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

Yousef S. Al-Zeghayer

Abstract—The partial oxidation of ethane to ethylene and acetic acid was examined over catalyst based on unsupported and supported Mo-V-Nb oxides with and without Pd. The supports are different types of titania. Catalyst characterization was carried out uxing XRD, SEM, and BET surface area. The reaction was carried out in differential reactor at temperature range 200-275°C and total pressure 200 psi. Unsupported Mo₁₆V_{6.37}Nb_{2.05}O_x showed activity and selectivities resemble those reported previously. Titania with different grades was examined as a support for Mo₁₆V_{6.37}Nb_{2.05}O_x. The selectivities of products kept without significant change when titania P25 was used as a support for Mo₁₆V_{6.37}Nb_{2.05}O_x whereas the other grades cristal AF4.60, AF7.70, and AF12.5 showed either low catalytic activities and/or combustion reactions. Supported $Mo_{16}V_{6.37}Nb_{2.05}O_x$ over $TiO_2(P25)$ led to increase the catalyst surface area from 30 to 38.58 m²g⁻¹. The introduction of trace amounts of Pd led to the depletion of ethylene and to a significant increase in acetic acid synthesis rate.

Index Terms—Acetic acid, ethane, ethylene, MoVNbPd catalyst, partial oxidation.

I. INTRODUCTION

Commercially, acetic acid is mainly produced from methanol carbonylation, which gives rise to many problems, such as corrosion and waste disposal. Methanol carbonylation accounts for 65% of the world capacity.

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 promise. As an example, a process using palladium-based heteropoly acids catalysts for ethylene oxidation to acetic acid was commercialized by Showa Denko of Japan in 1997.

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, allows selectivities to acetic acid as high as 80%. Combining this technology with low cost ethane may result in production economics competitive with methanol carbonylation technology.

The main reaction equations describing the oxidation of ethane are

 C_2H_6 + 1/2 O_2 → C_2H_4 + H_2O $\Delta H 600$ 0K = - 24.59 kcal/mole C_2H_4

$$C_2H_6 + 3/2 O_2 \rightarrow CH_3COOH + H_2O \Delta H 600 {}^0K =$$

Manuscript received August 13, 2013; revised November 5, 2013.

- 116.54 kcal/mole CH₃COOH

C₂H₆ + 5/2 O₂ → 2CO + 3H₂O Δ H 600 ⁰K = - 90.13 kcal / mole CO

C₂H₆ + 7/2 O₂ → 2CO₂ + 3H₂O Δ H 600 ⁰K = -157.92 Kcal / mole CO₂

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.* [1] and Young and Thorsteinson [2]. 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 about 20 atm and acetic acid selectivity is about 20%, while ethylene selectivity is about 70%.

Three patents by Karim *et al.*[3]-[5] have been granted to SABIC as a result of work carried out at King Saud University. In these patents, it is shown that the addition of Pd to the MoVNb catalyst greatly increases the selectivity to acetic acid to about 80% and completely oxidizes CO to CO₂. The same idea was also discovered by Borchert and Dingerdissen [6]. The mechanism and the kinetics of the reaction were presented by Linke *et al.* [7], [8].

Li and Iglesia [9], [10] found that precipitation of Mo, V,and Nb salts solution in the presence of colloidal TiO₂ (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/Si O₂, led to the near complete depletion of ethylene and to a significant increase in acetic acid synthesis rate.

In this paper, we examine the partial oxidation of ethane to ethylene and acetic acid over catalyst based on unsupported and titania supported Mo-V-Nb oxides with and without the addition of Pd. Different grades of titania are used.

II. EXPERIMENTAL

A. Catalyst Preparation

Mo-V-Nb oxides catalyst was prepared using a slurry method. Three aqueous solutions were prepared (a) 0.57 g ammonium m-vanadate dissolved in 25 ml of water while stirring and heating at 87^{0} C. A yellow color solution resulted. (b) 2.16 g ammonium p-molybdate in 20 ml of water while stirring and heating at 60^{0} C. A colorless solution resulted, (c) 0.97 g niobium oxalate (21.5% Nb₂O₅) in 20 ml of water while stirring and heating at 63^{0} C. A white colour solution was formed. 1.5 g oxalic acid powder was added gradually to

Y. S. Al-Zeghayer is with Department of Chemical Engineering and is a Director of Industrial Catalysts Chair, King Saud University (Riyadh, Saudi Arabia) (e-mail: yszs@ksu.edu.sa).

vanadate solution and stirred again at 87^oC. Foam resulted while adding oxalic acid and it breaks fast. The solution color 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, 5.0 gm of support (titania with different grades) is added to the Mo-solution while stirring and heating at 85^oC until the liquid evaporated. For catalysts containing palladium, 10 % Pd on charcoal in oxidized form is added in the appropriate amount.

