Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

CO_2 Assisted Ethane Oxidative Dehydrogenation Over MoO_x catalysts supported on Reducible CeO_2-TiO_2

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Supporting Information

S1 Synthesis parameters and physicochemical characterization of mixed CeO_2-TiO_2

Table S1: Synthesis details and properties of bare supports

Materials	Calcination Temperature (°C)	Molar ratio of Ce to Ti	BET surface area (m^2/g)	Literature surface area (m^2/g)
1CeTi	600	0.01	41.5	51[1], 31-59[2]
5CeTi	600	0.05	69.1	
10CeTi	600	0.1	88.4	
P25	-	0	55	-
5Mo/1CeTi	600	0.01	28.1	-
5Mo/5CeTi	600	0.05	46.2	-
5Mo/10CeTi	600	0.1	52.5	-
5Mo/P25	600	0	41.4	-

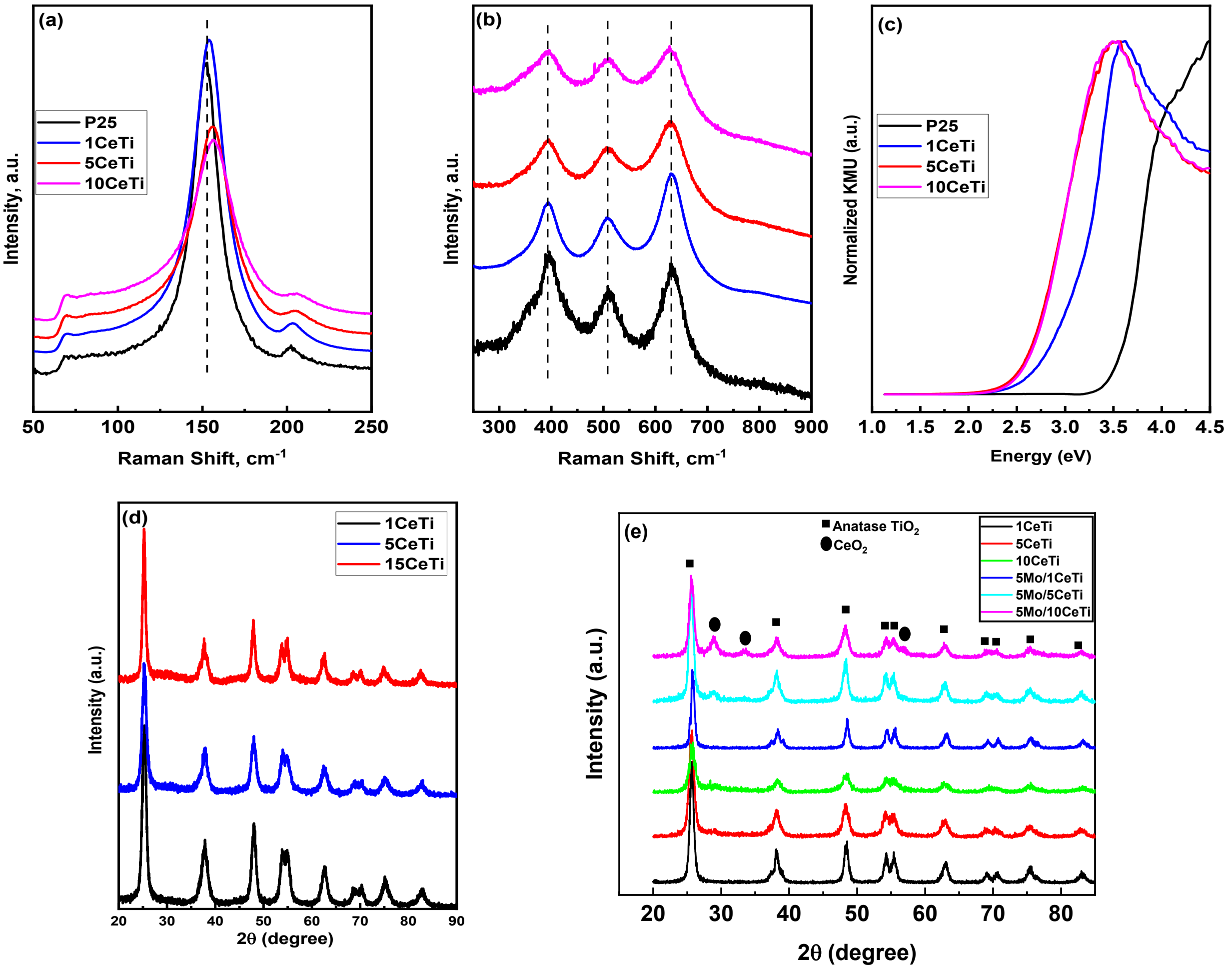

Figure S1: Physicochemical characterization of all bare supports by utilizing (a and b) Raman spectroscopy, (c) UV-vis spectroscopy, (d) X-ray diffraction of supports and (e) X-ray diffraction of all catalysts

