SUPPORTING INFORMATION

Reactivity of Vanadyl pyrophosphate catalyst in ethanol ammoxidation and β-picoline oxidation: advantages and limitations of bi-functionality features

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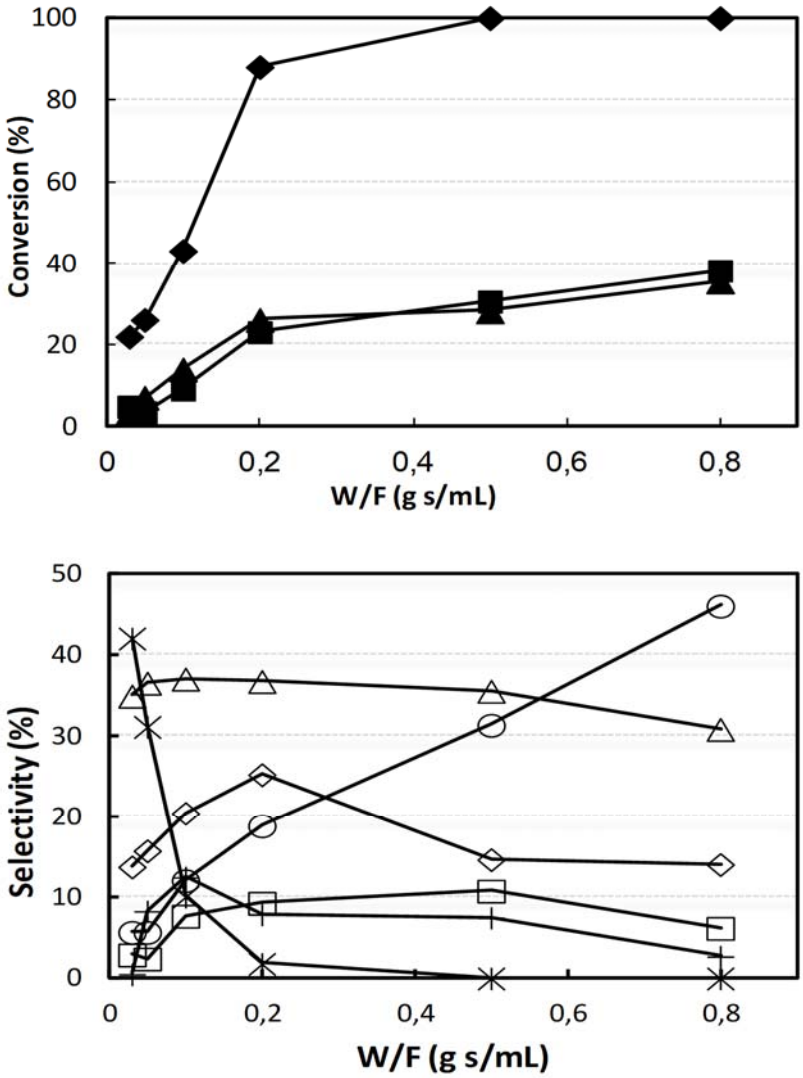


Figure S1. Effect of W/F ratio on reactants conversion (top figure) and on selectivity to products (bottom figure). Reaction conditions: T 440°C, feed composition (molar %): ethanol (azeotrope)/ammonia/oxygen/inert 5/13/13/69. Symbols: ethanol conversion (◆), ammonia conversion (▲) and oxygen conversion (■). Selectivity to: acetonitrile (◇), acetaldehyde (∗), ethylene (△), $CO+CO_2$ (○), HCN (□), and heavy compounds (+). Catalyst VPP.