The resulting paste was aged for 24 hours, then dried for 16 h at 120° C and calcinated for 0.5h at 350° C.The bulk standard catalyst is donated herein as (M) ; $Mo_{16}V_{6.37}Nb_{2.05}$.

The catalyst weight for a supported catalyst is between 7.10 - 7.20 gm.

B. Catalyst Characterization

Crystalline phase of TiO₂ and TiO₂-supported catalysts were 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 2Θ = 5-70 degrees. SEM images were taken on NOVA NANO LAB microscope.BET surface area of the catalysts were determined by N₂ adsorption at liquid nitrogen temperature using a Micromeritics ASAP 2020 automated system and the Brunauer–Emmet–Teller (BET) method using nitrogen adsorption- desorption at 77 K.

The scanning electron microscopy (SEM) results for Pd on activated charcoal (Fig .1) show that Pd O is in a nano form.



Fig. 1. SEM for Pd on charcoal.

C. Catalytic Tests Set up

Catalytic activity and selectivity tests were carried out in an apparatus comprised of a reaction section and analysis section.

1) Reaction section

Reaction section mainly consists of (Fig. 2)

- Oven is a convection zone that surrounds the reactor and where the sample valves are fixed. It is a stainless steel box with $40 \times 40 \times 40$ cm dimensions. The oven was designed with maximum temperature around 350° C and its temperature is controlled by Omega temperature controller.
- Reactor which is Micro-reactor overall length is 150 mm with inside diameter of made of 6.35 mm stainless steel and surrounded by brass block. The block is surrounded by mica band heater. Reactor temperature can be measured by a thermocouple touched reactor wall. The reactor is fixed inside the oven where the

temperature is stable. The authors of the accepted manuscripts will be given a copyright form and the form should accompany your final submission.

The reaction products which exit from reactor are analyzed in gas chromatography.

2) Analysis section

The Gas Chromatography that is shown in Fig. 2 is a Shamudzu equipment of model AS2010. Thermal conductivity detector (TCD) is used for the analysis. It was conFigd to analyze reaction products as well as feed mixture using Propack Q and carboxeen 1000 as columns.



Fig. 2. Schematic of experimental setup, reactants mass flow controller (MFC's), feed sample valve (FSV), products sample valve (PSV).

III. RESULTS AND DISCUSSION

A. Ethane Oxidation to Ethylene and Acetic Acid on Bulk $Mo_{16}V_{6.37}Nb_{2.05}O_x$ Catalyst

 $Mo_{16}V_{6.37}Nb_{2.05}O_x$ catalyst is considered as a high active and selective catalyst as well as its superior long-term stability compared to other systems for ethane oxidation. Oxidations rates and products selectivities on bulk $Mo_{16}V_{6.37}Nb_{2.05}O_x$ (M) catalyst were measured at temperature range 225-275 ^oC and 200 psi total pressure. The reactants flow rate was maintained at 15 ml/min. Bulk $Mo_{16}V_{6.37}Nb_{2.05}O_x$ catalyst gave 23-35% acetic acid selectivity and 62-76% ethylene selectivity at ethane conversion 6-17% (Fig. 3) these selectivities resemble those reported in previous works.

It is seen that acetic acid selectivities increased slightly with ethane conversion (from 23% to 35%), while ethylene selectivities concurrently decreased (from 76% to 62%), consistent with the involvement of ethylene as a reactive intermediate in acetic acid synthesis. The non zero acetic acid selectivity, evident by extrapolation to zero ethane conversion (Fig. 3 & Table I) suggests, however that a substantial fraction of the acetic acid forms via direct oxidation of ethane.

B. Support Effects on Ethane Oxidation Catalyzed by Supported $Mo_{16}V_{6.37}Nb_{2.05}O_x$

Titania with different grades has been used as supports in the study of support effect on $Mo_{16}V_{6.37}Nb_{2.05}O_x$ activities. Standard catalyst $Mo_{16}V_{6.37}Nb_{2.05}O_x$ was supported over four different grades of Titania. In Table II, the BET surface areas of the different supports as well as the bulk and supported catalyst are given.

Cat.	T(°C)	0	Ed	Select	ivity (%)	Yield *10 ⁻² (%)		Space time yield(gm/kgh)		
Name		Oxygen Con. (%)	Ethane Con. (%)	Ethylene	Acetic Acid	Ethylene	Acetic Acid	Ethylene	Acetic Acid	
М	225	27.31	5.5	75.71	22.82	4.16	1.26	127.9	83.2	
М	250	61.99	12.35	67.78	67.78 29.74		8.37 3.67		241.8	
М	275	88.76	16.93	61.42	35.04	10.4	5.93	319.8	390.7	

TABLE I: SUMMARY OF EXPERIMENTAL RUNS OF BULK MO16V6.37Nb2.05Ox(M) CATALYST (REACTION PRESSURE: 200 PSI FOR, F/W: 50 ML/MIN.G. CAT.)



