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Influence of Bi–Fe additive on properties of vanadium phosphate catalysts for *n*-butane oxidation to maleic anhydride

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Abstract

The physico-chemical and catalytic properties of three ways of modified catalysts were studied, i.e. (i) the addition of both Bi and Fe (nitrate form) during the refluxing $VOPO_4\cdot 2H_2O$ with isobutanol (Catalyst A), (ii) the simultaneous addition of BiFe oxide powder in the course of the synthesis of precursor $VOHPO_4\cdot 0.5H_2O$ (Catalyst B) and (iii) the mechanochemical treatment of precursor $VOHPO_4\cdot 0.5H_2O$ and BiFe oxide in ethanol (Catalyst C). It was found that surface area of the modified catalysts has increased except Catalyst B. The reactivity of the oxygen species linked to V^{5+} and V^{4+} was studied by using H_2-TPR, which also affected the catalytic performance of the catalyst. The conversion of *n*-butane decreases with an increment of oxygen species associated with V^{5+}.

Keywords: Vanadium phosphate; *n*-Butane; Oxidation; Oxygen species; Maleic anhydride

1. Introduction

Since the discovery of production of maleic anhydride (MA) from *n*-butane over vanadium phosphorus oxide (VPO) catalyst by Bergmann and Frisch and followed by Monsanto succeeded in commercial this reaction in 1974 [1], many of efforts have been made to improve the catalytic properties of VPO catalyst [2]. One of the methods to improve the catalytic performance of the VPO catalyst is by addition of metal dopants [3]. Most of the research papers and patents on doped VPO catalyst were employed more than one metal dopants in the formulations of their preparation method for the improvement of the activity and selectivity [4–8].

The bismuth (Bi) and iron (Fe) are the most studied dopants for VPO catalysts. Bismuth has been used as a dopant for VPO catalysts by some researchers for the past two decades [7–9], reporting an increase in selectivity to maleic anhydride upon the addition of bismuth. Sajip et al. [10] proposed that Fe could play the role as electronic promoter for $(VO)_2P_2O_7$, which enable the re-oxidation of the catalyst or increased the oxygen mobility. They also claimed that iron may associate with the disordered phase that enhanced the catalytic performances of VPO catalysts. In our previous study, we have reported that the BiFe-doped VPO catalysts prepared by refluxed $VOPO_4\cdot 2H_2O$ with the metal dopant [11]. Catalytic test for *n*-butane partial oxidation to MA shown a significant lower activity which due to the increased of oxygen species (O^{2-}) associated to V^{5+} phase. Our previous result on Bi-promoted VPD catalysts shows an enhancement of the activity [12] whereas Fe was found to reduce the conversion of the catalyst [13]. In this study, the VPO catalyst were modified in three different ways by using BiFe additive in order to investigate the effect of physico-chemical and catalytic properties of the catalysts.

2. Experimental

2.1. Catalysts preparation

The $VOPO_4\cdot 2H_2O$ was prepared by reacting V_2O_5 (12.00 g from Fluka) with 115 g of *ortho*-phosphoric acid, H_3PO_4 (85% from Merck) in water (24 ml H_2O/g solid) under refluxed for 24 h. The yellow solid was then recovered by filtration, washed

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sparingly with water and followed by acetone. It was dried in an oven at 383 K and then identified by XRD analysis as $VOPO_4{\cdot}2H_2O$. After that, the unmodified precursor was prepared by adding well synthesised of $VOPO_4{\cdot}2H_2O$ (4.0 g) to isobutanol (80 cm^3 from BDH). The mixture was refluxed for 21 h with continuous stirring. Then, the blue solid was recovered by filtration, washed and dried in an oven at 383 K for 16 h.

The above prepared precursor was divided into three portions and used to prepare modified catalysts in three different ways. In the first method of modification, the $VOPO_4{\cdot}2H_2O$ (4.0 g) and the desire quantity of $Fe(NO_3)_3{\cdot}9H_2O$ (from Hamburg Chemical) as well as bismuth nitrate, $Bi(NO_3)_3{\cdot}5H_2O$ from Sigma with the ratio of Bi:Fe of 2:1 were suspended by rapid stirring into isobutanol (80 cm^3 from BDH). The mixtures were refluxed for 21 h with continuous stirring. Then, the blue solids were recovered by filtration, washed and dried at 383 K for 16 h. The precursor is referred as Precursor A.

