EFFECT OF SUPPORT ON THE ACTIVITY OF MoVCeZr CATALYST FOR PROPANE AMMOXIDATION REACTION

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ABSTRACT

Mixed metal oxide catalysts based on Mo-V have been known as the most active and selective in the ammoxidation of propane to ACN. A series of MoVCeZr (5% wt/wt) supported with MOR, TiO_2 and MgO have been prepared by incipient wetness impregnation method for propane ammoxidation reaction to ACN. The catalyst was calcined in a two step calcination process in static air between 350-600 ^{o}C for a total of 10h. The surface area and pore size of these catalysts were measured using physical adsorption of nitrogen following Brunauer, Emmet and Teller (BET) equation. The textural and morphological of these catalysts were determined using scanning electron microscopy (SEM) and X-ray Diffraction (XRD). The activities of all catalysts were tested using a fixed-bed reactor with online gas chromatography (GC) at 420 ^{o}C and atmospheric pressure in the presence of 0.5 ml catalyst with composition consisting of 5.8 : 7 : 17.4 (propane : ammonia : air) and helium as carrier to give a total flow of 120 ml. Results show that MoVCeZr supported with MOR, TiO_2 and MgO give a better conversion due to the surface area and pore size characteristic of catalyst.

INTRODUCTION

Acrylonitrile (ACN) is an intermediate chemical used by manufactures to produce other products such as acrylic fiber for clothing, carpeting and other fabrics; durable plastics for computer and TV housing; nitrile rubber for oil-resistant hoses at gasoline stations and under car hood. Presently, ACN is produced by ammoxidation of propene in a fluidized-bed reactor using mixed metal oxide catalysts [1]. High yields of ACN from propane have been reported on a Mo-V-Te-Nb catalyst since the early 1990s. However, neither catalyst has been commercialised. Apparently, the new propane ammoxidation processes have yet to be successful in challenging the existing commercial process, which utilizes propylene as the starting material and is very efficient [2].

In recent years many researchers have been trying to develop catalysts for the selective conversion of propane to acrylonitrile (ACN) because of the considerable price difference between propane and propene, the increasing world demand for ACN and derived products and the risk of propylene shortage due to its increasing consumption. However the selective conversion of propane to ACN is more difficult than that of

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propene due to the low reactivity of propane. All existing commercial processes for the production of ACN use propene as a feed stock [3]. In 1997 British Petroleum started a demonstration plant to make acrylonitrile using propane and estimated to decrease production costs ca. 20% compared with conventional propylene-based technology. In this reaction, the activation of propane is the limiting step. Since the adsorption rate of propane is nearly 10 times smaller than that of propylene the conversion of propane is at least 10 times smaller than that of propylene. The reaction conditions to activate the C-H bond in propane are more energy demanding which has negative effect on selectivity [4].

The catalysts reported previously for the ammoxidation of propane are composed of multicomponent oxides, which could be mainly divided into 2 categories as follows: i) V-Sb based oxide catalyst with the rutile structure, ii) Bi-V-Mo base oxide catalyst with the scheelite structure. According to BP/Sohio, V-Sb based oxides catalysts have low selectivity to ACN, whereas Bi-V-Mo based catalysts had high selectivity to ACN. Therefore they prepared a catalytic mixture of V-Sb based oxide catalysts and Bi-Ce-Mo based oxide catalysts for propane ammoxidation [3]. Among the most active and selective propene ammoxidation catalyst, Mo is thought to play the role of NH^{2-}-insertion onto the allylic intermediate. This element is also present in a new class of propane ammoxidation catalyst based on V/Mo/Nb/Sb/O mixed oxide. While the active phase of these catalysts has a structure and a composition very different from the rutile-type, the same cooperation between V, Mo and co-elements based on the same principle is observed [4].

In this research, catalysts of MoV supported with zeolite mordenite, titania and magnesia were synthesized where the catalyst was doped with combination of metals cerium (Ce) and zirconia (Zr). The auxiliary of this metal doped were investigated in ammoxidation reaction.

EXPERIMENT DETAILS

Catalyst Preparation
A series of Mo-V catalyst promoted with Ce and Zr (5 wt %) supported on MOR (Zeolysts International, AR), TiO_2 (Riedel-de-Haën, AR) and MgO (Fluka, 97%) were prepared by an incipient wetness impregnation method. Ammonium meta vanadate (R&M, AR) and oxalic acid (Fisher, AR) were dissolved in a required amount of deionised water and added to a solution containing ammonium molybdate (R&M, AR), cerium (III) nitrate hexahydrate (Acros, AR) and zirconyl (IV) nitrate hydrate (Acros, AR). For the supported catalysts, the mixture was then added to the supports and left to stand for 2 hours. The impregnated samples were dried for 17 hours. Finally they were calcined in air at 350-600 $^\circ$C for total of 10 hours.