Fig. 3. Product selectivities as a function of ethane conversion for ethane oxidation on Mo₁₆V_{6.37}Nb_{2.05}O_x catalyst (T=225-275C, P=200 psi, F/W: 50 ml/min.g. Cat.)

TABLE II: BET SURFACE AREAS OF THE DIFFERENT SUPPOR	T
---	---

Cristal	Cristal BET surface area (m ² /g)
AF (4.60)	26.96
AF (7.70)	33.8
AF (12.5)	2.5
Degussa P25	54.0

The surface area of the standard catalyst is 30 m2/g The surface area of the standard catalyst supported on P25 is 38.58 m2/g.

Cristal titania have mainly anatase structure. Degussa P25 contains about 81% anatase and 19% rutile phase.

The prepared catalysts are:

1)	$Mo_{16}V$	/ _{6.37} Nb ₂	_{.05} O _x /	AF(4.6)	$S_{4.60}M$
----	------------	-----------------------------------	---------------------------------	---------	-------------

2)
$$Mo_{16}V_{6.37}Nb_{2.05}O_x / AF(7.7) = S_{7.70}M$$

3)
$$Mo_{16}V_{6.37}Nb_{2.05}O_x/AF(12.5)$$
 $S_{12.5}N_x$

4) $Mo_{16}V_{6.37}Nb_{2.05}O_x/P25$ $S_{25}M$

The catalytic activity of the prepared catalysts was evaluated at temperature range 200-275 C and feed flow rate 15ml/min. Total pressure was maintained at 200 psi. The results of catalysts testing are presented in Table III and Figs (4-6).



Fig. 4. Ethane conversion as a function on reaction temperature for ethane oxidation over different supported Mo₁₆V_{6.37}Nb_{2.05}O_x catalysts (P=200 psi, F/W: 15 ml/min.g. Cat.)



Fig. 5. Ethylene yield as a function on reaction temperature for catalytic ethane oxidation over different supported Mo₁₆V_{6.37}Nb_{2.05}O_x catalysts (P=200 psi, F/W: 15 ml/min.g.Cat.)



Fig. 6. Acetic acid yield as a function on reaction temperature for catalytic ethane oxidation over different supported Mo₁₆V_{6.37}Nb_{2.05}O_x catalysts (P=200 psi, F/W: 15 ml/min.g. Cat.)

From the results, it is clear that the catalytic activity practically S25M is sensitive to reaction temperature. In case of $S_{25}M$, ethane conversion was increased from 1.31% at 200C to 10.53% at 275^oC where oxygen conversion was increased from 7.74% to 81.39% at the same temperature range. On the other hand $S_{7.70}M$ catalyst showed lower activity than $S_{25}M$ and the highest ethane and oxygen conversions were 4.06% and 19.37% respectively.

 $S_{4.6}M$ and $S_{12.5}M$ catalysts have shown too lower or almost no activities if they are compared with $S_{25}M$ and $S_{7.7}M$.

Good performance of P25 and cristal 7.7 should be correlated to their relatively large surface area.

The activities of these catalysts significantly reflected on products selectivities where the same order of the catalytic activity was repeated when we talk about catalytic productivities. Again, $S_{25}M$ occupied the first one in products yields where ethylene and acetic acid yield reordered 5% and 4.23% respectively to become the heights values obtained.

As a result, these supported catalysts can be arranged based on their activities and products yield to become $S_{25}M$ is the best which has shown the highest activity and products yield. $S_{7.7}M$ came the second with lower activity than $S_{25}M$. $S_{4.6}M$ and $S_{12.5}M$ have shown almost no activity for $S_{12.5}M$ or too low activity for $S_{4.6}M$.

