catalysts

Supplementary Information

The list of catalysts is presented in Table S1. According to the results of the Rietveld refinement, all samples are represented by a mixture of solid solutions and simple oxides of Mn. The diffraction pattern of the Mn0.3Ce0.1Zr0.6 catalyst did not allow us to determine its phase composition; therefore, this sample is not presented in further analysis.

Table S1. List of catalysts.

Catalyst	Mn	Ce	Zr	T_{50} (CO), °C	T_{50} (C_3H_8), °C
Mn0.5Ce0.25Zr0.25	0.5	0.25	0.25	140	267
Mn0.6Ce0.2Zr0.2	0.6	0.2	0.2	142	270
Mn0.4Ce0.3Zr0.3	0.4	0.3	0.3	147	276
Mn0.7Ce0.15Zr0.15	0.7	0.1	0.15	151	271
Mn0.4Ce0.5Zr0.1	0.4	0.5	0.1	157	274
Mn0.8Ce0.1Zr0.1	0.8	0.1	0.1	158	273
Mn0.3Ce0.35Zr0.35	0.3	0.35	0.35	159	268
Mn0.5Ce0.5	0.5	0.5	0	160	259
Mn0.3Ce0.2Zr0.5	0.3	0.2	0.5	162	258
Mn0.2Ce0.4Zr0.4	0.2	0.4	0.4	163	293
Mn0.3Ce0.6Zr0.1	0.3	0.6	0.1	164	267
Mn0.3Ce0.5Zr0.2	0.3	0.5	0.2	164	284
Mn0.3Zr0.7	0.3	0	0.7	172	314
Mn0.3Ce0.1Zr0.6	0.3	0.1	0.6	175	355
Mn0.3Ce0.7	0.3	0.7	0	178	309
Mn0.2Ce0.5Zr0.3	0.2	0.5	0.3	179	315
Mn0.1Ce0.5Zr0.4	0.1	0.5	0.4	191	375
Mn0.1Ce0.45Zr0.45	0.1	0.45	0.45	196	342
Ce0.5Zr0.5	0	0.5	0.5	389	471
MnOx	1	0	0	191	285

For all other samples, the correlations between the catalytic activity in the oxidation of CO and propane and other characteristics, such as the initial ratio of cations, Mn content in the solid solution composition, phase composition, solid solution lattice parameter, CSR, were studied. The temperature of 50% conversion T50 (°C) was used as a measure of catalytic activity.

The following calculation method was used to estimate the position occupancies in the solid solution. In the case of the Ce0.5Zr0.5 catalyst, according to the Rietveld method, sample contains 40 wt.% CeO_2 and 60 wt.% ZrO_2. Analysis of call parameters indicates that there are two solid solutions, for which the following designations are chosen: $Ce_{x1}Zr_{1-x1}O_2$ (40 wt.%) and t-$Ce_{x2}Zr_{1-x2}O_2$ (60 wt.%). Since in this case, both solid solutions consist only of Ce, Zr and O, it is possible to use the calibration curve (Vegard's rule) constructed from the lattice parameter for Ce-Zr solid solutions according to the literature data. This calculation showed the occupancy of Ce in the first solid solution x1 = 0.95, and in the second x2 = 0.24. This agrees with the initial ratio Ce/Zr = 1 during synthesis: after calculation Ce/Zr=0.34/0.37..

In the case of the Mn0.5Ce0.5 sample, for $Mn_{1-x}Ce_xO_2$ solid solutions, there are no literature data to build a calibration from the lattice parameter values. Therefore, in this case, the calculation will be made according to the quantitative phase composition and molar masses. We use the following designation for a solid solution: $Ce_xMn_{1-x}O_2$. The occupancy of Mn – x – is unknown, but it is possible to estimate the amount of Mn and Ce, knowing their molar mass, and then choose such a value of x, so that the Mn/Ce ratio is close to the ratio when loading (Mn/Ce = 1). Thus, the phase composition of Mn0.5Ce0.5 contains 87% $Ce_{0.63}Mn_{0.37}O_2$, 8% Mn_2O_3, 5% Mn_3O_4.

