Supporting Information

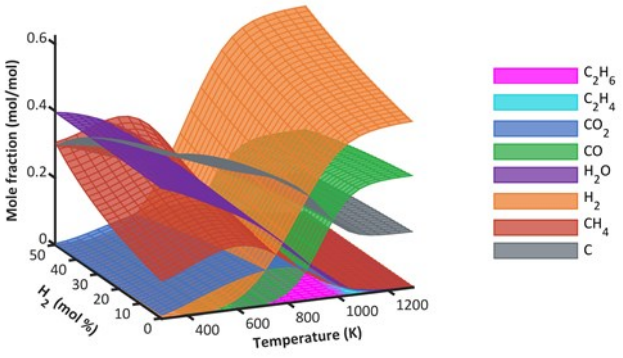

Figure S1 – Thermodynamically predicted equilibrium composition of the CO_2-ODH total system as a function of temperature and H_2 co-feeding, at a feed composition of CO_2 : C_2H_6 of 1 and 1 bar pressure.

Gibbs free energy (ΔG) of total system as a function of temperature and pressure, with n_i, the molar concentration and μ_i, the chemical potential of species i.

$$\Delta G^{system}_{T,P} = \sum n_i \mu_i \qquad \text{S-Eq.1}$$

with

$$\mu_i^{T,P} = \Delta G_T^f + RTln\frac{\frac{n_i}{\sum n}P}{100kPa} \qquad \text{S-Eq. 2}$$

and

$$\Delta G_T^f = T\left(\frac{\Delta G^f_{298K}}{T_0} - \left[\left(-aT_0 - \frac{1}{2}bT_0^2 + \frac{c}{T_0} - \frac{1}{3}dT_0^3 + \Delta H^f_{298K}\right)\left(\frac{1}{T_0} - \frac{1}{T}\right) + a(lnT - lnT_0) + \frac{1}{2}b(T - T_0) + \frac{1}{2}c\left(\frac{1}{T^2} - \frac{1}{T_0^2}\right) + \frac{1}{6}d(T^2 - T_0^2)\right]\right) \qquad \text{S-Eq. 3}$$

Thermodynamic properties from Knacke et al.[1] and Barin[2].

The conversion of the reactant (i) is defined as follows:

$$X_{reactant\ i}(\%) = \left(\frac{[i]_{inlet} - [i]_{outlet}}{[i]_{inlet}}\right) \cdot 100\% \qquad \text{S-Eq. 4}$$

The selectivity of a carbonaceous product i is defined as the concentration of product i corrected to the number of carbons in the product, devided by the sum of all products corrected to the number of carbons in each product:

$$S_{carbon\ product\ i}(C - \%) = \left(\frac{n_C^i \cdot [i]}{\sum n^i \cdot [i]}\right) \cdot 100\% \qquad \text{S-Eq. 5}$$

Ethylene yield is defined as the concentration of ethylene devided by the inlet concentration of ethane:

$$Y_{C_2H_4}(\%) = \left(\frac{[C_2H_4]}{[C_2H_6^{inlet}]}\right) \cdot 100\% \qquad \text{S-Eq. 6}$$

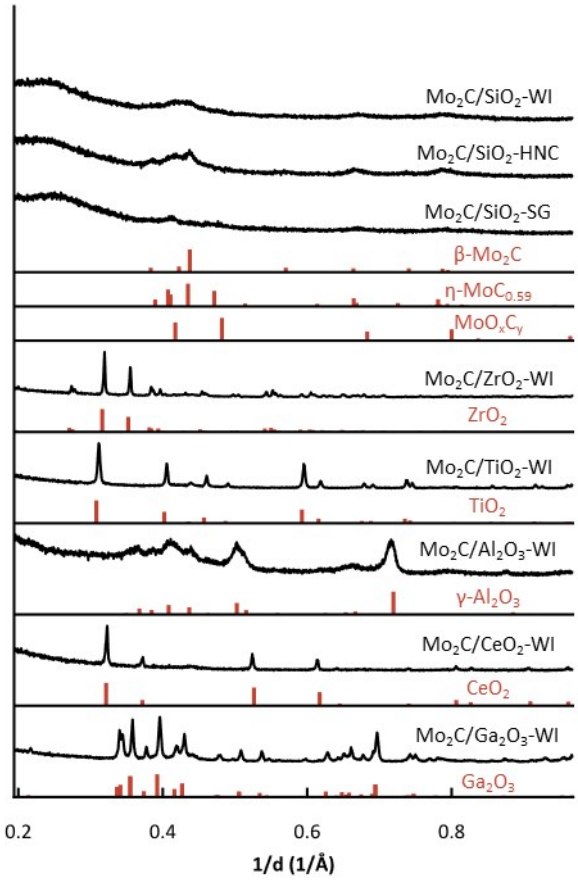

Figure 2. XRD profiles of freshly carburized catalysts (in black) and their corresponding reference patterns (in red)

