Electronic Supplementary Information

Current status and perspectives in oxidative, non-oxidative and CO_2-mediated dehydrogenation of propane and iso-butane over metal oxide catalysts

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Table S1 V-containing Catalysts and reaction conditions for the ODP reaction with co-fed propane and oxygen. The catalysts with propene selectivity above 70% at propane conversion larger than 10% have been selected from about 700 V-containing catalysts reported from 2008. All other catalysts do not fulfil these requirements.

Catalysts	T/K	$p(C_3H_8)$ / bar	$p(O_2)$ / bar	$X(C_3H_8)$ / %	$S(C_3H_6)$ / %		Ref.
Ga-Si-Mg-VO_x	843	0.75	0.25	16.8	78.6	2.9·10-1	[137]
VO_x(6 mol%)-AlF_3	773	0.30	0.51	11.0	90.2	$1.2\cdot10^{0}$	[138]
VO_x(8 mol%)-AlF_3	773	0.30	0.51	11.8	74.9	$1.1\cdot10^{0}$	[138]
$VSiO_x$-Flame pyrolysis	823	0.2	0.2	14.0	76.4	$1.4\cdot10^{-1}$	[139]
VO_x(4.5 wt.%)/SBA-15Si	873	0.17	0.17	15.0	85.0	$1.4\cdot10^{-1}$	[140]
$V_2Mo_4(O)_x/Al_2O_3$	773	0.60	0.20	13.0	78.6	$1.0\cdot10^{0}$	[141]
$Sr_{0.5}V_2Mo_4(O)_x/Al_2O_3$	773	0.60	0.20	14.3	81.7	$1.2\cdot10^{0}$	[141]
VO_x(1 wt.%)/SiO_2-(1000)	823	0.1	0.1	15.4	72.4		[142]
VO_x(5 wt%)Al_2O_3_flower	743	0.10	0.20	10.2	78.3	$7.1\cdot10^{-1}$	[143]
VO_x(5 wt%)Al_2O_3_sphere	743	0.10	0.20	10.7	81.6	$7.7\cdot10^{-1}$	[143]
V(2.72 wt%)-SiO_x	848	0.11	0.06	20	71.4	$9.5\cdot10^{-2}$	[73]
VO_x(3 wt%)/Al_2O_3	773	0.29	0.14	12.5	75.9	$4.2\cdot10^{-1}$	[144]
VO_x(6 wt%)/Al_2O_3	773	0.29	0.14	10.1	71.9	$3.3\cdot10^{-1}$	[144]

Table S2 V-free Catalysts and reaction conditions for the ODP reaction with co-fed propane and oxygen. The catalysts with propene selectivity above 70% at propane conversion larger than 10% have been selected reported from literature since 2008.

Catalysts	T/K	$p(C_3H_8)$ / bar	$p(O_2)$ / bar	$X(C_3H_8)$ / %	$S(C_3H_6)$ / %	STY(C3H6) / $kg \cdot kg^{-1} \cdot h^{-1}$	Ref.
70wt%NiO-$Cs_{2.5}H_{0.5}PMo_{12}O_{40}$	723	0.04	0.16	11.0	75.0	$3.7 \cdot 10^{-2}$	162
$MnMgAlO_x$	873	0.67	0.33	12.9	70.3	$1.0 \cdot 10^{0}$	170
$NiMoO_4$ Direct grinding	873	0.1	0.1	24.9	71.7	$4.0 \cdot 10^{-1}$	163
$NiMoO_4$ co-precipitation	873	0.1	0.1	11.6	71.8		163
Ni-Mo-MgO_x (10 wt%Ni, Ni:Mo=1)	873	0.1	0.05	11.3	81.4	$1.5 \cdot 10^{0}$	164
CrO_x(1 wt%)/C	643	0.68	0.34	11.3	74.8	$4.7 \cdot 10^{-1}$	169
CrO_x(1.5 wt%)/C	673	0.68	0.34	19.8	84	$9.6 \cdot 10^{-1}$	169
CrO_x(5 wt%)/MgO	723	0.68	0.34	10.8	84.1	$5.1 \cdot 10^{-1}$	168
$NiMoO_4$	748	0.1	0.13	14.1	72.0	$3.0 \cdot 10^{-2}$	165
β-$NiMoO_4$	773	0.1	0.1	15.5	74.5	$1.3 \cdot 10^{-1}$	166
BNOH	803	0.17	0.25	20.6	80.6	$3.4 \cdot 10^{-2}$	156
B	763	0.3	0.15	16.4	77.9	$1.1 \cdot 10^{1}$	155
β-$NiMoO_4$,	748	0.1	0.13	14.1	72.0		167
NiO-CeO_2	773	0.18*	0.18	52.0	72.0	$3.8 \cdot 10^{1}$	152
0.5Pt-5Sn/SiO_2(beta)	823	0.1	0.05	48.0	79.0	$1.4 \cdot 10^{0}$	153
Hexagonal BN	833	0.09	0.09	11.3	71.8		157
B(1.2 wt%)/SiO_2	773	0.3	0.15	10.1	73.2		158
B(1.7 wt%)/SiO_2	773	0.3	0.15	10.1	72.6		158
B_2O_3@BPO_4-600	823	0.3	0.15	14.8	76.5	$1.5 \cdot 10^{-1}$	159
B_2O_3@BPO_4-1000	823	0.3	0.15	19.2	70.7	$1.8 \cdot 10^{-1}$	159
B_2O_3@BPO_4-1200	823	0.3	0.15	18.4	71.3	$1.8 \cdot 10^{-1}$	159
B_2O_3(40 wt%)/SiO_2	823	0.3	0.15	12.0	74.4	$1.2 \cdot 10^{-1}$	159
γ-C_3N_4	773	0.45	0.11	12.8	74.0	$1.2 \cdot 10^{-1}$	171
Borosilicate	787	0.17	0.25	20.0	82.0	$7.4 \cdot 10^{-1}$	160
h-BN/Cordierite	776	0.17	0.25	25.7	77.9		161