For the preparation of doped precursors, the well synthesised of $VOPO_4{\cdot}2H_2O$ (4.0 g) and 1 wt% Bi–Fe oxide with the ratio of Bi:Fe of 2:1 obtained by coprecipitation were suspended by rapid stirring into 80 cm^3 of isobutanol. The mixtures were refluxed for 21 h with continuous stirring. Then, the blue solid was recovered by filtration and washed with distilled water (100 cm^3) and followed by acetone (100 cm^3). The resulting blue solid was further refluxed in hot water (24 ml H_2O/g solid) for 3h to remove $VO(H_2PO_4)_2$. After that, it was filtered immediately, washed with hot water (100 cm^3), dried in air at 385 K overnight and denoted as Precursor B.

The mechanochemical treatment of $VOHPO_4{\cdot}1/2H_2O$ and Bi–Fe oxide was carried out by using planetary ball mill (model Pulverisette 4 from Fritsch) with an agate bowl having 250 cm^3 volume together with 50 agate balls (diameter = 10 mm). About 8.0 g of the $VOHPO_4{\cdot}1/2H_2O$, 1 wt% Bi–Fe complex oxide (Bi/Fe = 2) and 50 cm^3 of ethanol as solvent were put together inside the bowl. The ball milling process was performed at the speed of 1400 rpm for 30 min. Then, it was dried and denoted as Precursor C.

All precursors were calcined under a reaction flow of *n*-butane/air mixture (0.75% *n*-butane in air) for 75 h at 673 K. The resulting modified catalysts were denoted Catalyst A, Catalyst B and Catalyst C according to their method of modification.

2.2. Catalysts characterisation

BET surface area measurement was carried out by using nitrogen adsorption–desorption at 77 K using a ThermoFinnigan Sorptomatic 1990 instrument.

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

X-ray diffraction (XRD) patterns were obtained using a Shimadzu diffractometer model XRD-6000 Diffractometer employing Cu Kα radiation.

Scanning electron microscopy (SEM) micrograph was obtained by using a JEOL JSM-6400 electron microscope.

Temperature-programmed reduction (TPR) in H_2/Ar experiment was performed using ThermoFinnigan TPDRO 1100 apparatus provided with thermal conductivity detector. It was done in H_2/Ar stream (5% H_2, 1 bar, 25 $cm^3\ min^{-1}$) of fresh catalysts raising the temperature from ambient to 1173 K at $5^\circ\ min^{-1}$ in that stream.

2.3. Catalytic testing

The oxidation of *n*-butane was carried out at 673 K with GHSV = 2400 h^{-1} in a fixed-bed microreactor with a standard mass of catalyst (250 mg). *n*-Butane and air were fed to the reactor via calibrated mass flow controllers to give a feedstock composition of 1.5% *n*-butane in air. The products were then fed via heated lines to an on-line gas chromatograph for analysis. The reactor comprised a stainless steel tube with the catalyst held in place by plugs of quartz wool. A thermocouple was located in the centre of the catalyst bed and temperature control was typically ±1 °C. Carbon mass balances of $\geq$95% were typically observed.

3. Results and discussion

3.1. BET surface area and chemical analysis

The Catalyst A has slightly higher surface area of 17.6 $m^2\ g^{-1}$ than unmodified catalyst (16.1 $m^2\ g^{-1}$). In comparison of the other two methods on introducing Bi–Fe dopants into VPD system, i.e. the Catalyst A produced by simultaneous addition of BiFe oxide powder in the course of the synthesis of VPD precursor with that Catalyst C obtained by the mechanochemical treatment of VPD precursor and BiFe oxide in ethanol medium for 30 min, it can be seen that the Catalyst B consisted of remarkably lower surface area, i.e. 7.2 $m^2\ g^{-1}$ compared to unmodified catalyst and Catalyst C. The higher surface area of Catalyst C may due to the repeating fracture of the solids cause by mechanochemical treatment.

