Supporting information

Ethanol Gas-Phase Ammoxidation to Acetonitrile: the Reactivity of Supported Vanadium Oxide Catalysts

Table S1. Catalytic ammoxidation of alcohols in gas and liquid phase.

Catalyst	T (°C) (GP/LP)	Alcohol	Alcohol/H_2O/NH_3/O_2 (molar ratios)	Alcohol conv., RCN yield (%)	Main byproducts	Ref
MnO_2	100, LP	Benzyl alcohol	0.5 mmol/--/ 0.85MPa/0.5MPa	100, 100	-	[25]
Co_3O_4	100, LP	Benzyl alcohol	0.5 mmol/--/ 0.85MPa/0.5MPa	96, 94	-	[25]
V/P/Sb/O-Al_2O_3	400, GP	Ethanol	Ethanol/water ½ v/v; NH_3/air 2.1/1	84, 82	acetaldehyde	[33]
SAPO	350, GP	Ethanol	1/1/5/air	100, 99	-	[31]
VAPO	350, GP	Ethanol	1/1/5/air	100, 96.5*	acetaldehyde	[32]
$Ru(OH)_3$-Al_2O_3	120, LP	Benzyl alcohol	NH_3/alcohol 1.8/1; air 6 bar	-, 72		[29]

* We were not able to reproduce these results

Table S2. Porosimetry of catalysts.

Sample	BET (m^2/g)	VO_x surface density (nm^{-2})*	t-Plot Micropore Area (m^2/g)
TiO_2	22,0		9,5
ZrO_2	26,5		0,6
V/Ti/O	21,3	21,8	4,6
V/Zr/O	24,2	19,1	1,9

*The VO*x* surface density was calculated according to the following equation:

$$n_S(\mathrm{VO}_x\,\mathrm{nm}^{-2}) = \frac{c_W N_A}{M_W S_{BET} \times 10^{18}(\mathrm{nm}^2/\mathrm{m}^2)}.$$

In the above equation, c_w (g/g) is the Vanadium content of catalysts, N_A the Avogadro's number (6.022×10^{23} mol^{-1}), M_w the molecular weight of Vanadium (50.94 g mol^{-1}) and S_{BET} (m^2 g^{-1}) is the surface area of the catalysts.

