

EFFECT OF ORGANIC SPECIES ON THE CHARACTERISTICS OF MOLYBDENUM-VANADIUM OXIDE

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ABSTRACT

In this study, molybdenum-vanadium oxide samples were prepared via reflux method. Urea and hexane were applied in the mixture in order to improve the physicochemical properties of the mixed oxide. A control sample without the presence of organic species was also prepared. X-ray diffraction analysis showed that the precursors were in a complex mixed phase. All of the precursors were calcined in N₂ flow at 573, 623, 673, 723 and 773 K for 2 hours. Calcined samples were denoted as Cont_{calc}, Ur_{calc} and Hex_{calc}. Samples calcined at 573 K were still in a complex mixed phases. When calcined at 623 K, Cont_{calc} and Hex_{calc} showed a hexagonal MoVO_x phase while Ur_{calc} was in a monoclinic MoO_x phase. However, calcination at 773 K has managed to transform all samples into the monoclinic MoO_x phase. On specific surface area analysis, Ur_{calc} gave the highest value, which was 10.8 m²g⁻¹.

INTRODUCTION

Propane selective oxidation is one of the recent challenges in selective oxidation field. The one-step direct conversion to acrylic acid has especially attracted much attention in industries for fundamental and economical reasons with a view to replace the current two-steps propene-to-acrolein and acrolein-to-acrylic acid process. The propane to acrylic acid process is reportedly active and selective through heterogeneous oxidation over molybdenum-vanadium-based oxides. Many works have been focused into developing this oxide. Ueda *et al.* (2004) successfully prepared Mo-V-O based catalyst by employing the hydrothermal method to produce single phased binary MoVO metal oxides [1]. There are also many reports on the addition of organic species in the preparation of metal oxide catalysts. In the case of homogeneous precipitation, urea acts as a precipitant. Since urea decomposed at around 373 K to produce carbon dioxide and ammonia, it increases the pH of the solution at which metal cation precipitation takes place [2].

Le *et al.* (2004) [3] reported that citric acid was used as a complexant in the process of producing yield which are better intermixed and more highly dispersed through a three-dimensional organic network of metallic components, which is responsible for pore structure and surface area of the catalyst. However, when the molar ratio of the organic species to bismuth exceeded 3, the precursors were inappropriately sticky [3]. In this study, the reflux method with the combination of the usage of urea and hexane in the

preparation process of the catalyst was explored. The molar ratio of Mo:V is fixed at 10:3 [4] by basing on the catalytic activity which is strongly dependant on the content of V^{4+} . Calcination conditions that were reported thus far varied in temperature and condition. Most reports suggested a 773 K in N_2 flow heat treatment for 2 hours in air [1,5]. Others suggested heat treatment of only up to 673 K to avoid decomposition of the active phase of VMo_3O_{11} [6,7,8]. In exploring the method used to prepare the MoVOx samples, various calcination temperatures were studied as well, to clarify the various information in hand.

EXPERIMENTAL

Ammonium heptamolybdate tetrahydrate (0.010 Moles) from Merck were dissolved in deionised water to form a clear solution. Vanadium sulphate (0.021 Moles) from Aldrich was dissolved in deionised water to obtain a clear blue solution. The number of moles of the starting materials corresponds to the molar atomic ratio of Mo:V of 10:3 [4]. The two solutions were mixed together. At this stage, organic species was added with the molar atomic ratio of Mo:organic species of 1:3 [3,7]. The sample was refluxed for an hour and aged for 1 hour. Then, the mixture is heated below 333 K until it becomes pasty textured. The sample was dried in a desiccator which later were ground into powder form. All the precursors were denoted as $Cont_{pre}$, Ur_{pre} and Hex_{pre} for the control samples, and the urea and hexane added samples respectively. The precursor powders were then characterised by X-ray diffraction using a Shidmazu Model XRD-6000 Diffractometer. The precursors were heat treated in N_2 flow 573, 623, 673, 723 and 773 K for 2 hours [1,5,6,7,8]. The calcined samples ($Cont_{calc}$, Ur_{calc} , Hex_{calc}) were characterised by a Sorptomatic 1990 series to measure the BET surface area measurements, XRD and a Thermo-Finnigan TPDRO 1100 series TPR.