Chemical analysis using ICP indicated that all modified catalysts had increased the phosphorus content due to an increase in the P/V atomic ratio from 1.04 (unmodified) to 1.09 for Catalyst A and Catalyst C and 1.11 for Catalyst B, as shown in Table 1. Chemical analysis confirmed the presence of Bi and Fe in Catalyst A with Bi/V and Fe/V atomic ratios of 0.024 and 0.014, respectively. It also showed the existence of the Bi and Fe in Catalyst B catalyst with the Bi/V and Fe/V atomic ratios of 0.026 and 0.007, respectively, whereas Catalyst C gave the Bi/V and Fe/V atomic ratios of 0.028 and 0.011, respectively.

Table 1
Atomic ratio and surface area of unmodified and modified catalysts

Catalyst	Atomic ratio (ICP)			Surface area ($m^2\ g^{-1}$)
	P/V	Bi/V	Fe/V	
Unmodified	1.00	–	–	16.1
Catalyst A	1.09	0.024	0.014	17.6
Catalyst B	1.11	0.026	0.007	7.2
Catalyst C	1.09	0.028	0.011	18.1

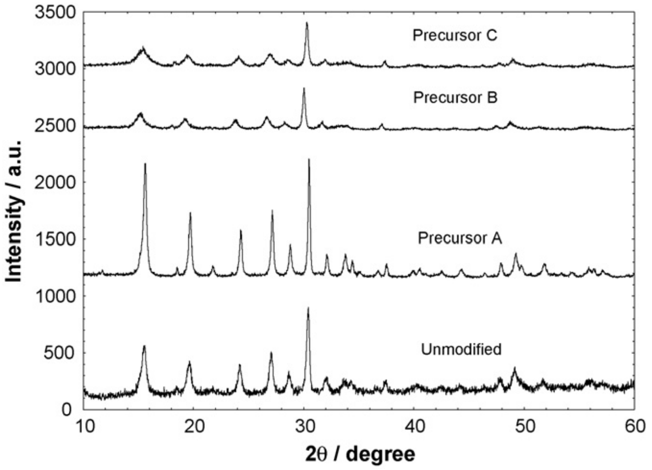

Fig. 1. XRD patterns of unmodified and modified catalysts.

3.2. X-ray diffraction (XRD)

The XRD patterns of the difference of Bi–Fe oxide addition into the precursor (Fig. 1) gave only the characteristic reflection of vanadyl hydrogen phosphate hemihydrate, $VOHPO_4\cdot 1/2H_2O$ (JCPDS File No. 37-0269), with the main peaks appeared at $2\theta = 15.6$, 19.7, 24.3, 27.1, 28.8, 30.4, 37.6 and 49.2° which correspond to (0 0 1), (1 0 1), (0 2 1), (1 2 1), (2 0 1), (1 3 0), (0 4 0) and (3 3 1) planes, respectively, which is similar with unmodified catalyst. However, the diffraction lines for precursors B and C were in lower intensity and also shifted towards lower angle.

The XRD patterns of unmodified and Catalyst B (Fig. 2) exhibit only the characteristic reflection of vanadyl pyrophosphate with the main peaks at $2\theta = 18.5$, 22.7, 28.2, 29.8, 33.8, 43.2 and 58.4° which correspond to (2 0 0), (0 2 0), (2 0 4), (2 2 1), (1 0 6), (0 0 8) and (3 1 9) reflections, respectively. However, the addition of Bi–Fe dopants into Catalyst A promoted the formation of α_{II}-$VOPO_4$ phase ($2\theta = 29.2°$). Besides, ball milled Catalyst C produced additional of some V^{5+} phases, i.e. α_{II}-$VOPO_4$ ($2\theta = 19.5°$), γ-$VOPO_4$ phase ($2\theta = 23.8°$) and $VOPO_4$ ($2\theta = 21.9°$) which is identified according to Abdelouahab et al. [13].

