Supporting information

Upgrading the Reflux Method as Novel Route for Competitive Catalysts in Alkane Selective Oxidation

by

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Summary

References

Table S1. Rietveld method quantification of the majority crystalline phases present in the XRD of the catalysts.

Catalyst[a]	**M1**	**Mo_5O_{14}**	**$TeMo_5O_{16}$**	**Amorphous**
P8-N	14.2	34.5	40.1	11.0
P10-N	27.3	20.1	30.2	22.3
P11-N	66.1	12.5	11.8	9.6
P11A-N	76.7	9.0	10.0	4.3
P11B-N	44.6	20.4	15.9	8.1
P11C-aN	73.2	1.8	12.3	12.6

a) Catalyst heat-treated at 600ºC in N_2 atmosphere; b) Catalyst initially calcined at 250ºC in air and then heat-treated at 600ºC in N_2 atmosphere.

Table S2. Catalytic results during the partial oxidation of propane over MoVTeNbO catalysts.[a]

Catalyst	Temp. (ºC)	Conv. (%)	S_{AA} (%)	$S_{C3=}$ (%)	S_{HAc} (%)	S_{COx} (%)	Y_{AA} (%)
P8-N	375	9.7	28.4	16.5	7.1	48.0	2.8
P10-N	391	18.5	54.9	10.8	3.4	30.9	10.1
P11-N	372	21.2	55.5	10.2	3.9	30.4	11.8
	400	40.5	57.0	5.3	6.0	31.7	23.1
P11A-N	380	56.7	63.2	2.1	2.8	25.9	35.8
	400	70.5	58.5	1.5	9.0	31.0	41.2
P11B-N	372	29.9	36.9	10.9	2.2	50.0	11.0
P11C-aN	380	60.7	63.7	1.7	8.5	26.1	38.7
	400 [b]	50.6	64.0	1.7	8.4	25.9	32.4
	400	74.4	59.0	1.5	8.8	30.7	43.9

a) Reaction conditions: Contact time, W/F, 407 $g_{cat}\,h^{-1}\,mol_{C3H8}^{-1}$; $C_3H_8/O_2/H_2O/He$= 4/8/30/58; total flow 25 mL min^{-1}.

b) Selectivity to acrylic acid (AA), acetic acid (HAc), propylene (C3=), and carbon oxides ($CO+CO_2$).

c) Contact time, W/F, 203 $g_{cat}\,h^{-1}\,mol_{C3H8}^{-1}$; $C_3H_8/O_2/H_2O/He$= 4/8/30/58; total flow 50 mL min^{-1}.

Table S3. Catalytic results during the ethane oxidative dehydrogenation over MoVTeNbO catalysts.[a]

Catalyst	Temp. (ºC)	Conversion (%)	S_{C2H4} (%)	S_{CO} (%)	S_{CO2} (%)	Y_{C2H4} (%)
P8-N	412	5.5	90.6	6.2	3.2	
	433	7.6	92.4	5.0	2.6	7.0
P10-N	408	11.9	94.1	4.0	1.9	11.2
	428	18.5	93.4	4.7	2.0	17.2
P11-N	408	12.4	95.4	3.0	1.6	11.8
	428	19.4	94.7	3.5	1.8	18.3
P11A-N	386	26.2	96.1	2.3	1.7	25.2
	407	39.1	94.8	3.2	2.0	37.1
	429	54.2	92.4	4,8	2.7	50.1
P11B-N	408	16.4	93.7	4.3	2.0	15.4
	428	25.7	92.5	5.3	2.2	23.7
P11C-aN	391	34.3	94.3	3.8	1.9	32.3
	412	49.6	92.7	5.0	3.1	46.0
	432	65.3	89.4	7.5	4.3	58.4

a) Reaction conditions: $C_2H_6/O_2/He$= 9/35/56; contact time, W/F, of 140 $g_{cat}\ h^{-1}\ mol_{C2H6}^{-1}$; total flow 30 mL min^{-1}.

b) Selectivity to ethylene (C_2H_4), and carbon oxides (CO and CO_2).