Catalyst Characterization
The surface area determination was carried out following a BET procedure using nitrogen gas in a Micrometics ASAP-2010. The X-ray powder diffraction data were

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recorded on a Bruker DS Advance diffractometer using a Cu Kα radiation with the scanning angles (2θ) from 2° to 80° at room temperature. The morphology of the catalysts was studied by Scanning Electron Microscope (SEM) using LEO 1530 EFSEM at magnification of 10 kx where the samples were coated with platinum using a Sputter Coater.

Catalytic Activity Test
Activity measurements were performed using a conventional plug flow fixed-bed reactor with on-line gas chromatography at atmospheric pressure. The correctness of the analytical determinations was checked by carbon balance (based on propane converted). The tests were made using 0.5 g sample with particle size of 212-425 μm range. The feed gas molar ratio are 5.8% propane, 7.0% ammonia, 17.4% oxygen and 69.8% helium with temperature reaction at 420 ^{o}C. The total flow rate was 120 ml min^{-1} corresponding to a gas-space velocity (GHSV) of about 1200 h^{-1}.

RESULTS AND DISCUSSION

The specific surface area of all catalysts as determined by N_2 physisorption is presented in Table 1 where unsupported MoVCeZr catalyst has a very low surface area (1.91 m^{2}g^{-1}). The surface area of the supported catalysts is higher than that of unsupported catalyst. The higher surface area in the supported catalysts is predominantly given by the characteristic of the supports which have surface areas in the range of 36.17-407.60 m^{2}g^{-1}. However, the surface areas of the support reduced significantly when MoVCeZr was loaded into them. The surface area of the MOR support is 407.60 m^{2}g^{-1} and the pore size of 0.42 nm. When 5% (w/w) MoVCeZr was loaded onto the MOR, the surface area of the catalyst reduced significantly to 213.40 m^{2}g^{-1} and the average pore size is 0.42 nm.

Table 1: BET Surface area (m^{2}g^{-1}) of the samples with different supported

Catalyst	Surface Area (m^{2}g^{-1})	Pore Size (nm)
MoVCeZr	1.91	2.77
MoVCeZr/MOR	213.40	0.42
MoVCeZr/TiO$_2$	8.07	1.08
MoVCeZr/MgO	26.24	1.41
MOR	407.60	0.42
TiO$_2$	10.41	0.42
MgO	36.17	1.47

The surface area and average pore size of TiO$_2$ support are 10.41 m^{2}g^{-1} and 0.42 nm, respectively. However, loading of 5% (w/w) MoVCeZr onto the pores significantly reduced the surface area of the catalyst to 8.07 m^{2}g^{-1} while the average pore size increased to 1.08 nm. The surface area of the MgO is 36.17 m^{2}g^{-1}. After 5% (w/w) of MoVCeZr was loaded into the MgO the surface area also decreased to 26.24 m^{2}g^{-1}.

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Reduction of the surface area are due to some of the deposition has closed some of the pore opening, thus it reducing the pore volume of the catalyst.