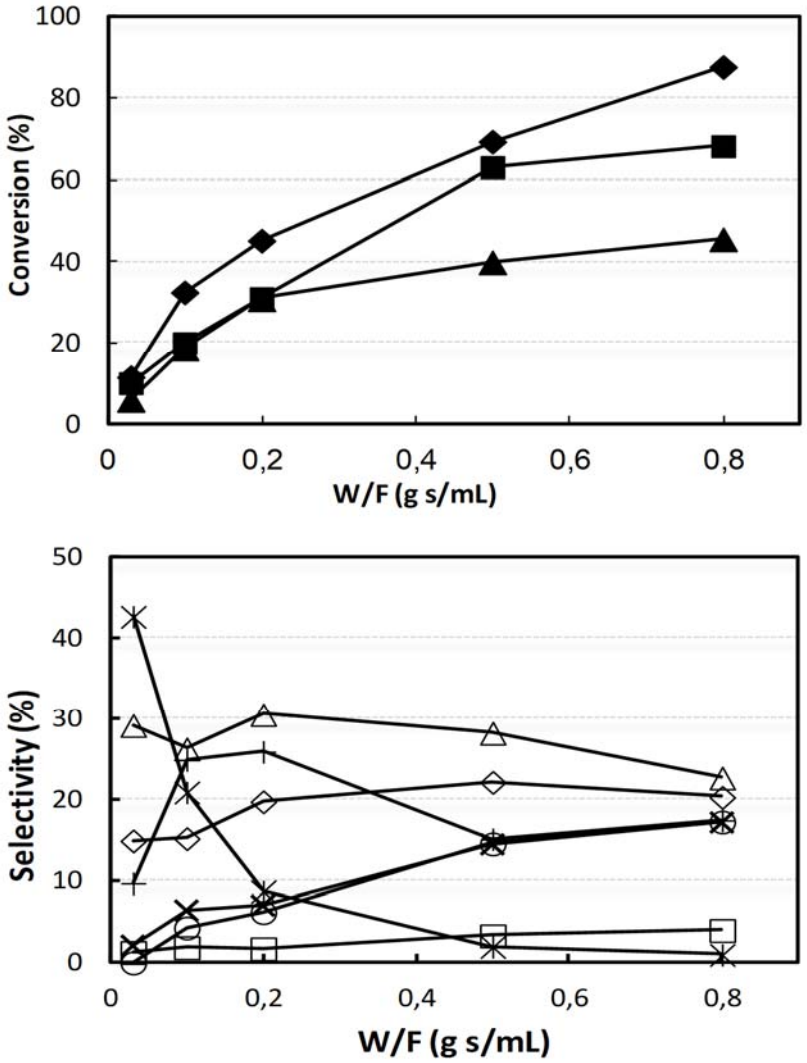


Figure S2. Effect of W/F ratio on reactants conversion (top figure) and on selectivity to products (bottom figure). Reaction conditions: T 440°C, feed composition (molar %): ethanol (azeotrope)/ammonia/oxygen/inert 7.5/13/13/66.5. Symbols: ethanol conversion (◆), ammonia conversion (▲) and oxygen conversion (■). Selectivity to: acetonitrile (◇), acetaldehyde (∗), ethylene (△), CO (○), CO_2 (×), HCN (□), and heavy compounds (+). Catalyst VPP.

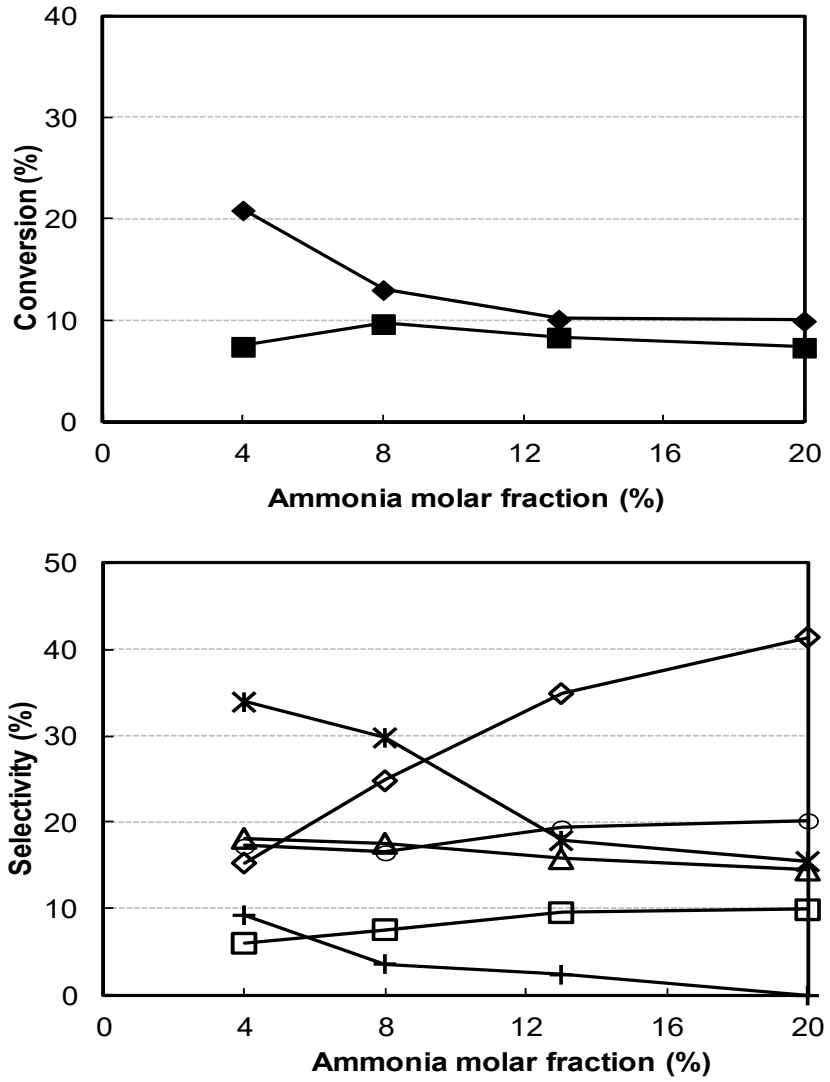


Figure S3. Effect of ammonia inlet molar fraction on reactants conversion (top figure) and on selectivity to products (bottom figure). Reaction conditions: W/F ratio 0.8 g s ml^{-1}, T 370°C, feed composition (molar %): ethanol (azeotrope)/ammonia/oxygen/inert 5/x/13/82-x. Symbols: ethanol conversion (◆), and oxygen conversion (■). Selectivity: acetonitrile (◇), acetaldehyde (✳), ethylene (△), $CO+CO_2$ (○), HCN (□), heavy compounds (+). Catalyst VPP.

