OXIDATIVE DEHYDROGENATION OF ETHANE TO ETHYLENE OVER MOLYBDENUM BASED CATALYSTS

Supakorn Samangain [a], _Boonyarach Kitiyanan_ [a,*], _Sitthipong Pengpanich_ [b], _Kaew-arpha Thavornprasert_ [b]

[a] The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Thailand
[b] PTT Global Chemical Public Company Limited

Keywords : Oxidative dehydrogenation of ethane (ODH), Molybdenum oxide catalysts, Mixed metal oxide catalysts

ABSTRACT
Molybdenum based catalysts with second metal (Me) supported on alumina (γ-Al_2O_3) were studied for oxidative dehydrogenation of ethane to obtain ethylene. The catalysts, Mo-Me/Al_2O_3 mixed oxide catalysts at the ratio Me/Mo+Me (varying from 0 to 1), were prepared by using incipient wetness impregnation technique with total metal loading fixed at 20% by wt. The catalysts were investigated for their activity toward the reaction at temperature of 400, 450 and 500 ºC under atmospheric pressure. The reaction was carried out in a fixed-bed reactor with feed ratio of 20% ethane to 10% oxygen balanced by helium. The W/F ratio (W = catalyst weight, F = total feed flow rate) was fixed at 0.54 g.s.cm^{-3}. In addition, the catalysts were characterized by several techniques, such as BET surface area analysis and XRD. Among the tested catalysts, the best catalyst provides relatively high ethylene yield (>20%) at 500 ºC. Nonetheless, the ethylene selectivity is decreased with increasing Me/Mo+Me ratio while the CO selectivity is increased.
* Boonyarach.k@chula.ac.th

INTRODUCTION

Ethylene is one of the most important petrochemicals to produce several downstream products, such as polyethylene, ethylene oxide, ethylene dichloride, ethyl benzene and etc. The global demand of ethylene has been forecasted to increases by 6 million metric tons per year.(Advisors, 2016) Currently, ethylene is commercially produced by steam cracking or catalytic cracking of naphtha. However, there are some disadvantages of these processes for example, high energy consumption due to high reaction temperature, catalyst deactivation due to coke formation. Ethylene can also be produced from ethane via dehydrogenation. With the advent of shale gas, ethane is available at relatively low cost. Therefore, ethane from shale gas is economically considered to produce ethylene. Instead of direct dehydrogenation, oxidative dehydrogenation (ODH) of ethane is an attractive route to the conventional process of making ethylene. Oxidative dehydrogenation requires lower energy consumption because it is an exothermic reaction. In addition, the presence of oxygen in feed gas help prohibiting coke deposition on catalyst. However, the drawback of ethane ODH is that the yield of ethylene is relatively lower than the steam cracking, due to the lower conversion and the formation of undesired products (e.g. carbon monoxide and

carbon dioxide). Therefore, an active and selective catalyst to efficiently convert ethane to ethylene is necessary.(Gärtner et al., 2013) The aim of this research is to test Mo based catalysts for the ODH process with high catalytic activity, selectivity and to investigate the effect of adding vanadium on catalytic activity of Mo based catalysts. The effect of reaction temperature on ethane conversion, product selectivity and ethylene yield are also investigated. Moreover, the prepared catalysts are characterized by BET surface area analysis and XRD techniques in order to gain more information of the catalysts.

EXPERIMENTAL

A. Catalyst preparation
Transition metal oxide catalysts were prepared by incipient wetness impregnation of γ-Al_2O_3 with ammonium molybdate and ammonium metavanadate. The alumina and metals were purchased from Sigma-Aldrich. Metal solutions containing the precursor salts with appropriate amounts were dissolved and heated in deionized water at 70 ℃. After that prepared metal solutions were impregnated on alumina support. Samples were dried at 120 ℃ overnight and then calcined in the air at 500 ℃ for 5 h.

B. Catalyst characterization
B.1 Surface area analysis
Surface area analysis (BET): surface area of the catalysts was determined by using the multi-point BET analysis method. Prior to N_2 adsorption, 0.1-0.2 g of catalysts was degassed by using a vacuum at 250 °C for 10 h. The relative pressure used (P/P_0) in the range of 0.001 to 0.999 with a number of adsorption equal to 15 points and desorption 10 points.