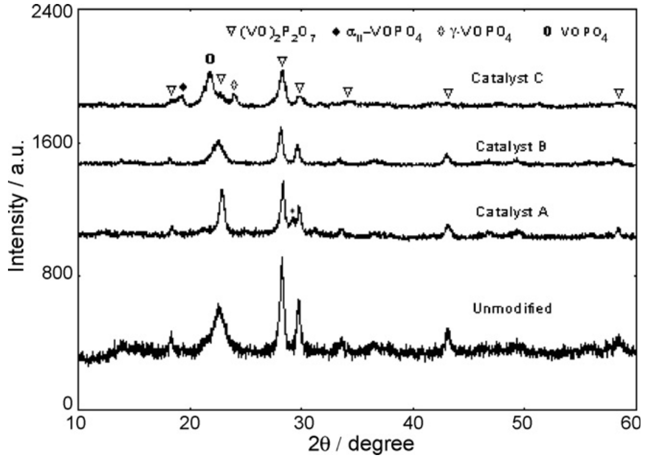

Fig. 2. XRD patterns of unmodified and modified catalysts.

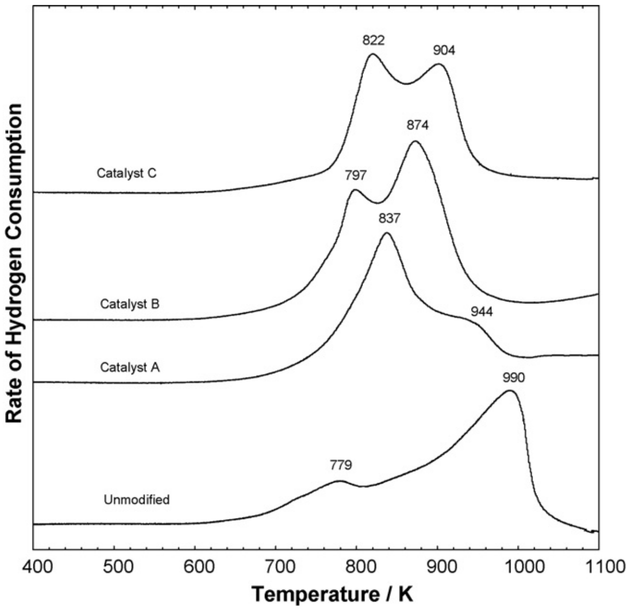

Fig. 3. H_2-TPR profile of unmodified and modified catalysts.

3.3. Temperature-programmed reduction (TPR) in H_2/Ar

The H_2-TPR experiments were used to investigate the redox properties of the catalysts, as shown in Fig. 3. Total amount of oxygen removed, the values of reduction activation energies and coverage obtained by temperature programmed reduction in H_2/Ar (H_2-TPR) are shown in Table 2.

The unmodified catalyst gave a characteristic of two reduction peaks which occurred at 779 and 990 K, where the first peak is associated to the reduction of V^{5+} phase whereas the latter peak is assigned to the removal of lattice oxygen from V^{4+} phase [15,16]. The peak attributed to V^{4+} associated to the removal O^{-} anion and the peak from V^{5+} is related to the oxygen species of O^{2-} [14,15]. The amount of oxygen removed from each peak is 3.85×10^{20} and 1.20×10^{21} atom g^{-1} which corresponds to the coverage of 2.41×10^{15} and 7.52×10^{15} atom cm^{-2}, respectively. The ratio of oxygen atom removed from V^{5+}/V^{4+} is about 0.32.

By introducing the Bi–Fe dopants into Catalyst A, the reduction patterns are significant change with the reduction of V^{5+} species appeared to be the major peak, whereas the reduction peak of V^{4+} was remarkably decreased. The removal amount of oxygen species associated with V^{5+} greatly increased to more than 250% to 1.24×10^{21} atom g^{-1}. The amount of oxygen removed from the second reduction peak, which is assigned to the reduction of V^{4+} phase tremendously decreased to 5.57×10^{20} atom g^{-1}. Hence, the ratio of oxygen removed from V^{5+} and V^{4+} for Catalyst A was significantly increased to 2.23. Too much of oxygen species associated to V^{5+} phase removal suggested that these catalysts will show a poor activity with higher selectivity, which will be discussed in the following section.