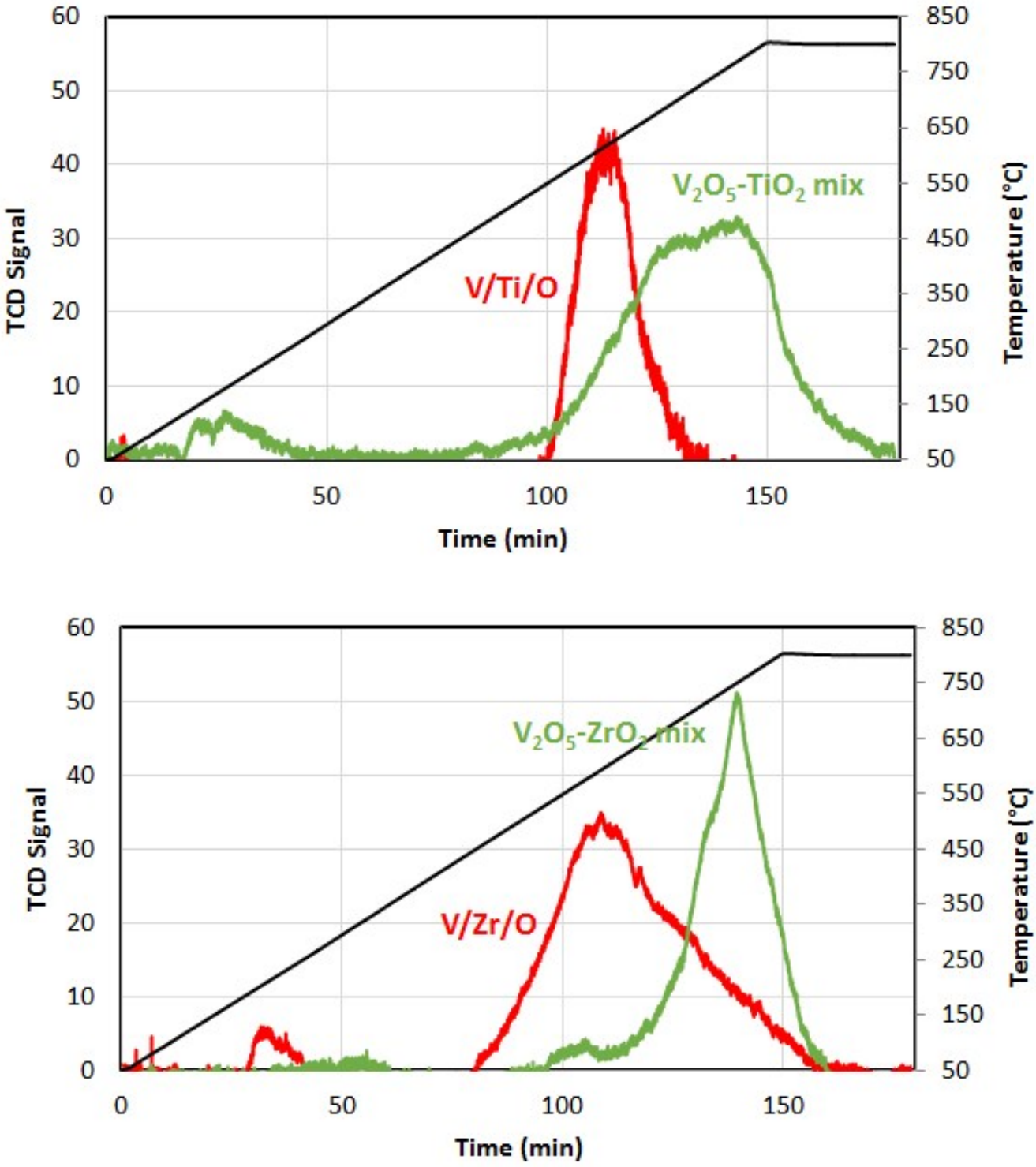

Figure S1. TPR profiles of V/Ti/O (top) and V/Zr/O (bottom) catalysts, and profiles of two reference catalysts prepared by mixing and calcination of 7 wt% V_2O_5 with bare supports.