Table S1. Overview of chemical and physical properties of fresh catalysts determined using BET and ICP-OES analysis.

Sample Name	Mo content (wt.-%)	BET (m^2/g)	Pore volume (cm^3/g)	Pore width (Å)
Mo_2C/SiO_2-WI[3]	18	123	0.95	335
Mo_2C/SiO_2-SG[3]	18	176	0.86	174
Mo_2C/SiO_2-HNC	15	119	0.79	272
Mo_2C/ZrO_2-WI	20	8	0.03	181
Mo_2C/TiO_2-WI	21	19	0.12	301
Mo_2C/Al_2O_3-WI	17	84	0.54	255
Mo_2C/CeO_2-WI	17	8	0.05	220
Mo_2C/Ga_2O_3-WI	19	7	0.03	255

Table S2. Raman bands observed in literature of their respective metal oxide materials.

	MoO_3-orthorhombic[4]	ZrO_2-monoclinic	TiO_2-rutile[5]	CeO_2[6]	β-Ga_2O_3[7]
Raman bands	114 cm^{-1}	117-189 cm^{-1} pair	134 cm^{-1}	250 cm^{-1}	201 cm^{-1}
	127 cm^{-1}	222 cm^{-1}	231 cm^{-1}	464 cm^{-1}	350 cm^{-1}
	158 cm^{-1}	330 cm^{-1}	438 cm^{-1}	550 cm^{-1}	417 cm^{-1}
	196 cm^{-1}	376 cm^{-1}	604 cm^{-1}	595 cm^{-1}	527 cm^{-1}
	218 cm^{-1}	473 cm^{-1}		830 cm^{-1}	631 cm^{-1}
	245 cm^{-1}	633 cm^{-1}		860 cm^{-1}	653 cm^{-1}
	283 cm^{-1}			950 cm^{-1}	767 cm^{-1}
	292 cm^{-1}			1170 cm^{-1}	
	335 cm^{-1}				
	364 cm^{-1}				
	379 cm^{-1}				
	665 cm^{-1}				
	817 cm^{-1}				
	995 cm^{-1}				