Table S4. Catalytic parameters during the oxidation of ethane and propane over MoVTeNbO catalysts.[a]

Catalyst[a]	Propane oxidation		Ethane oxidation	
	Areal rate[b]	Rate per area and per M1-content[c]	Areal rate[b]	Rate per area and per M1-content[c]
P8-N	2.57	18.0	2.63	18.5
P10-N	3.71	13.6	4.56	16.7
P11-N	9.14	13.4	9.66	14.7
P11A-N	9.83	12.8	14.3	18.6
P11B-N	5.72	12.8	5.82	13.1
P11C-aN	7.36	10.1	16.0	21.8

[a] Reaction conditions as in Table S2 (at 380ºC) and S3 (at 412ºC); [b] Areal rate in $g_{C3}\,m^{-2}\,h^{-1}$ or $g_{C2}\,m^{-2}\,h^{-1}$; [c] Rate per area and per M1-content has been obtained by dividing the areal rate by %/100 of M1 in the catalyst.

Figure S1. XRD patterns of as-synthesized materials a) P8-as; b) P10-as; c) P11-as; d) P11A-as; e) P11B-as; f) P11C-as. Characteristics of catalysts as in **Table 1**.

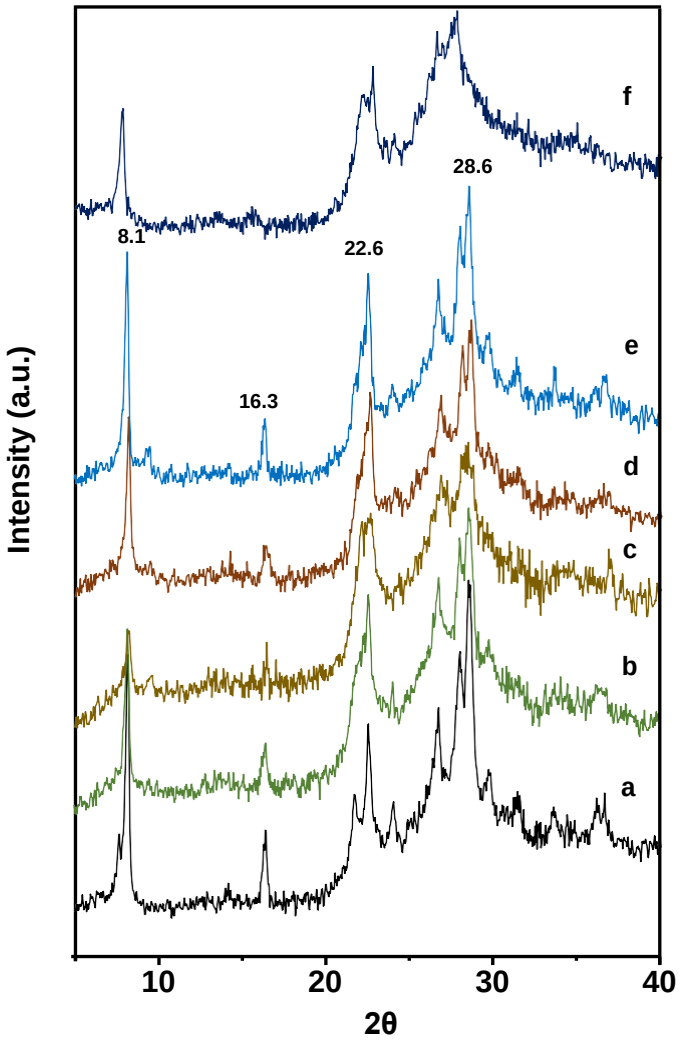


Figure S2. Infrared spectra of as-synthesized materials: a) P11-as; b) P11A-as; c) P11B-as; d) P11C-as. Characteristics of catalysts as in **Table 1**.