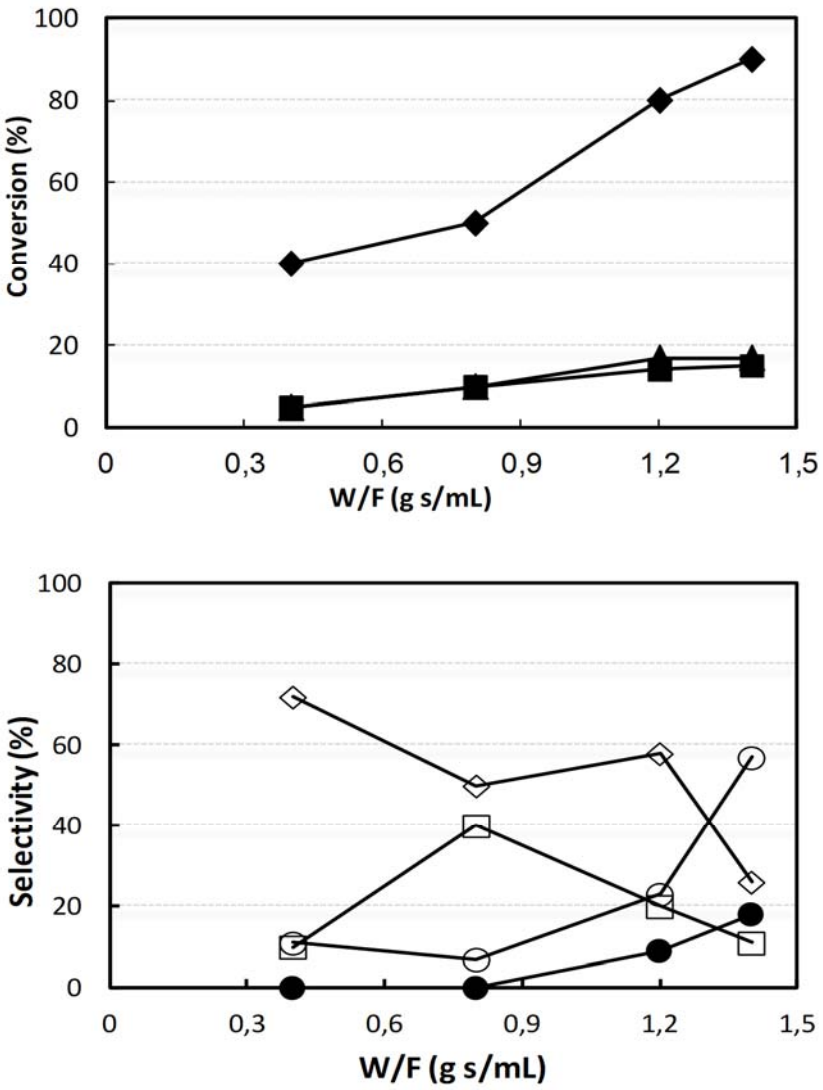


Figure S4. Effect of W/F ratio on reactants conversion (top figure) and on selectivity to products (bottom figure). Reaction conditions: temperature 350°C, feed composition (molar %): acetaldehyde/ammonia/oxygen/inert 0.5/13/13/73.5. Symbols: acetaldehyde conversion (◆), ammonia conversion (▲) and oxygen conversion (■). Selectivity: acetonitrile (◇), $CO+CO_2$ (○), HCN (□), and N_2 (calculated with respect to converted ammonia) (●). Catalyst VPP.

