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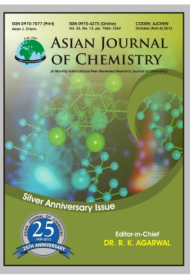

Partial Oxidation of Ethane to Acetic Acid on Titania Supported MoVNbPd Catalyst

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Partial oxidation of ethane was studied on unsupported and supported Mo-V-Nb oxides. Different grades of titania (Crystal-AF4.60, AF7.70 and AF12.5 and Degussa P25) were explored as supports. Samples of the catalyst were characterized using XRD, SEM and BET surface area. The reaction was carried out at 200-275 °C and 200 psi. At ethane conversion (6 %), unsupported samples exhibited selectivities to ethylene and acetic acid of 76 and 23 %, while for Degussa P25-supported sample, the values were 54 and 35 %, respectively. Addition of Pd (0.196 %) led to an increase in selectivity to acetic acid of 75 %.

Key Words: Ethane, Ethylene, Acetic acid, Partial oxidation, MoVNbPd catalyst.

INTRODUCTION

The catalytic conversion of C1-C4 components of natural gas to valuable chemicals or intermediates is a long-term goal of the petrochemical industry. Currently, olefins are the most important link between the relatively low cost and abundant supply of natural gas and a variety of chemicals that are in high demands. Partial oxidations such as that of propane to acrylic acid and ethane to ethylene/acetic acid are important demonstrations of the potential of using alkanes as direct raw materials for production of chemicals[1,2]. Commercially, acetic acid is mainly produced from methanol carbonylation. The route accounts for 75 % of the world capacity[3]. However, it has many challenge, such as corrosion and waste disposal. Considerable efforts have been made to develop alternative approaches for acetic acid production, among which the direct oxidation of ethane and ethylene to acetic acid has shown promising results[4,5]. Most of the catalysts reported are based on MoVNb mixed oxides[6,7].

The main reaction equations describing the partial oxidation of ethane are:

$$C_2H_6 + 1/2O_2 \rightarrow C_2H_4 + H_2O \qquad \Delta H_{600\ K} = -24.59\ \text{kcal/mol}\ C_2H_4$$

$$C_2H_6 + 3/2O_2 \rightarrow CH_3COOH + H_2O \qquad \Delta H_{600\ K} = -116.54\ \text{kcal/mol}\ CH_3COOH$$

$$C_2H_6 + 5/2O_2 \rightarrow 2CO + 3H_2O \qquad \Delta H_{600\ K} = -\ 90.13\ \text{kcal/mol CO}$$

$$C_2H_6 + 7/2O_2 \longrightarrow 2CO_2 + 3H_2O \qquad \Delta H_{600\ K} = -157.92\ \text{Kcal/mol}\ CO_2$$

Thus, all the reactions are highly exothermic and mainly irreversible.

The study of MoVNb catalyst for the partial oxidation of ethane to ethylene and acetic acid was pioneered by the work of Thorsteinson *et al*.[8,9]. The use of high pressure and the addition of steam to the feed improve the selectivity to acetic acid. The process requires a pressure of *ca.* 20 atm to obtain selectivity to acetic acid of 20 % and that to ethylene of 70 %. There were many attempts to improve the performances of the catalysts; such as the one that focused on getting better insight into the reaction network[10]. In 2005, SABIC of Saudi Arabia commercialized a 30,000 tons/year acetic acid plant based on a proprietary catalytic oxidation process. The catalyst is a calcined mixture of oxides of Mo, V, Nb and Pd. Three patents have been granted to SABIC as a result of work carried out on the catalysts at King Saud University[11-13]. It was shown that the addition of Pd to the MoVNb catalyst greatly increases the selectivity to acetic acid to *ca.* 80 % and completely oxidizes CO to CO_2. Combining this technology with low cost ethane may result in production competitive with methanol carbonylation technology.

Similar catalysts composition was reported by Borchert and Dingerdissen[14]. The mechanism and kinetics of the reaction were presented by Linke *et al*.[15,16]. Li and Iglesia[17,18] found that precipitation of Mo, V and Nb salts solution in the presence of colloidal TiO_2 (titania P25 from Degussa) led to a 10-fold increase in ethylene and acetic acid rates (per active oxide) without significant changes in selectivity relative to unsupported samples. The introduction of trace amounts of Pd (0.0025-0.01 wt. %) as a physical mixture of separate 0.3 (wt. %) Pd/SiO_2 led to the near complete depletion of ethylene and to a significant increase in acetic acid synthesis rate. Based on foregoing discussion, the aim of this study was to explore the partial oxidation of ethane to ethylene and acetic acid over catalyst based on unsupported and supported Mo-V-Nb oxides with and without the addition of Pd addition. Different grades of titania were used as supports.