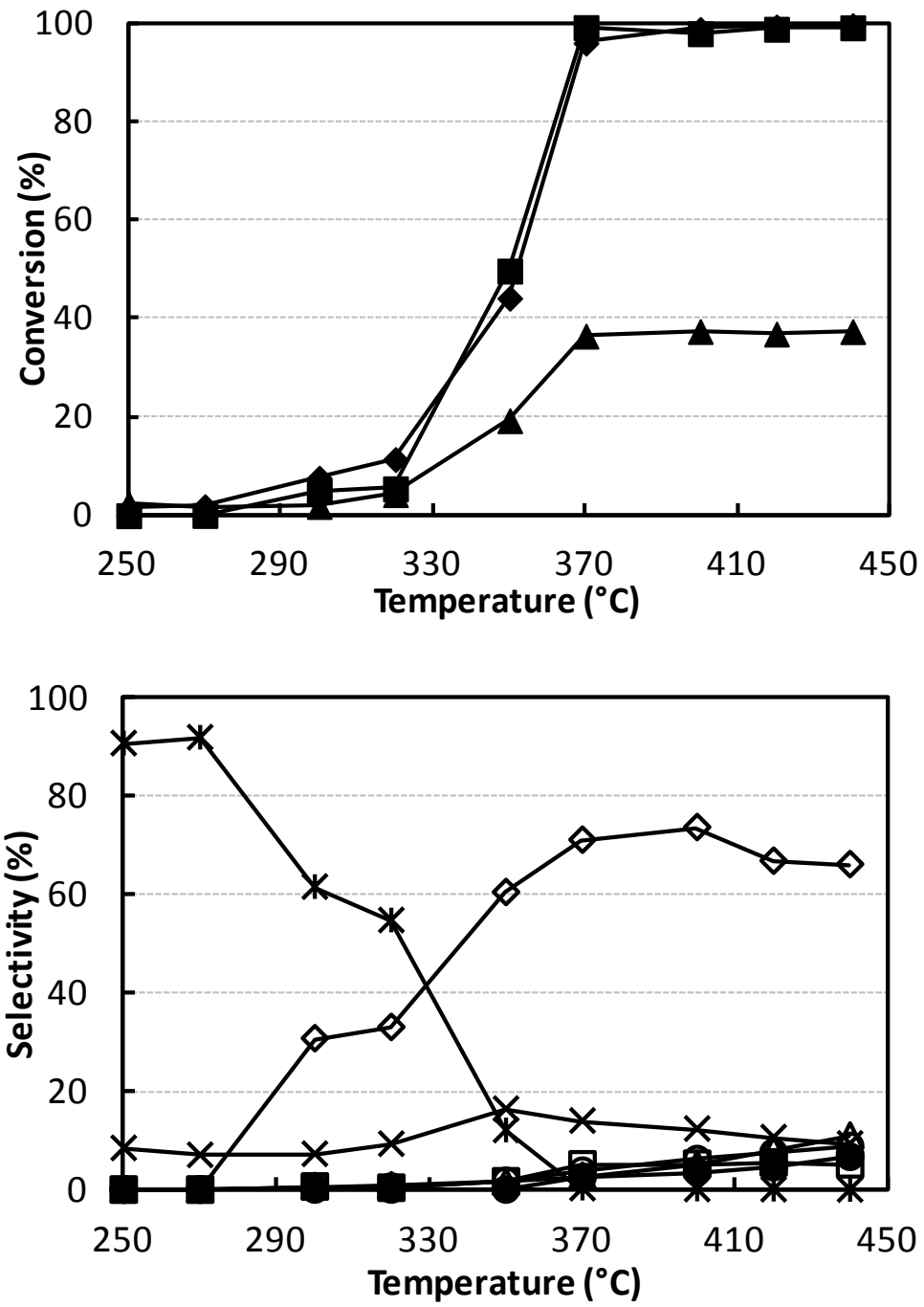

Figure S2. Effect of temperature on reactant conversion (top figure) and on selectivity to products (bottom figure). Reaction conditions: W/F ratio 0.1 g s mL^{-1}, feed composition (molar %): ethanol (azeotrope)/ammonia/oxygen 5/13/6. Symbols: ethanol conversion (◷), ammonia conversion (□) and oxygen conversion (○). Selectivity to: acetonitrile (✳), acetaldehyde (➲), ethylene (❒), CO (ᨒ), CO_2 (ᨓ), HCN (●) and N_2 (calculated with respect to converted ammonia) (ᨔ). Catalyst V/Zr/O.

