CHAPTER 7

DISCUSSION, CONCLUSIONS AND RECOMMENDATIONS

OXIDATIVE DEHYDROGENATION OF ETHANE OVER REDUCED HETEROPOLYANION CATALYSTS

7.1 Discussion

The performances of both $Nb_xPMo_{11}VPyr$ and $Nb_xPMo_{12}Pyr$ compare favorably to other ethane and ethylene oxidation catalysts in the open literature (Table 7.1). Production of ethylene is one order of magnitude greater than that of any other ethane oxidation catalyst at atmospheric pressure except for Mo-V-Te-Nb oxide. Other than $Nb_xPMo_{11}VPyr$ and $Nb_xPMo_{12}Pyr$, only VO_x/TiO_2 is able to produce acetic acid from ethane at atmospheric pressure. Both Mo-V-Nb and Mo-V-Nb-Pd oxides are able to catalyze the production of acetic acid from ethane at elevated pressure, but space time yield remains one order of magnitude below that of $Nb_xPMo_{11}VPyr$ and $Nb_xPMo_{12}Pyr$.

Catalyst	Feed	T °C	P atm	Flow mL/min[a]	Conv. %C_2	Sel %		STY[b]		Ref
						C_2H_4	AcA	C_2H_4	AcA	
$Nb_{0.6}PMo_{12}Pyr$	C_2H_6	380	1	16:8:16:20	16	29	9	5.3e-2	1.5e-2	this work
	C_2H_4	340	1		26	-	29	-	1.8e-1	this work
$Nb_{0.68}PMo_{12}Pyr$	C_2H_6	380	1	16:8:16:20	7.4	36	12	2.2e-2	7e-3	this work
$Mo_{0.73}V_{0.18}Nb_{0.09}Ox$	C_2H_6	350	1	13.3: 8.8: 125.2: 0	58	65	-	7.9E-03	-	1
			20	6: 3.6: 14.4: 0	32	44	2.5	1.9E-02	1.1E-03	2
	C_2H_4	260	20	9:5:10:0	12	-	56	-	1.3E-02	2
$Mo_1V_{0.25}Nb_{0.12}Pd_{0.0005}O_x$	C_2H_6	246	14.8	11:2.2:12.4:1.8	4.7	19	62	3.8E-03	1.2E-02	3
	C_2H_4	247	5.2	2:24:40:40	99	-	93	-	1.0E-01	3
VO_x/TiO_2	C_2H_6	250	1	142:8.3:16.7:0	1	18	36	3.5E-03	6.9E-03	4
$Mo_1V_{0.39}Te_{0.16}Nb_{0.17}O_x$	C_2H_6	380	1	4.9:1.6:9.8	40	94	-	1.0e-1	-	5

[a] C_2:O_2:inert:steam quoted at standard temperature and pressure

[b] STY calculation based on flow rates taken at standard temperature and pressure

Table 7.1: Comparison of ethane and ethylene oxidation catalysts. STY = space time yield (mmol/min/g_{cat}).

Both $Nb_xPMo_{11}VPyr$ and $Nb_xPMo_{12}Pyr$ are able to effectively oxidize ethane to acetic acid and ethylene at atmospheric pressure. The catalysts are also extremely active for the production of acetic acid from ethylene. Both activity towards ethane and selectivity to ethylene and acetic acid are enhanced when vanadium is absent from the catalysts. This result is unprecedented for ethane oxidation over molybdenum oxide catalysts. Usually, vanadium is not only found to enhance selectivity to acetic acid, but is required for significant activity.[2,3,5-8] This is most likely because vanadium is the active site for ethane activation in a variety of mixed molybdenum oxide systems.[3-5,7,9] In the absence of vanadium, only ethylene can be produced by molybdenum-based oxide catalysts.[2,10-12] However, although vanadium has been identified as the active site for ethane oxidation in many molybdenum mixed oxide systems, its role as active site is not universally accepted for all systems. In the case of Mo-V-Nb mixed oxides, Mo^{5+} has been proposed as the activation and oxygen insertion center.[1,6,13] Furthermore, both V^{4+} and Mo^{5+} may be responsible for taking alkenes formed after initial activation on to their respective acids.[8,14] Thus, while unprecedented, a vanadium free molybdenum based mixed oxide catalyst highly active for the conversion of ethane to ethylene and acetic acid is not inconsistent with findings in the literature.