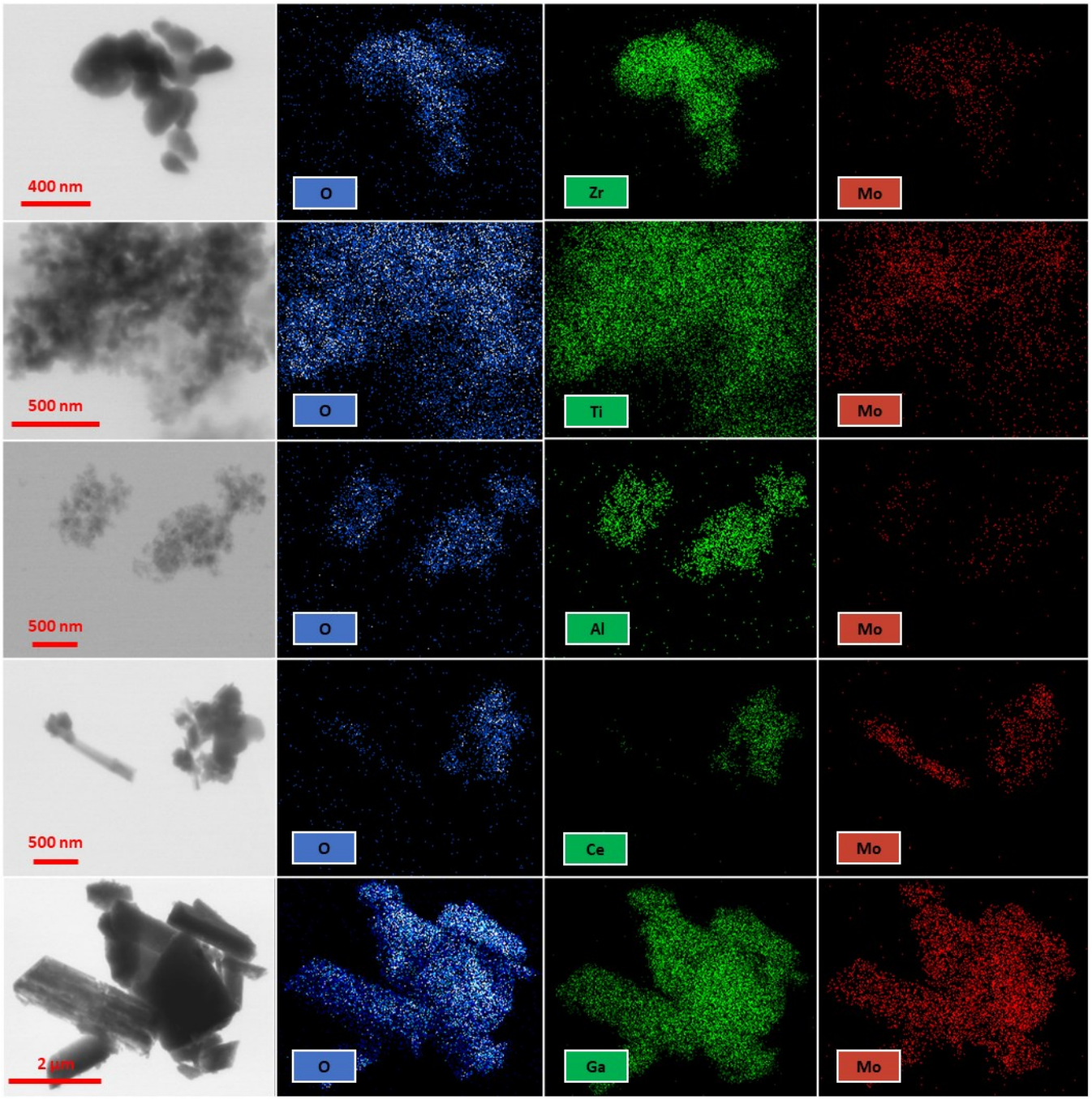

Figure S3. SEM-EDS images and elemental mapping of Mo_2C supported on various metal oxide supports via wet impregnation.

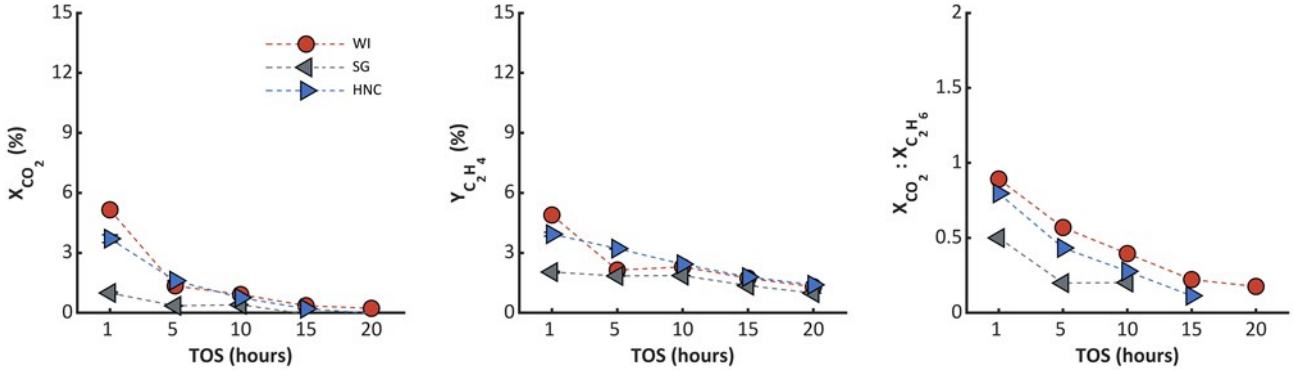

Figure S4. CO_2 conversion, ethylene yield and conversion ratio of Mo_2C/SiO_2-WI, Mo_2C/SiO_2-SG and Mo_2C/SiO_2-HNC. Conditions: T = 873 K, P = 1 bar, SV = 15 L/h·g_{cat}^{-1}, $CO_2 : C_2H_6$ = 1.