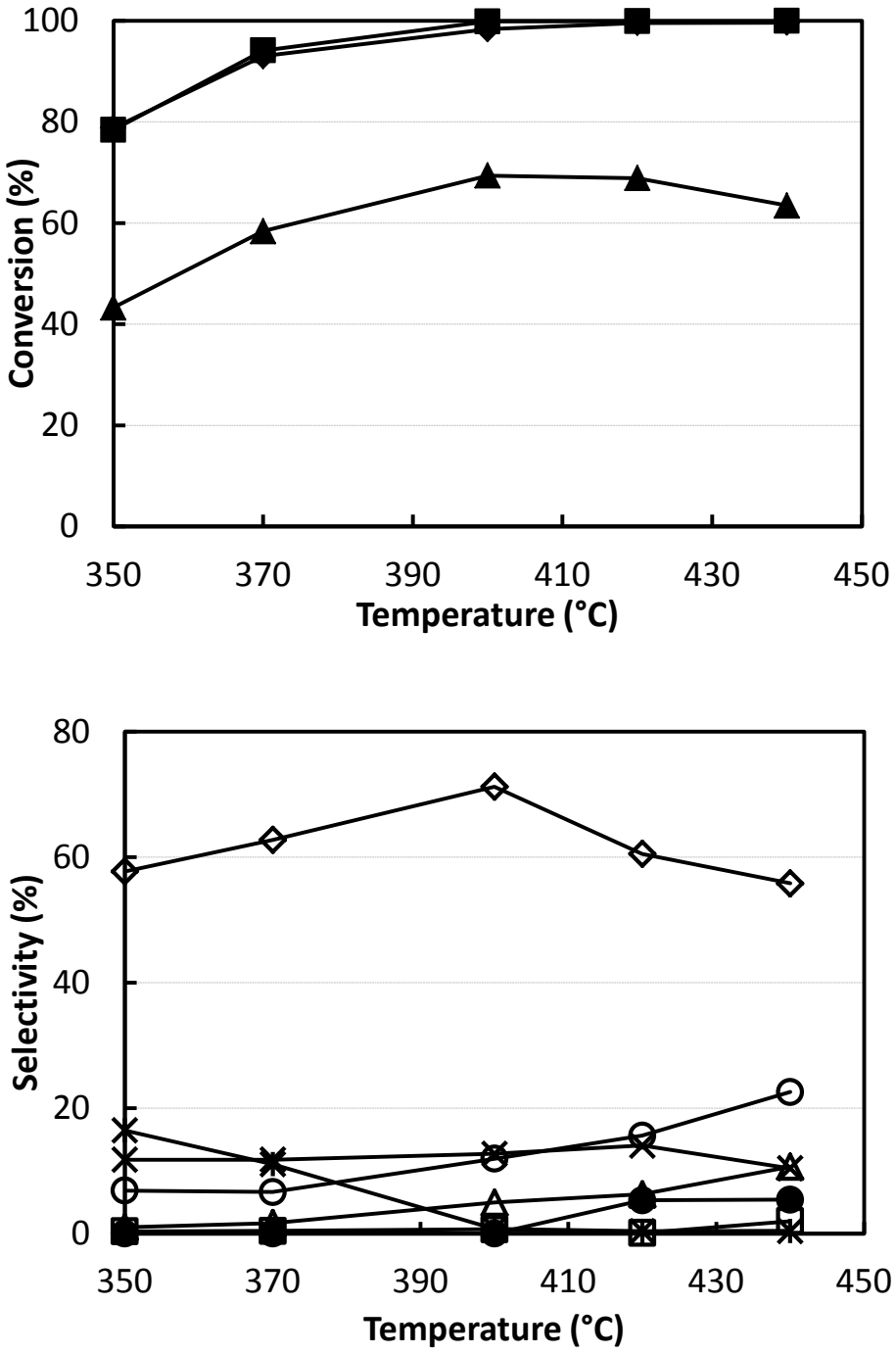

Figure S3. Effect of temperature on reactant conversion (top figure) and on selectivity to products (bottom figure). Reaction conditions: W/F ratio 0.1 g s mL^{-1}, feed composition (molar %): ethanol (azeotrope)/ammonia/oxygen 10/12/10. Symbols: ethanol conversion (◷), ammonia conversion (□) and oxygen conversion (○). Selectivity to: acetonitrile (✳), acetaldehyde (➲), ethylene (❒), CO (🝖), CO_2 (🝗), HCN (●) and N_2 (calculated with respect to converted ammonia) (ᔓ). Catalyst V/Zr/O.

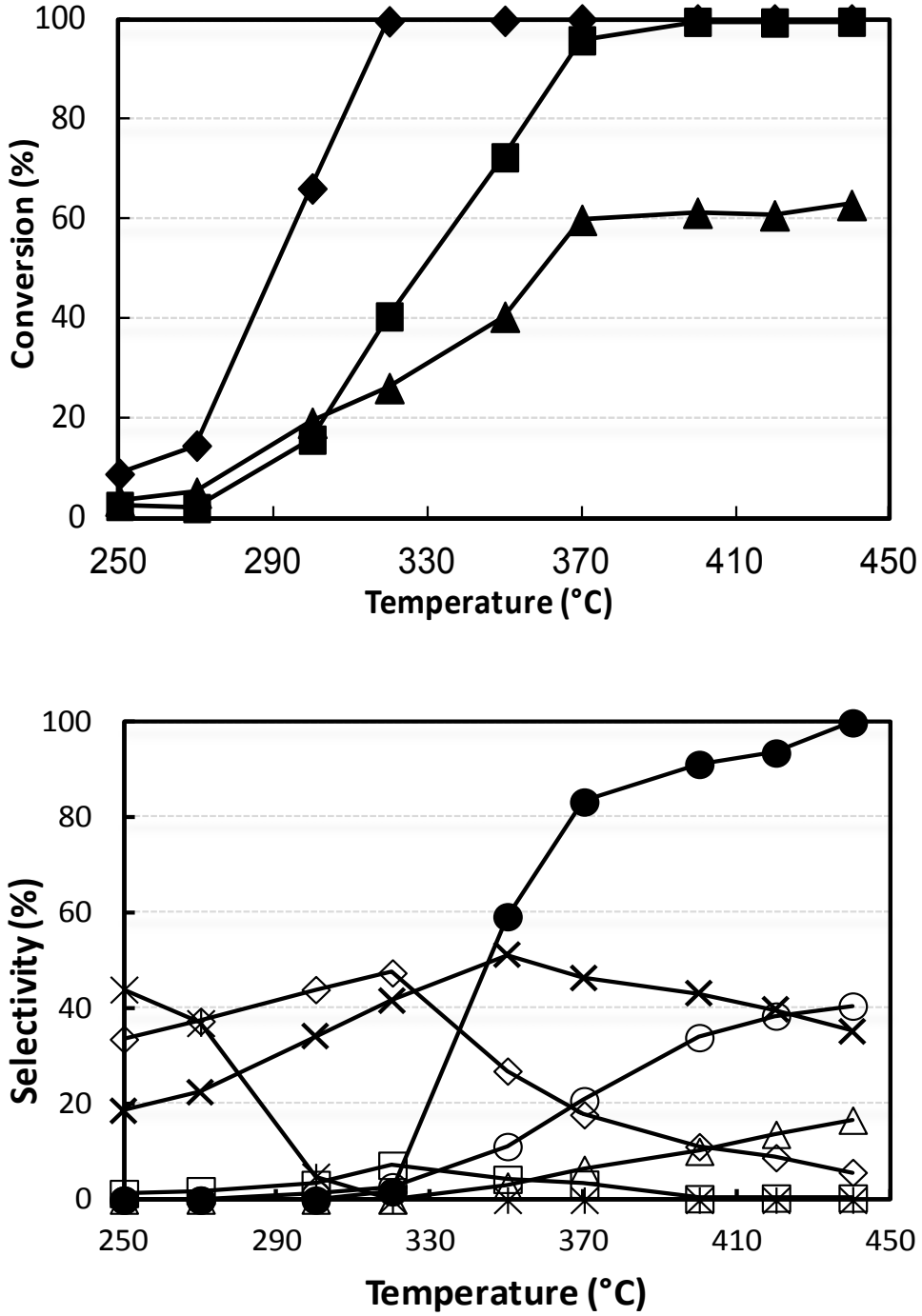

Figure S4. Effect of temperature on reactant conversion (top figure) and on selectivity to products (bottom figure). Reaction conditions: W/F ratio 0.8 g s mL^{-1}, feed composition (molar %): ethanol (azeotrope)/ammonia/oxygen/inert 5/13/13/69. Symbols: ethanol conversion (◴), ammonia conversion (◘) and oxygen conversion (O). Selectivity to: acetonitrile (❋), acetaldehyde (➲), ethylene (❒), CO (ᨒ), CO_2 (ᨓ), HCN (❍) and N_2 (calculated with respect to converted ammonia) (ᨔ). Catalyst V/Ti/O.