Cat.	T (C)	Oxygen	Ethane	Selecti	vity (%)	Yiel	d *10 ⁻²	Space time yield(gm/kgh)		
Name		Con. (%)	Con. (%)	Ethylene	Acetic Acid	Ethylene	Acetic Acid	Ethylene	Acetic Acid	
S4.6M	200	0.4	0.15	100	0	0.15	0	4.6	0	
S4.6M	225	1.09	0.33	97.24	0	0.32	0	9.8	0	
S4.6M	250	4.85	0.91	96.68	0	0.88	0	27.1	0	
S7.7M	200	0.86	0.87	29.01	70.26	0.25	0.61	7.7	40.2	
S7.7M	225	2.36	1.17	45.44	53.25	0.53	0.62	16.3	40.9	
S7.7M	250	8.55	2.11	78.03	19.21	1.65	0.41	50.7	27	
S7.7M	275	19.37	4.06	71.75	24.2	2.91	0.98	89.5	64.6	
S12.5M	200	1.09	0.02	60.75	0	0.01	0	0.3	0	
S12.5M	250	1.9	0.11	83.05	0	0.09	0	2.7	0	
S12.5M	275	1.95	0.13	71.6	0	0.09	0	2.7	0	
S25M	200	7.74	1.31	76.7	19.14	1	0.25	30.7	16.5	
S25M	220	20.16	3.44	66.53	28.13	2.29	0.97	70.4	63.9	
S25M	250	59.01	7.99	54.23	34.71	4.33	2.77	133.1	182.5	
S25M	275	81.39	10.53	48	40	5	4.23			

TABLE III: SUMMARY OF EXPERIMENTAL RUNS OF SUPPORTED M016V6.37Nb205Ox(MI) CATALYSTS (Reaction pressure: 200 psi for, F/W: 15 mL/MIN.G. CAT.)

This comparison leads us clearly to choose TiO₂ P25 as a support of $Mo_{16}V_{6.37}Nb_{2.05}O_x$ catalyst for partial oxidation of ethane in this study. This choice is compatible with the findings of the previous works. Li & Iglesia [9] concluded that TiO₂ P25 favor the formation of active structures without forming unselective linkages between active oxides and support surfaces or other unselective or inactive structures.



Fig. 7. Ethylene selectivity as a function of ethane conversion for Ethane oxidation on Mo₁₆V_{6.37}Nb_{2.05}O_x and Mo₁₆V_{6.37}Nb_{2.05}O_x /TiO₂ catalysts (T=200-275C: P=200 psi, F/W: 15 ml/min.g.cat)



Fig. 8. Acetic acid selectivity as a function of ethane conversion for Ethane oxidation on $Mo_{16}V_{6.37}Nb_{2.05}O_x$ and $Mo_{16}V_{6.37}Nb_{2.05}O_x$ /TiO2 catalysts (T=200-2750C:P=200 psi, F/W: 15 ml/min.g. Cat.)

Fig. 7 and Fig. 8 show ethane oxidation on supported $Mo_{16}V_{6.37}Nb_{2.05}O_x$ / TiO $Mo_{16}V_{6.37}Nb_{2.05}O_x$ powders (23-35%).Ethylene selectivities concurrently decreased to (66-48%) as a result of its subsequent conversion to acetic acid and CO_x . Thus, the structures formed during preparation

in the presence of TiO_2 appear to have a higher surface area (38.58 m²g⁻¹) exposed to ethane reactants. These conclusions corresponds largely with the findings of Li & Iglesia [9] who found 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.

C. Ethane Oxidations in the Presence Nano-Palladium as Co-Catalysts

Ethane oxidation on Mo₁₆V_{6.37}Nb_{2.05}O_x and $Mo_{16}V_{6.37}Nb_{2.05}O_x$ /TiO₂ gave in the best condition around 40% acetic acid selectivity and more than 48% ethylene selectivity. Thus, it appears that higher acetic acid selectivities require the incorporation of catalytic functions for ethylene oxidation to acetic acid. The source of palladium is 10% palladium on activated charcoal in an oxidized form. The present study focus on the discussion of ethane oxidation when palladium in nano forms are involved. In this section we will look for the optimum content of both Pd that can be added to get the highest selectivity of acetic acid.

1) 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 as list below:

1) $Mo_{16}V_{6.37}Nb_{2.05}Pd_{1.844}O_x/AF 4.60$ $S_{4.60}M PC21$ 2) $Mo_{16}V_{6.37}Nb_{2.05}Pd_{1.844}O_x/AF 7.70$ $S_{7.70}M PC21$ 3) $Mo_{16}V_{6.37}Nb_{2.05}Pd_{1.844}O_x/AF 12.50$ $S_{12.5}M PC21$ 4) $Mo_{16}V_{6.37}Nb_{2.05}Pd_{1.844}O_x/P25$ $S_{25}MPC21$

Palladium loading for these catalysts was 2.1%. The reaction conditions were mentioned as before where the temperature range was 200-275^oC and the feed flow rate and total pressure were 15ml/min and 200 psi respectively. The reactions results are Table IV and represented in Figs. 9-11.