Figure 1a shows the diffractogram of the unsupported MoVCeZr catalysts having 2 types of crystal phases, namely monoclinic and orthorhombic. The strong peaks appear at 2θ values of 21.57^o, 25.24^o, and 27.97^o representing the monoclinic structures of V_2MoO_8 phase. The minor peak belong to V2MoO8 appeared at 2θ value of about 18.28^o, 33.19^o, 34.39^o, 47.29^o, 50.54^o, 51.17^o, 55.58^o and 58.51^o. The peaks at 2θ of 20.80^o, 26.16^o and 31.06^o are referred to the orthorhombic structures of V_2O_5 while the other monoclinic structures of Mo_4O_{11} were observed at 2θ of about 22.97^o, 24.67^o and 31.87^o.
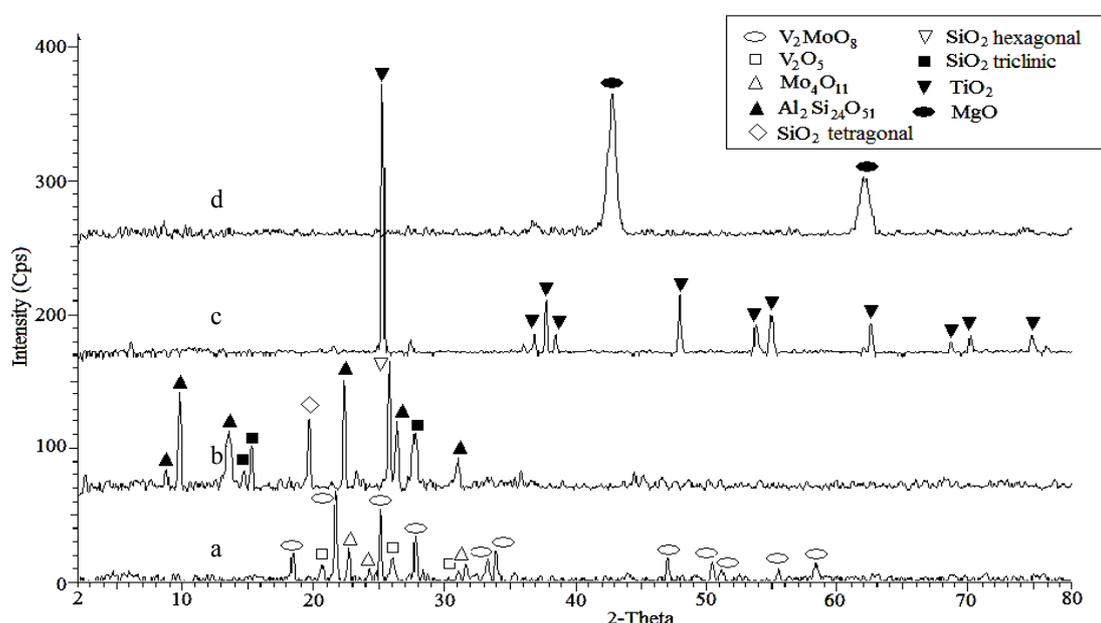

Figure 1: X-ray diffraction pattern for the catalysts (a) MoVCeZr, (b) MoVCeZr/MOR, (c)MoVCeZr/ TiO2, (d)MoVCeZr/MgO

The supported catalyst diffractogram show no new crystallographic phase corresponding to metallic compounds is observed since only 5% metal loading was applied. Figure 3b show the difractogram of the MoVCeZr/MOR catalyst. The diffractogram show 2 types of phase were observed in MoVCeZr/MOR catalyst i.e. SiO_2 and $Al_2Si_{24}O_{51}$ where SiO_2 has 3 type structures tetragonal, hexagonal and triclinic. The strong peaks appear at 2θ values of 25.66^o and 23.20^o representing the hexagonal structures of SiO_2 and $Al_2Si_{24}O_{51}$ phase respectively. The peaks at 2θ of 8.97^o, 9.96^o, 13.41^o, 26.49^o and 31.03^o are referred to the $Al_2Si_{24}O_{51}$. The peak at 2θ value of 15.11^o, 19.54^o and 27.86^o are referred to SiO_2 triclinic while the tetragonal structure of SiO_2 was observed at 2θ of about 22.45^o.

The difractogram of the MoVCeZr/TiO2 are shown in figure 3c. The intense peak were observed at 2θ 25.31^o where it is referred to TiO2 support. The minor peaks owing to

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the crystalline phases of TiO_2 were observed at 2θ values of 36.95^o, 37.79^o, 38.57^o, 48.04^o, 53.89^o, 55.07^o, 62.69^o, 68.76^o, 70.30^o and 75.05^o. Figure 3d shows the diffractogram of MoVCeZr/MgO support catalyst. It shows the appearance of strong peaks in the 2θ values of 42.92^o and 62.30^o which is due to supported MgO.

Study on the textural properties of the solids was completed by means of SEM. Figure 2 shows the images at 10kx magnification correspond to the MoVCeZr, MoVCeZr/MOR, MoVCeZr/TiO$_2$ and MoVCeZr/MgO. All catalyst show the presence of agglomerates particles which there are 4 types of morphologies and local composition characteristic for the crystallites could be detected which MoVCeZr show a needle-like structure, MoVCeZr/MOR show a combination of slabs and crystal rod. MoVCeZr/TiO$_2$ and MoVCeZr/MgO show a crystal like fiber and powdery respectively with no specific morphology.