EXPERIMENTAL

Catalysts preparation: Mo-V-Nb-O catalyst was prepared using a slurry method. Three aqueous solutions were prepared. (a) 0.57g ammonium *m*-vanadate was dissolved in 25 mL of water while stirring and heating at 87 ºC. A yellow colour solution was obtained. (b) 2.16 g ammonium *p*-molybdate was dissolved in 20 mL of water while stirring and heating at 60 ºC. A colourless solution was obtained. (c) 0.97g niobium oxalate (21.5 % Nb_2O_5) in 20 mL of water while stirring and heating at 63 ºC. A white colour solution was formed. 1.5 g oxalic acid powder was added gradually to vanadate solution and stirred again at 87 ºC. Foams were observed while adding oxalic acid, but they broke-up fast. The solution colour changed from yellow to dark blue. The molybdate solution was then mixed with the previous solution and stirred again for 10 min at 87 ºC before adding (drop-wise) the niobium solution. The mixture was stirred for additional 10 min at 87 ºC. The water was then evaporated.

In case of supported catalyst, 5 g of respective support (titania with different grades) was added to the Mo-solution while stirring and heating at 85 ºC until the water was evaporated. This makes the active components to be about 30 wt % on support.

Furthermore, other catalysts containing palladium were prepared. Appropriate amount of a 10 % Pd on charcoal in oxidized form was added. The resulting paste was left for 24 h at room temperature. It was then dried for 16 h at 120 ºC and calcined for 0.5 h at 350 ºC. Based on the respective amounts of metals added, the bulk unsupported catalyst ($Mo_{16}V_{6.37}Nb_{2.05}$) is donated herein as 'M'. Then, for the supported samples, corresponding supported name is added. The metals ratio and corresponding catalysts names are given in the Table-1.

TABLE-1
SUPPORTS BET SURFACE AREA (m^2/g) AND NAMES OF THE SAMPLES (AS USED IN THE TEXT) M = $Mo_{16}V_{6.37}Nb_{2.05}O_x$, S = SUPPORT AND PC = PALLADIUM WEIGHT PER CENT

Support type	Surface area (m^2)	Name in text	Pd (wt %)	Name in text
Cristal AF (4.60)	27	S4.60M	2.100000	S25MPC21*
Cristal AF (7.70)	34	S7.70M	1.100000	S25MPC11
Cristal AF (12.5)	3	S12.5M	0.100000	S25MPC1
Degussa P25	54	S25M	0.050000	S25MP0.5

*$Mo_{16}V_{6.37}Nb_{2.05}Pd_{1.844}O_x$/P25, the Pd ratio varies accordingly for other samples.

Characterization of catalysts: Crystalline phase of the TiO_2-supported catalysts was analyzed by powder X-ray diffraction (XRD, Ultima IV) with Cu radiation (40 kV, 40 mA). The XRD patterns were collected at a scan rate of 2.0 degree/min in the range of $2\theta = 5$-7º. SEM images were taken on NOVA NANO LAB microscope. BET surface areas of the catalysts were determined by N_2 adsorption at liquid nitrogen temperature using a Micromeritics ASAP 2020 automated system and the Brunauer-Emmett-Teller (BET) method using nitrogen adsorption-desorption at 77 K.

Catalytic tests: The catalytic activities tests were measure at reaction temperatures of 225-275 ºC and total pressure of 200 psi. The reactants flow rate was maintained at 15 mL/min (ethane and oxygen with volume percent of 82 and 18 %, respectively). The tests were carried out in an apparatus comprised of a reaction section and analysis section. As shown in Fig. 1, the reaction section mainly consists of oven and a reactor. Oven is a convection zone that surrounds the reactor and where the sample valves are fixed. It is a stainless steel box with 40 cm × 40 cm × 40 cm dimensions. The oven was designed with maximum operating temperature of 350 ºC. The temperature is controlled by Omega temperature controller. The Micro-reactor was made of stainless steel - length of 150 mm and inside diameter of 6.4 mm. It is surrounded by brass block. The block is surrounded by mica band heater. The reactor was fixed inside the oven. Reactor temperature is measured by a thermocouple that touched reactor wall.