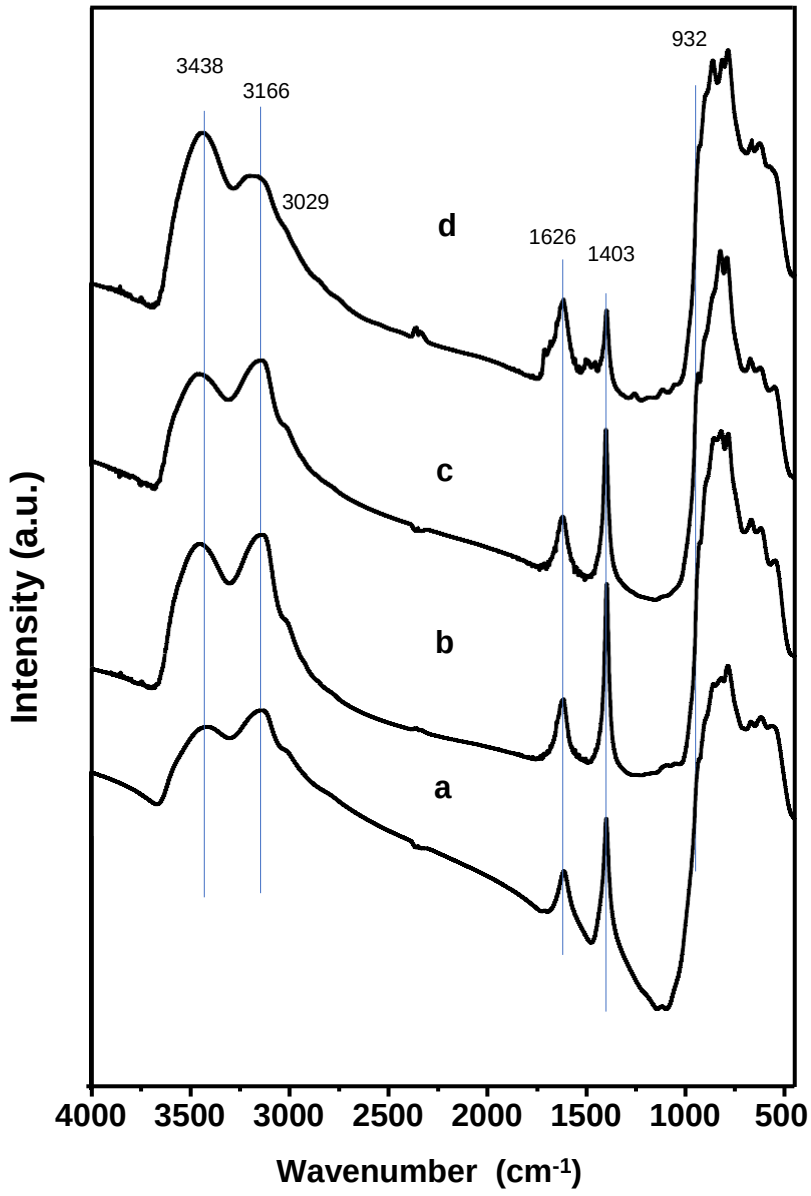


Figure S3. Low magnification FESEM micrographs of: a) **P8-N**, b) **P10-N**, c) **P11-N**, d) **P11A-N**, e) **P11B-N** and f) **P11C-aN** catalysts.