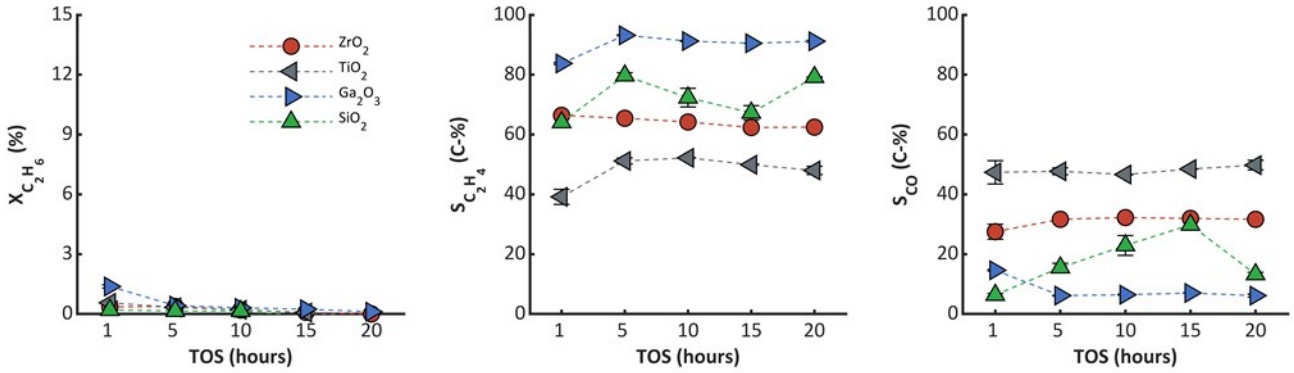

Figure S5. C_2H_6 conversion, C_2H_4 selectivity and CO selectivity of pure metal oxides, ZrO_2, TiO_2, Ga_2O_3 and SiO_2. Conditions: temperature = 873 K, pressure = 1 bar, space velocity = 15 L/h·g_{cat}^{-1}, $CO_2 : C_2H_6$ ratio = 1.

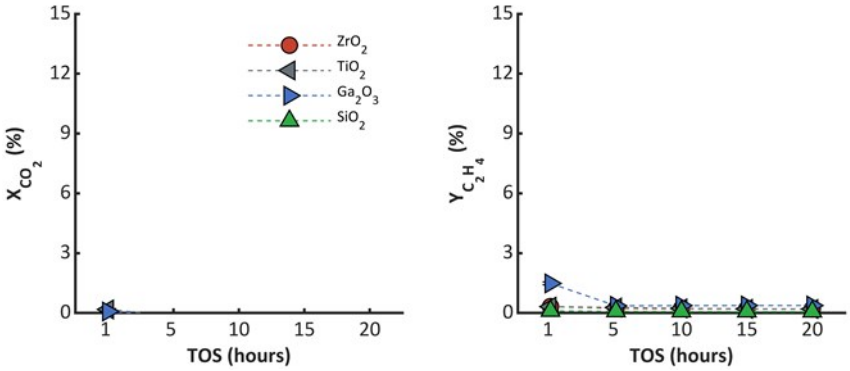

Figure S6. CO_2 conversion and ethylene yield of bulk support materials. Conditions: T = 873 K, P = 1 bar, SV = 15 L/h·g_{cat}^{-1}, $CO_2 : C_2H_6$ = 1.