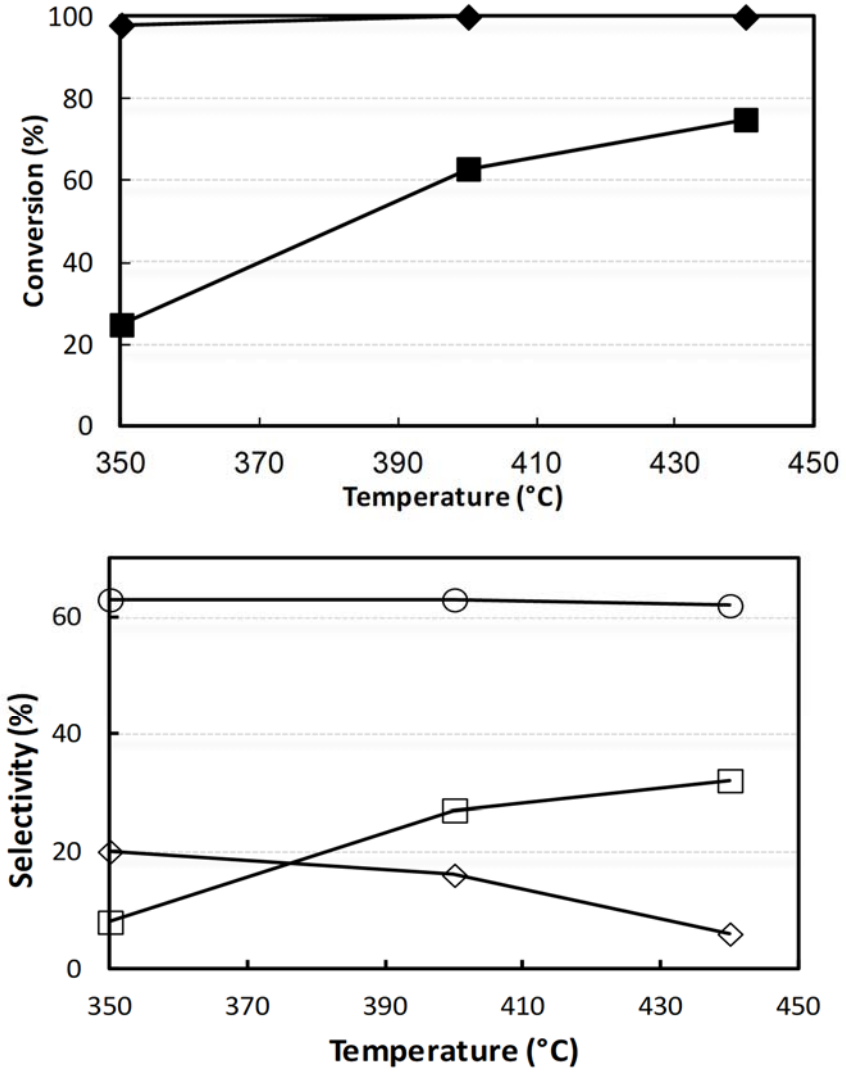


Figure S5. Effect of temperature on reactants conversion (top figure) and on selectivity to products (bottom figure). Reaction conditions: W/F ratio 0.8 g s ml^{-1}, feed composition (molar %): ethylamine/oxygen/inert 0.9/13/86.1. Symbols: ethylamine conversion (◆), and oxygen conversion (■). Selectivity to: acetonitrile (◇), $CO+CO_2$ (○), and HCN (□). Catalyst VPP.

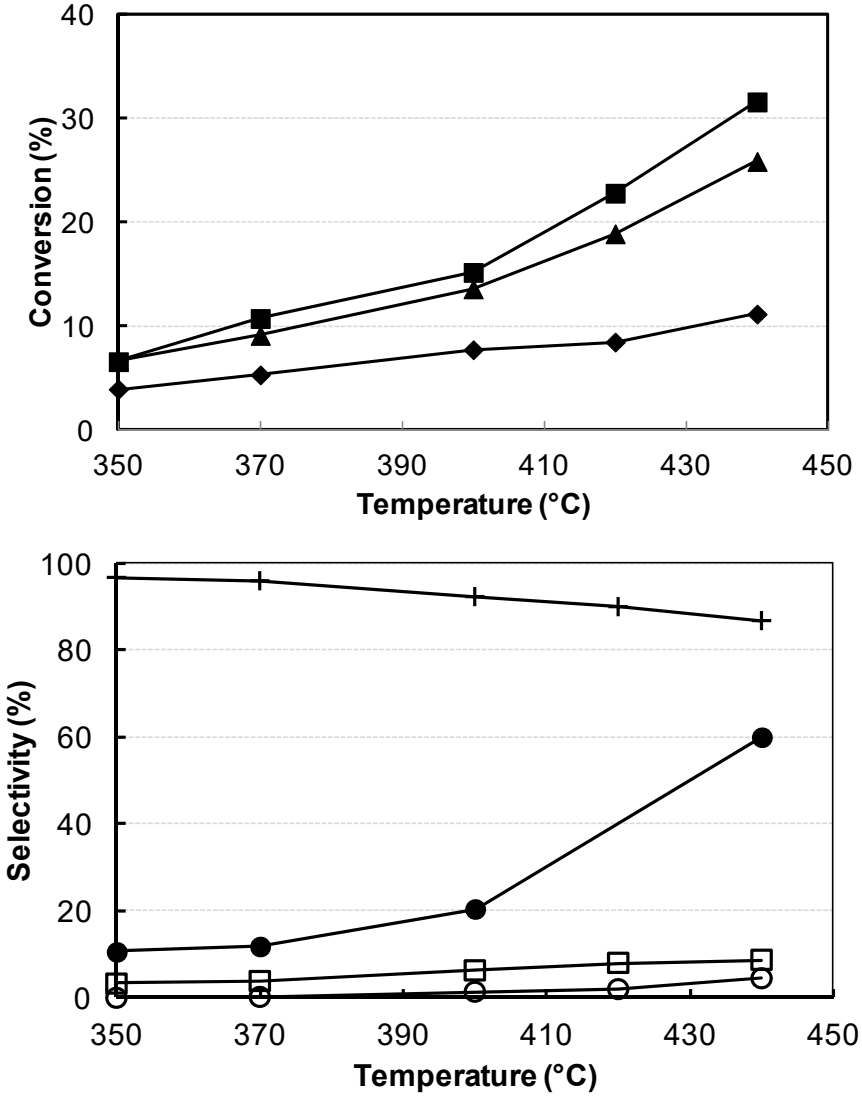


Figure S6. Effect of temperature on reactants conversion (top figure) and on selectivity to products (bottom figure). Reaction conditions: W/F ratio 0.8 g s ml^{-1}, feed composition (molar %): ethylene/ammonia/oxygen/inert 7.5/13/13/66.5. Symbols: ethylene conversion (◆), ammonia conversion (▲) and oxygen conversion (■). Selectivity to: $CO+CO_2$ (○), HCN (□), unknown compound (possibly toluene, +) and N_2 (calculated with respect to converted ammonia) (●). Catalyst VPP.