RESULTS AND DISCUSSION

The XRD patterns of the precursors are shown in Figure 1. The precursors were all multiphasic. A hexagonal molybdenum vanadate and a monoclinic molybdenum oxide hemihydrate have been identified. Other phases of molybdenum-vanadium oxides could not be ruled out.

Figure 3 (a), (b), and (c) shows the XRD patterns of $Cont_{calc}$, Ur_{calc} and Hex_{calc} respectively for samples calcined at 573, 623, 673, 723 and 773 K.

After calcination at 573 K, peaks appeared indicate that all three samples are in a mixture phases of anorthic ammonium molybdates, orthorhombic molybdenum vanadate and anorthic molybdenum vanadate. The presences of other phases could not be ruled out. Upon calcination at 623 K, $Cont_{calc}$ and Hex_{calc} showed the hexagonal molybdenum vanadate peaks whereas Ur_{calc} showed monoclinic molybdenum oxide peaks. Once calcined at 673 K, more developed peaks were observed for $Cont_{calc}$. For the Hex_{calc} and Ur_{calc} , the samples remained unchanged up to 723 K. However, $Cont_{calc}$ peaks observed were becoming less intense. This implies crystallinity deterioration,

which is probably due to transformation from one crystal structure to another. Upon calcination at 773 K, all samples showed monoclinic MoO_2 with the appearance of slight unidentified peaks.

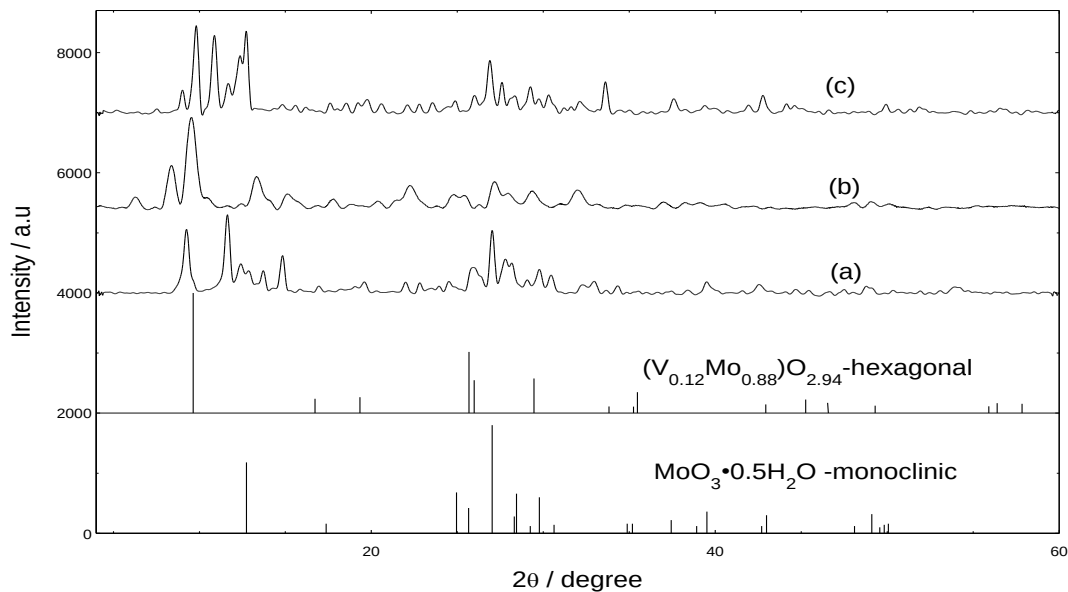
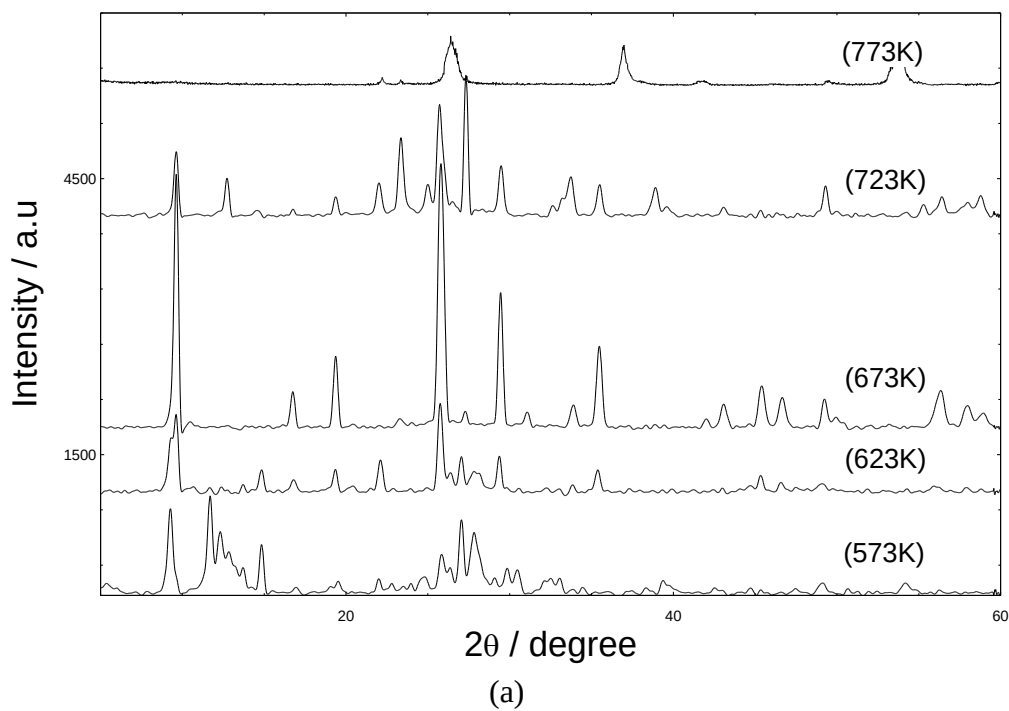