The occupancies of positions in the solid solution in the Mn0.3Zr0.7 sample were calculated in a similar way. In the case of ternary oxides, two phases of a solid solution of the composition Mnx1Cey1Zr1-x1-y1O2 and Mnx2Cey2Zr1-x2-y2O2 are formed, as indicated by the analysis of X-ray diffraction patterns by the Rietveld method. An exact calculation by the previous method with so many unknowns is impossible. Therefore, in this case, to estimate the populations, the approximation of one solid solution MnxCeyZr1-x-yO2 with an average lattice parameter and total phase content was used.

Table S2. Phase composition of catalysts.

Catalyst	Phase composition, wt %	Catalyst	Phase composition, wt %
Mn0.1Ce0.5Zr0.4	$Ce_{0.5}Mn_{0.1}Zr_{0.4}O_2$	Mn0.3Ce0.7	$Ce_{0.7}Mn_{0.3}O_2$
Mn0.2Ce0.5Zr0.3	98% $Ce_{0.52}Mn_{0.17}Zr_{0.31}O_2$ 2% Mn_2O_3	Mn0.3Zr0.7	54% amorphous 40% $Mn_{0.25}Zr_{0.75}O_2$ 6% Mn_2O_3
Mn0.3Ce0.5Zr0.2	96% $Ce_{0.54}Mn_{0.25}Zr_{0.21}O_2$ 4% Mn_2O_3	Mn0.1Ce0.45Zr0.45	$Ce_{0.45}Mn_{0.1}Zr_{0.45}O_2$
Mn0.4Ce0.5Zr0.1	92% $Ce_{0.58}Mn_{0.3}Zr_{0.12}O_2$ 6% Mn_2O_3 2% Mn_3O_4	Mn0.2Ce0.4Zr0.4	$Ce_{0.4}Mn_{0.2}Zr_{0.4}O_2$
Ce0.5Zr0.5	40% $Ce_{0.95}Zr_{0.05}O_2$ 60% $Ce_{0.24}Zr_{0.76}O_2$	Mn0.3Ce0.35Zr0.35	94% $Ce_{0.39}Mn_{0.23}Zr_{0.38}O_2$ 6% Mn_2O_3
Mn0.5Ce0.5	87% $Ce_{0.63}Mn_{0.37}O_2$ 8% Mn_2O_3 5% Mn_3O_4	Mn0.4Ce0.3Zr0.3	92% $Ce_{0.35}Mn_{0.3}Zr_{0.35}O_2$ 4% Mn_2O_3 4% Mn_3O_4
Mn0.3Ce0.6Zr0.1	20% amorphous 74% $Ce_{0.71}Mn_{0.17}Zr_{0.12}O_2$ 6% Mn_2O_3	Mn0.5Ce0.25Zr0.25	82% $Ce_{0.34}Mn_{0.32}Zr_{0.34}O_2$ 7% Mn_2O_3 11% Mn_3O_4
Mn0.3Ce0.5Zr0.2	96% $Ce_{0.54}Mn_{0.25}Zr_{0.21}O_2$ 4% Mn_2O_3	Mn0.6Ce0.2Zr0.2	73% $Ce_{0.32}Mn_{0.36}Zr_{0.32}O_2$ 12% Mn_2O_3 15% Mn_3O_4
Mn0.3Ce0.35Zr0.35	94% $Ce_{0.39}Mn_{0.22}Zr_{0.39}O_2$ 6% Mn_2O_3	Mn0.7Ce0.15Zr0.15	50% $Ce_{0.41}Mn_{0.18}Zr_{0.41}O_2$ 38% Mn_2O_3 12% Mn_3O_4
Mn0.3Ce0.2Zr0.5	91% $Ce_{0.23}Mn_{0.19}Zr_{0.58}O_2$ 9% Mn_2O_3	Mn0.8Ce0.1Zr0.1	33% $Ce_{0.465}Mn_{0.07}Zr_{0.465}O_2$ 30% Mn_2O_3 22% Mn_3O_4 15% MnO_2
Mn0.3Ce0.1Zr0.6	amorphous CeO_2 Mn_2O_3	MnOx	Mn_2O_3