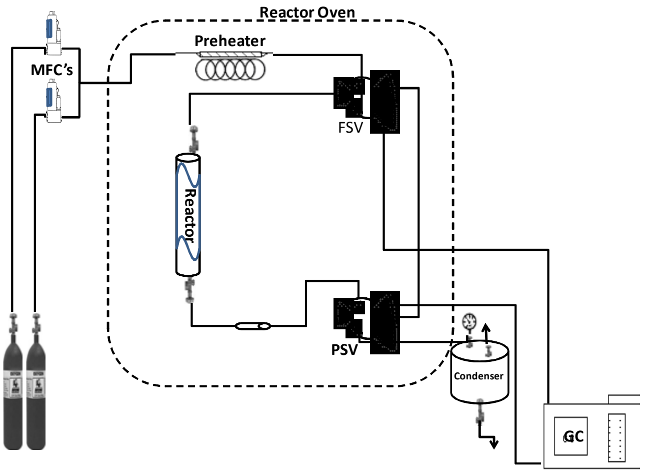

Fig. 1. Schematic of experimental setup, MFC's reactants mass flow controller, FSV feed sample valve, PSV products sample valve

The reaction products which exit from reactor are analyzed in gas chromatography-a Shimadzu equipment of model AS2010. All gases and acetic acid were detected by Thermal conductivity detector, TCD. Porapak Q 80/100 column was used as separation columns. Helium was the carrier gas. The temperature programming was: 35 ºC (hold 9 min) 20 ºC/min to 135 ºC (hold 12 min).

RESULTS AND DISCUSSION

Sample Characterizations: Many catalysts samples were prepared. Effects of types of support and addition of dopant were explored. The most important difference among the supports is the variation in their surface areas (Table-1). The lowest and highest areas are 3 and 54 m^2/g, respectively. A sample (S25MCP0.125) that exhibited the best performance was characterized using X-ray diffraction (Fig. 2). It indicates strong peaks for the anatase and rutile forms of the TiO_2 support and a weak line at 22.58° for Mo_5O_{14}-like structure. The major XRD peak for the rutile is at $2\theta = 27.42°$ and that of anatase at $2\theta = 25.30°$. Bulk sample has a strong line at a 2θ value of 22.58° and weaker lines at 25.30°. These lines have been assigned to Mo_5O_{14}-like structures formed when V or Nb substitute into Mo_5O_{14}[15]. The catalyst was prepared using appropriate amount of a 10 % Pd on charcoal in oxidized form. SEM image (Fig. 3) of the charcoal shows that the Pd was dispersed nano-micro size clusters on the surface of the charcoal.