* In the presence of HCl

Table S3 Catalysts and reaction conditions for the ODP reaction with alternating feeds of propane and air. The catalysts with propene selectivity above 70% at propane conversion larger than 10% have been selected from literature since 2008.

Catalysts	T/K	$p(C_3H_8)$ / bar	X(C3H8) / %	$S(C_3H_6)$ / %	Ref.
VO_x(5 wt%)/γ-Al_2O_3	823		11.7	85.9	[146]
VO_x(7 wt%)/γ-Al_2O_3	823		13.4	75.3	[146]
VO_x(10 wt%)CaO-γ-Al_2O_3 (1:4)	933	1	31	73	[147]
VO_x(10 wt%)CaO-γ-Al_2O_3 (1:1)	933	1	65	85	[147]
VO_x(2.5 wt%)/γ-Al_2O_3	754	1	17.3	82.7	[148]
VO_x(5 wt%)/γ-Al_2O_3	752	1	25.6	88.5	[148]
VO_x(7.5 wt%)/γ-Al_2O_3	750	1	25.7	89.3	[148]
VO_x(2.5 wt%)/ZrO_2-γ-Al_2O_3 (1:1)	726	1	16	85.1	[148]
VO_x(5 wt%)/ZrO_2-γ-Al_2O_3 (1:1)	741	1	25.1	89.7	[148]
VO_x(7.5 wt%)/ZrO_2-γ-Al_2O_3 (1:1)	763	1	24.8	93	[148]
VO_x(10 wt%)/CaO-γ-Al_2O_3 (1:1)	913	1	25.5	94.2	[149]
VO_x(7.5 wt%)/ZrO_2-γ-Al_2O_3 (1:1)			25.5	94	[150]
$MoVO_x$(V/Mo=6)			36	89	[151]

Table S4 Turn over frequency of propene formation ($TOF(C_3H_6)$) and primary ($X(C_3H_8)<10\%$) propene selectivity ($S(C_3H_6)$) over different catalysts.