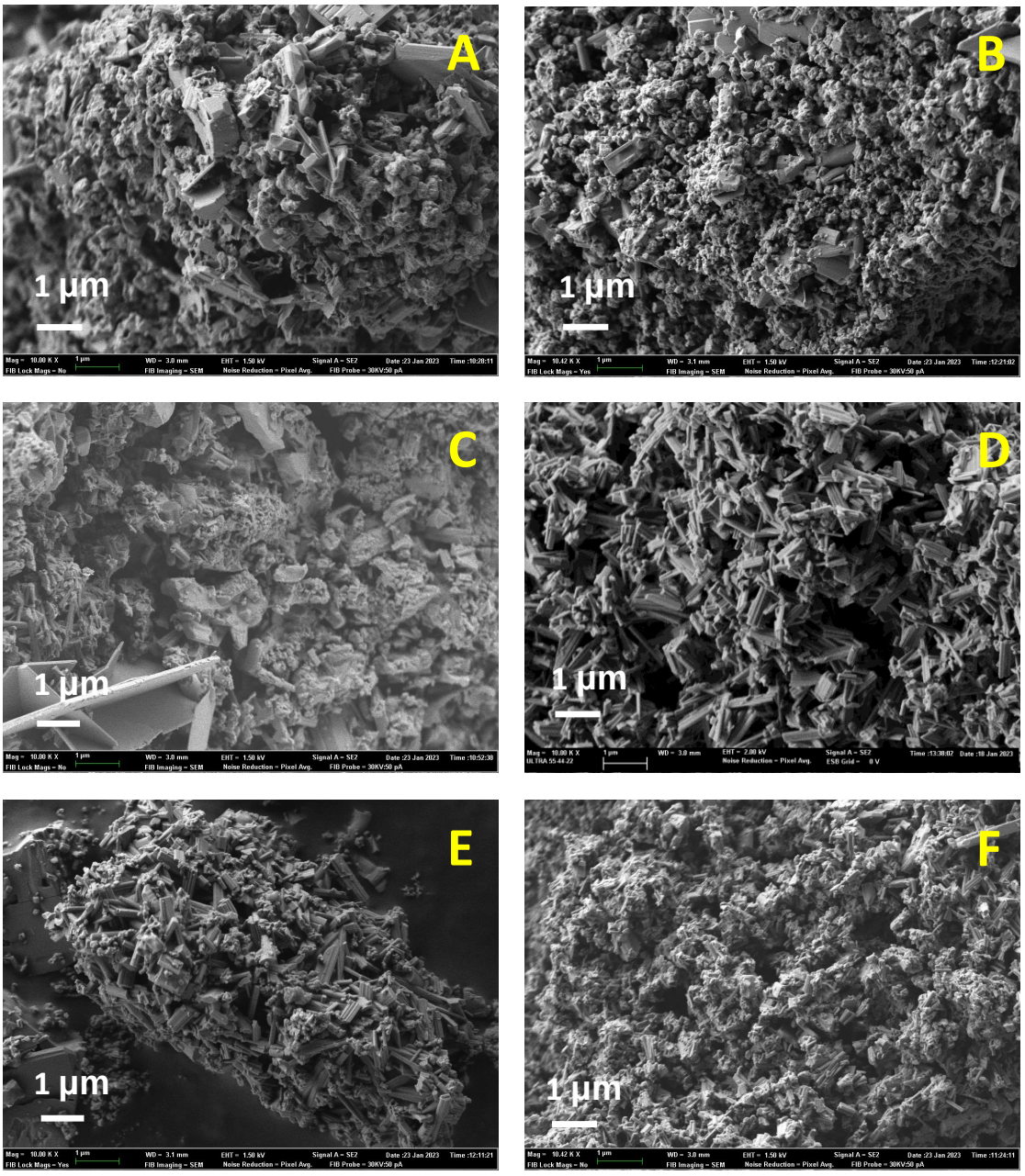


Figure S4. HRTEM micrographs of: a) **P8-N**, b) **P11-N**, c) **P11A-N** and d) **P11C-aN** catalysts.