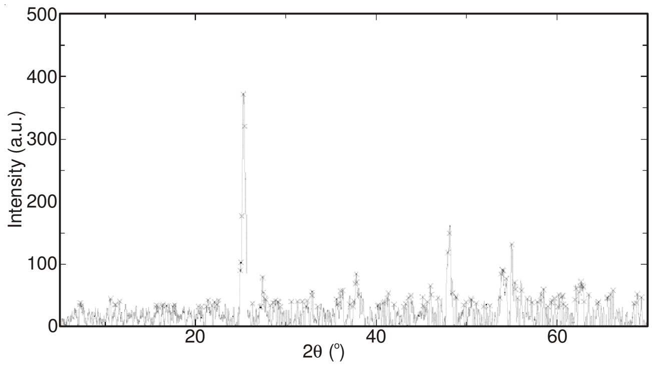

Fig. 2. XRD pattern for $Mo_{16}V_{6.37}Nb_{2.05}Pd_{1.844}O_x/TiO_2$-P25

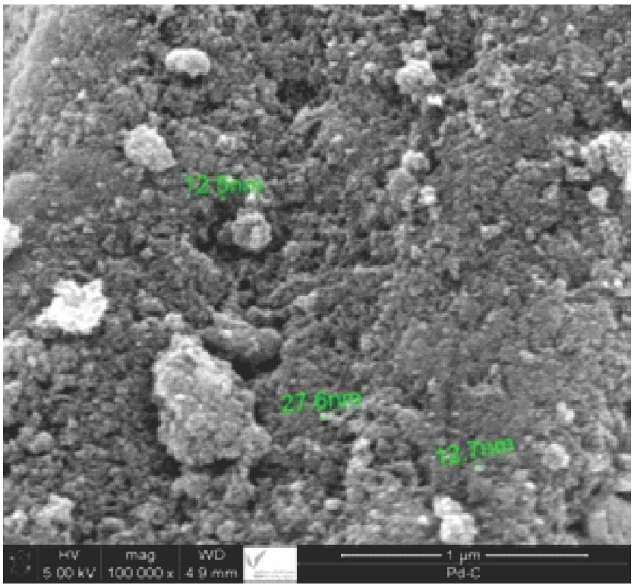

Fig. 3. SEM for Pd on charcoal

Ethane oxidation to ethylene and acetic acid on bulk $Mo_{16}V_{6.37}Nb_{2.05}O_x$ catalyst: $Mo_{16}V_{6.37}Nb_{2.05}O_x$ is considered as a highly active and selective catalyst. Also it has superior long-term stability compared to other systems for ethane oxidation[11,12]. Oxidations rates and selectivities to products on bulk $Mo_{16}V_{6.37}Nb_{2.05}O_x$ (subsequently referred to as M) catalyst were measured at temperature range 225-275 °C and 200 psi total pressure. The reactants flow rate was maintained at 15 mL/min. As shown in Fig. 4, bulk M catalyst gave selectivity to acetic acid of 23-35 % and selectivity to ethylene of 62-76 % at ethane conversion 6-17 %. It is observed that as the ethane conversion increased, the selectivity to acetic acid increased slightly (23-35 %) with corresponding decrease in selectivity to ethylene (76-62 %). This is consistent with the involvement of ethylene as a reactive intermediate in acetic acid production route. However, the non-zero selectivity to acetic acid, evident by extrapolation to zero ethane conversion suggests that a substantial fraction of the acetic acid forms *via* direct oxidation of ethane.

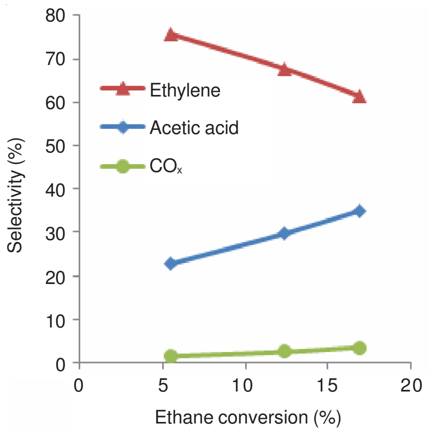

Fig. 4. Product selectivities as a function of ethane conversion for ethane oxidation on $Mo_{16}V_{6.37}Nb_{2.05}O_x$ catalyst: T = 225-275 °C, P = 200 psi, F/W= 50 mL/min g catalyst

Support effects on ethane oxidation catalyzed by supported $Mo_{16}V_{6.37}Nb_{2.05}O_x$: The performance of catalyst M was further explored using four different grades of titania as supports. The activities of the catalysts were evaluated at temperature range of 200-275 °C and feed flow rate of 15 mL/min. Total pressure was maintained at 200 psi. The results are presented in Figs. 5-7. The S25M has the highest conversion with increase in reaction temperature. The ethane conversion was increased from 1 to 11 % in the temperature range. The oxygen conversion (not shown) was increased from 8 to 81 %. S7.7M exhibited lower conversion for both ethane and oxygen with values of 4 and 19 %, respectively at 275 °C. Also S4.6M and S12.5M catalysts have shown relatively very low activities compared with S25M and S7.7M. The superior performance of P25 and cristal 7.7 may be associated with their relatively higher surface area.

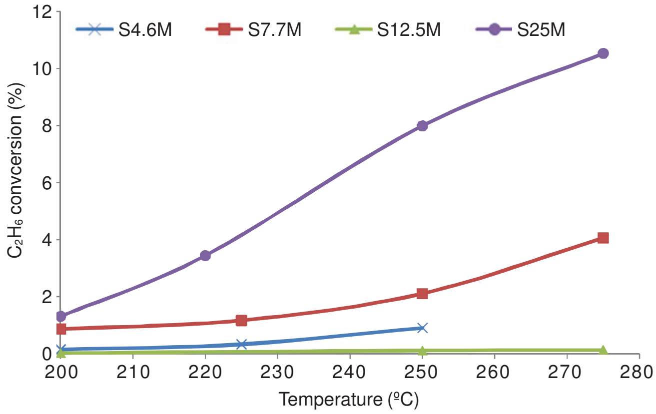

Fig. 5. Ethane conversion as a function on reaction temperature for ethane oxidation over different supported $Mo_{16}V_{6.37}Nb_{2.05}O_x$ catalysts: P = 200 psi, F/W = 15 mL/min g catalyst

The same catalyst exhibited higher yields to both ethylene and acetic acid (Figs. 6 and 7). Again, S25M showed ethylene and acetic acid yields of 5 and 4 %, respectively. There are significant effects of the supports towards enhancing the ethane conversion and selectivities to ethylene and acetic acid. This suggests that TiO_2-P25 is best supports for $Mo_{16}V_{6.37}Nb_{2.05}O_x$ as a catalyst in partial oxidation of ethane to ethylene and acetic acid. This is similar to the observation in previous workers[17]. It was shown that TiO_2-P25 led to the formation of active structures without forming unselective linkages between active oxides and support surfaces or other unselective or inactive structures.