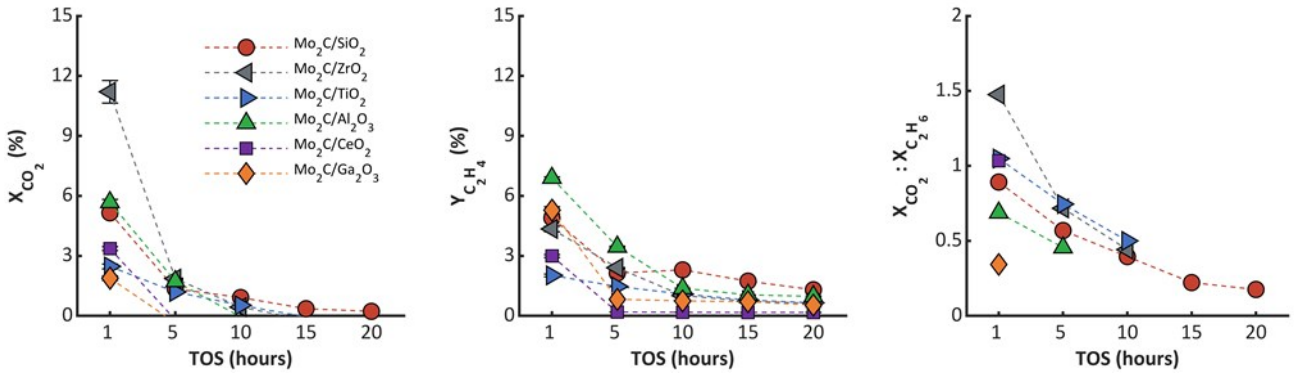

Figure S7. CO_2 conversion, ethylene yield and conversion ratio of Mo_2C/MOx-WI on various metal oxide support materials. Conditions: T = 873 K, P = 1 bar, SV = 15 L/h·g_{cat}^{-1}, CO_2 : C_2H_6 = 1.

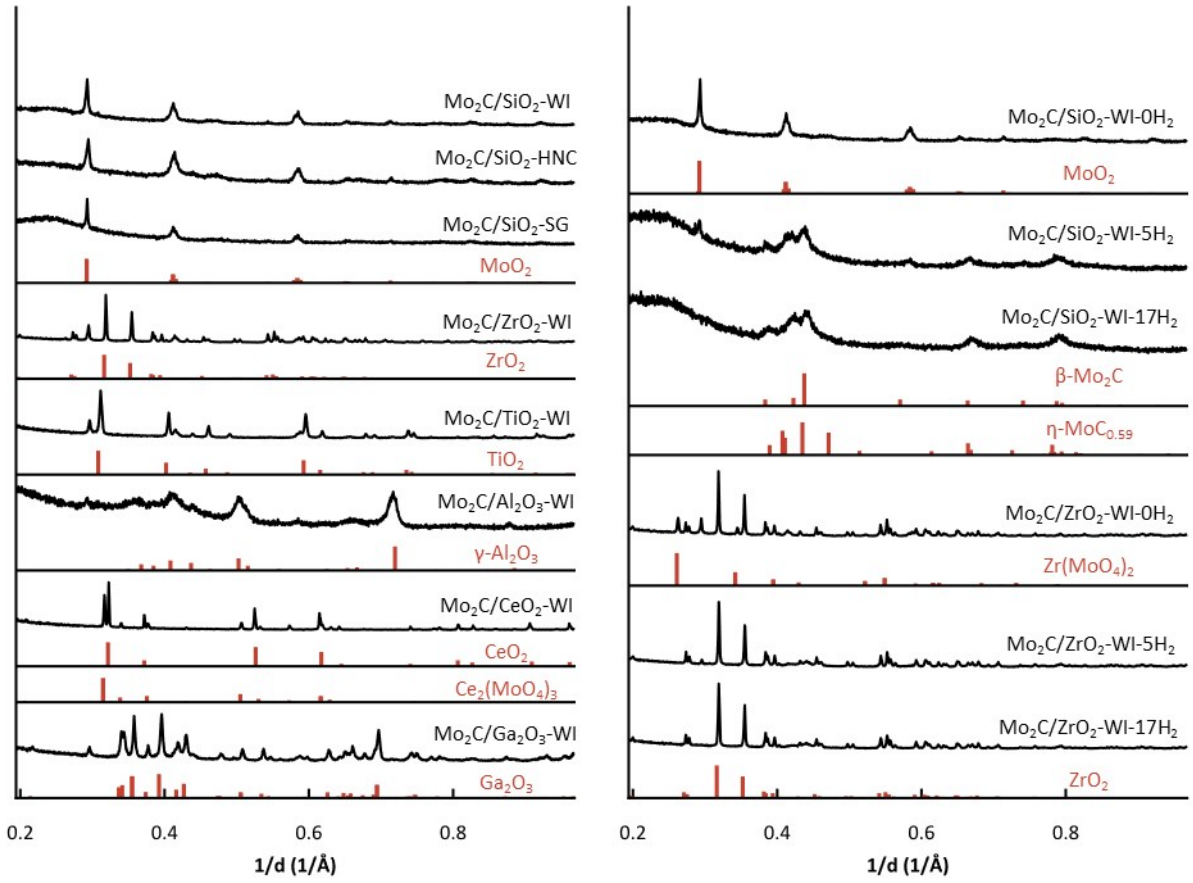

Figure S8. XRD profiles of spent CO_2-ODH (left) and CO_2/H_2-ODH (right) catalysts (in black) and their corresponding reference patterns (in red).