The presence of niobium is essential for efficient ethane activation to ethylene and acetic acid. Attempts at replacing the niobium with vanadium, iron, gallium, or antimony did not result in active catalysts. This result is consistent with results from Holles et al. whom found that the niobium outperformed other metal cations for butane and propane oxidation.[15] Additionally, the presence of niobium in molybdenum based pyridine exchanged heteropolyanion catalysts has previously been demonstrated to vastly improve the activity and productivity of butane oxidation to maleic acid and propane oxidation to acrylic acid.[15,16] The beneficial effect of niobium has also been demonstrated in a variety of other alkane oxidation systems.[1,3,9,13,14,17-19] The presence of niobium can improve the oxidation of light alkanes by modifying catalyst acidity,[18] improving site isolation,[13] affecting the distribution or redox centers,[18] improving the stability of the active sites,[6] and by electronic promotion of the active sites.[19] Although pyridine exchange of the heteropolyanion in the absence of niobium does allow for maleic and acrylic acids during butane and propane oxidation,[15] respectively, the extension to ethane oxidation and acetic acid is not observed here. No acetic acid is formed in the absence of niobium during ethane activation although small amounts of ethylene may be produced without niobium.[20]

While niobium is essential to ethane activity and the production of acetic acid, conversion and selectivity to acetic acid do not increase monotonically with Nb/P ratio. These data indicate that niobium itself is not the active center, which is consistent with Fourier transform-ion cyclotron resonance (FT-ICR) studies indicating that small niobium clusters are very unreactive to ethane.[21] However, when data from the Nb/P experiments are plotted as selectivity versus conversion, a linear relationship is obtained. This suggests that niobium modifies the active center in balance with another factor which is related to the amount of niobium present. The Nb/P ratio affects the temperature onset of phase transition to MoO_2. However, despite an initial decrease in onset temperature and increase in catalytic activity until Nb/P =0.2, attempts to correlate catalytic activity to the temperature of MoO_2 phase transition were unsuccessful. Since the amount of niobium also adjusts the amount of pyridine that may be protonated during synthesis, it is likely that a balance of acidity and niobium are important for an active catalyst. Indeed, in Mo-V based oxides synthesized in the presence of ammonia, the active site for propane oxidation is believed to a combination of molybdenum and vanadium working in conjunction with a nearby acid site left behind during ammonia desorption.[22] As expected, when pyridinium chloride was used in place of pyridine during catalyst synthesis to produce a more acidic catalyst precursor, the resulting catalytic activity was shifted to lower conversion on the selectivity versus conversion curve constructed as a function of Nb/P ratio. Thus, the data in the present system support the hypothesis of a molybdenum ethane activation site enhanced by niobium and the presence of acid sites. This conclusion is consistent with other studies on Mo-V-Nb-O_x systems.[1,6] The specific benefit on molybdenum provided by niobium remains unknown.

The same trends and conclusions can be drawn for $Nb_xPMo_{11}SbPyr$ and $Sb_xPMo_{11}NbPyr$. Activity and selectivity do not increase monotonically with X/P ratio. However, product selectivity is a relatively linear, although weak, function of conversion. This is true regardless of the initial position of niobium. Thus, even when the niobium content of the catalyst is fixed, adjusting X/P results in the same behavior as when X = Nb. This result lends further support to the claim that niobium itself is not the active site for ethane activation. Thus, although niobium is required for ethane activation to acetic acid, it must be balanced with the complementary effect of X/P. The similarity of the results from $Nb_xPMo_{11}SbPyr$ and $Sb_xPMo_{11}NbPyr$ at identical X/P further suggests that like niobium,[23] antimony is mobile during thermal treatment such that its initial position is not indicative of its final position following thermal treatment and during reaction.

Niobium is also required for the active oxidation of ethylene to acetic acid. Although some acetic acid can be formed from ethylene without the presence of niobium, addition of niobium greatly improves overall conversion and production of acetic acid. Furthermore, the activity of the catalysts tends to increase with increasing niobium loading. Selectivity to acetic acid also increases with niobium except for the very highest Nb/P ratios. Data collected during the oxidation of ethanol demonstrate that niobium increases the oxidizing ability of the catalysts. Thus, the decrease in selectivity to acetic acid during ethylene oxidation at high Nb/P ratio can be explained by more complete oxidation to carbon oxides as a result of increased niobium loading. Niobium, specifically Nb^{4+} as determined by EXAFS experiments[23], therefore, must be directly involved in the transformation of ethylene to acetic acid. This finding is also consistent with FT-ICR studies of small niobium clusters.[21] Niobium alone is not sufficient to take ethylene onto acetic acid, although it is very capable of taking ethylene to ethanol.[24] When tungsten was substituted for molybdenum, very little catalytic activity was observed. Thus, molybdenum and niobium must work synergistically to promote ethylene oxidation to acetic acid.