Figure 1: XRD patterns of precursor samples (a) Cont_{pre} , (b) Ur_{pre} and (c) Hex_{pre}



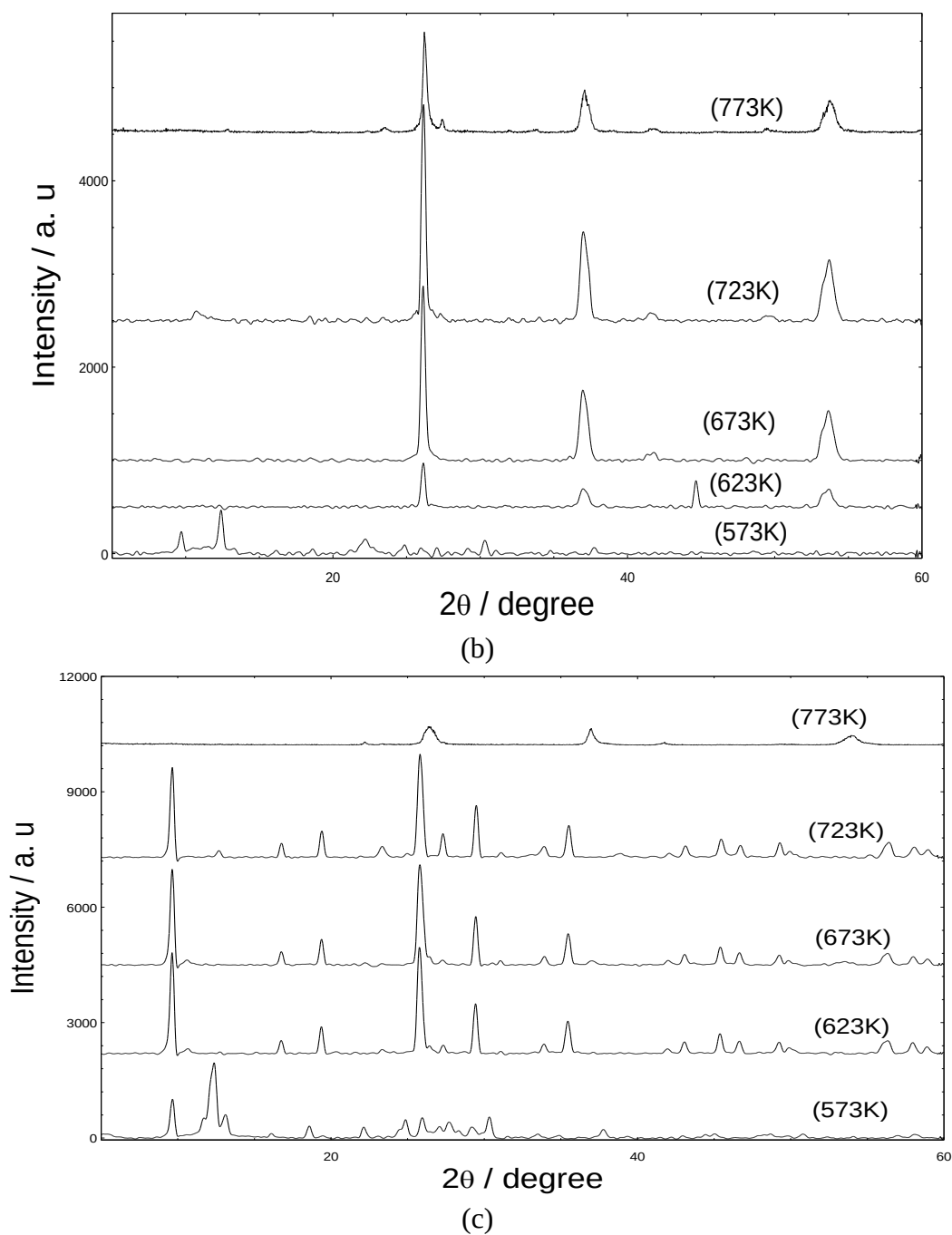


Figure 3: XRD patterns of (a) Cont_{calc}, (b) Ur_{calc}, and (c) Hex_{calc} for samples calcined at various temperatures

The particles size was calculated by the Debye Scherrer equation:

$$t = \frac{0.9 \lambda}{\beta_{hkl} \cdot \cos \theta_{hkl}}$$

where t is the crystallite size, λ is 1.5438Å and β_{hkl} is the FWHM (in radian). In general the crystallite size falls in the range between 28.0 to 83.0 nm. BET surface area measurements showed that urea treated sample gives the highest surface area. Table 1 presents the crystallite size t and the specific surface area of the samples prepared.