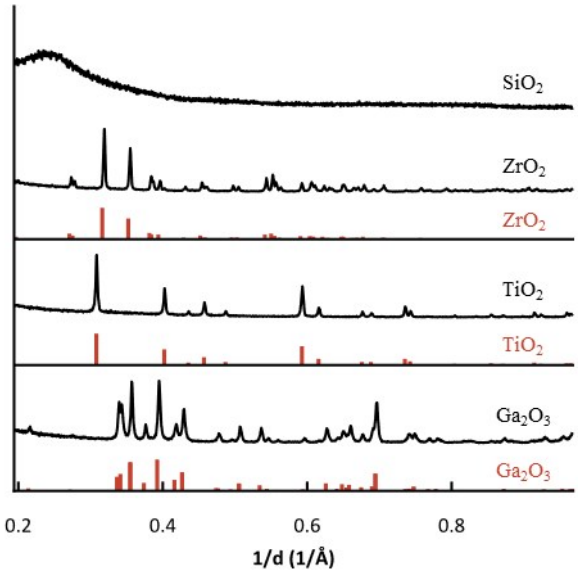

Figure S9. XRD profiles of spent CO_2-ODH bulk metal oxide support materials.

Table S3. Overview of phase quantification and crystallite size determined via Rietveld refinement of spent catalysts, with and without H_2 co-feeding. Bracketed values for SiO_2 supported samples are normalized to total Mo content obtained by ICP-OES. Mo_2C/SiO_2-WI and Mo_2C/SiO_2-SG are adapted from Marquart et al.[3].

Sample Name	Support		β-Mo_2C		η-$MoC_{0.59}$		MoO_xC_y		MoO_2		MoO_3		$Ce_2(MoO_4)_3$ / $Zr(MoO_4)_2$	
	wt.-%	nm	wt.-%	nm	wt.-%	nm	wt.-%	nm	wt.-%	nm	wt.-%	nm	wt.-%	nm
Spent catalysts – CO_2 ODH														
Mo_2C/SiO_2-WI	-	-	-	-	29.3 ± 0.9 (Norm. 5.6)	6.5 ± 0.4	-	-	70.2 ± 1.2 (Norm. 13.5)	30.5 ± 0.9	0.5 ± 1.1 (Norm. 0.1)	57.9 ± 25.6		
Mo_2C/SiO_2-SG	-	-	-	-	-	-	33.8 ± 2.1 (Norm. 6.5)	6.6 ± 0.8	66.2 ± 2.1 (Norm. 12.7)	49.7 ± 3.0	-	-	-	-
Mo_2C/SiO_2-HNC	-	-	-	-	50.1 ± 0.7 (Norm. 7.8)	4.9 ± 0.2	-	-	49.9 ± 0.7 (Norm. 7.8)	22.3 ± 0.8	-	-	-	-
Mo_2C/ZrO_2-WI	79.6 ± 0.3	75.3 ± 1.0	-	-	-	-	-	-	18.9 ± 0.2	46.4 ± 1.4	-	-	1.5 ± 0.2	59.8 ± 14.7
Mo_2C/TiO_2-WI	89.2 ± 0.2	39.2 ± 0.5	-	-	-	-	-	-	10.8 ± 0.2	31.9 ± 1.4	-	-	-	-
Mo_2C/Al_2O_3-WI	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Mo_2C/CeO_2-WI	47.2 ± 0.4	113.1 ± 2.5	-	-	-	-	-	-	-	-	-	-	52.8 ± 0.4	94.3 ± 3.7
Mo_2C/Ga_2O_3-WI	85.5 ± 0.5	29.6 ± 0.3	2.0 ± 0.2	15.9 ± 2.2	7.2 ± 0.4	3.6 ± 0.3	-	-	5.3 ± 0.2	28 ± 1.8	-	-	-	-
Spent catalysts – H_2/CO_2 ODH														
Mo_2C/SiO_2-WI-0H_2	-	-	-	-	37.7 ± 0.8 (Norm. 7.3)	5.7 ± 0.3	-	-	62.3 ± 0.8 (Norm. 12.0)	34.0 ± 1.1	-	-	-	-
Mo_2C/SiO_2-WI-5H_2	-	-	40.8 ± 1.7 (Norm. 7.9)	6.2 ± 0.4	52.3 ± 1.7 (Norm. 10.1)	3.6 ± 0.2	-	-	6.9 ± 0.6 (Norm. 1.3)	46.0 ± 8.3	-	-	-	-
Mo_2C/SiO_2-WI-17H_2	-	-	53.9 ± 2.0 (Norm. 10.4)	4.6 ± 0.3	46.1 ± 2.0 (Norm. 8.9)	6.1 ± 0.4	-	-	-	-	-	-	-	-
Mo_2C/ZrO_2-WI-0H_2	76.1 ± 0.3	74.3 ± 1.0							12.0 ± 0.2	48.8 ± 2.1	-	-	11.9 ± 0.2	48.9 ± 2.1
Mo_2C/ZrO_2-WI-5H_2	79.9 ± 0.4	69.6 ± 0.9	17.5 ± 0.4	5.3 ± 0.2	-	-	-	-	2.6 ± 0.1	88.9 ± 12.9	-	-	-	-
Mo_2C/ZrO_2-WI-17H_2	79.8 ± 0.4	66.9 ± 0.9	20.2 ± 0.4	4.3 ± 0.2	-	-	-	-	-	-	-	-	-	-