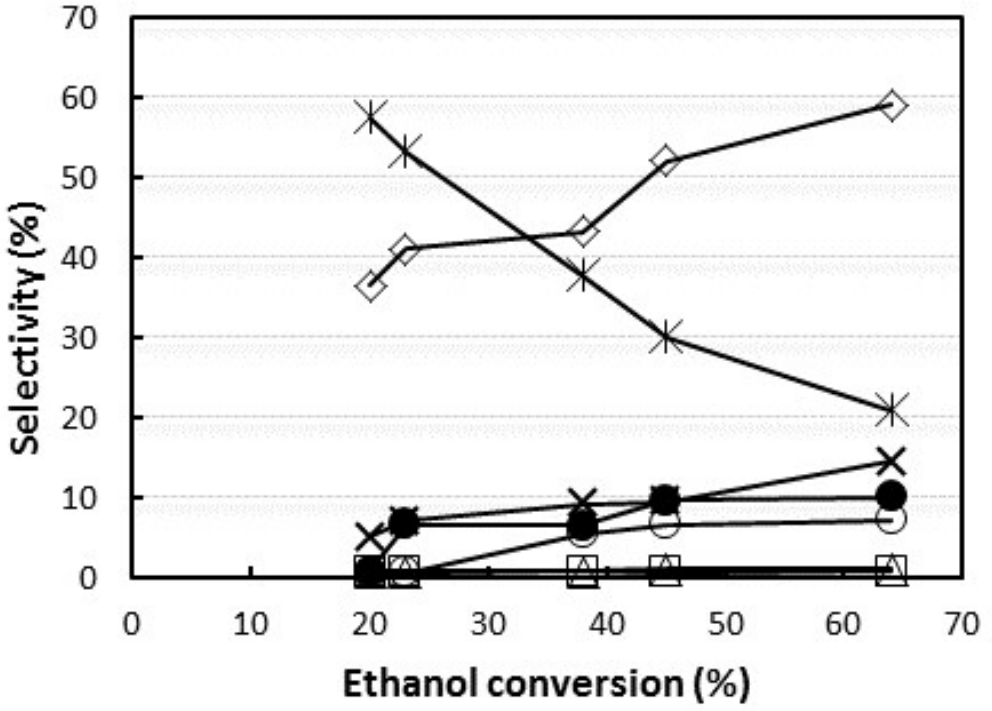

Figure S5. Effect of conversion on selectivity to products. Reaction conditions: temperature 320°C, feed composition (molar %): ethanol (azeotrope)/ammonia/oxygen 1.4/3.6/1.7. Contact time was varied. Symbols: Selectivity to: acetonitrile (❋), acetaldehyde (➲), ethylene (❒), CO (🝖), CO_2 (🝗), HCN (●) and N_2 (calculated with respect to converted ammonia) (🝘). Catalyst V/Ti/O.