Table 1: Crystallite size of $\text{Cont}_{\text{calc}}$, Ur_{calc} and Hex_{calc} calcined at 723 K

Sample	(hkl)	2 θ (degree)	FWHM	t (nm)	Surface area (m ² g ⁻¹)
$\text{Cont}_{\text{calc}}$	1 (011)	23.3	0.1624	50.0	4.3
	2 (040)	25.7	0.1624	50.3	
	3 (021)	27.3	0.1299	63.1	
Ur_{calc}	1 (011)	26.1	0.1624	50.3	10.8
	2 (-211)	36.9	0.2598	32.3	
	3 (022)	53.7	0.3168	28.2	
Hex_{calc}	1 (100)	9.7	0.0974	81.4	1.8
	2 (211)	25.8	0.1624	50.3	
	3 (101)	26.0	0.0974	83.9	

Figure 4 is the TPR profile obtained by passing hydrogen in argon stream (5% hydrogen, 1 bar, 25ml min⁻¹) over the fresh samples.

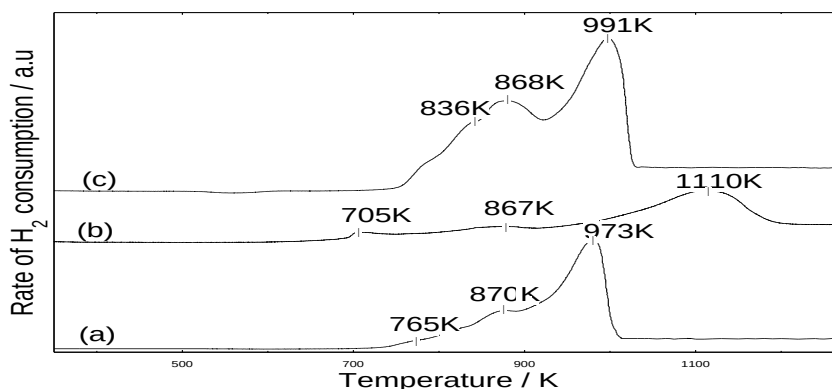
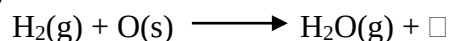