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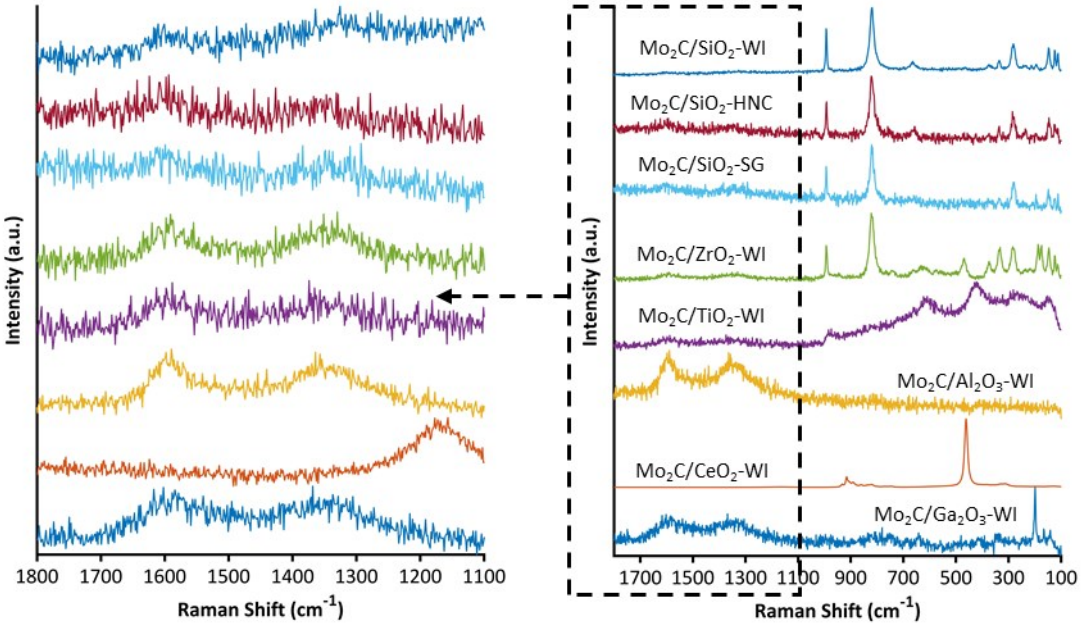

Figure S10. Raman spectra collected of spent CO_2-ODH supported Mo_2C catalysts.