While water is required for the formation of acetic acid from ethane, it is also a product of ethylene production. During ethane oxidation over $Nb_{0.6}PMo_{12}Pyr$, increasing steam flow increased the selectivities of ethylene and acetic acid. However, activity passed through a maximum at 33% steam feed. A possible explanation of this effect is competitive adsorption of steam, ethane, and acetic acid on the surface of the catalyst.[3,4] Water of formation due to ethylene production was eliminated by feeding ethylene instead of ethane, thereby reducing the amount of water present on the surface of the catalyst during reaction. Both activity and selectivity to acetic acid increased with increasing steam feed during ethylene oxidation over the same catalyst as used for ethane oxidation steam studies; this indicates that competitive adsorption is most likely the cause of the decreased ethane activity at high steam flow. Additionally, while activity and selectivity to acetic acid increase with increasing steam flow, carbon oxide production is decreased. This is consistent with previous results showing that water may aid in the desorption of acetic acid from the surface of mixed oxide catalysts thus preventing further oxidation to carbon oxides.[4,25]

The activity of many mixed metal oxides for alkane activation benefits from the addition of promoting metals. Both palladium[3,26] and tellurium[5,27] have been shown to effectively enhance the oxidation of ethane to acetic acid in the Mo-V-Nb-O catalyst system. In heteropolyanion systems, iron,[10,11] gallium,[28-31] and antimony[12,32] have all shown beneficial effects on alkane oxidation. Polyatom substitution of iron for molybdenum did not result in significantly increased catalytic activity in oxidizing or reducing conditions when compared to $Nb_xPMo_{12}Pyr$. Therefore, the ability of iron to aid in reducing or oxidizing the catalyst under oxidizing or reducing environments[11,33,34] was not found to be important for the pyridine exchanged catalyst system. Polyatom substitution of molybdenum with gallium, thought to aid in C-H bond activation,[30,31,35] did result in slightly increased conversion when compared to $Nb_xPMo_{12}Pyr$, but also led to increased carbon oxides at the expense of acetic acid. The incorporation of antimony as a polyatom resulted in drastically decreased catalyst activity. However, antimony was able to stabilize the catalyst towards temperature when included as a polyatom, consistent with previous studies.[12] In general, promotion of $Nb_xPMo_{12}Pyr$ with additional metal cations does not significantly improve catalytic activity.

Although the benefit of partially reduced heteropolyanions is well known,[15,16,23,32,33] none of the reference systems make use of an organic exchange cation for the purpose of in—situ reduction of the catalyst prior to reaction like the $Nb_xPMo_{12}Pyr$ system. Hence, the number of possible redox pairs is limited unless synthesis or reaction conditions are adjusted to promote some reduction of the catalyst. When the catalyst is not, or only slightly, reduced, this effect explains why the ability of iron to aid in the redox cycle improves catalyst activity for cesium exchanged heteropolyanions. Copper ions in cesium salts of heteropolyanions have been found to play a similar role, though only in reducing environments.[10] Antimony has been shown to partially reduce the Keggin ion during synthesis, resulting in enhanced catalytic performance.[32] It follows that, insensitivity to promoters in the $Nb_xPMo_{12}Pyr$ system is likely due to the partial reduction of catalysts during thermal treatment prior to reaction resulting in sufficient redox pairs on the surface of the catalysts.

The reducing effect of pyridine may also partially explain why reduction potential of the synthesized Keggin catalyst has little to do with catalyst activity in the current system. Pyridine provides a very powerful in-situ reductant, reducing 58% of the molybdenum from Mo^{6+} to Mo^{5+} and 100% of the niobium from Nb^{5+} to Nb^{4+} during thermal treatment.[23] Thus, small adjustments to reduction potential made by position and identity of transition metals in the catalysts are dominated by the reducing ability of pyridine desorption during thermal treatment. This allows the identity of the metal atoms to dominate the reactive properties of the catalytic materials, as shown by results of ethylene oxidation.

