| Samples[a]	T_{max} (K)	Reduction activation energy, E_r (kJ mol^{-1})	Oxygen atom removed from the catalysts (mol g^{-1})	Oxygen atom removed from the catalysts (atom g^{-1})
MoV(control)	1059	177	1.2×10^{-2}	7.3×10^{21}
MoV(AA)	971	162	3.0×10^{-2}	1.8×10^{22}
MoV(MA)	1028	172	5.5×10^{-2}	3.3×10^{22}
MoV(PVA)	1023	171	2.4×10^{-2}	1.4×10^{22}

Figure 3: Temperature programmed reduction of hydrogen of a) MoV(control), b) MoV(AA), c) MoV(MA) and d) MoV(PVA)

Conclusion

Treatment of MoV oxides with organic species has a positive effect on the properties of the catalysts. Addition of organic species to the precursor leads to formation of a highly crystalline compound with Mo-V-O orthorhombic structure which is reported to be active and selective for the propane oxidation. Fascinating results in which high surface area values (S_{BET}) are obtained in the range of 10 to 20 m^2 g^{-1}. Encouraging results were also obtained through temperature programmed reduction studies where addition of organic species into the sample was found to induce the removal of strongly bonded oxygen species at lower reduction activation energy as compared to untreated sample.

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