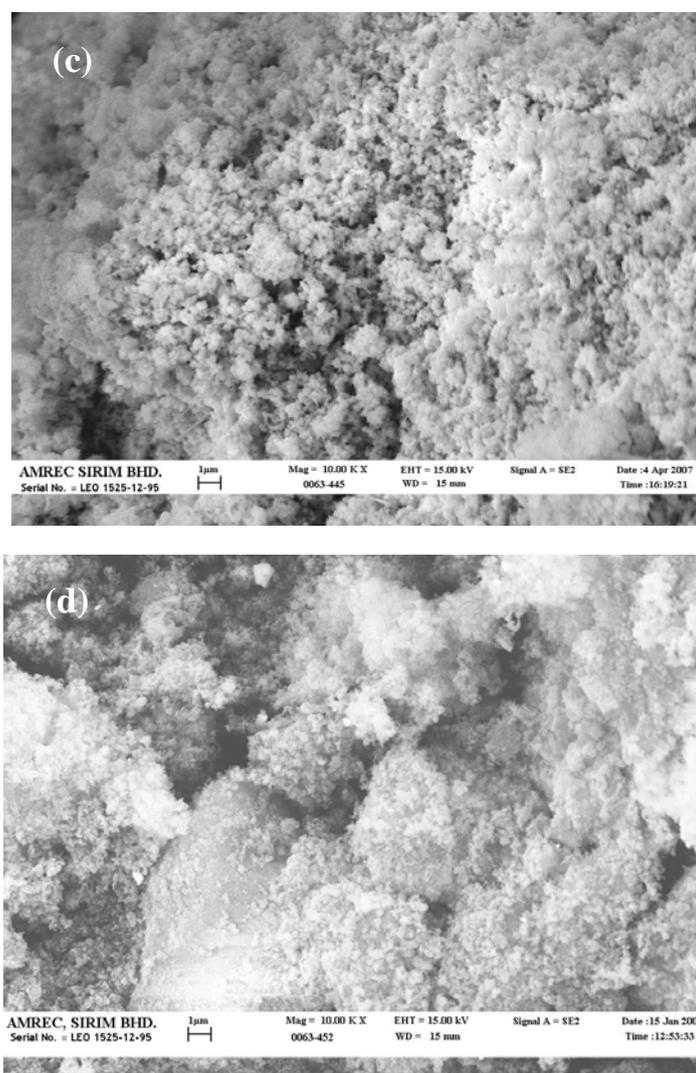Corresponding Author: anita_ramli@sirim.my
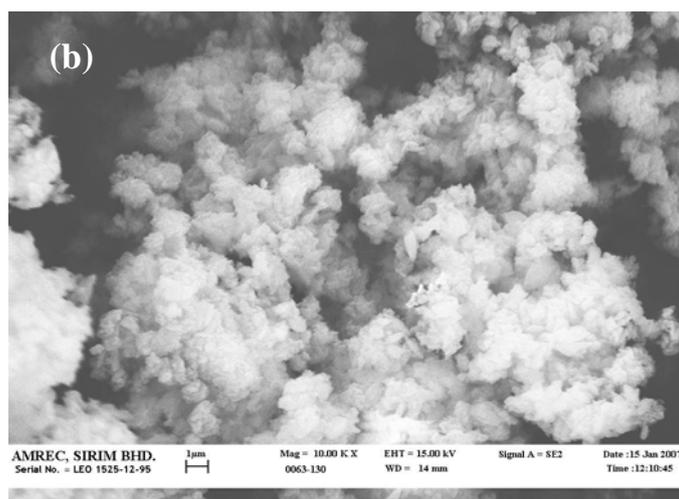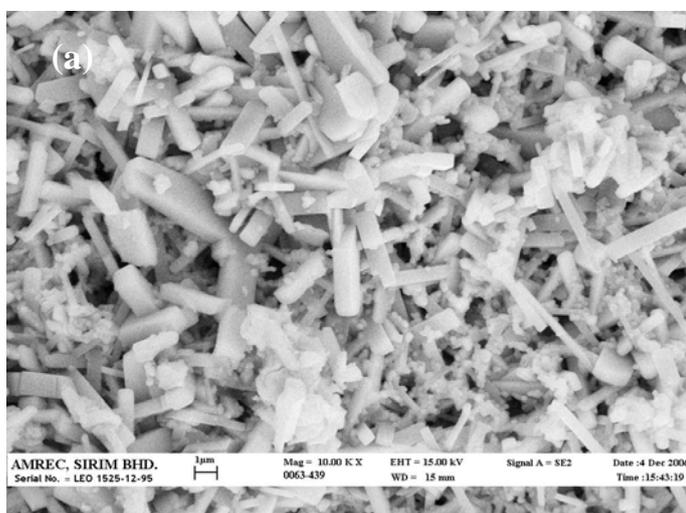
Figure 2: SEM micrograph for (a) MoVCeZr, (b) MoVCeZr/MOR, (c) MoVCeZr/TiO$_2$ and (d) MoVCeZr/MgO