Although the exact mechanism of reaction cannot be determined, the data suggest a reaction scheme, shown in Figure 7.1. Ethane can be oxidized directly to ethylene and acetic acid, although acetic acid is a minor product. Ethylene is either collected as product or further oxidized to acetic acid. Ethane, ethylene and acetic acid can be oxidized to carbon oxides. Reactivity studies with ethylene and ethanol show that both substrates are converted to acetic acid in high yield. The conversion of ethylene to acetic acid results in significant oxidation to carbon oxides, however, indicating that readsorption and oxygen insertion are rather difficult processes for ethylene. These effects can be mitigated by increasing steam flow. Under reducing environments, transformation of ethanol to acetic acid and ethylene is extremely efficient, even at 300°C. Although only two values of space time were tested for ethane oxidation, extrapolation of the results to zero conversion indicates that carbon oxides and ethylene are the major products. A very small amount of acetic acid is theoretically produced. However, more importantly, when space time is decreased ethylene production increases but acetic acid production is decreased by nearly 30%. This result strongly suggests that acetic acid is a secondary product rather than a primary product. These combined results indicate that although some acetic acid may be formed directly from ethane, the majority of acetic acid must be a secondary product from ethylene conversion.

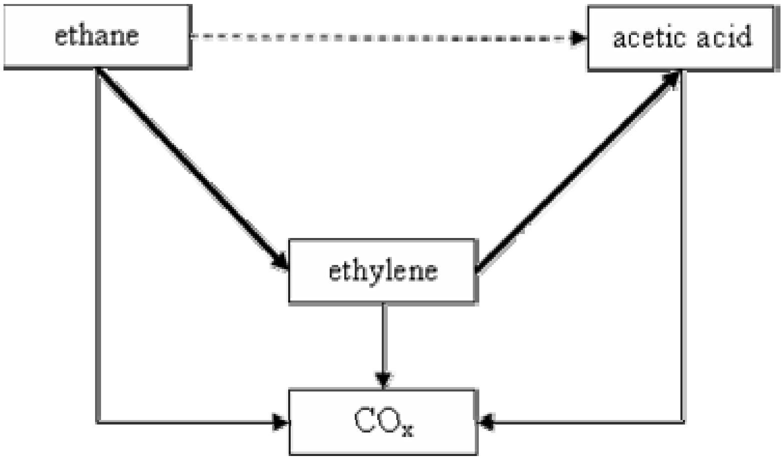

Figure 7.1: Reaction scheme for the production of ethylene and acetic acid over partially reduced niobium exchanged phosphomolybdic Keggin type heteropolyanions. The major pathway to acetic acid is emphasized by bold arrows.

If an ethoxy intermediate is involved in the conversion of ethane to both ethylene and acetic acid, it must preferentially produce ethylene rather than acetic acid. This assertion is supported by the results of ethanol oxidation which show a fivefold excess of ethylene compared to acetic acid. Initially produced ethylene could be readsorbed and subsequently converted to acetic acid with significant carbon oxide formation. Bypassing the ethoxy intermediate is also possible through the formation of an ethyl group on the catalyst surface followed by desorption and reaction with gaseous oxygen to give ethylene.

This mechanism has been suggested by kinetic modeling of the VPO catalyst system.[36] However, EXAFS measurements of the heteropolyanion based catalyst system indicate that the catalyst surface is partially oxidized during butane and propane oxidation in reducing environments.[23] Thus, it seems more likely that ethane oxidation in the heteropolyanion based system proceeds via the Mars and van Krevelen mechanism.[37] Therefore, ethylene formation should originate from an initial ethoxy intermediate formed by surface oxygen insertion rather than an initial surface ethyl group. The results of temperature studies during ethane oxidation are consistent with the formation of an ethoxy intermediate which is then transformed to ethylene by β-H abstraction or acetic acid by subsequent α-H extractions.

7.2 Conclusions

Niobium and pyridine exchanged salts of phosphomolybdic and phosphovanadomolybdic acids, which, when partially reduced at 420°C, form solids that catalyze the oxidative dehydrogenation of ethane to ethylene and acetic acid in high yield at atmospheric pressure and moderate temperature under reducing conditions. The same catalysts also effectively convert ethylene to acetic acid in high yield under similar conditions. The production of acetic acid from ethane or ethylene over the catalytic materials exceeds that reported in the literature for Mo-V-Nb-O_x systems at atmospheric or elevated pressure. Unlike other mixed metal oxide systems reported in the literature, catalysts that do not contain vanadium are able to catalyze the formation of acetic acid from ethane and are more active and selective than catalysts including vanadium. The presence of niobium is required for significant activity and for the production of acetic acid from ethane. Other metal cations such as antimony, iron, and gallium in polyatom or exchange position are not able to replicate the function of niobium in ethane or ethylene oxidation. The initial position of the niobium is relatively unimportant but the balance of protonated pyridine and niobium present in the catalyst precursor affects catalytic activity and selectivity for the oxidation of ethane or ethylene.