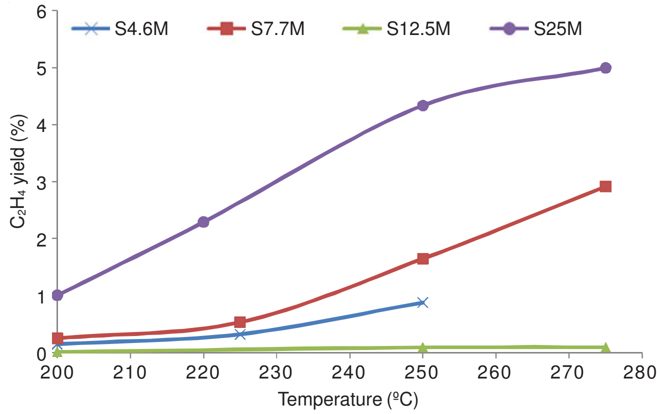

Fig. 6. Ethylene yield as a function on reaction temperature for catalytic ethane oxidation over different supported $Mo_{16}V_{6.37}Nb_{2.05}O_x$ catalysts: P = 200 psi, F/W = 15 mL/min g catalyst

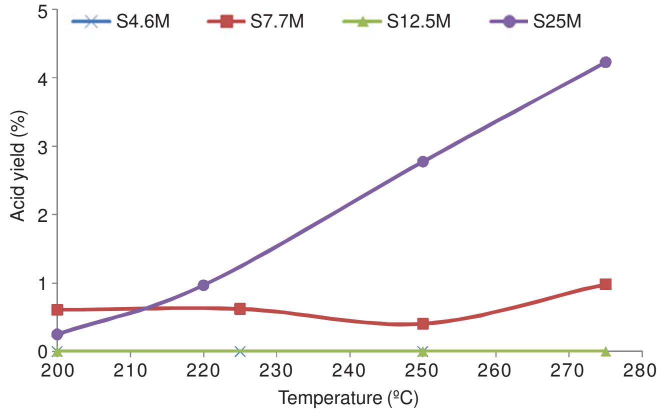

Fig. 7. Acetic acid yield as a function on reaction temperature for catalytic ethane oxidation over different supported $Mo_{16}V_{6.37}Nb_{2.05}O_x$ catalysts: P = 200 psi, F/W = 15 mL/min g catalyst

Figs. 8 and 9 show the performances of supported $Mo_{16}V_{6.37}Nb_{2.05}O_x/TiO_2$-P25 and unsupported $Mo_{16}V_{6.37}Nb_{2.05}O_x$ catalysts in the reaction. They indicate the products selectivities as functions of ethane conversion based on variation of the reaction temperature. Supported $Mo_{16}V_{6.37}Nb_{2.05}O_x$ species gave higher acetic acid selectivities (28-40 %) than $Mo_{16}V_{6.37}Nb_{2.05}O_x$ powders (23-35 %). Ethylene selectivities concurrently decreased (66-48 %) as a result of its subsequent conversion to acetic acid and CO_x. This suggests modification of surface structure of the catalyst that improves the selectivity to acetic acid. It was reported that the synthesis rate of acetic acid was enhanced by structural dispersion of active oxides on TiO_2 more than ten times higher synthesis rate was achieved with similar selectivities to all the products[17].

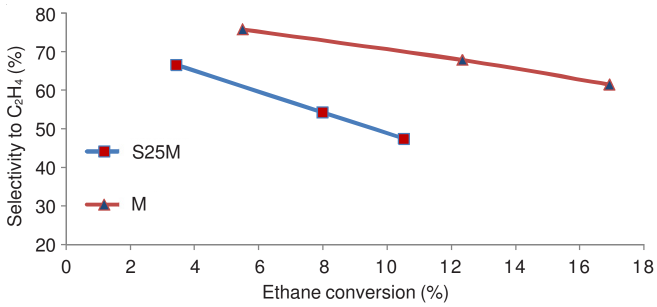

Fig. 8. Ethylene selectivity as a function of ethane conversion for ethane oxidation on $Mo_{16}V_{6.37}Nb_{2.05}O_x$ and $Mo_{16}V_{6.37}Nb_{2.05}O_x/TiO_2$ catalysts: T = 200-275 ºC, P = 200 psi, F/W = 15 mL/min g catalyst

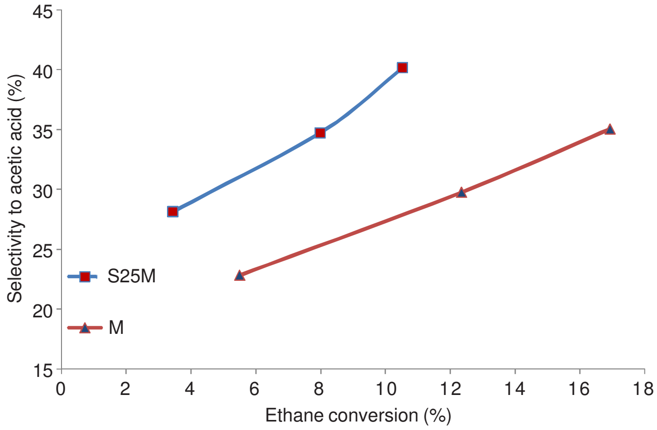

Fig. 9. Acetic acid selectivity as a function of ethane conversion for ethane oxidation on $Mo_{16}V_{6.37}Nb_{2.05}O_x$ and $Mo_{16}V_{6.37}Nb_{2.05}O_x$ /TiO_2 catalysts: T = 200-275 ºC, P = 200 psi, F/W= 15 mL/min g catalyst