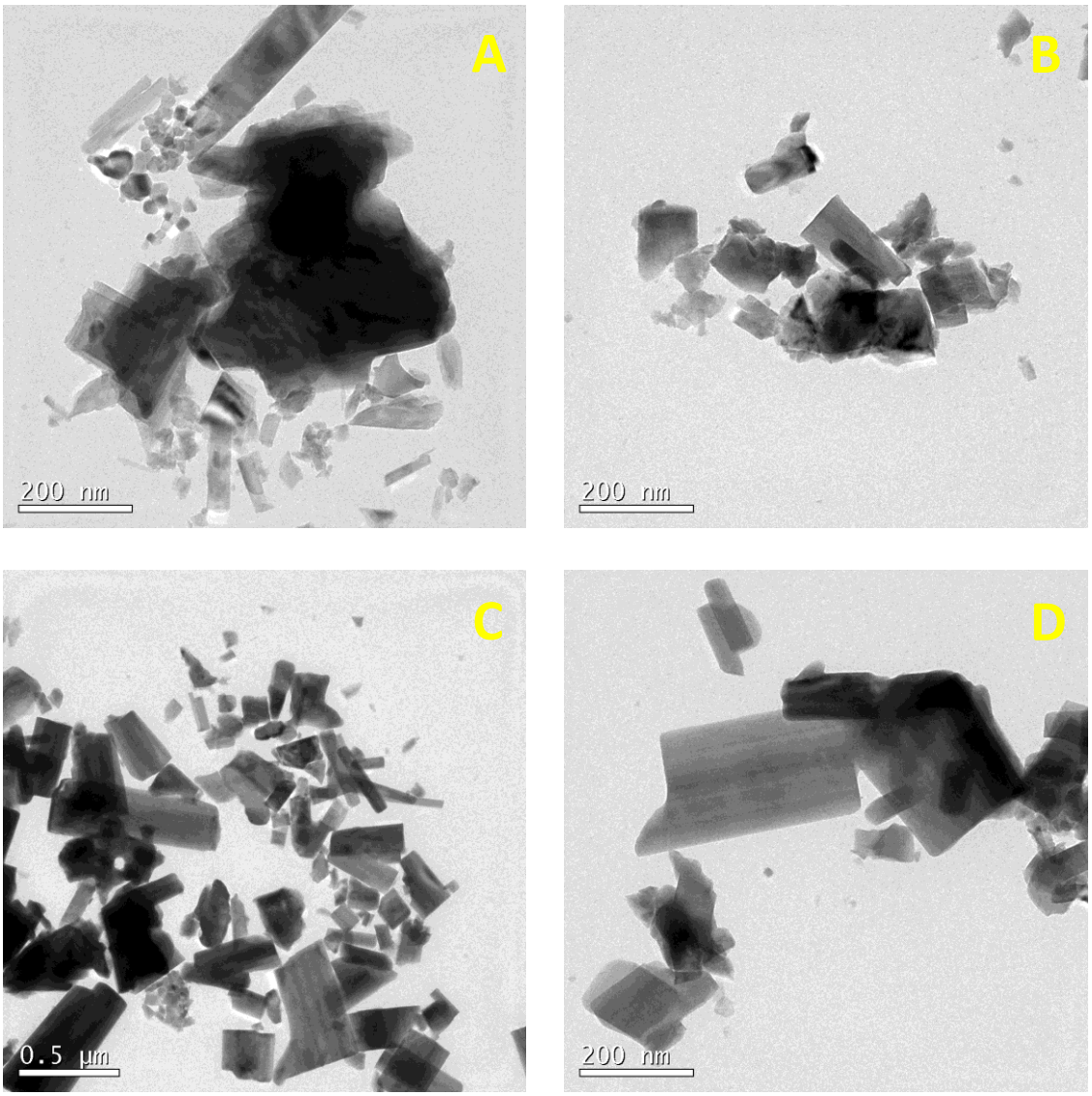


Figure S5. XPS spectra of Mo *3d* (**A, B**), Te *3d* (**C, D**) and Nb *3d* (**E, F**) core level.