Cat.	T (C)	Oxygen	Ethane	Select	ivity (%)	Yie	ld *10 ⁻²	Space time yield(gm/kgh)	
Name		Con. (%)	Con. (%)	Ethylene	Acetic Acid	Ethylene	Acetic Acid	Ethylene	Acetic Acid
S4.6MPC21	200	0.39	0.17	92.54	0	0.16	0	4.9	0
S4.6MPC21	225	3.57	0.57	74.46	17.24	0.42	0.1	12.9	6.6
S4.6MPC21	250	5.84	1.3	56.01	33.5	0.73	0.44	22.4	29
S7.7MPC21	200	2.45	0.12	73.71	0	0.09	0	2.8	0
S7.7MPC21	225	5.13	0.4	45.39	36.15	0.18	0.15	5.5	9.9
S7.7MPC21	250	13.53	1.28	25.19	55.9	0.32	0.72	9.8	47.4
S7.7MPC21	275	45.66	3.31	9.86	57.3	0.33	1.9	10.1	125.2
S12.5MPC21	200	9.21	0.52	0	52.76	0	0.27	0	17.8
SM12.5PC21	225	69.47	3.37	7.47	29.69	0.25	1	7.7	65.9
SM12.5PC21	240	99.06	5.37	12.21	23.75	0.66	1.28	20.3	84.3
S25MPC21	200	15.56	1.37	0	80.89	0	1.11	0	73.2
S25MPC21	220	46.8	3.72	0	73.54	0	2.74	0	180.5
S25MPC21	250	99.23	9.06	0	75.3	0	6.82	0	449.4

TABLE IV: SUMMARY OF EXPERIMENTAL RUNS OF SUPPORTED M016V6.37Nb2.05Pd0.196Ox (SIMPC21) CATALYSTS (REACTION PRESSURE: 200 PSI FOR, F/W: 15 ML/MIN.G. CAT.)

Obviously, catalytic activity of $S_{12.5}M$ PC21 has dramatically changed by adding palladium where ethane conversion has risen from almost nothing at 240^oC to 5.37% with full oxygen conversion. On the other hand, $S_{4.60}M$ PC21 has shown no change in the activity compared with the same catalyst without palladium where its activity was too low.

Such addition of palladium, also affected on the catalyst supported over AF (7.7) support. $S_{7.70}M$ PC21 has shown slightly dropping in ethane conversion where oxygen conversion was doubled at the same range of temperature. For instance, at $275^{0}C$ ethane conversion decreased from 4.06% for the catalyst without palladium to 3.31% for the same catalyst but in presence palladium where oxygen conversion was increased from 19.37% to 45.66%.

Supported MoVNb over P25 was also affected by presences of palladium and this leads to a significant increase in oxygen conversion. For example, at 275C while the change in ethane conversion was within 1%, oxygen conversion changed from 59% to almost full conversion.

However, we can say tentatively that the effect of palladium on catalytic activity clearly reflected on oxygen conversion where all catalysts have shown increasing in oxygen conversion.



Fig. 9. 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. Cat.)

It is also seen that for all catalysts increase oxygen conversion was accompanied by decreasing of ethylene selectivity and increasing selectivities of both acetic acid and carbon oxides. So we can link these variables where some oxygen was consumed in ethylene oxidation to produce acetic acid and/or Cox. This explains the high change in oxygen conversion while a slight change of ethane conversion take place.

The presence of the Pd-based co-catalyst did not influence ethane oxidation rate but markedly increased acetic acid synthesis rate by merely converting ethylene intermediates to acetic acid. Acetic acid selectivities increased from ~ 40% to ~75% while ethylene selectivities decreased from ~ 66% to nearly depleted from the reactor effluent.

If these catalysts are compared with each other, $S_{25}M$ PC21 showed good activity and it recorded the best selectivity and yield for acetic acid. For instance at $250^{\circ}C$ it gave 75.3% and

 6.83×10^{-2} acetic acid selectivity and yield respectively where the nearest values were recorded is 57.3 and $1.9*10^{-2}$ for S_{7.70}M PC21 at 275C.



Fig. 10. Ethylene Yield as a function on reaction temperature for ethane oxidation over different supported Mo₁₆V_{6.37}Nb_{2.05} Pd_{1.844} O_x catalysts (P=200 psi, F/W: 15 ml/min.g. Cat.)

In spite of the high activity of $S_{12.5}M$ PC21, it tended to produce undesirable products at expense of ethylene and acetic acid. The highest selectivity and then yield of carbon oxides were got for this catalyst. For example, at 240C where oxygen conversion was 99% Cox selectivity was 64% and their yield was 3.44×10^-2.Cox selectivities 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 and COx.

Therefore, these catalysts can be arranged based on their activities and selectivities of desirable products to become $S_{25}M$ PC21 is the best one and the second is $S_{7.7}M$ PC21 and then $S_{12.5}M$ PC21 and finally $S_{4.6}M$ PC21.