Ethane oxidations in the presence of nano-palladium additive: Ethane partial oxidation on $Mo_{16}V_{6.37}Nb_{2.05}O_x$ and $Mo_{16}V_{6.37}Nb_{2.05}O_x/TiO_2$ gave best performance with selectivity to acetic acid of 40 % and that to ethylene of more than 48 % ethylene. Thus, it appears that higher acetic acid selectivities require the incorporation of catalytic functions for ethylene oxidation to acetic acid. Therefore, we explored the effects of Pd addition on the reaction. The source of palladium is 10 % palladium on activated charcoal in an oxidized form. We studied the optimum amount of Pd for the reaction based on selectivity to ethylene and acetic acid.

Effect of palladium content: The same supports in previous study were also used to explore the effect of palladium contents. Mo-V-Nb standard catalyst containing fixed amount of nano-palladium was prepared and supported on the different grades of titanium dioxide, four catalysts were prepared:

$Mo_{16}V_{6.37}Nb_{2.05}Pd_{1.844}O_x$/AF4.60	S4.60MPC21
$Mo_{16}V_{6.37}Nb_{2.05}Pd_{1.844}O_x$/AF7.70	S7.70MPC21
$Mo_{16}V_{6.37}Nb_{2.05}Pd_{1.844}O_x$/AF12.50	S12.5MPC21
$Mo_{16}V_{6.37}Nb_{2.05}Pd_{1.844}O_x$/P25	S25MPC21

Palladium loading for these catalysts was 2.1 %. The reactions results are shown in Figs. 10-12. By adding palladium, catalytic activity of S12.5MPC21 drastically changed. At 240 ºC, ethane conversion increased from 0.1 to 5 % after Pd addition. The corresponding oxygen conversions are 2 and 99 %, respectively. On the other hand, S4.60MPC21 showed no change in the activity compared with the same catalyst without palladium. Such addition also affected the performance of

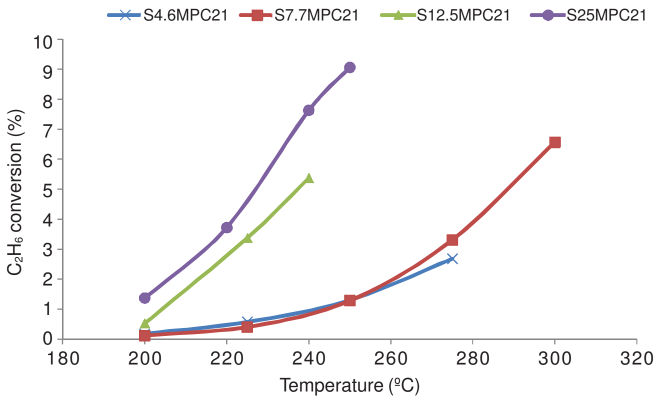

Fig. 10. Ethane conversion as a function on reaction temperature for ethane oxidation over different supported $Mo_{16}V_{6.37}Nb_{2}.05$ $Pd_{1.844}O_x$ catalysts: P = 200 psi, F/W: 15 mL/min g catalyst

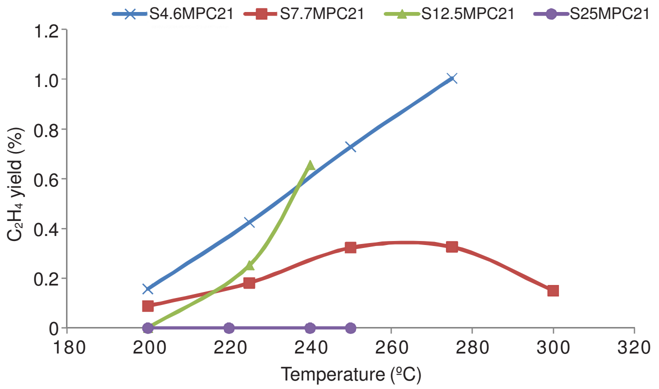

Fig. 11. Ethylene yield as a function on reaction temperature for ethane oxidation over different supported $Mo_{16}V_{6.37}Nb_{2}.05$ $Pd_{1.844}O_x$ catalysts: P = 200 psi, F/W: 15 mL/min g catalyst