Figure 4 shows the propane conversion and selectivity to ACN given by each catalyst. The unsupported MoVCeZr has a very low propane conversion (27%) which could be due to the low surface area of the catalyst (1.91 m^{2}g^{-1}), limiting the conversion of propane from taking place. However, the selectivity to ACN is quite high, owing to the existence of some crystalline phases V$_2$MoO$_8$, Mo$_4$O$_{11}$ and V$_2$O$_5$ required for the formation of ACN. Introduction of a support improves the conversion of propane by two-fold to seventy-fold due to improvements in the surface area of the MoVCeZr supported catalysts enabling the reaction to occur. However, the selectivity to ACN reduces as insufficient formation of crystalline phases within the supported catalysts.

Among the supported catalysts, MoVCeZr/MOR shows a better selectivity to ACN

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(24%) due to the characteristic of zeolite MOR as a reactant selectivity, product selectivity and reaction intermediate selectivity. Zeolite MOR has small and uniform pores where only the molecules smaller than the pores can react and only the molecules that able to diffuse out of the pores appear as product [5].

The selectivity is reduced further in MoVCeZr/MgO catalyst but increased the propane conversion. In this case, MgO plays the role of basic centre as was discussed by Bettehar et al. [6] about the VMgO system for oxydehydrogenation of propane to propylene. It shows that MgO system catalyst gives a better selectivity in partial oxidation of propane and it is responsible for high propylene. This research proves that MoVCeZr/MgO gives a higher conversion of propane and it also shows that propane was converted to other byproduct such as propylene as the selectivity decreased.
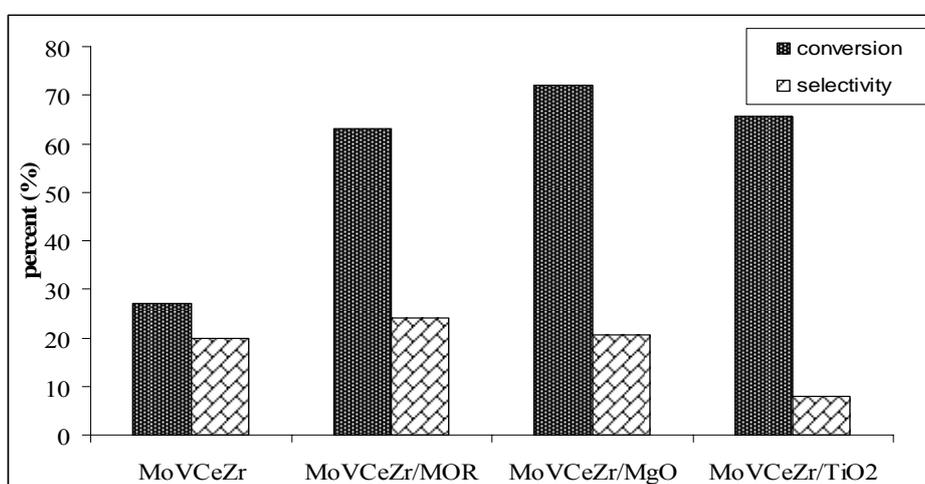

Figure 4: Catalytic behaviour in the propane ammoxidation for all catalysts

The MoVCeZr/TiO$_2$ catalyst has the lowest selectivity of only 8% as there was no existence of any crystalline phase of V$_2$MoO$_8$, Mo$_4$O$_{11}$ and V$_2$O$_5$ detected within the catalyst. Even though MoVCeZr/TiO$_2$ has a higher conversion of propane but almost more than half of the propane fed was being converted to other byproducts instead to ACN, thus a decreasing in catalyst selectivity to ACN was observed.

CONCLUSION

Supporting the MoVCeZr catalyst with MOR, MgO and TiO$_2$ improves the surface area of the catalyst, thus increases the propane conversion. However, the introduction of these supports hindered the formation of crystalline phases required for the amoxidation to ACN. Insufficient existence of these crystalline phases reduces the selectivity to ACN.

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