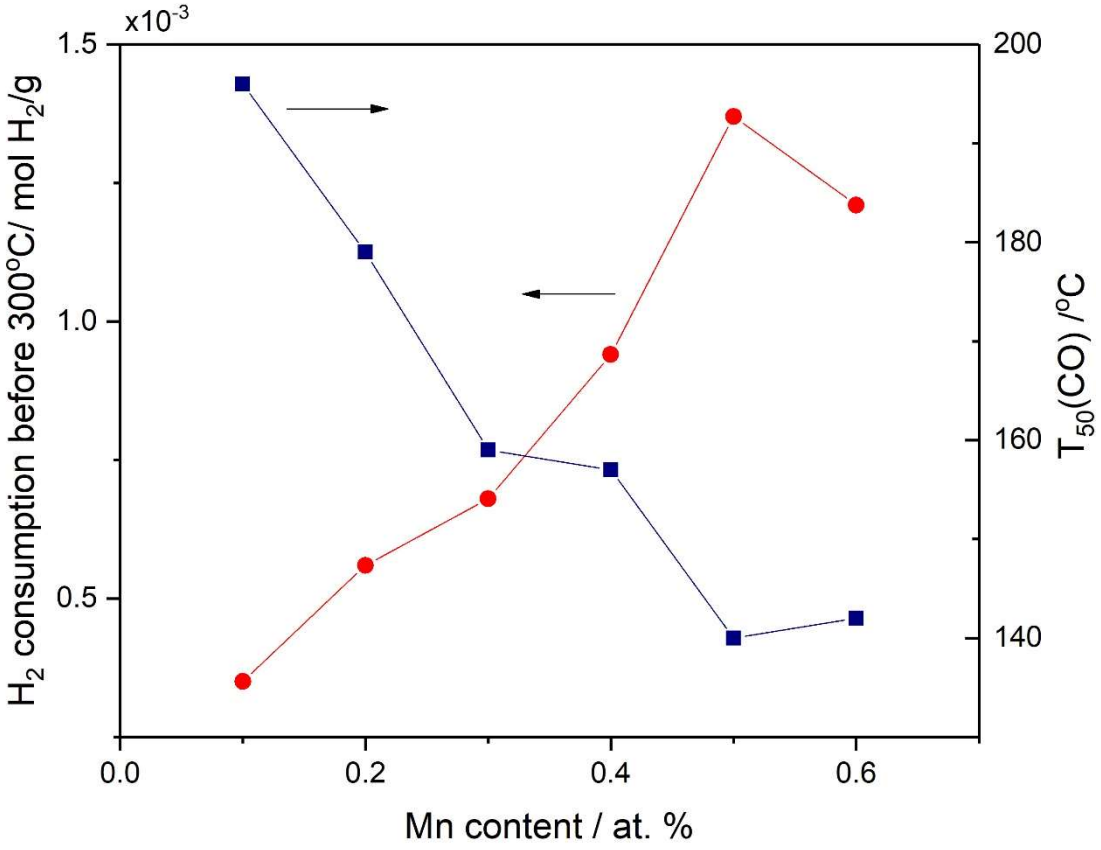

Figure S1. Temperature of 50% CO conversion (blue) and H_2 consumption before 300°C (red) versus the Mn content.