The Catalyst B gave similar characteristic of two reduction peaks with unmodified catalyst. The first peak occurred at higher temperature at 797 K and the later peak significantly

Table 2
Total amount of oxygen atoms removed, values of reduction activation energies and ratio for oxygen removal of V^{5+}/V^{4+} by reduction in H_2/Ar for unmodified and modified catalysts

Sample	Peak	T_{max} (K)	Reduction activation energy, E_r (kJ mol^{-1})	Total amount of oxygen removed (mol g^{-1})	Total amount of oxygen removed (atom g^{-1})
Unmodified	1	779	130.3	6.39×10^{-4}	3.85×10^{20}
	2	990	165.5	2.00×10^{-3}	1.20×10^{21}
	Total			2.64×10^{-3}	1.59×10^{21}
Catalyst A	1	837	140.0	2.06×10^{-3}	1.24×10^{21}
	2	944	157.9	9.25×10^{-4}	5.57×10^{20}
	Total			2.99×10^{-3}	1.80×10^{21}
Catalyst B	1	797	133.3	1.30×10^{-3}	7.82×10^{20}
	2	874	146.1	2.41×10^{-3}	1.45×10^{21}
	Total			3.71×10^{-3}	2.23×10^{21}
Catalyst C	1	822	137.5	1.41×10^{-3}	8.51×10^{20}
	2	904	151.2	1.36×10^{-3}	8.19×10^{20}
	Total			2.77×10^{-3}	1.67×10^{21}

shifted to a lower temperature, 874 K. However, the amount of oxygen removed from these two peaks increased to 7.82×10^{20} and 1.45×10^{21} atom g^{-1}, respectively. This result consequently increased the ratio for oxygen species of V^{5+}/V^{4+} to about 0.54. As compared to Catalyst A gave a small amount of lattice oxygen associated to V^{4+} where the TPR pattern showed the first reduction peak as the major peak. However, Catalyst B gave a markedly increment for the reduction of V^{4+} (second reduction peak) with the first reduction peak remain unchanged. The result indicated that an addition of Bi–Fe dopants by co-precipitation method leads to the enhance of the amount of oxygen species associated with V^{4+} without any effect on the oxygen species associated with V^{5+}. However, for milled Catalyst C, the oxygen species linked to V^{4+} reduced to 8.19×10^{20} atom g^{-1}, but the oxygen removed from V^{5+} phase was increased to 8.51×10^{20} atom g^{-1}. The amount of oxygen ratio of the V^{5+} reduction peak to the V^{4+} reduction peak is significantly increased to 1.04.

3.4. Selective oxidation of *n*-butane to maleic anhydride

Fig. 4 shows conversion of *n*-butane as a function of the reaction temperature, whereas the selectivity to maleic anhydride (MA) is plotted against the reaction temperature in the range of 613–673 K is given in Fig. 5. The detail of the catalytic performance data at 673 K is shown in Table 3. It can be seen that the addition of Bi–Fe oxide into the catalyst system had lowered the conversion of *n*-butane. For Catalyst B which produced by simultaneous addition of Bi–Fe oxide powder in the course of the synthesis of unmodified precursor gave the highest *n*-butane conversion (72%) than Catalyst A (43%) synthesised via refluxing Bi and Fe nitrate with $VOPO_4{\cdot}2H_2O$