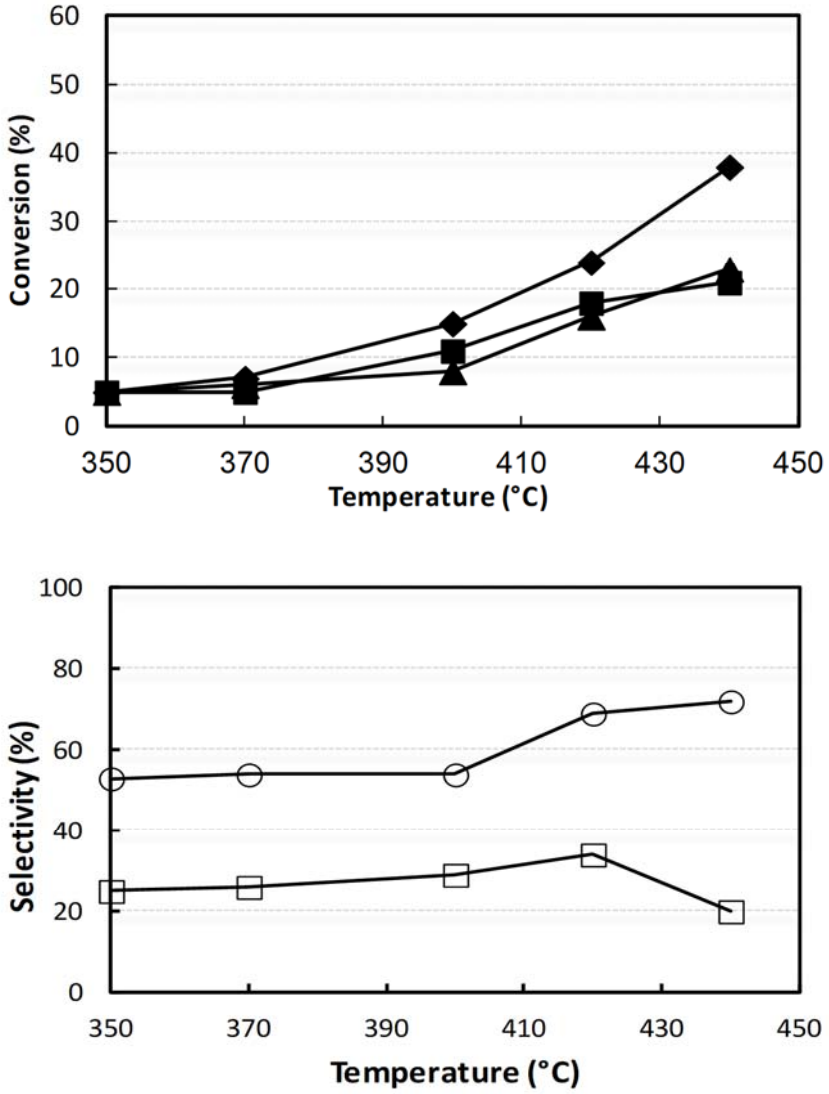
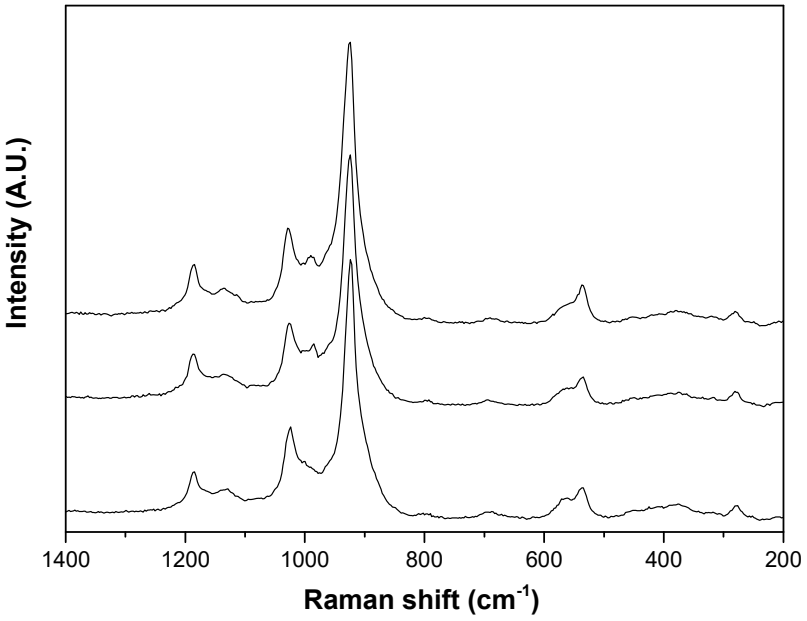


Figure S7. Effect of temperature on reactants conversion (top figure) and on selectivity to products (bottom figure). Reaction conditions: W/F ratio 0.8 g s ml^{-1}, feed composition (molar %): acetonitrile/ammonia/oxygen/inert 1/13/13/66.5. Symbols: acetonitrile conversion (◆), ammonia conversion (▲) and oxygen conversion (■). Selectivity to: $CO+CO_2$ (○), and HCN (□).