Fig.11. Acetic Acid Yield as a function on reaction temperature for ethane oxidation over different supported Mo₁₆V_{6.37}Nb_{2.05} Pd_{1.844} O_x catalysts (P=200 psi, F/W: 15 ml/min.g. Cat.)

2) Optimum loading of nano-PdOX

After TiO₂ P25 was selected as the best support for $Mo_{16}V_{6.37}Nb_{2.05}Ox$ catalyst in partial oxidation of ethane and how activity and acetic acid selectivity was enhanced in presence of palladium, it is important to discuss the effect of palladium loading to find out the optimum loading of nano-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 loading shown in Table IV. Ethane oxidation over these catalysts was carried out at three reaction temperature 220C, 230C, and 240C and total pressure 200 psi with 15ml/min feed flow rate. The results are shown in Table V-VII and Figs. 12-16.

It is seen that when nano-PdO_X loading was above 0.05% all trends are almost the same with difference in catalytic activities. So we will focus on catalysts contain nano-PdO_X loading below 0.05% and at 240C (only one reaction temperatures will be discussed due to different temperatures have almost shown the same trends).

Depending on the results, it is seen that the activity of catalysts were increased as nano-palladium oxides loading increase and it is clear in the range below 0.0125%. Ethane and oxygen conversions were recorded the highest value at 0.0125% loading where their values were 8.49% and 84.47% respectively. The high activity of $Mo_{16}V_{6.37}Nb_{2.05}Pd_{0.011}Ox/TiO2$ (S₂₅MPC0.125) reflected on acetic acid selectivity where it was shown the heights selectivity and yield among the different loading. S₂₅M PC0.125% reordered 78.4% and 6.66×10^{-2} acetic acid selectivity and yield respectively.

In contrast, ethylene recorded the top selectivity and yield at palladium loading 0.000625% which were 63.5% and $4.91*10^{-2}$ % respectively. S₂₅M PC0.00625% also has shown the lowest selectivity and yield of carbon oxides which were 6.34% and 0.49*10⁻²%. However we can conclude that 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).



Fig. 12. Effect of nano-PdOx loading on Ethane conversion for $Mo_{16}V_{6.37}Nb_{2.05}PdIO_x/TiO_2$ (P25) catalyst at various reaction temperatures, 200 psi and 15 ml/min



Fig. 13. Effect of nano-PdOx loading on Acetic Acid Selectivity for $Mo_{16}V_{6.37}Nb_{2.05}PdIO_x/TiO_2$ (P25) catalyst at various reaction temperatures, 200 psi and 15 ml/min



Fig.14. Effect of nano-PdOx loading on Ethane Conversion for Mo₁₆V_{6.37}Nb_{2.05}PdIO_x/TiO₂ (P25) catalyst at 2200C and 240C reaction temperatures, 200 psi and 15 ml/min



Fig. 15. Effect of nano-PdOx loading on Acetic Acid Selectivity for Mo₁₆V_{6.37}Nb_{2.05}PdIO_x/TiO₂ (P25) catalyst at 2200C and 240C reaction temperatures, 200 psi and 15 ml/min.

International Journal of Chemical Engineering and Applications, Vol. 5, No. 1, February 2014

Г	ABLE. V: SUMMARY	OF EXPERIME	ENTAL RUNS (OF MO16V6.37N	Jb2.05PdIOx/TiO2 (P25) (S25M	IPCI) CATALYSTS WITH DIFFE	RENT LOADING OF PD (REACTION	N
			TEMPERATUR	E 220C; REA	CTION PRESSURE: 200 PSI FOR	, F/W: 15 ML/MIN.G. CAT.)		
	C .							

Cat. Name	Pd	Oxygen	Ethane	Selecti	Selectivity (%) Yie		d *10 ⁻²	Space time yield(gm/kgh)	
	(%) Con. (%		Con. (%)	Ethylene	Acetic Acid	Ethylene	Acetic Acid	Ethylene	Acetic Acid
S25MPC21	2.1	46.8	3.72	0	73.54	0	2.74	0	180.5
S25MPC11	1.1	51.36	3.96	0	70.73	0	2.8	0	184.5
S25MPC1	0.1	44.61	3.67	0.06	76.74	0	2.82	0	185.8
S25MP0.5	0.05	38.66	3.58	1.82	79.69	0.07	2.85	2.2	187.8
S25MP0.343	0.034	62.1	4.22	1.63	79.45	0.07	3.35	2.2	220.7
S25MP0.25	0.025	41	3.72	3.44	77.29	0.13	2.88	4	189.8
S25MPC0.125	0.0125	34.24	3.27	10.28	75.71	0.34	2.48	10.5	163.4
S25MPC0.0625	0.00625	30.49	3.68	42.54	47.78	1.57	1.76	48.3	116
S25MPC0.00625	0.000625	26.03	4.19	76.33	19.12	3.2	0.8	98.4	52.7
S25M	0	20.16	3.44	66.53	28.13	2.29	0.97	70.4	63.9