Figure 4 : TPR profile of fresh samples (a) $\text{Cont}_{\text{calc}}$ (b) Ur_{calc} (c) Hex_{calc}

Water evolution occurs as a result of the hydrogen reaction with adsorbed oxygen according to the following reaction:



where (g), (s) is gaseous or surface species and $\square$ is the oxygen vacancy. An estimate of the amount of oxygen taken up by the catalyst in each sample can be made by calculating the area under the peak. The results are shown in Table 2. The reduction activation energies can be obtained from a modified Redhead equation:

$$\frac{E_r}{RT_m^2} = \left(\frac{A_r}{\beta} \right) [H_2]_m \exp \left(\frac{-E_r}{RT_m} \right)$$

where T_m is the peak maximum temperature (K) in the rate of production of H_2 , E_r is the reduction activation energy (kcalmol^{-1}), A_r is the reduction pre-exponential term ($\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$) which is given a standard collision number of $10^{13}\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$ and $[H_2]_m$ is the gas phase concentration of hydrogen (molcm^{-3}) at the peak maximum. The values obtained for the peaks in $\text{Cont}_{\text{calc}}$ at 765, 870 and 973 K are 128.0, 145.5 and 162.7 kJmol^{-1} respectively. The values obtained for the peaks in Ur_{calc} at 705, 867 and 1110 K, are 117.9, 145.0 and 185.6 kJmol^{-1} respectively. The values obtained for the peaks in Hex_{calc} at 836, 868 and 991 K, are 139.8, 145.1 and 165.7 kJmol^{-1} respectively. These are a very high E_r value; therefore the oxygen may be strongly bonded to the surface of the catalysts. The numbers of oxygen atoms removed are 2.1×10^{21} , 7.4×10^{21} and 1.9×10^{21} atoms g^{-1} for $\text{Cont}_{\text{calc}}$, Ur_{calc} and Hex_{calc} respectively.

Table 2: Reduction activation energy and total number of oxygen removed

Peaks	T_{max} (K)	Reduction activation energy (kJmole^{-1})	Oxygen removed (moles g^{-1})	Oxygen removed (atoms g^{-1})
Cont_{calc} 1	765	128.0	8.5×10^{-5}	5.1×10^{19}
2	870	145.5	8.6×10^{-4}	5.2×10^{20}
3	973	162.7	2.5×10^{-3}	1.5×10^{21}
Total			3.5×10^{-3}	2.1×10^{21}
Ur_{calc} 1	705	117.9	8.0×10^{-4}	1.1×10^{21}
2	867	145.0	1.7×10^{-3}	6.6×10^{20}
3	1110	185.6	9.7×10^{-3}	4.2×10^{21}
Total			1.2×10^{-2}	6.0×10^{21}
Hex_{calc} 1	836	139.8	2.2×10^{-4}	1.3×10^{20}
2	868	145.1	10.0×10^{-4}	6.0×10^{20}
3	991	165.7	1.9×10^{-3}	1.1×10^{21}
Total			3.1×10^{-3}	1.9×10^{21}

CONCLUSION

All of the samples prepared ($\text{Cont}_{\text{calc}}$, Ur_{calc} and Hex_{calc}) were obtained through mixed phases route. Upon calcination at various temperatures, phase evolution was observed. $\text{Cont}_{\text{calc}}$ and hex_{calc} showed a hexagonal phase once calcined at 623 K whereas Ur_{calc} showed monoclinic phase. However, when calcined at 773 K all of the samples transformed into monoclinic phase. BET surface area showed that urea will improve the sample surface area rather than using hexane as an organic species.

ACKNOWLEDGMENT

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