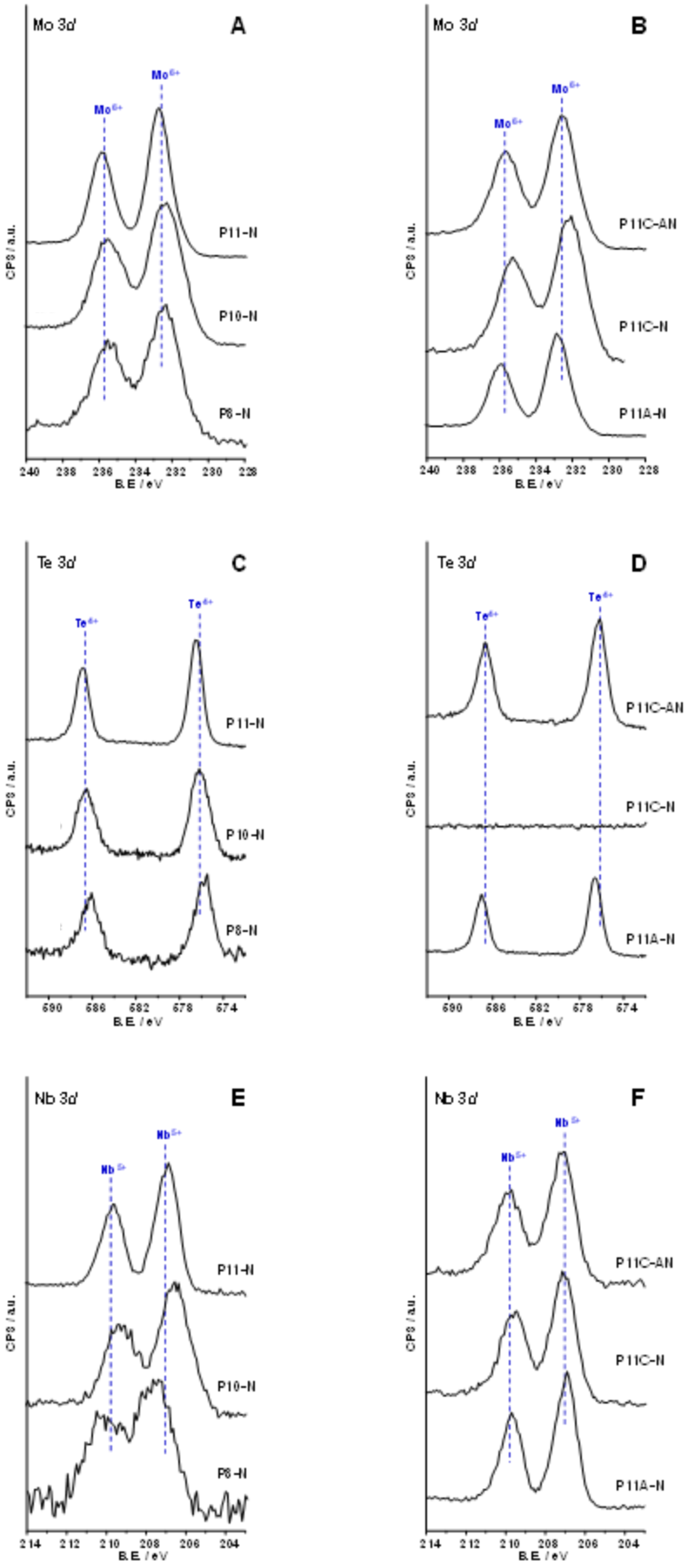


Figure S6. Relationship between the areal rate for both propane (**A**) and ethane (**B**) oxidation and the % of the orthorhombic M1 phase in the catalysts. Reaction conditions as in Table S4.