 $TABLE.VI. SUMMARY OF EXPERIMENTAL RUNS OF MO_{16}V_{6.37}Nb_{2.05}PdIO_x/TiO_2 (P25) (S25MPCI) CATALYSTS WITH DIFFERENT LOADING OF PALLADIUM AND ADDING OF PALLADIUM AND ADDING OF PALLADIUM AND ADDING ADD$ (REACTION TEMPERATURE 230C; REACTION PRESSURE: 200 PSI FOR, F/W: 15 ML/MIN.G. CAT.)

Cat. Name	Pd loading	Oxygen	Ethane Con. (%)	Select	ivity (%)	Yiel	d *10 ⁻²	Space time yield(gm/kgh)	
	(70)	Con. (%)		Ethylene	Acetic Acid	Ethylene	Acetic Acid	Ethylene	Acetic Acid
S25MPC21	2.1	55.86	4.6	0	74.83	0	3.442	0	226.7
S25MPC11	1.1	78.15	5.97	0	69.16	0	4.129	0	271.5
S25MPC1	0.1	59.59	5.3	0.08	78.07	0.004	4.138	0.1	272.1
S25M0.5	0.05	55.69	5.26	1.29	79.91	0.068	4.203	2.1	276.7
S25M0.343	0.0343	85.24	5.64	1.07	79.48	0.06	4.483	1.8	295.2
S25M0.25	0.025	53.79	4.62	2.82	76.05	0.13	3.514	4	231.3
S25MPC0.125	0.0125	61.43	6.06	5.3	76.95	0.324	4.663	10	307
S25MPC0.0625	0.00625	49.58	5.95	27.82	59.22	1.655	3.524	50.9	231.9

 $TABLE. \ VII. \ Summary \ of \ Experimental \ Runs \ of \ Supported \ Mo_{16}V_{6.37}Nb_{2.05}PdIO_x/TiO_2(P25) \ (S25MPCI) \ Catalysts \ with \ different \ Loading \ of \ Mo_{16}V_{6.37}Nb_{2.05}PdIO_x/TiO_2(P25) \ (S25MPCI) \ Catalysts \ With \ different \ Loading \ of \ Mo_{16}V_{6.37}Nb_{2.05}PdIO_x/TiO_2(P25) \ (S25MPCI) \ Catalysts \ With \ different \ Loading \ of \ Mo_{16}V_{6.37}Nb_{2.05}PdIO_x/TiO_2(P25) \ (S25MPCI) \ Catalysts \ With \ different \ Loading \ of \ Mo_{16}V_{6.37}Nb_{2.05}PdIO_x/TiO_2(P25) \ (S25MPCI) \ Catalysts \ With \ different \ Mo_{16}V_{6.37}Nb_{2.05}PdIO_x/TiO_2(P25) \ (S25MPCI) \ Catalysts \ With \ different \ Mo_{16}V_{6.37}Nb_{2.05}PdIO_x/TiO_2(P25) \ (S25MPCI) \ Catalysts \ With \ different \ Mo_{16}V_{6.37}Nb_{2.05}PdIO_x/TiO_2(P25) \ (S25MPCI) \ Catalysts \ With \ different \ Mo_{16}V_{6.37}Nb_{2.05}PdIO_x/TiO_2(P25) \ (S25MPCI) \ Catalysts \ With \ different \ Mo_{16}V_{6.37}Nb_{2.05}PdIO_x/TiO_2(P25) \ (S25MPCI) \ Catalysts \ With \ different \ Mo_{16}V_{6.37}Nb_{2.05}PdIO_x/TiO_2(P25) \ (S25MPCI) \ Catalysts \ With \ Mo_{16}V_{6.37}Nb_{2.05}PdIO_x/TiO_2(P25) \ (S25MPCI) \ Catalysts \ With \ Mo_{16}V_{6.37}Nb_{2.05}PdIO_x/TiO_2(P25) \ (S25MPCI) \ Catalysts \ With \ Mo_{16}V_{6.37}Nb_{2.05}PdIO_x/TiO_2(P25) \ (S25MPCI) \ (S25MPC$ PALLADIUM (R

REACTION TEMPERATURE 240C;	REACTION PRESSURE: 200 PSI FOR, F/W: 15 ML/MIN.G. CAT.)