Materials	Molar ratio of Ce to Ti	TiO_2-Anatase Crystallite size (nm)	Unit cell parameters TiO_2 - Anatase		` Unit cell parameters Cubic CeO_2
			a	*c*	*a*
1CeTi	0.01	16.9	3.7852	9.5109	-
5CeTi	0.05	11.3	3.7905	9.512	-
10CeTi	0.1	10.2	3.798	9.527	-
5Mo/1CeTi	0.01	22.9	3.785	9.509	-
5Mo/5CeTi	0.05	15.2	3.788	9.511	5.414
5Mo/10CeTi	0.1	13.3	3.789	9.510	5.413

Table S2: Analysis of XRD data, crystallite size and unit cell parameters

Characterization techniques including BET, Raman spectroscopy, UV-vis spectroscopy, XRD were performed and the results were summarized in **Table S1, Table S2** and **Figure S1**. When ceria was introduced into anatase phase via sol-gel method, UV-vis absorption features of mixed oxide were shifted to lower energy region as reported in the literature[26]. It could be observed that the surface area of mixed oxide supports was larger than pure, commercial anatase material and were comparatively similar to flame synthesized titania (P25). It was reported that mixed CeO_2-TiO_2 samples had larger surface area since the great difference of Ti^{4+} and Ce^{4+} radii caused significant difficulties in particle agglomeration and phase sintering[26]. As a result, as more ceria was incorporated in the mixed oxide materials, the crystallinity of the TiO_2 anatase phase decreased, as demonstrated in the literature[26-28,30,32,33]. This behavior was also seen in the characterization via XRD and Raman spectroscopy. As more ceria was added into the mixed oxide,

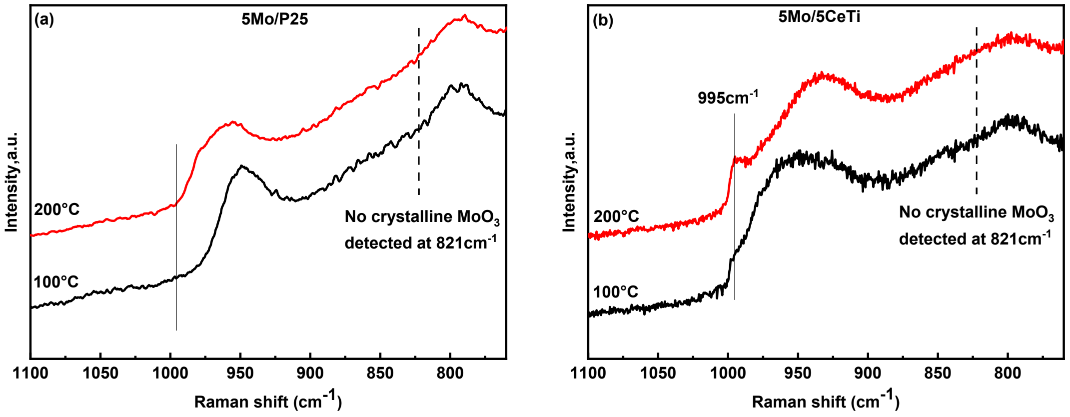

Figure S2: Low temperature Raman spectra of (a) 5Mo/P25 and (b) 5Mo/5CeTi catalysts.

the intensity of the main peaks in XRD and Raman spectra results representing anatase phase were significantly reduced featuring the smaller crystallite size of this phase. Since features of rutile and ceria phases were absent in Raman and XRD characterization, it could be argued as suggested in other reports that small ceria domains could hinder the formation of rutile while remaining as small dispersed clusters [22,25–28].