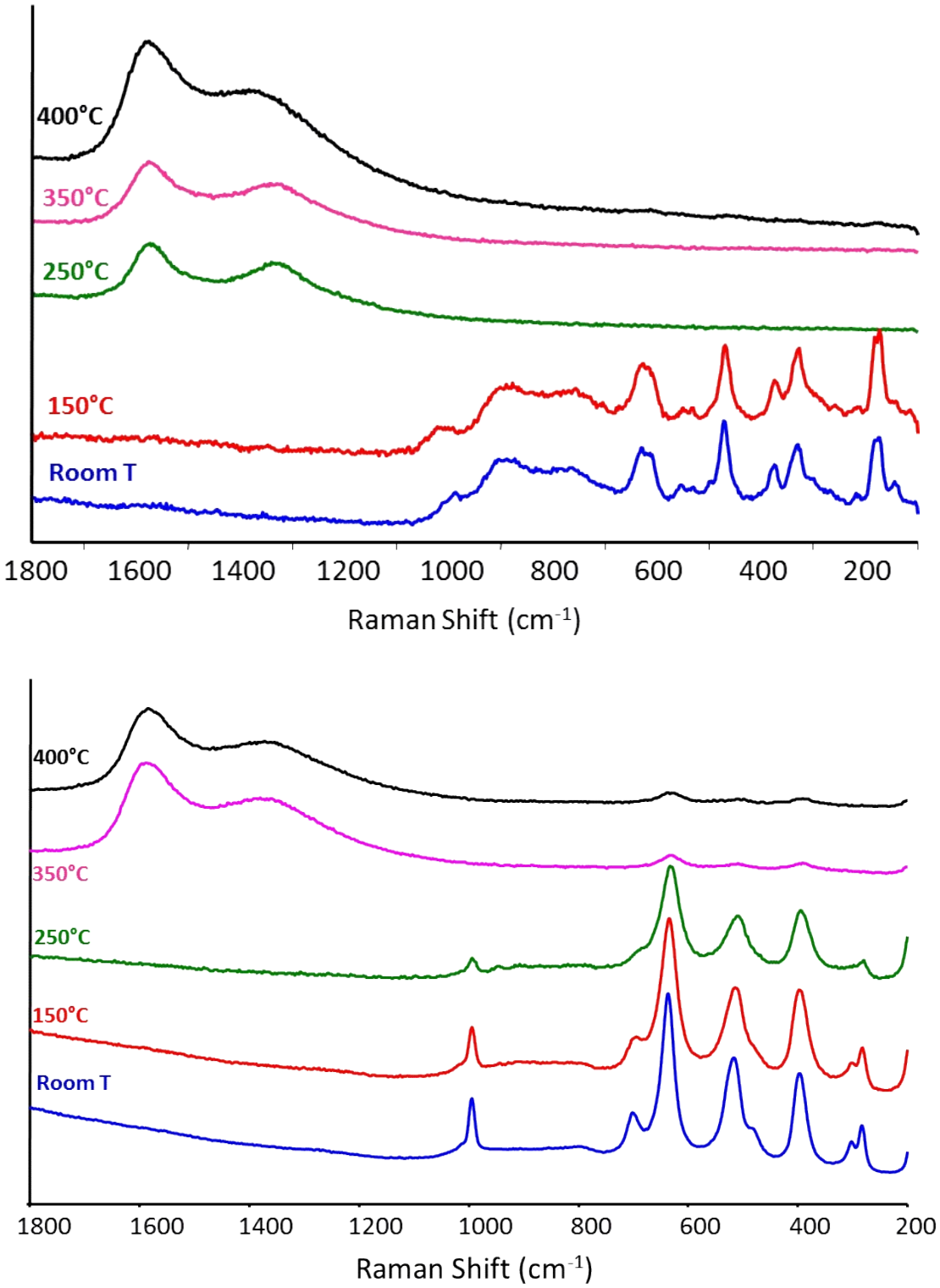

Figure S6. Raman spectra recorded while heating samples under an ethanol/He feed. Catalysts: V/Zr/O (top) and V/Ti/O (bottom).