B.2 X-Ray diffraction
X-ray diffraction (XRD) patterns were obtained with a Rigaku SmartLab RINT 2000 diffractometer employing with Cu-Kα radiation (λ = 1.542 Å). The catalysts were scanned from 2θ = 5° to 80° at a rate of 5°/min and their diffraction patterns was analyzed with the aim of determining crystalline structures. The mean crystallite size was calculated by using the Scherrer's equation from the XRD data.

C. Catalytic activity testing
The catalytic activity of the catalysts was known by performing the reaction in a packed-bed quartz tube reactor at atmospheric pressure with W/F of 0.54 g s/cm^3. The catalyst was activated in flowing oxygen at 500 °C for 30 min. The total flow was 50 cm^3/min with the composition of reaction mixture of $C_2H_6/O_2/He$ = 20%/10%/70%. The furnace temperature was raised to the desired reaction temperature. The reaction products were analyzed by gas chromatograph equipped with a flame-ionization detector (FID) and thermal conductivity detector (TCD).

RESULTS AND DISCUSSION

A. Effect of adding V to Mo/Al₂O₃ catalysts and reaction temperature

A. Effect of adding V to Mo/Al_2O_3 catalysts and reaction temperature

In this work section, the vanadium was added into molybdenum based catalysts with total metal loading fixed at 20wt.% similar to the work done by Christodoulakis et al. (2006) and the V/(Mo+V) ratio were varied from 0 to 1. The prepared V-Mo catalysts were tested for ethane ODH reaction using packed-bed reactor with W/F of 0.54 g s/cm^3 at temperature of 500 ℃. As shown in Figure 1, the ethylene selectivity is decreased with increasing V/(Mo+V) ratio. However, ethane conversion is relatively constant with V/(Mo+V) ratio. Furthermore, CO selectivity is increased with V/(Mo+V) ratio. For the optimum V/(Mo+V) ratio, it was found that V/(Mo+V) ratio of 0.2 provided the highest ethylene selectivity and ethylene yield comparing to the other V/(Mo+V) ratio. Meanwhile, V/(Mo+V) ratio of 0.8 obtained the highest CO and CO_2 selectivity. The effect of reaction temperature on activity of 20wt.%$Mo_{0.8}V_{0.2}/Al_2O_3$ catalyst was investigated at temperature of 400, 450 and 500 ℃. The data in the Table 1 shows that ethane conversion is increased with increasing reaction temperature because ethane is favorable to be converted toward desired and undesired products at high reaction temperature. As expected, the ethylene selectivity is not similar tendency as ethane conversion. Nonetheless, the CO and CO_2 selectivity are increased with increasing reaction temperature.

Table 1 The catalytic activity of 20wt.%$Mo_{0.8}V_{0.2}/Al_2O_3$ catalyst at reaction temperature of 400, 450 and 500 ℃

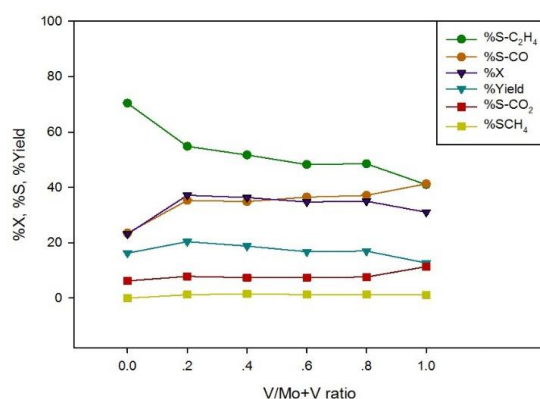| Temperature	Conversion (%)	Selectivity (%)				Yield (%)
		C_2H_4	CH_4	CO_2	CO	
400	12.6	63.7	0.0	7.2	28.2	8.0
450	32.1	59.0	1.2	7.6	31.7	18.8
500	37.2	55.1	1.2	7.9	35.5	20.4

Figure 1 The catalytic activity of 20wt.%$Mo_{1-x}V_x/Al_2O_3$ catalysts (x = 0.2, 0.4, 0.6, 0.8, 1) at reaction temperature of 500 ℃, X : conversion (%), S : selectivity (%) and Y : yield (%)