Catalysts	ω_V / nm^{-2}	T / K	$p(C_3H_8)$ / bar	$p(O_2)$ / bar	$TOF(C_3H_6)$ / s^{-1}	$S(C_3H_6)$ / %	Ref.
V-based catalysts							
VO_x/Al_2O_3	$2.33 \cdot 10^0$	723	0.29	0.14	$5.35 \cdot 10^{-3}$	57.0	[178]
VO_x/Al_2O_3	$5.66 \cdot 10^0$	723	0.29	0.14	$3.25 \cdot 10^{-2}$	46.0	[178]
VO_x/Al_2O_3	$1.04 \cdot 10^1$	723	0.29	0.14	$1.53 \cdot 10^{-2}$	43.0	[178]
VO_x/Al_2O_3	$1.68 \cdot 10^1$	723	0.29	0.14	$1.33 \cdot 10^{-2}$	42.0	[178]
VO_x/Al_2O_3	$1.45 \cdot 10^0$	723	0.48	0.06	$6.04 \cdot 10^{-2}$	56.0	[179]
$VO_x/Ca_5[OH\|(PO_4)_3]$	$2.23 \cdot 10^0$	723	0.14	0.40	$1.43 \cdot 10^{-4}$	36.4	[180]
$VO_x/Ca_5[OH\|(PO_4)_3]$	$12.57 \cdot 10^0$	723	0.14	0.40	$3.18 \cdot 10^{-5}$	37.4	[180]
VO_x/CeO_2	$6.03 \cdot 10^0$	723	0.17	0.09	$1.54 \cdot 10^{-3}$	89.0	[181]
VO_x/CeO_2	$7.16 \cdot 10^1$	723	0.17	0.09	$1.75 \cdot 10^{-4}$	92.0	[181]
VO_x/CeO_2	$1.65 \cdot 10^0$	723	0.1	0.1	$2.53 \cdot 10^{-3}$	11.5	[182]
VO_x/CeO_2	$4.14 \cdot 10^0$	723	0.1	0.1	$2.97 \cdot 10^{-3}$	35.0	[182]
VO_x/CeO_2	$8.27 \cdot 10^0$	723	0.1	0.1	$2.81 \cdot 10^{-3}$	62.4	[182]
VO_x/CeO_2	$1.65 \cdot 10^1$	723	0.1	0.1	$1.67 \cdot 10^{-3}$	69.7	[182]
VO_x/CeO_2	$1.05 \cdot 10^0$	723	0.1	0.1	$1.89 \cdot 10^{-3}$	8.4	[182]
VO_x/CeO_2	$2.62 \cdot 10^0$	723	0.1	0.1	$1.64 \cdot 10^{-3}$	20.3	[182]
VO_x/CeO_2	$5.24 \cdot 10^0$	723	0.1	0.1	$2.11 \cdot 10^{-3}$	40.2	[182]
VO_x/CeO_2	$1.05 \cdot 10^1$	723	0.1	0.1	$1.67 \cdot 10^{-3}$	61.3	[182]
VO_x/MgO	$6.95 \cdot 10^0$	723	0.05	0.05	$1.66 \cdot 10^{-4}$	35.0	[183]
VO_x/MgO	$3.48 \cdot 10^0$	723	0.05	0.05	$4.90 \cdot 10^{-4}$	69.0	[183]
VO_x/SiO_2	$1.55 \cdot 10^0$	723	0.67	0.33	$1.66 \cdot 10^{-3}$	87.0	[191]
VO_x/SiO_2	$1.83 \cdot 10^0$	723	0.67	0.33	$1.72 \cdot 10^{-3}$	84.0	[191]
VO_x/SiO_2	$2.19 \cdot 10^0$	723	0.67	0.33	$1.88 \cdot 10^{-3}$	83.0	[191]
VO_x/SiO_2	$2.58 \cdot 10^0$	723	0.67	0.33	$1.99 \cdot 10^{-3}$	73.0	[191]
VO_x/SiO_2	$3.08 \cdot 10^0$	723	0.67	0.33	$2.47 \cdot 10^{-3}$	71.0	[191]
VO_x/TiO_2	$1.61 \cdot 10^0$	723	0.48	0.06	$6.04 \cdot 10^{-2}$	56	[179]
VO_x/ZrO_2	$2.9 \cdot 10^0$	723	0.05	0.08	$0.81 \cdot 10^0$		[192]
Zn-based catalysts							
ZnO_x/SiO_2	$4.56 \cdot 10^0$	723	0.29	0.14	$6.56 \cdot 10^{-5}$	62.0	[186]
ZnO_x/SiO_2	$9.12 \cdot 10^0$	723	0.29	0.14	$2.54 \cdot 10^{-5}$	24.0	[186]
ZnO_x/SiO_2	$1.37 \cdot 10^1$	723	0.29	0.14	$2.54 \cdot 10^{-5}$	24.0	[186]
ZnO_x/SiO_2	$1.82 \cdot 10^1$	723	0.29	0.14	$2.54 \cdot 10^{-5}$	24.0	[186]
ZnO_x/ZrO_2	$8.69 \cdot 10^0$	723	0.29	0.14	$1.20 \cdot 10^{-4}$	8.0	[186]
ZnO_x/ZrO_2	$1.30 \cdot 10^1$	723	0.29	0.14	$9.90 \cdot 10^{-5}$	9.0	[186]
ZnO_x/ZrO_2	$1.74 \cdot 10^1$	723	0.29	0.14	$1.02 \cdot 10^{-4}$	11.0	[186]
ZnO_x/TiO_2	$1.10 \cdot 10^1$	723	0.29	0.14	$3.51 \cdot 10^{-4}$	20.0	[186]