Cat.	Pd	Oxygen	Ethane	Selectivity (%)		Yield *10 ⁻²		Space time yield(gm/kgh)	
Name	(%)	Con. (%)	Con. (%)	Ethylene	Acetic Acid	Ethylene	Acetic Acid	Ethylene	Acetic Acid
S25MPC21	2.1	94.09	7.63	0	72.28	0	5.515	0	363.4
S25MPC11	1.1	99.1	7.56	0	68.42	0	5.173	0	340.8
S25MPC1	0.1	80.78	7.01	0.02	76.8	0.001	5.384	0.3	354.8
S25M0.5	0.05	84.08	7.87	0.88	79.1	0.069	6.225	2.1	410.2
S25M0.343	0.0343	84.2	7.9	1.2	78.8	0.095	6.225	2.9	410.2
S25M0.25	0.025	83.92	7.58	1.7	76.76	0.129	5.818	3.9	383.3
S25MPC0.125	0.0125	84.47	8.49	3.6	78.4	0.306	6.656	9.4	438.6
S25MPC0.0625	0.00625	68.2	7.69	22.56	62.74	1.735	4.825	53.4	317.9
S25MPC0.00625	0.000625	49.69	7.73	63.51	30.15	4.909	2.331	151	153.6
S25M	0	41.69	5.9	62.47	27.51	3.686	1.623	113.3	106.9



Fig. 16. Effect of nano-PdOx loading on Ethylene Selectivity for Mo₁₆V_{6.37}Nb_{2.05}PdIO_x/TiO₂ (P25) catalyst at 220C and 240C reaction temperatures, 200 psi and 15 ml/min.

IV. 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). Titania-containing catalysts merely reflect a higher dispersion of the active Mo-V-Nb oxides species without detectable change in their intrinsic reactivity. However, negative effects were observed when supporting on the other titania grades cristal AF4.60, AF7.70, and AF12.5 because of the low surface area.

Ethane oxidation in the presence of nano-palladium oxides shifted the reaction toward acetic acid formation. The presence of nano-PdO_x based co-catalyst did not influence ethane oxidation rates, but markedly increased acetic acid synthesis rates by merely converting ethylene intermediates to acetic acid.

Acetic acid recorded a high value of selectivity where ethylene was nearly depleted from the reactor effluent. The optimum loading of nano-PdO_x was recorded at 0.0125%.

ACKNOWLEDGMENT

The authors acknowledge the support provided by King AbdulAziz City for Science and Tecgnology for the support of this research under grant number AR-29-256.

REFERENCES

- E. M. Thorsteinson, Wilson, *Journal of Catalysis*, vol. 52, pp. 116, 1978.
- [2] F. G. Young, E. M. Thorsteinson, U. S. Patent 4 250 346, 1981.
- [3] K. Karim, E. Mamedov, M. H. Al-Hazmi, A. H. Fakeeha, M. A. Soliman, Y. S. Al-Zeghayer, A. S. Al-Fatish, A. A. Al-Arify, U.S. Patent 6 030 920, 2000.
- [4] K. Karim, E. Mamedov, M. H. Al-Hazmi, A. H. Fakeeha, M. A. Soliman, Y. S. Al-Zeghayer, A. S. Al-Fatish, A. A. Al-Arify, U.S. Patent 6 310 241, 2001.
- [5] K. Karim, E. Mamedov, M. H. Al-Hazmi, A. H. Fakeeha, M. A. Soliman, Y. S. Al-Zeghayer, A. S. Al-Fatish, A. A. Al-Arify, U. S. Patent 6 383 977, 2002.
- [6] H. Borchert, U. Dingerdissen, Ger.offen.de patent 19 630 832, 1998.
- [7] D. Linke, D. Wolf, U. Dingerdissen, S. Zeyb, M. Baerns, "Catalytic partial oxidation of ethane to acetic acid over Mo1 V0.25 Nb0.12 Pd0.0005 Ox Part I: Catalyst performance and reaction mechanism," *Journal of Catalysis*, vol. 205, pp. 16-31, 2002.
- [8] D. Linke, D. Wolf, U. Dingerdissen, S. Zeyb, M. Baerns, "Catalytic Partial oxidation of ethane to acetic acid over Mo1 V0.25 Nb0.12 Pd0.0005 Ox Part II: Kinetic modeling," *Journal of Catalysis* vol. 205, pp. 32, 2002.
- [9] X. Li, E.Iglesia, Applied Catalysis A: General. vol.334, pp. 339, 2008.
- [10] X. Li, E. Iglesia, J. Phys. Chem. B, vol. 112, pp 15001, 2008.



Yousef S. Al-Zeghayer is an associate professor at the Department of Chemical Engineering and Director of Industrial Catalysts Chair, King Saud University, Riyadh, Sudi Arabia.