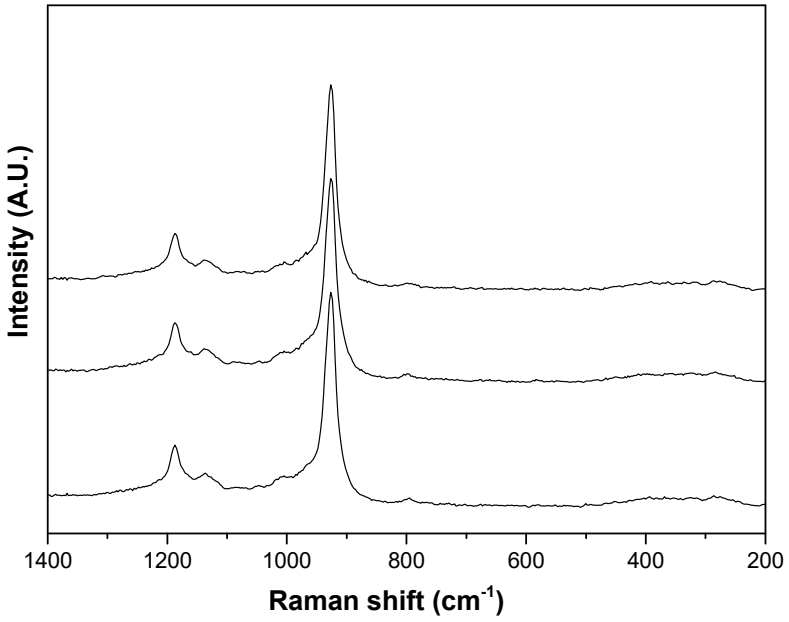


Figure S8. Raman spectra of the fresh calcined VPP catalyst (top) and of the used catalyst after ethanol ammoxidation (bottom). In the latter case, only bands attributable to $(VO)_2P_2O_7$ are shown, whereas in the calcined catalyst also bands attributable to α_I-$VOPO_4$, in the 500-to-600 cm^{-1} spectral range, are shown.

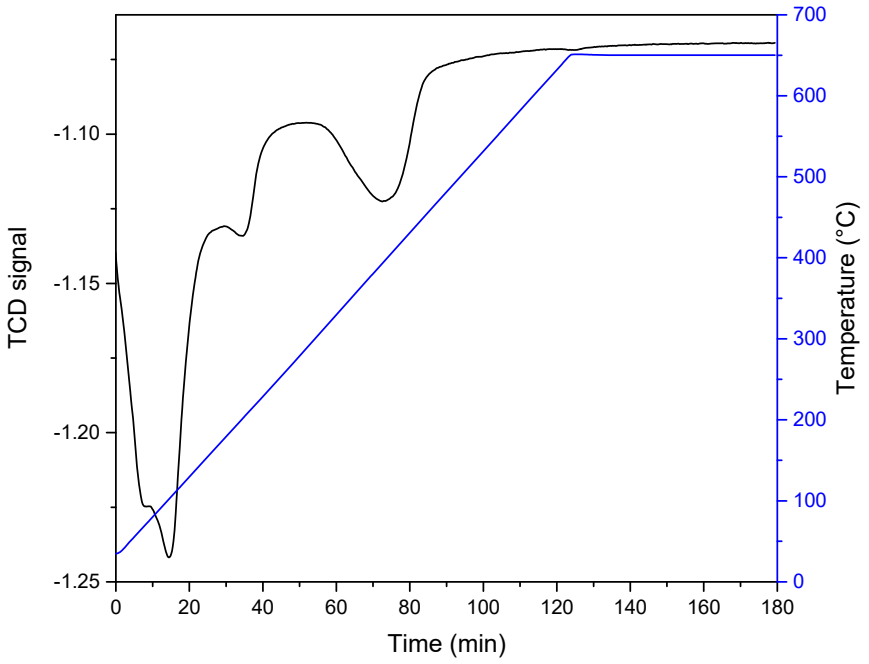


Figure S9. TPD profile recorded by heating the VPP sample in He until 650°C, with no pre-adsorption. The TCD signal was coincident with the m/e = 18 signal (H_2O) recorded by MS.