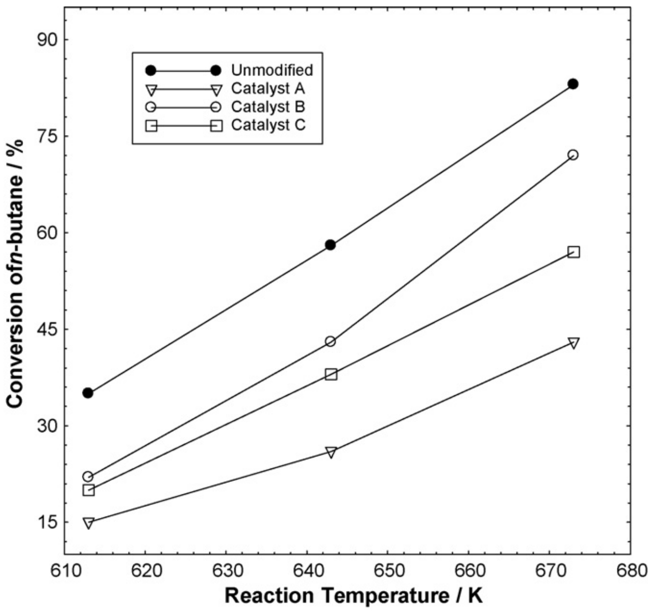

Fig. 4. *n*-Butane conversion of as a function of the reaction temperature.

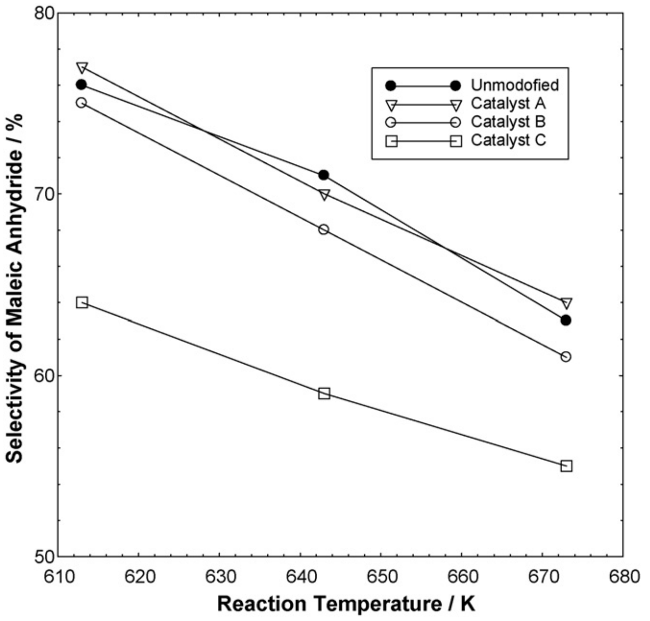

Fig. 5. MA selectivity as a function of the reaction temperature.

Table 3
Catalysts performance of unmodified and modified catalysts[a]

Catalyst	n-Butane conversion (%)	Product selectivity (%)			Intrinsic activity[b] (10^{-5} mol MA m^{-2} h^{-1})
		MA	CO	CO_2	
Unmodified	83	63	18	19	4.18
Catalyst A	43	64	17	19	2.01
Catalyst B	72	61	16	23	7.85
Catalyst C	57	55	17	28	2.23

[a] Reaction conditions: 673 K, 1.5% n-butane in air, GHSV = 2400 h^{-1}.
[b] Intrinsic activity: mol maleic anhydride (MA) formed m^{-2} catalyst h^{-1}.

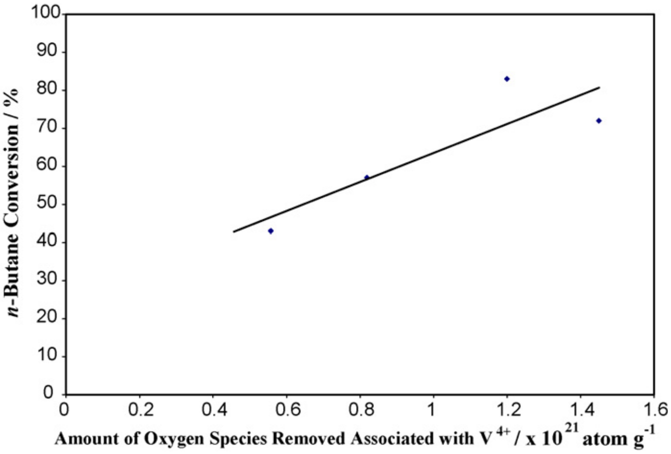

Fig. 6. Correlation of n-butane conversion with the amount of oxygen species removal associated with V^{4+}.