Catalysts	ω_V / nm^{-2}	T / K	$p(C_3H_8)$ / bar	$p(O_2)$ / bar	$TOF(C_3H_6)$ / s^{-1}	$S(C_3H_6)$ / %	Ref.
ZnO_x/TiO_2	$1.46 \cdot 10^1$	723	0.29	0.14	$2.84 \cdot 10^{-4}$	20.0	[186]
ZnO_x/Al_2O_3	$4.38 \cdot 10^0$	723	0.29	0.14	$6.67 \cdot 10^{-5}$	63.0	[186]
ZnO_x/Al_2O_3	$8.77 \cdot 10^0$	723	0.29	0.14	$4.55 \cdot 10^{-5}$	10.0	[186]
ZnO_x/Al_2O_3	$1.32 \cdot 10^1$	723	0.29	0.14	$2.26 \cdot 10^{-5}$	8.0	[186]
ZnO_x/Al_2O_3	$1.75 \cdot 10^1$	723	0.29	0.14	$1.14 \cdot 10^{-5}$	8.0	[186]
Fe-based catalysts							
$FeO_x/Ca_5[OH\|(PO_4)_3]$	$3.62 \cdot 10^0$	723	0.06	0.03	$1.67 \cdot 10^{-2}$	50.0	[189]
$FeO_x/Ca_5[OH\|(PO_4)_3]$	$6.69 \cdot 10^0$	723	0.06	0.03	$8.29 \cdot 10^{-3}$	51.5	[189]
$FeO_x/Ca_5[OH\|(PO_4)_3]$	$8.95 \cdot 10^0$	723	0.06	0.03	$5.81 \cdot 10^{-3}$	50.0	[189]
$FeO_x/Ca_5[OH\|(PO_4)_3]$	$1.12 \cdot 10^1$	723	0.06	0.03	$4.08 \cdot 10^{-3}$	34.0	[189]
$FeO_x/Ca_5[OH\|(PO_4)_3]$	$1.23 \cdot 10^1$	723	0.06	0.03	3.19·10-3	31.0	[189]
Co-based catalysts							
$CoO_x/MgAlO_x$	$2.56 \cdot 10^0$	723	0.29	p(oxidant), bar	$1.07 \cdot 10^{-3}$	96.4	[188]
$CoO_x/MgAlO_x$	$9.96 \cdot 10^0$	723	0.29	0.14	$4.37 \cdot 10^{-4}$	96.6	[188]
$CoO_x/MgAlO_x$	$9.80 \cdot 10^0$	723	0.29	0.14	$1.63 \cdot 10^{-4}$	92.5	[188]
$CoO_x/MgAlO_x$	$1.79 \cdot 10^1$	723	0.29	0.14	$2.73 \cdot 10^{-4}$	92.6	[188]
B-based catalysts							
B/C	$1.07 \cdot 10^0$	723	0.03	p(oxidant), bar	$2.42 \cdot 10^{-4}$	51.9	[187]
B/C	$2.67 \cdot 10^0$	723	0.03	0.03	$7.93 \cdot 10^{-5}$	54.7	[187]
B/C	$5.40 \cdot 10^0$	723	0.03	0.03	$2.43 \cdot 10^{-5}$	57.6	[187]
B/C	$8.79 \cdot 10^0$	723	0.03	0.03	$1.23 \cdot 10^{-5}$	64.0	[187]
B/C	$1.64 \cdot 10^1$	723	0.03	0.03	$4.83 \cdot 10^{-6}$	61.7	[187]

Table S5 Turn over frequency of propene formation ($TOF(C_3H_6)$) and primary ($X(C_3H_8)<10\%$) propene selectivity ($S(C_3H_6)$) over different V-based catalysts at different temperatures.