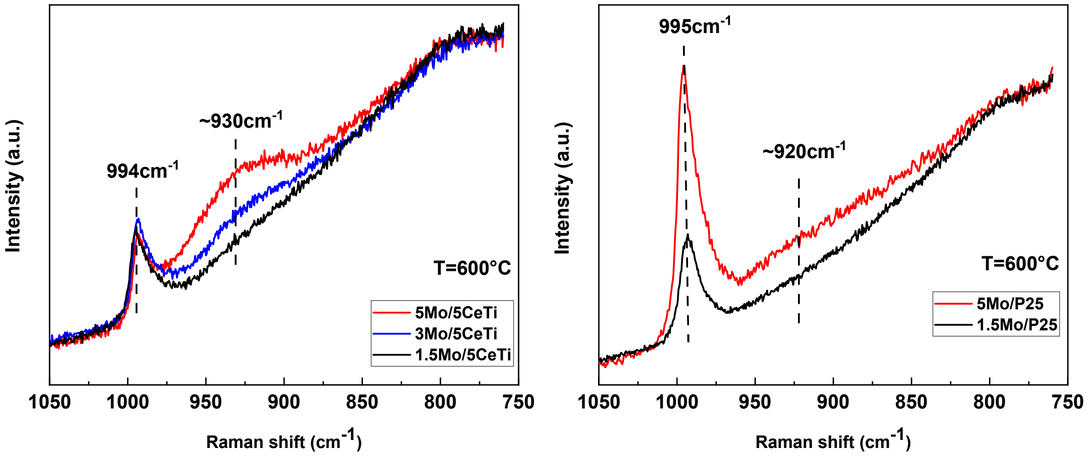

Figure S3: Raman spectra of 1.5Mo/5CeTi, 3Mo/5CeTi, 5Mo/5CeTi and 1.5Mo/P25, 5Mo/P25 at 600 °C under an air flow

S2. Catalytic performance of supported Mo on P25 and mixed CeO_2-TiO_2

Selectivity data of the bare supports as well as supported catalysts are summarized in Table S2. P25 shows an 11.5% ethane conversion while the initial ethylene selectivity is 82%. By incorporating different amounts of CeO_2 in the mixed supports significant changes pertaining to ethylene selectivity can be seen. The ethane conversion decreased at high CeO_2 content. Initial selectivity to total COx, as oxidation/combustion products is reported as:

$$\%S_{COx} = 100 - S_{C_2H_4} - S_{CH_4}$$

Table S3: Carbon balance and selectivity to detected products over all materials at 600 °C under a flow of 20 mL containing 5 % C_2H_6, 5 % CO_2 and 90 % N_2

Catalyst	C_2H_6 conversion (%)	C_2H_4 selectivity (%)	CH_4 selectivity (%)	CO_x selectivity (%)	Overall carbon balance (%)
TiO_2 (Anatase)	0.87	80	-	19.85	99.8
P25	11.55	82.36	2	17.6	98.8
1CeTi	12.40	82.37	2	17.6	98.5
5CeTi	11.04	59.33	0.6	24.3	98.7
10CeTi	6.77	57.71	1.3	42.3	98.2
5Mo/TiO_2 (Anatase)	1.93	46	-	53.34	99.3
5Mo/P25	17.21	56.52	2.9	36.8	99.2
5Mo/1CeTi	15.88	68.40	0.5	25.5	99.3
5Mo/5CeTi	15.37	72.49	1.23	26.8	99.8
5Mo/10CeTi	10.62	65.03	-	30.9	98.2