and Catalyst C (57%) obtained by the mechanochemical treatment of unmodified precursor with Bi–Fe oxide. It is also noted that Catalyst A gave 3–9% higher MA selectivity compared to Catalyst B and C. Interestingly, Catalyst B gave remarkably higher intrinsic activity, although it had lower surface area compared to the other catalysts. This may due higher amount and reactivity of oxygen species removed associated with V^{4+} which occurred at lower temperature. A good correlation was observed (Fig. 6) of n-butane conversion for all the catalysts and the amount of oxygen species removed associated with V^{4+} phase which is in agreement with our previous report [16,17]. However, the conversion was lower than the unmodified catalyst caused by a higher amount of oxygen species associated with V^{5+}. Higher amount of this oxygen species not only favour the selectivity but also inhibited the activity of the catalyst. We had also shown that the existence of too high V^{5+} phase would reduce the n-butane conversion [16]. A slight improvement of mechanochemical treated catalyst (Catalysts C) shows that the mechanochemcial is also potential method for enhancing the activity. However, the activity is still lower than the unmodified catalyst due to the existence of higher amount of some V^{5+} phases as shown in XRD as described in the previous literatures [18,19] and oxygen species associated with them.

4. Conclusions

Although the BiFe modified catalysts gave poor catalytic performance of the vanadium phosphate catalysts, but this study showed that the oxygen species associated with V^{4+} played an important role in activity of the catalyst, whereas the oxygen species linked to V^{5+} is needed in formation of maleic anhydride. Additional of dopants in oxide form was shown to enhance the activity without much effect on the selectivity.

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References

[1] B.C. Trivedi, B.M. Culbertson, Maleic Anhydride, Plenum Press, New York, 1982, p. 1.
[2] G. Centi, Catal. Today 16 (1993) 5.
[3] B.K. Hodnett, Catal. Rev. -Sci. Eng. 27 (1985) 373.
[4] G.J. Hutchings, J. Mater. Chem. 14 (2004) 3385.
[5] M. Otake, US Patent 4,337,173 (1982) assigned to Mitsubishi Chem. Ind. (Tokyo).
[6] G.J. Hutchings, R. Higgins, J. Catal. 162 (1996) 153.
[7] R.C. Edwards, US Patent 4 515 904 (1985) assigned to Standard Oil Company (Indiana).
[8] A. Bortinger, US Patent 5,885,919 (1999) assigned to Scientific Design Company, Inc. (Little Ferry).
[9] S.H. Sookraj, D. Engelbrecht, Catal. Today 49 (1999) 161.
[10] S. Sajip, J.K. Bartley, A. Burrows, M.T. Sananes, A. Tuel, J.C. Volta, C.J. Kiely, G.J. Hutchings, New J. Chem. 25 (2001) 125.
[11] Y.H. Taufiq-Yap, K.P. Tan, K.C. Waugh, M.Z. Hussein, I. Ramli, M.B. Abdul Rahman, Catal. Lett. 89 (2003) 87.
[12] Y.H. Taufiq-Yap, C.K. Goh, K.C. Waugh, Y. Kamiya, React. Kinet. Catal. Lett. 84 (2005) 271.
[13] F.B. Abdelouahab, R. Olier, N. Guilhaume, F. Lefebvre, J.C. Volta, J. Catal. 134 (1992) 151.
[14] J.C. Volta, C. R. Acad. Sci. Paris, Série IIc, Chimie/Chemistry 3 (2000) 717.
[15] M. Abon, J.M. Herrmann, J.C. Volta, Catal. Today 71 (2001) 121.
[16] Y.H. Taufiq-Yap, C.K. Goh, G.J. Hutchings, N. Dummer, J.K. Bartley, J. Mol. Catal. A: Chem. 260 (2006) 24.
[17] Y.H. Taufiq-Yap, J. Nat. Gas Chem. 15 (2006) 144.
[18] V.V. Guliants, J.B. Benziger, S. Sundaresan, I.E. Wachs, J.M. Jehng, J.E. Roberts, Catal. Today 28 (1996) 275.
[19] M. Abon, K. Bere, A. Tuel, P. Delichere, J. Catal. 156 (1995) 28.