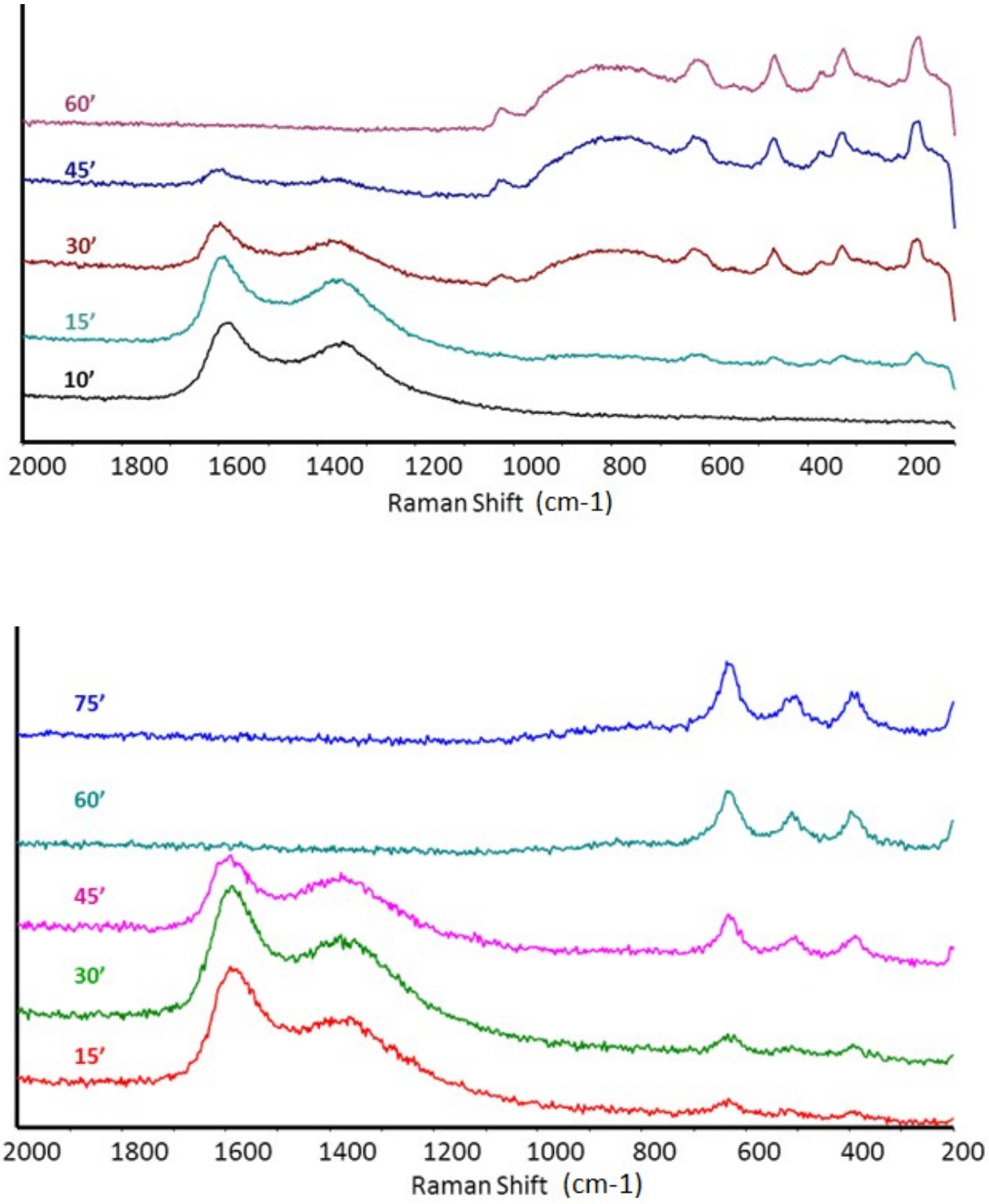

Figure S7. Raman spectra recorded at 400°C in N_2 flow after recording of spectra reported in Figure S6. Catalysts: V/Zr/O (top) and V/Ti/O (bottom).