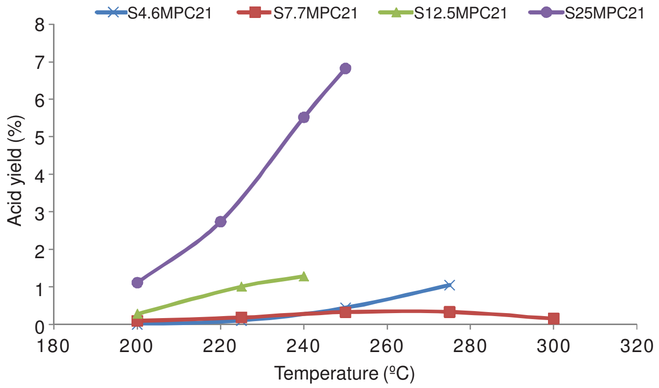

Fig. 12. Acetic acid yield as a function on reaction temperature for ethane oxidation over different supported $Mo_{16}V_{6.37}Nb_{2}.05$ $Pd_{1.844}O_x$ catalysts: P = 200 psi, F/W: 15 mL/min g catalyst

the catalyst supported over AF(7.7). S7.70M PC21 has shown slight decrease in ethane conversion whereas oxygen conversion was doubled at the same temperature range. For instance, at 275 ºC ethane conversion was maintained at 4 % (with or without palladium) whereas oxygen conversion was increased from 19-46 %.

Supported MoVNb over P25 was also affected by presences of palladium and this led to a significant increase in oxygen conversion. At 275 ºC while the change in ethane conversion was within 1 %, oxygen conversion changed from 59 % to almost complete conversion. It is observed that the addition of palladium on catalytic activity manifested more on oxygen conversion where all catalysts have shown significant increase in oxygen conversion. It is also seen that for all catalysts, increases in oxygen conversion was accompanied by decrease in selectivities to ethylene and increase in selectivities to both acetic acid and carbon oxides. So, the presence of Pd may be associated with the change in redox properties of the sample. This facilitates oxygen mobility and its insertion into the product structure. This manifested in relatively higher oxygen conversions and no significant difference in ethane conversion with the addition of Pd. The presence of the additive did not show significant change in ethane oxidation rate but markedly increased acetic acid synthesis rate by converting ethylene intermediates to acetic acid. Selectivity to acetic acid increased from 40 to 75 % while that to ethylene decreased from 66 % to a negligible amount in the reactor effluent.

Overall, S25MPC21 showed good activity and it recorded the best selectivity and yield for acetic acid. For instance, at 250 ºC it exhibited 75 and 7 % selectivity to acetic acid and yield, respectively whereas the respective values recorded were 56 and 0.7 % for S7.70M PC21 at same temperature. High ethane conversion was observed on S12.5M PC21. But it exhibited highest selectivity to undesirable products at expense of ethylene and acetic acid. At 240 ºC, oxygen conversion was 99 %, selectivity to CO_x was 64 % and their yield was 3 %. Selectivity to CO_x increased while ethylene and acetic acid decreased indicating that unselective structure formed by interaction between $Mo_{16}V_{6.37}Nb_{2.05}O_xPd$ and S12.5 surfaces catalyzed oxidation of ethylene and acetic acid to CO_X. Therefore, these catalysts can be arranged based on their activities and selectivities to desirable products. S25MPC21 is considered to be the best followed by S7.7MPC21, S12.5MPC21 and finally S4.6MPC21.

Optimum loading of Nano-PdO$_X$: After TiO_2 P25 was selected as the best support for $Mo_{16}V_{6.37}Nb_{2.05}O_x$ catalyst in partial oxidation of ethane and how activity and acetic acid selectivity was enhanced in presence of palladium, we explored further the effect of palladium. Supported Mo-V-Nb over P25 was promoted with different amounts of nano-PdO$_X$. Ten different catalysts were prepared using different nano-palladium oxides loadings shown. Ethane oxidation over these catalysts was carried out at three reaction temperatures-220, 230 and 240 ºC and total pressure of 200 psi with 15 mL/min feed flow rate. The results are shown in Tables 2-4. It is observed that when nano-PdO$_X$ loading was above 0.05 wt %, the samples showed similar trends with no significant differences in ethane and oxygen conversions. In addition, the catalyst exhibited similar trends at different temperatures. So we will focus on samples with nano-PdO$_X$ loading below 0.05 wt % and at 240 ºC.