Catalysts	ω_V / nm^{-2}	ω_{Me} / nm^{-2}	T /K	$p(C_3H_8)$ / bar	$p(O_2)$ / bar	$TOF(C_3H_6)$ / s^{-1}	$S(C_3H_6)$ / %	Ref.
MoO_x as a promoter for VO_x								
VO_x/SiO_2	0.72		713	0.1	0.05	$4.0 \cdot 10^{-4}$	57.4	[204]
$Mo\text{-}VO_x/SiO_2$	0.76	0.49	713	0.1	0.05	$2.6 \cdot 10^{-4}$	75.5	[204]
$Mo\text{-}VO_x/SiO_2$	0.56	0.79	713	0.1	0.05	$2.4 \cdot 10^{-4}$	79.6	[204]
$Mo\text{-}VO_x/SiO_2$	0.5	1.26	713	0.1	0.05	$2.2 \cdot 10^{-4}$	80.2	[204]
$Mo\text{-}VO_x/SiO_2$	0.36	1.82	713	0.1	0.05	$2.4 \cdot 10^{-4}$	81.7	[204]
VO_x/SiO_2	0.72		733	0.1	0.05	$7.3 \cdot 10^{-4}$	58.3	[204]
$Mo\text{-}VO_x/SiO_2$	0.76	0.49	713	0.1	0.05	$5.0 \cdot 10^{-4}$	68.0	[204]
$Mo\text{-}VO_x/SiO_2$	0.56	0.79	713	0.1	0.05	$4.8 \cdot 10^{-4}$	72.9	[204]
$Mo\text{-}VO_x/SiO_2$	0.5	1.26	713	0.1	0.05	$4.7 \cdot 10^{-4}$	72.3	[204]
$Mo\text{-}VO_x/SiO_2$	0.36	1.82	713	0.1	0.05	$5.6 \cdot 10^{-4}$	75.1	[204]
F as a promoter for VO_x								
$F\text{-}VO_x/SiO_2$	4.79	$3.44 \cdot 10^{1}$	753	0.10	0.05	$4.43 \cdot 10^{-4}$	74.9	[201]
$F\text{-}VO_x/SiO_2$	4.79	$3.44 \cdot 10^{1}$	813	0.10	0.05		64.1	[201]
$F\text{-}VO_x/SiO_2$	5.23	$3.76 \cdot 10^{1}$	753	0.10	0.05	$2.15 \cdot 10^{-4}$	73.0	[201]
$F\text{-}VO_x/SiO_2$	5.23	$3.76 \cdot 10^{1}$	813	0.10	0.05	$3.55 \cdot 10^{-4}$	63.1	[201]
$F\text{-}VO_x/SiO_2$	5.81	$4.17 \cdot 10^{1}$	753	0.10	0.05	$1.82 \cdot 10^{-4}$	60.1	[201]
$F\text{-}VO_x/SiO_2$	5.81	$4.17 \cdot 10^{1}$	813	0.10	0.05		53.4	[201]
K_2O as promoter for VO_x								
$K\text{-}VO_x/SiO_2$	0.44	$1.58 \cdot 10^{-1}$	823	0.10	0.1	$1.69 \cdot 10^{-3}$	37.2	[207]
NbO_x as promoter for VO_x								
$Nb\text{-}VO_x/SiO_2$	0.89	$5.73 \cdot 10^{-1}$	773	0.10	0.05	$8.46 \cdot 10^{-4}$	81.8	[208]
$Nb\text{-}VO_x/SiO_2$	0.84	$5.43 \cdot 10^{-1}$	773	0.10	0.05	$9.78 \cdot 10^{-4}$	93.5	[208]
$Nb\text{-}VO_x/SiO_2$	0.88	$5.66 \cdot 10^{-1}$	773	0.10	0.05	$8.98 \cdot 10^{-4}$	92.8	[208]
vanadyl phosphate								
$P\text{-}VO_x/Al_2O_3$	4.7	4.7	723	0.05	0.03	$6 \cdot 10^{-3}$	71.9	[206]
$P\text{-}VO_x/ZrO_2$	4.7	4.7	723	0.05	0.03	$1.7 \cdot 10^{-2}$	57.9	[206]
$P\text{-}VO_x/TiO_2$	5.15	5.15	723	0.05	0.03	$1 \cdot 10^{-2}$	75.4	[206]
MgO as promoter for VO_x								
VO_x/Al_2O_3	5.6		773	0.05	0.05	$1.78 \cdot 10^{-2}$	66.6	[197]
$MgO\text{-}VO_x/Al_2O_3$	7.1	3.38	773	0.05	0.05	$9.75 \cdot 10^{-3}$	73.1	[197]
$MgO\text{-}VO_x/Al_2O_3$	6.0	3.0	773	0.05	0.05	$9.97 \cdot 10^{-3}$	74.8	[197]
$MgO\text{-}VO_x/Al_2O_3$	5.76	2.64	773	0.05	0.05	$8.39 \cdot 10^{-3}$	70.2	[197]