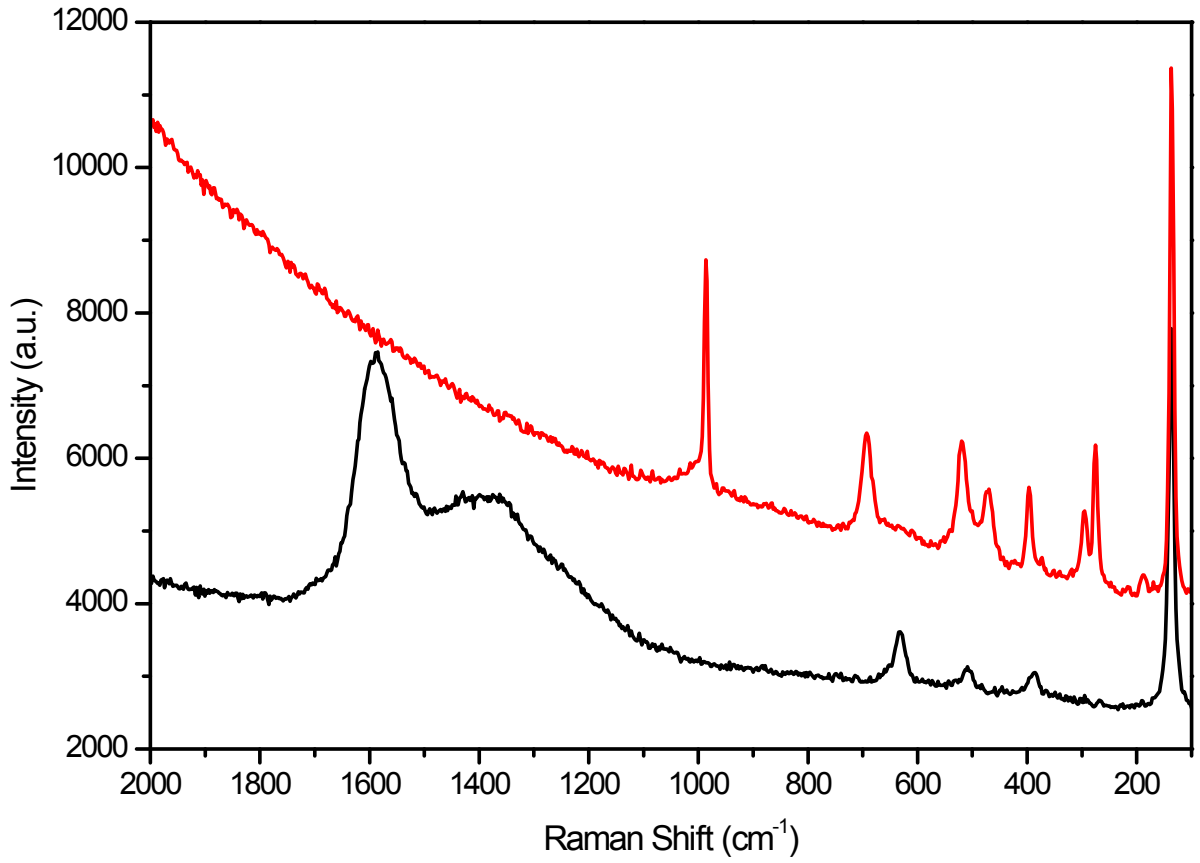

Figure S8. Raman spectra (recorded at 130°C) of used V/Zr/O (top) and V/Ti/O (bottom) catalysts after experiments carried out with ethanol/air feed.

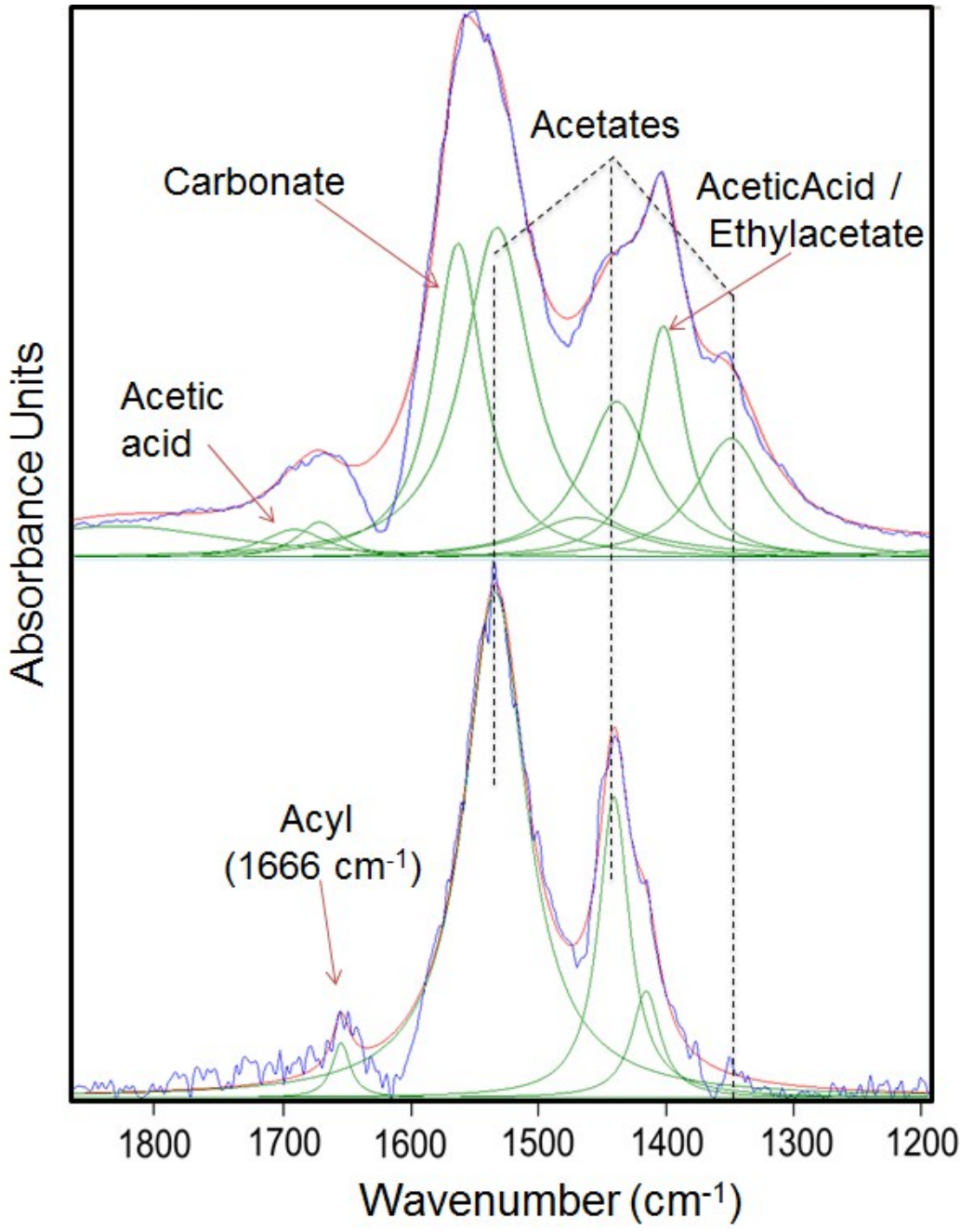

Figure S9. Detail of the DRIFT spectra recorded at 350°C for V/Ti/O (bottom) and V/Zr/O (top) catalysts after adsorption of ethanol.