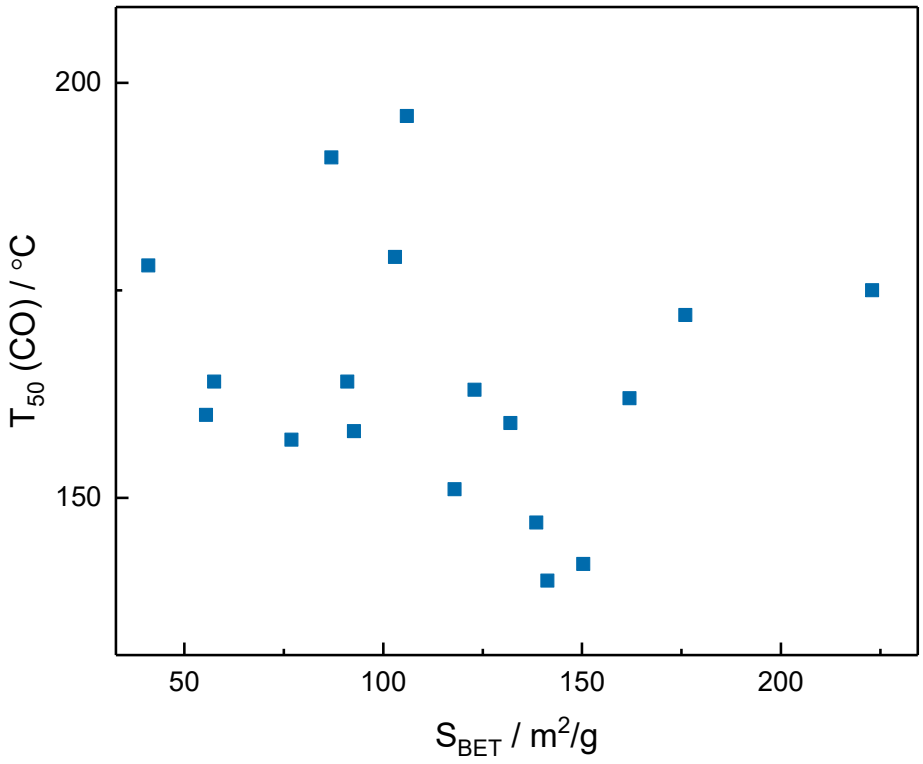

Figure S2. Temperature of 50% CO conversion versus the specific surface area (S_{BET}) for all catalysts.