B. Surface area analysis

The surface area and pore volume of alumina support and prepared catalysts are reported in Table 2. As a result, it exhibits that the specific surface area of alumina support was decreased after loading metal which was mainly attributed to the pore blocking of doped metal. The 20wt.%V/Al_2O_3 catalyst obtained lower specific surface area than 20wt.% Mo/Al_2O_3 catalyst. For the activity of 20wt.%Me/Al_2O_3 (Me = Mo and V) catalysts was independent from specific surface area. According to 20wt.%$Mo_{1-x}V_x$/Al_2O_3 catalysts, the diminishing of specific surface area was affected by increasing V/(Mo+V) ratio and also related to the catalytic activity. These results were also correlated with X-ray diffraction technique (XRD) which will be mentioned in the following section.

Table 2 Specific surface area, pore volume of the support and prepared catalysts

Catalyst	Surface area (m^2/g)	Pore volume (ml/g)
Commercial Al_2O_3	155	0.272
20wt.%Mo/Al_2O_3	109	0.196
20wt.%V/Al_2O_3	90	0.197
20wt.%$Mo_{0.8}V_{0.2}$/Al_2O_3	149	0.294
20wt.%$Mo_{0.6}V_{0.4}$/Al_2O_3	135	0.276
20wt.%$Mo_{0.4}V_{0.6}$/Al_2O_3	126	0.263
20wt.%$Mo_{0.2}V_{0.8}$/Al_2O_3	90	0.213

C. X-Ray diffraction

XRD patterns of γ-Al_2O_3, 20wt.%Me/Al_2O_3 (Me = Mo and V) is shown in Figure 2. The peaks at 2θ = 66.80°, 46.01° and 37.44° indicate the presence of γ-Al_2O_3 (Qiao et al., 2013). It is clearly noticed that the peaks at 2θ = 12.73°, 23.37°, 25.59°, 27.32° and 33.75° indicating the presence of $Al_2(MoO_4)_3$ crystallites from 20wt.%Mo/Al_2O_3 catalyst while the peaks at 2θ = 20.29°, 26.18° and 34.34° indicating the presence of V_2O_5 crystallites from 20wt.%V/Al_2O_3 catalyst. (Qiao et al., 2013) As illustrated in Figure 2, XRD patterns of 20wt.%$Mo_{1-x}V_x$/Al_2O_3 catalysts (x = 0.2, 0.4, 0.6) exhibit the peak at 2θ value of approximately 20.89° indicating the presence of Al-V-MoO_7 crystallites.(Khatib et al., 2006) The average particle size of $Al_2(MoO_4)_3$, Al-V-MoO_7 and V_2O_5 crystallites calculated by using the Scherrer's equation, is shown in the Table 3. It is obviously seen that the particle size of Al-V-MoO_7 crystallites is increased with increasing the V/(Mo+V) ratio. In case of the 0.8 V/(Mo+V) ratio, it is no peak appearance at 2θ value of 20.89° but it is found the peak at 2θ value of approximately 20.29° that indicates the presence of V_2O_5 crystallites. From the previous results, it was implied that the diminishing of specific surface areas was related to the increasing of crystalline size. It was possibly due to occurring of pore blockages from the large crystals. Furthermore, it can be mentioned that the ethylene yield of $Mo_{0.8}V_{0.2}$/Al_2O_3 catalyst was enhanced, due to the presence of Al-V-MoO_7 phases. In case of $Al_2(MoO_4)_3$ phases, it is possible to mention that the presence of

$Al_2(MoO_4)_3$ phases has no significant effect on ethylene yield comparing to the $Al-V-MoO_7$ phases. Another relevant problem is that the ethylene yield tends to decrease when both $Al-V-MoO_7$ and V_2O_5 crystalline size are increased.