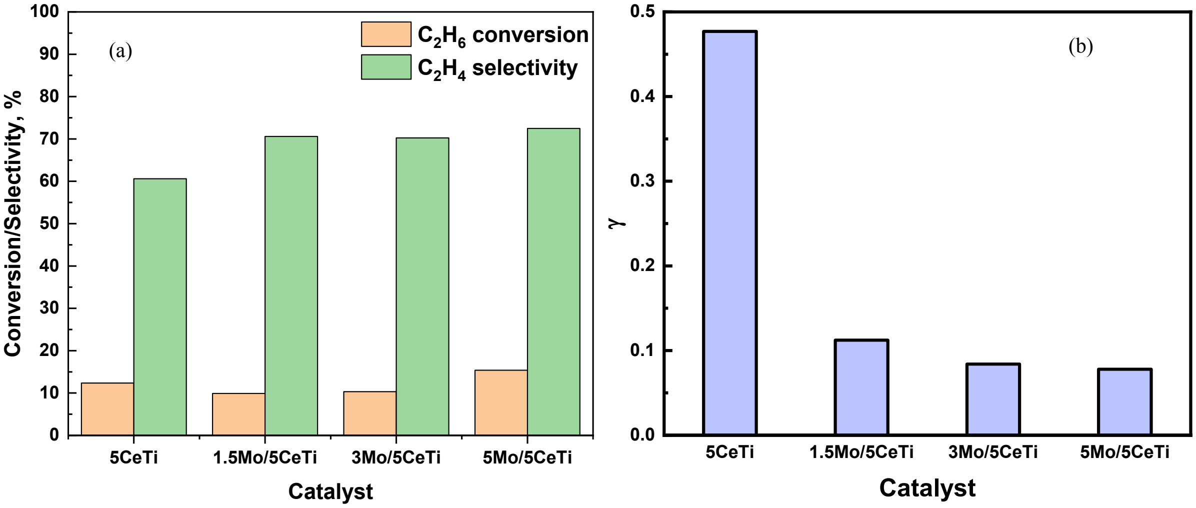

Figure S4: Dependence of catalytic performance over (a) Mo loadings at 600 °C under a flow of 20 mL containing 5 % C_2H_6, 5 % CO_2, and 90 % N_2. (b) The dependence of ratio on Mo loadings

γ

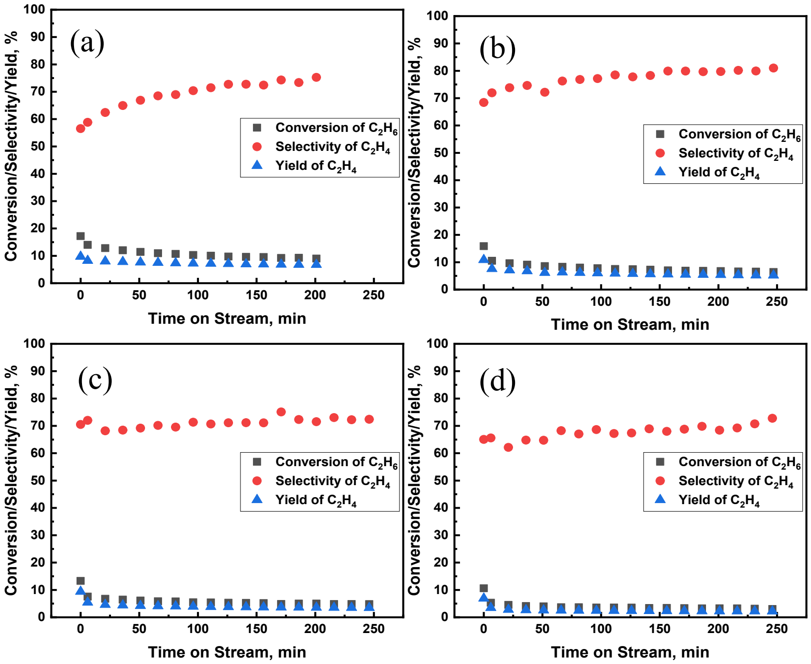

Figure S5: Ethane conversion, selectivity to ethylene, and yield of ethylene over supported Mo on (a) P25, (b) 1CeTi, (c) 5CeTi, (d)10CeTi at 600 °C, under a 20 mL/min flow containing 5 % C_2H_6, 5 % CO_2, and 90 % N_2

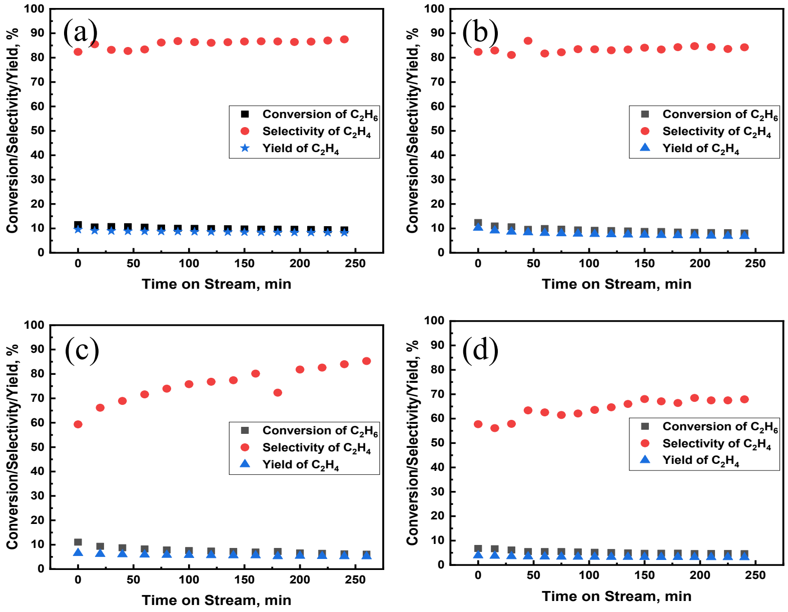

Figure S6 Ethane conversion, selectivity to ethylene, and yield of ethylene over bare support on (a) P25, (b) 1CeTi, (c) 5CeTi, (d)10CeTi at 600 °C, under a 20 mL/min flow containing 5 % C_2H_6, 5 % CO_2, and 90 % N_2