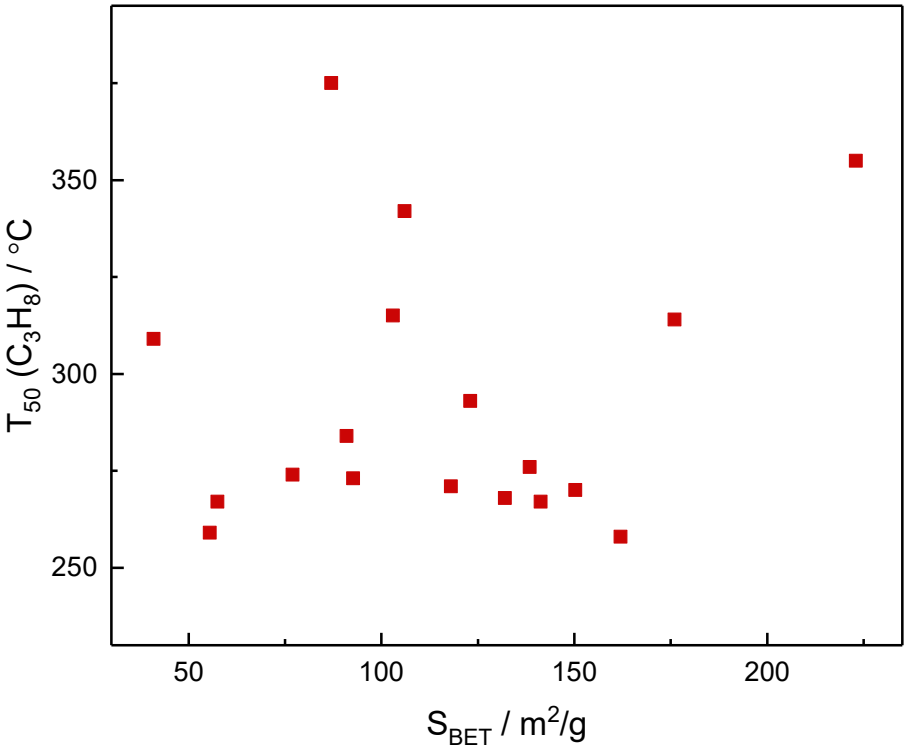

Figure S3. Temperature of 50% C_3H_8 conversion versus the specific surface area (S_{BET}) for all catalysts.

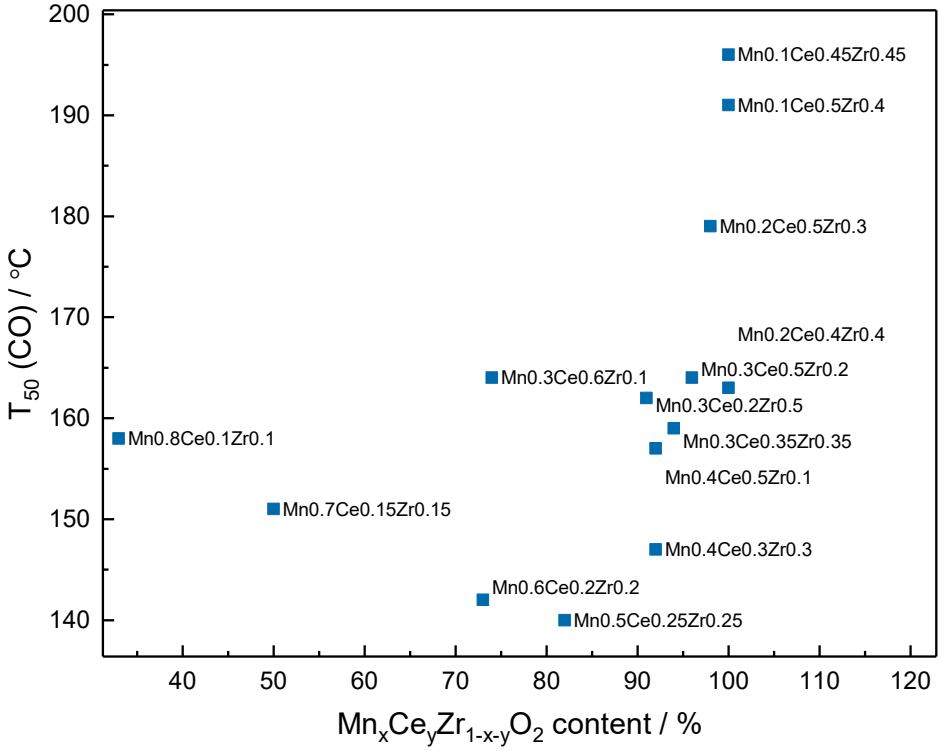

Figure S4. Temperature of 50% CO conversion versus the content of solid solutions for all catalysts.