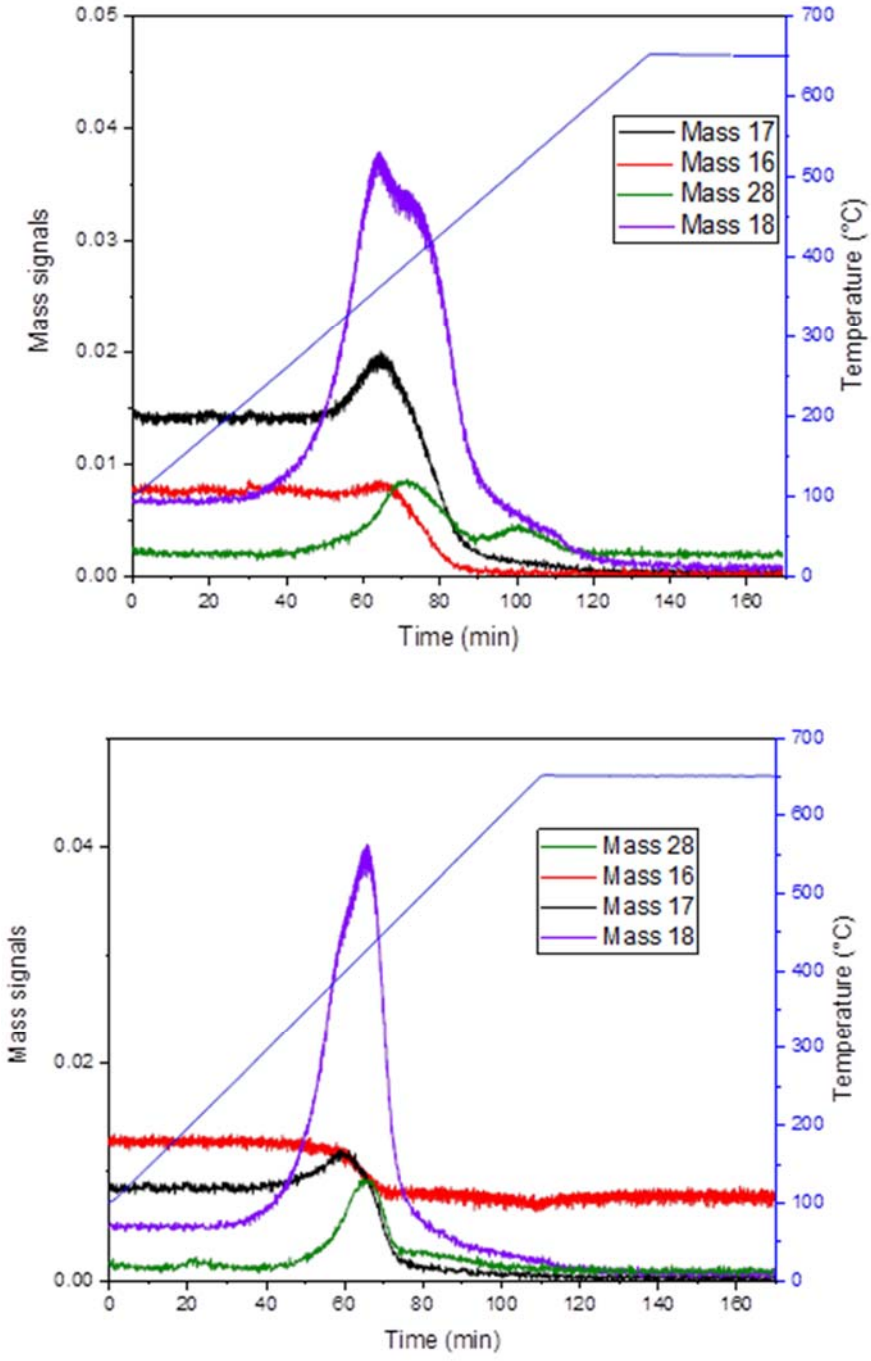


Figure S10. TPD profiles; experiments were carried out by first heating the sample in He until 350°C, then adsorbing NH_3 at 100°C, then making the TPD experiments by heating either in He (top) or in He with 5% O_2 (bottom). Red signal (mass 16): NH_3; Blu signal (mass 18): H_2O; Black signal (mass 17): H_2O and NH_3; Green signal (mass 28): N_2.