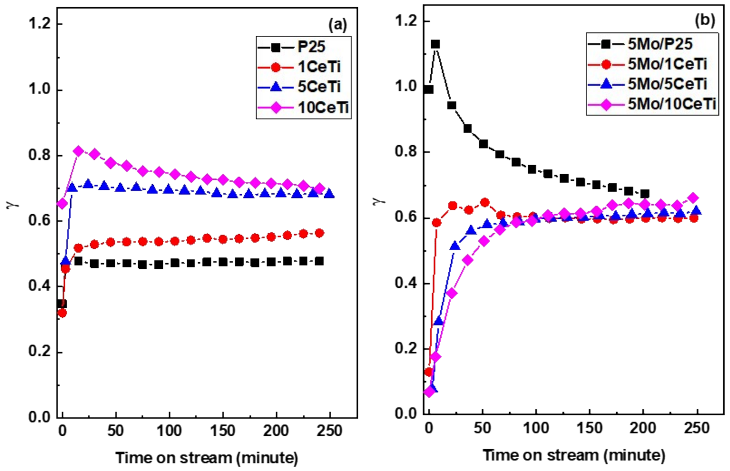

Figure S7: γ ratio of (a) bare supports and (b) Mo catalysts in reaction carried out 600 °C, under a 20 mL/min flow containing 5 % C_2H_6, 5 % CO_2, and 90 % N_2 and

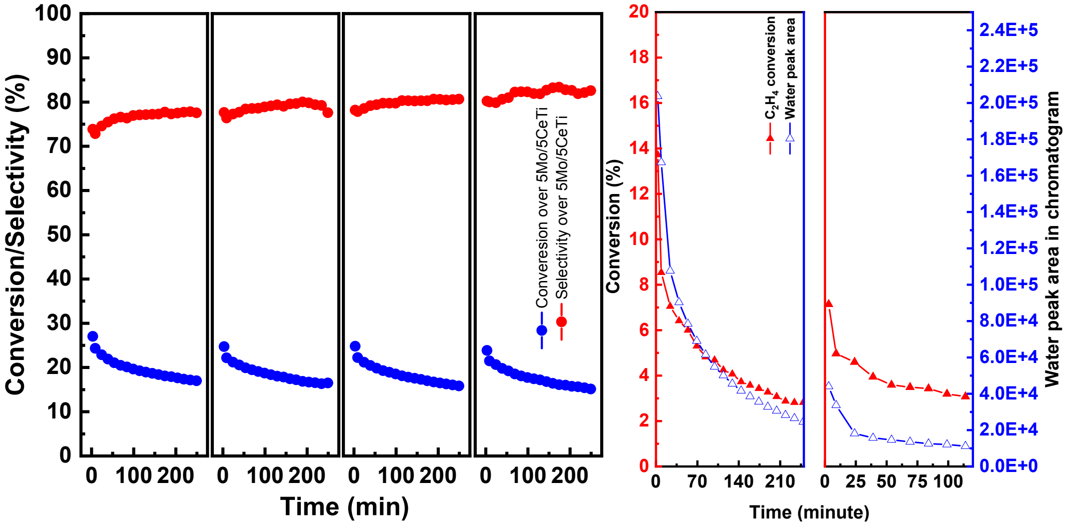

Figure S8: (a) Regeneration of 5Mo/5CeTi at 650 °C by O_2 in 30 minutes after 4hrs reaction with a flow of 20 mL/min containing 5% C_2H_6, 5% CO_2, and 90% N_2 (b) Regeneration of 5Mo/5CeTi at 600 °C by CO_2 in 1 hour after 4hrs reaction with a flow of 20 mL/min containing 5% C2H6, and 95% N2