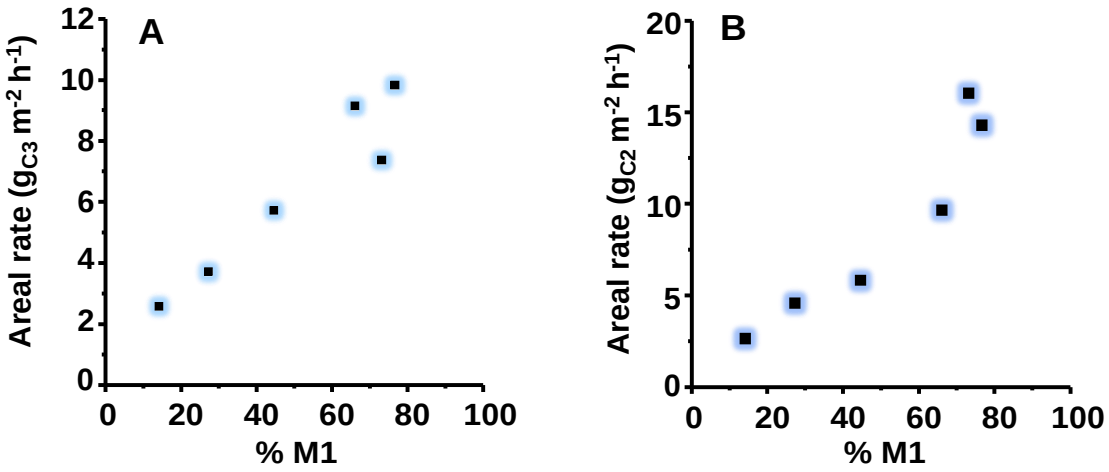
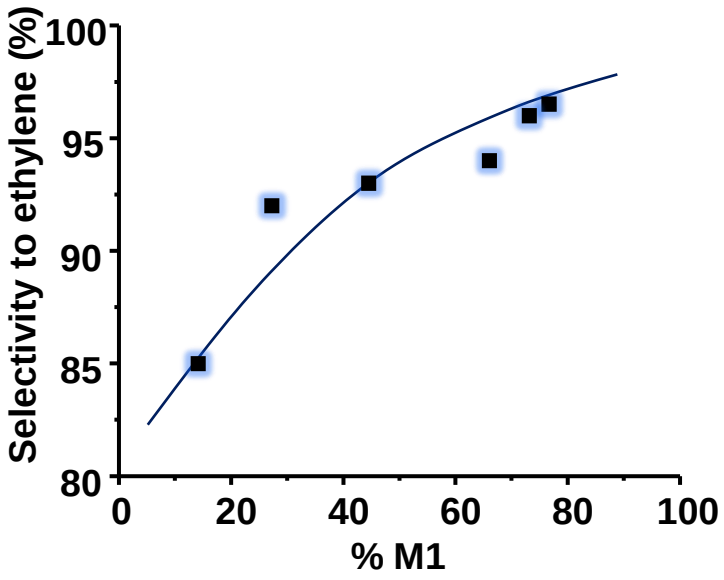
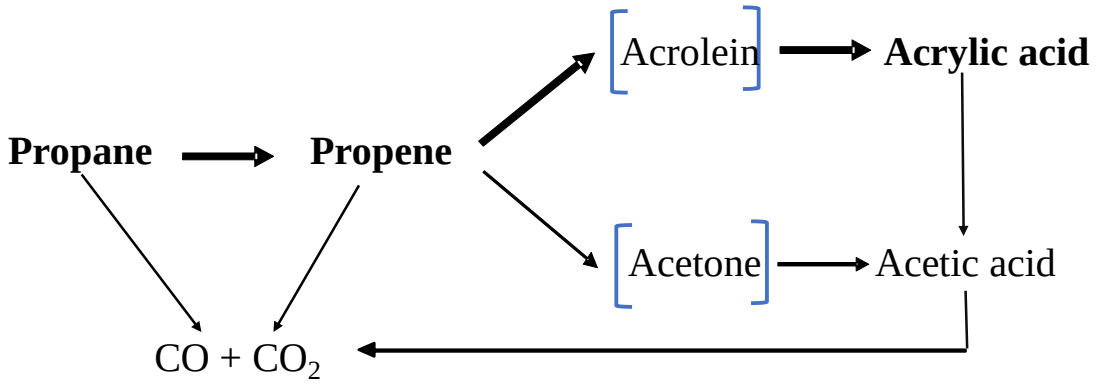


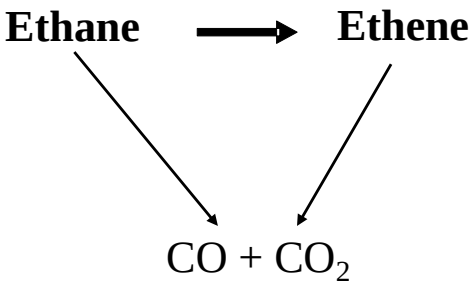
Figure S7. Relationship between the selectivity to ethylene and the % of the orthorhombic M1 phase in the catalysts. Reaction conditions: 25% conversion, 412 ºC and remaining conditions in the text.



Scheme S1. Reaction network for the selective oxidation of propane on mixed metal oxides. Adapted from ref. 1.



Scheme S2. Reaction network for the ethane ODH on mixed metal oxides. Adapted from ref. 2.



References

1. P. Concepción, P. Botella, J.M. López Nieto, Appl. Catal. A- Gen 278 (2004) 45–5.
2. T. Blasco, J.M. L6pez Nieto, Appl. Catal. A- Gen 157 (1997) 117-142.