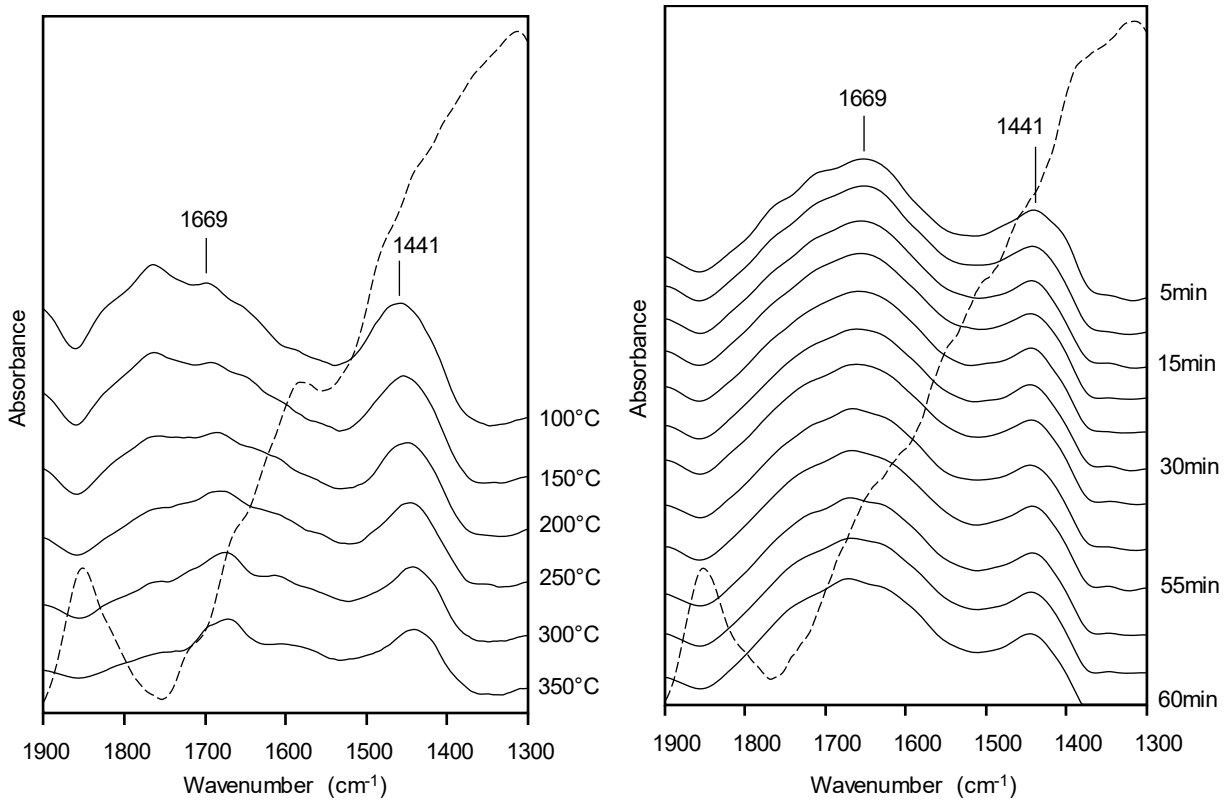


Figure S11. DRIFTS spectra; experiments were carried out by first heating VPP in He until 500°C, then adsorbing NH_3 at 100°C and recording its desorption with temperature (TPD) in He (left). Then ethanol was pulsed at 350°C, collecting spectra at increasing time-on-stream (right). Signals at 1441 and 1669 cm^{-1} are typical of ammonium cations ($\delta_s(NH_4)$, $\delta_{as}(NH_4)$). Spectra are obtained by subtracting the spectra of VPP (dotted line) and are in line with the results previously reported in literature. [1]

[1] G. Busca, G. Centi, F. Trifiro, and V. Lorenzelli. Phys. Chem. 1986, 90, 1337-1344.

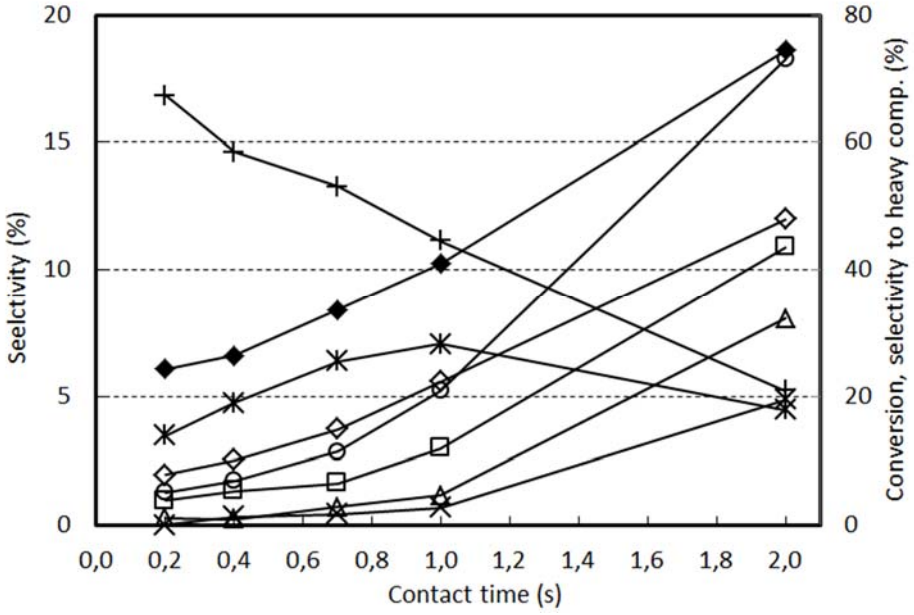


Figure S12. Effect of contact time on β-picoline conversion and on selectivity to products. Reaction conditions: feed composition (molar %): β-picoline/oxygen/inert 1/20/79; temperature 330°C. Symbols: β-picoline conversion (◆), selectivity to: nicotinic acid (◇), nicotinic aldehyde (✳), pyridine (△), cyanopyridine (□), CO (×), CO_2 (○) and heavy compounds (+). Catalyst VPP.