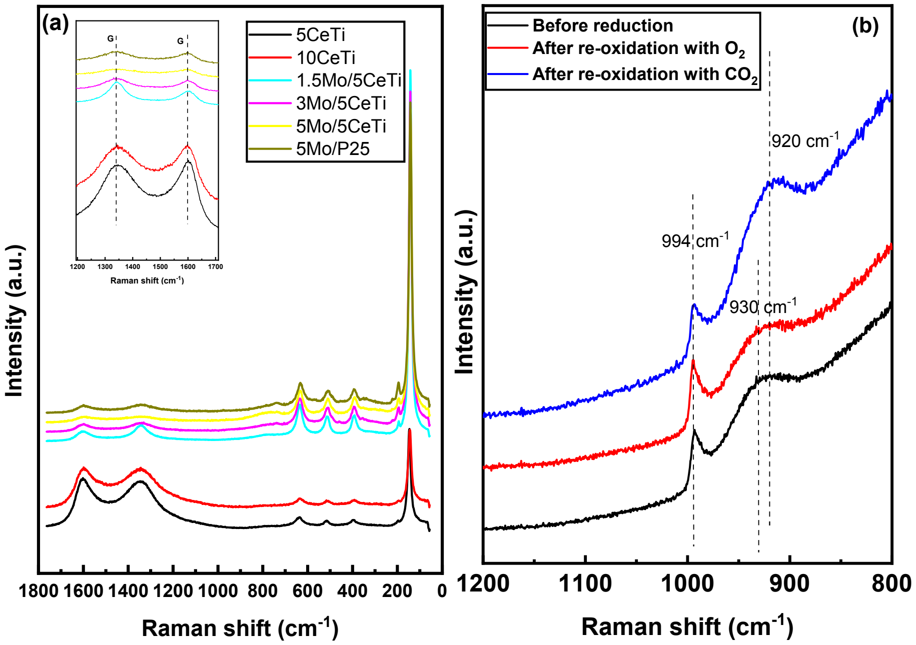

Figure S9: (a) Post-reaction Raman spectra of all materials. (b) Raman spectra of fresh 5Mo/5CeTi and after reduction following by reoxidation with O_2 and by reoxidation with CO_2 5Mo/5CeTi

TPR-H_2 measurements were performed over all samples and the results were plotted in Figure S10. For the bare supports, when ceria content increased, the onset of reduction shifted to lower temperature indicating the increase in the reducibility which can be assigned to the presence of added ceria. Recent literature showed that the high mobility of ceria could lead to low selectivity of olefin due to product oxidation. Such interpretation is agreement with our results in catalytic test for bare supports. When more ceria was added into the support, selectivity of ceria seemed to decrease. When Mo was added onto the surface of the bare supports, the amount of accessible oxygen significantly increased. One of the main reasons for such increase could be assigned to the oxygen from Mo amorphous structures. The TPR-H_2 results of supported Mo showed that there are different oxygen species reduced by H_2. Based on the Raman study, the more reducible species could be assigned to the terminal oxygen Mo=O and the less reducible

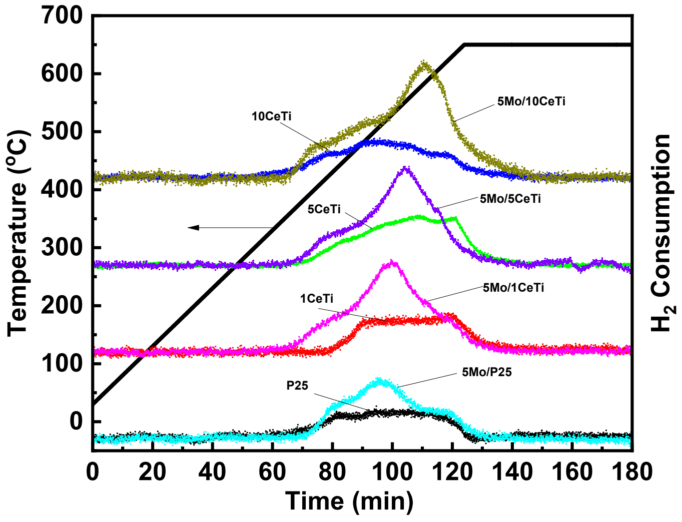

Figure 10: TPR-H_2 of bare support and supported Mo under a 40 mL/min flow of 2% H_2 in Ar with ramp rate of 5 ^{o}C/min from 25 ^{o}C to 650 ^{o}C

species could be assigned to the bridging oxygen Mo-O-X. Figure S10 showed that when more ceria was incorporated into the support, the more reducible species (Mo=O) became more reducible while the less reducible species (Mo-O-X) became less reducible. This observation is also in agreement with the dynamic in-situ Raman spectra. Moreover, as more ceria was added in the support, the ratio of less reducible species to more reducible species also increased. This partially explains also the increase in olefin selectivity for 5Mo/xCeTi as compared to 5Mo/P25.