Partial reduction of the catalyst precursor during thermal treatment dominates the redox properties of the activated catalyst. Small variations in the reduction potential of the catalyst precursors do not correlate with catalytic activity of the activated materials. The catalysts are most active and selective under reducing reaction conditions. The addition of steam to the reactive feed reduces conversion, but decreases the production of carbon oxides. The conversion of ethane is decreased by the addition of steam due to the competitive adsorption of steam and acetic acid on the surface of the catalyst during catalytic reaction. The addition of steam to the feed increases the yield to acetic acid by aiding in desorption of acetic acid from the catalyst surface, thereby preventing further oxidation to carbon oxides.

Although the exact nature of the active site remains unknown, results suggest that ethane activation occurs over a molybdenum center in close proximity to niobium and an acid site. Niobium is directly involved in the conversion of ethylene to acetic acid. The conversion of ethane to ethylene and acetic acid occurs through an initial ethoxy intermediate which is preferentially transformed to ethylene by β-H elimination. Although some acetic acid can be produced directly from the ethoxy intermediate by subsequent α-H eliminations, the majority of observed acetic acid is a secondary product formed from the readsorption and conversion of ethylene. The process of converting ethylene to acetic acid results in significant carbon oxide formation.

7.3 Recommendations

In order to better quantify the effect of Nb/P on the acidity of the thermally activated catalysts, temperature programmed desorption over the $Nb_xPMo_{12}Pyr$ series should be investigated. A correlation between the number and type of acid sites should be made with niobium loading and catalytic activity. The reactivity curve as a function of acid sites correlated to niobium loading should be complementary to the curve as a function of Nb/P ratio.

Detailed EXAFS and XANES measurements have been performed for $Nb_{0.4}PMo_{11}VPyr$.[23] However, no such studies have been performed for $Nb_xPMo_{12}Pyr$. Given the relatively large effect vanadium has on the reactivity of the $Nb_xPMo_{12}Pyr$ catalyst system and the fact that the ratio of X/P is important for catalyst reactivity, it would be interesting to compare the results from $Nb_{0.4}PMo_{11}VPyr$ to EXAFS and XANES of $Nb_xPMo_{12}Pyr$ as a function of Nb/P ratio during activation and reaction conditions. Comparing the structure of the catalyst during activation and reaction in the presence and absence of vanadium might elucidate how vanadium alters the active site of the catalyst and consequently yield more detail on the exact nature of the active site. Additionally, the effect of X/P on the structural parameters of the active catalyst may permit further identification of the active site of the catalytic material. Structural parameters such as extent of reduction of the metals, coordination number, and inter—atomic distance might be correlated to activity. This study should be coupled with detailed in—situ X—ray diffractometry measurements of the catalysts during thermal treatment. In-situ Raman measurements under reaction conditions at various temperatures and feed compositions (i.e. oxidizing versus reducing conditions) might further help in understanding the nature of the active site of the catalyst.

Coupled TGA/DSC – mass spectroscopy could provide understanding into the mechanism by which pyridine and pyridinium are desorbed from the catalyst. Since XANES measurements of $Nb_{0.4}PMo_{11}VPyr$ show that desorption of pyridine species results in reduction of the catalyst,[23] it would be interesting to determine how the pyridine and pyridinium are desorbed. This information may clarify the nature of the reductant of the catalyst precursor during thermal treatment and provide some information on the active site. For instance, if oxygen is removed from the catalyst during desorption, defect sites in the catalyst may be created and be responsible for catalytic activity. Careful calibration and comparison with TPD data may allow quantification of acid sites left behind specifically from desorption of the pyridine species.

More extensive testing of the effect of space velocity should be performed for ethane oxidation to better elucidate the reaction scheme to acetic acid. Although it is suggested that both ethylene and acetic acid may be formed directly from ethane, this preliminary result is based on only two space velocities. A more accurate assertion may be made by extending the study to higher space velocities and lower conversion.

The effect of niobium loading greater than Nb/P = 1.0 has not been examined. This could be achieved in the range of Nb/P = 1.0 – 2.0 by varying the amount of exchange niobium in the catalyst precursor $Nb_xPMo_{11}NbPyr$ to achieve the desired Nb/acid site balance. These studies would be easily performed since the synthesis of $PMo_{11}NbPyr$ is known. To achieve Nb/P > 2, the synthesis of $Nb_xPMo_{12-x}Nb_x$ would be required. Although $PMo_{12-x}V_x$ is available commercially, the incorporation of two or more niobium atoms in polyatom position is unknown for molybdophosphoric acids. Niobium in excess of Nb/P = 1.0 may result in additional oxidation to carbon oxides due to the oxidizing ability of niobium discovered during ethanol oxidation. However, increased carbon oxide production could be offset by increased carbon conversion.

7.4 References

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