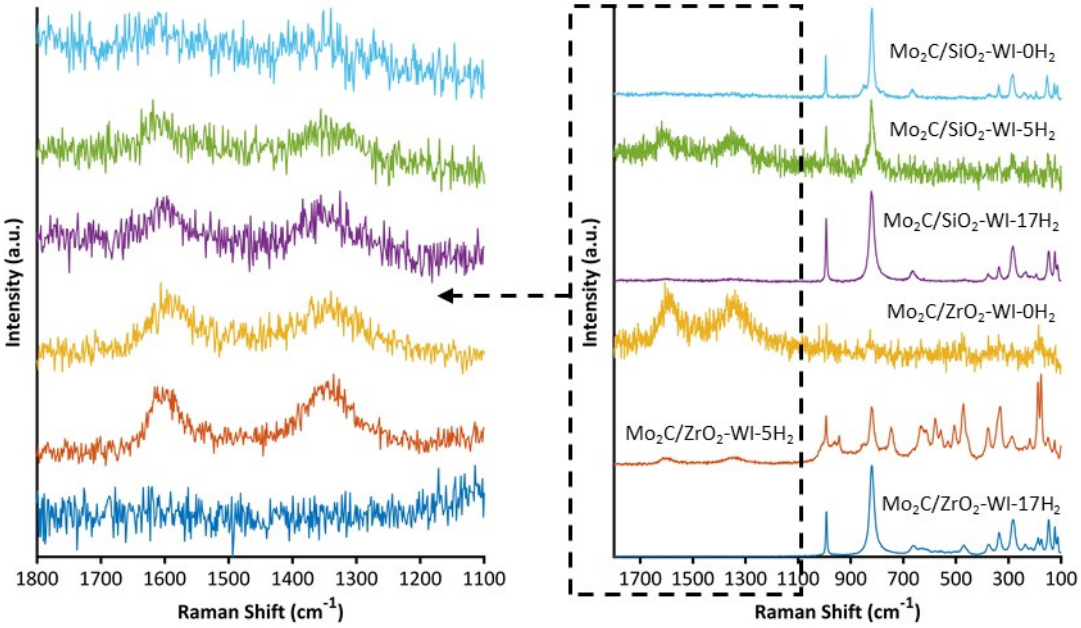

Figure S11. Raman spectra collected of spent H_2/CO_2-ODH supported Mo_2C catalysts.

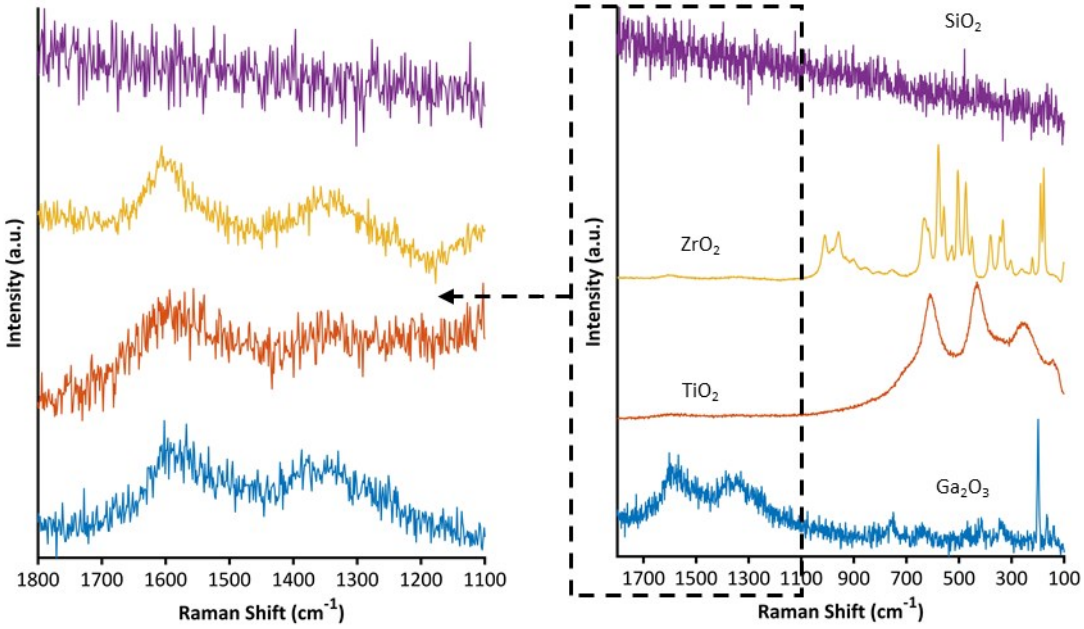

Figure S12. Raman spectra collected of spent CO_2-ODH bulk metal oxide support materials.

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