Catalysts	ω_V / nm^{-2}	ω_{Me} / nm^{-2}	T /K	$p(C_3H_8)$ / bar	$p(O_2)$ / bar	$TOF(C_3H_6)$ / s^{-1}	$S(C_3H_6)$ / %	Ref.
VO_x/Al_2O_3	5.56		773	0.05	0.05	$1.5 \cdot 10^{-2}$	68.4	[198]
MgO-VO_x/Al_2O_3	7.03	3.46	773	0.05	0.05	$3.7 \cdot 10^{-3}$	73.3	[198]
MgO-VO_x/Al_2O_3	6.7	5.97	773	0.05	0.05	$5.8 \cdot 10^{-3}$	78.8	[198]
MgO-VO_x/Al_2O_3	6.62	9.03	773	0.05	0.05	$3.7 \cdot 10^{-3}$	79.7	[198]
$VO_x/SiZrO_2$ (3.5 wt% SiO_2)	9		713	0.143	0.286	$1.28 \cdot 10^{-3}$	49.4	[205]
Sb-$VO_x/SiZrO_2$ (3.5 wt% SiO_2)	1.13	3.38	713	0.143	0.286	$1.49 \cdot 10^{-3}$	14	[205]
Sb-$VO_x/SiZrO_2$ (3.5 wt% SiO_2)	2.25	6.75	713	0.143	0.286	$9.87 \cdot 10^{-4}$	60.5	[205]
Sb-$VO_x/SiZrO_2$ (3.5 wt% SiO_2)	4.5	$1.35 \cdot 10^{1}$	713	0.143	0.286	$9.17 \cdot 10^{-4}$	43.5	[205]

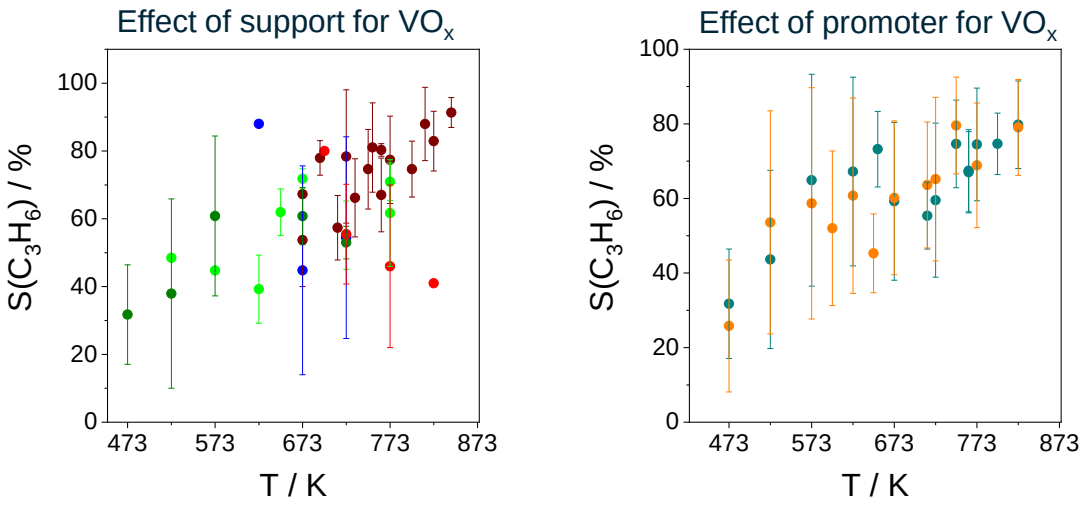

Figure S1 Averaged propene selectivity calculated from literature data obtained at a propane conversion below 10% at different temperatures. The colours distinguish different supports (Al_2O_3, CeO_2, SiO_2, TiO_2 or MgO), (●) supported catalysts with VO_x exclusively (●), all catalysts containing V (●).