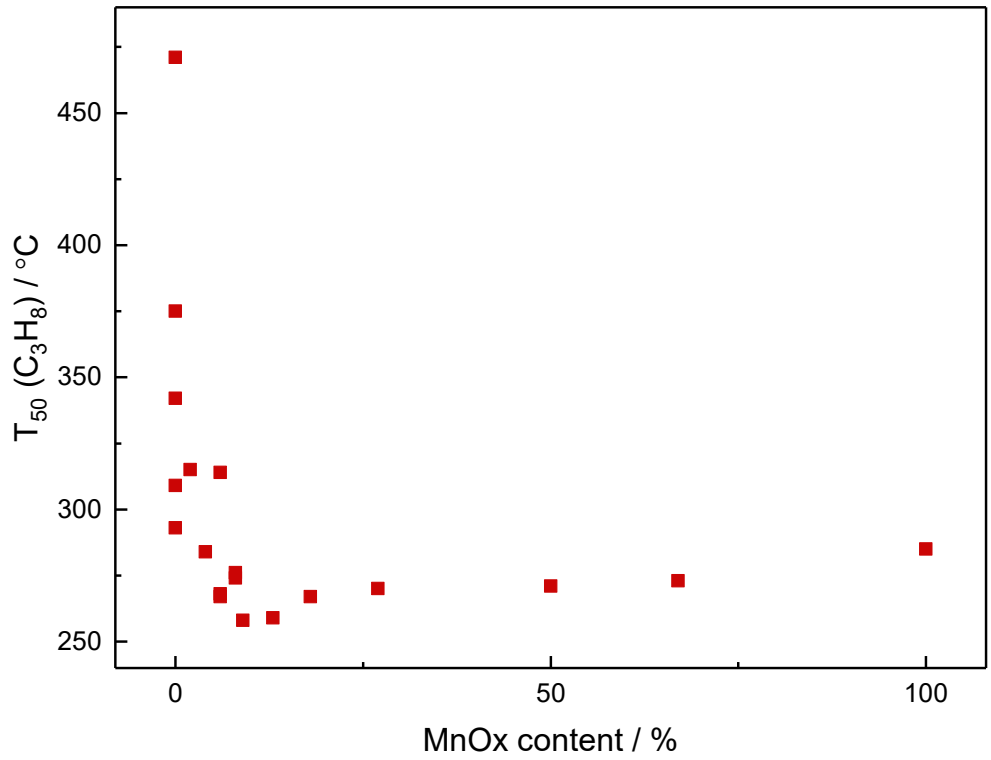

Figure S5. Temperature of 50% C_3H_8 conversion versus the content of crystalline Mn oxides for all catalysts.