Depending on the results, the activities of catalysts increased as nano-palladium oxides loading increased. Highest conversions of ethane and oxygen observed at 0.0125 wt % loading with values of 9 and 85 %, respectively. The corresponding selectivity and yield to acetic acid are 78 and 7 %, respectively. In contrast, ethylene recorded the highest selectivity and yield at palladium loading of 0.000625 wt % which were 64 and 5 %, respectively. S25MPC0.00625 also

TABLE-2
EFFECTS OF Pd LOADING ON THE PERFORMANCE OF $Mo_{16}V_{6.37}Nb_{2.05}Pd_1O_x/TiO_2$ (P25) AT 220 ºC; 200 psi AND F/W Of 15 mL/min g cat

Catalyst name	Pd (wt %)	Conversion (%)		Selectivity (%)		Yield (%)		Space time yield (g/kgh)	
		O_2	C_2H_6	Et	AA	Et	AA	Et	AA
S25MPC21	2.100000	47	4	0	74	0	3	0	181
S25MPC11	1.100000	51	4	0	71	0	3	0	185
S25MPC1	0.100000	45	4	0	77	0	3	0	186
S25MP0.5	0.050000	39	4	2	80	0	3	2	188
S25MP0.343	0.034000	62	4	2	79	0	3	2	221
S25MP0.25	0.025000	41	4	3	77	0	3	4	190
S25MPC0.125	0.012500	34	3	10	76	0	2	11	163
S25MPC0.0625	0.006250	30	4	43	48	2	2	48	116
S25MPC0.00625	0.000625	26	4	76	19	3	1	98	53
S25M	0.000000	20	3	67	28	2	1	70	64

Ethylene = Et and acetic acid = AA.

TABLE-3
EFFECTS OF Pd LOADING ON THE PERFORMANCE OF $Mo_{16}V_{6.37}Nb_{2.05}Pd_1O_x/TiO_2$ (P25) AT 230 ºC; 200 psi AND F/W OF 15 mL/min g cat

Catalyst name	Pd (wt %)	Conversion (%)		Selectivity (%)		Yield (%)		Space time yield (g/kgh)	
		O_2	C_2H_6	Et	AA	Et	AA	Et	AA
S25MPC21	2.10000	56	5	0	75	0	3	0	227
S25MPC11	1.10000	78	6	0	69	0	4	0	272
S25MPC1	0.10000	60	5	0	78	0	4	0	272
S25M0.5	0.05000	56	5	1	80	0	4	2	277
S25M0.343	0.03430	85	6	1	79	0	4	2	295
S25M0.25	0.02500	54	5	3	76	0	4	4	231
S25MPC0.125	0.01250	61	6	5	77	0	5	10	307
S25MPC0.0625	0.00625	50	6	28	59	2	4	51	232

TABLE-4
EFFECTS OF Pd LOADING ON THE PERFORMANCE OF $Mo_{16}V_{6.37}Nb_{2.05}Pd_1O_x/TiO_2$ (P25) AT 240 ºC; 200 psi AND F/W OF 15 mL/min g cat

Catalyst name	Pd (wt %)	Conversion (%)		Selectivity (%)		Yield (%)		Space time yield (g/kgh)	
		O_2	C_2H_6	Et	AA	Et	AA	Et	AA
S25MPC21	2.100000	94	8	0	72	0	6	0	363
S25MPC11	1.100000	99	8	0	68	0	5	0	341
S25MPC1	0.100000	81	7	0	77	0	5	0	355
S25M0.5	0.050000	84	8	1	79	0	6	2	410
S25M0.343	0.034300	84	8	1	79	0	6	3	410
S25M0.25	0.025000	84	8	2	77	0	6	4	383
S25MPC0.125	0.012500	84	8	4	78	0	7	9	439
S25MPC0.0625	0.006250	68	8	23	63	2	5	53	318
S25MPC0.00625	0.000625	50	8	64	30	5	2	151	154
S25M	0.000000	42	6	62	28	4	2	113	107

exhibited the lowest selectivity and yield of carbon oxides which were 6 and 0.5 %, respectively. Overall, 0.0125 % is the optimum loading of nano-palladium oxides for oxidation of ethane to acetic acid over $Mo_{16}V_{6.37}Nb_{2.05}Ox$ /TiO_2 (P25).

Conclusion

Partial oxidation of ethane to ethylene and acetic acid on multi-components oxides-$Mo_{16}V_{6.37}Nb_{2.05}O_x$-was enhanced by the structural dispersion of active oxides on titania (Degussa, P25) support. At ethane conversion of *ca.* 6 %, unsupported samples exhibited selectivities to ethylene and acetic acid of 76 and 23 %, while for Degussa P25-supported sample; the values were 54 and 35 %, respectively. Other supports tested - cristal AF4.60, AF7.70 and AF12.5 exhibited less significant increase in the conversion and selectivities. In the presence of nano-palladium oxides as additive, the reaction shifted toward acetic acid formation. Furthermore, at similar level of ethane conversion, addition of trace amounts of Pd (0.196 %) led to no production of ethylene and to a significant increase in selectivity to acetic acid of 75 %. Supported MoVNb-Pd is very active and selective catalyst for the reaction.

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