Table 3 Effect of crystalline size on surface area of 20wt.%$Mo_{1-x}V_x/Al_2O_3$ catalysts (x = 0.2, 0.4, 0.6, 0.8, 1)

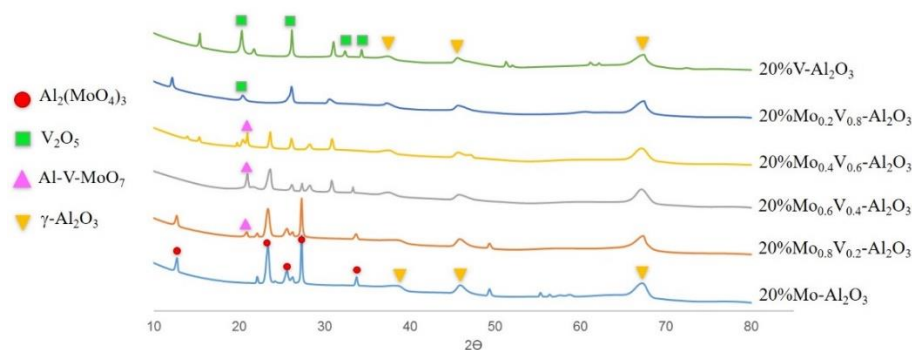| V/(Mo+V) ratio	Crystalline size (nm)			Surface area (m^2/g)	Yield (%)
	$Al_2(MoO_4)_3$	$Al-V-MoO_7$	V_2O_5		
0	21.4	-	-	109.0	16.3
0.2	17.7	27.2	-	149.0	20.4
0.4	17.5	30.2	-	135.4	19.1
0.6	17.1	40.2	17.9	125.6	17.3
0.8	-	-	19.6	90.3	17.1
1.0	-	-	30.8	90.2	13.0

Figure 2 X-Ray diffraction patterns of 20wt.%$Mo_{1-x}V_x/Al_2O_3$ catalysts (x = 0.2, 0.4, 0.6, 0.8, 1)

CONCLUSIONS

Mo-Me mixed catalysts with second metal (Me = V) supported on alumina, have been successfully synthesized by incipient wetness impregnation technique. Surface area analysis of 20wt.%$Mo_{1-x}V_x/Al_2O_3$ catalysts (x = 0.2, 0.4, 0.6 and 0.8) indicates the specific surface area of alumina support was decreased with increasing V/(Mo+V) ratio and also resulted in decreasing of ethylene yield. From XRD results, it revealed the presence of $Al-V-MoO_7$ crystallites at 2θ value of 20.89° belonging to 20wt.%$Mo_{1-x}V_x/Al_2O_3$ catalysts (x = 0.2, 0.4 and 0.6). At the V/(Mo+V) ratio of 0.8, there is no appearance of $Al-V-MoO_7$ crystallites but it discovered the presence of V_2O_5 crystallites. It was obviously seen that the increasing of $Al-V-MoO_7$ crystalline size resulted in decreasing of specific surface area and also ethylene yield, due to the pore blockades of large particle size. Among the tested catalysts, the 20wt.%$Mo_{0.8}V_{0.2}/Al_2O_3$ catalyst provided relatively high ethylene yield.

Nonetheless, the increasing of reaction temperature was favorable to increase ethane conversion while the ethylene selectivity was decreased.

ACKNOWLEDGEMENTS

REFERENCES

Advisors, S. (2016, 10 March 2016). Global Refining Outlook: 2016-2035. Retrieved 15 August, 2016, from https://stratasadvisors.com/

Christodoulakis, A., Heracleous, E., Lemonidou, A., & Boghosian, S. (2006). An operando Raman study of structure and reactivity of alumina-supported molybdenum oxide catalysts for the oxidative dehydrogenation of ethane. Journal of Catalysis, 242(1), 16-25.

Gärtner, C. A., van Veen, A. C., & Lercher, J. A. (2013). Oxidative Dehydrogenation of Ethane: Common Principles and Mechanistic Aspects. ChemCatChem, 5(11), 3196-3217.

Khatib, S., Guillopez, R., Pena, M., Fierro, J., & Banares, M. (2006). Alumina-supported V–Mo–O mixed oxide catalysts, the formation of phases involving aluminum: $AlVMoO_7$. Catalysis Today, 118(3-4), 353-359.

Qiao, A., Kalevaru, V. N., Radnik, J., Srihari Kumar, A., Lingaiah, N., Sai Prasad, P. S., & Martin, A. (2013). Oxidative dehydrogenation of ethane to ethylene over V_2O_5/Nb_2O_5 catalysts. Catalysis Communications, 30, 45-50.