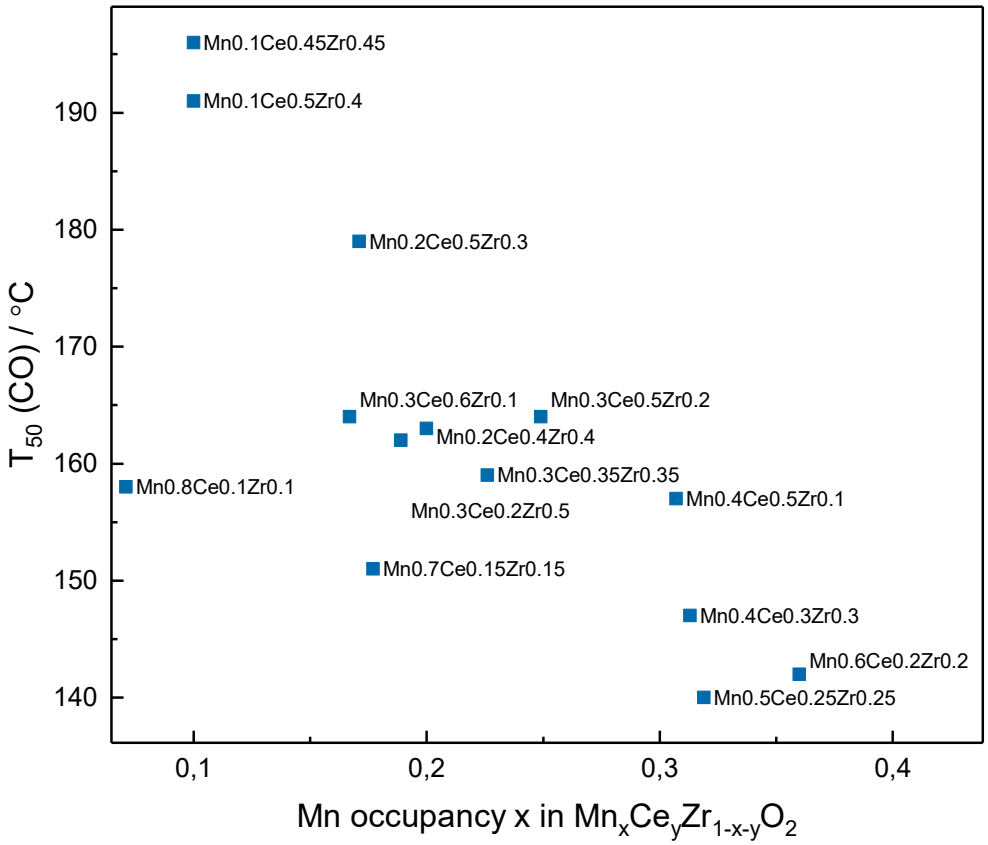

Figure S6. Temperature of 50% CO conversion versus the content of Mn (x) in $Mn_xCe_yZr_{1-x-y}O_2$ solid solution for all catalysts.

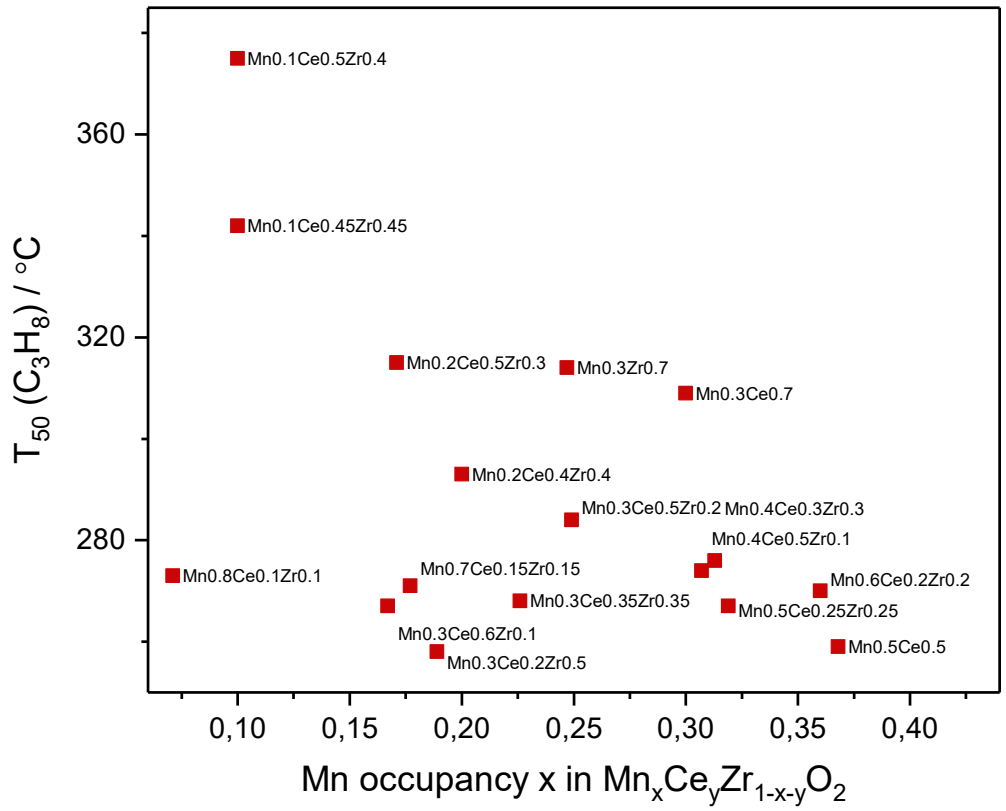

Figure S7. Temperature of 50% C_3H_8 conversion versus the content of Mn (x) in $Mn_xCe_yZr_{1-x-y}O_2$ solid solution for all catalysts.