ARTICLE

Supported Fe_xNi_y catalysts for the co-activation of CO_2 and small alkanes

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Electronic Supplementary Information ESI

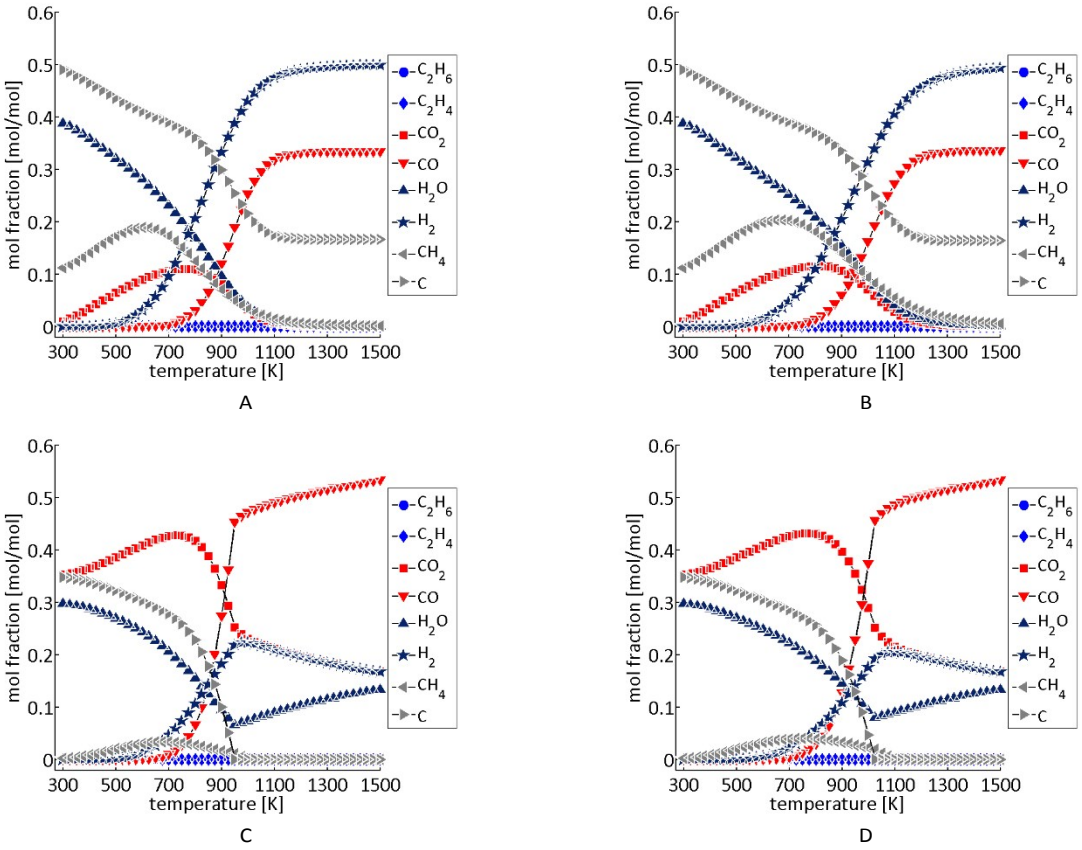

Fig. S1: Thermodynamic equilibrium composition of C_2H_6, C_2H_4, CO_2, CO, H_2O, H_2, CH_4 and C as function of temperature at a feed composition of (**A**) CO_2/C_2H_6 = 1 and 1 bar pressure, (**B**) CO_2/C_2H_6 = 1 and 5 bar pressure, (**C**) CO_2/C_2H_6 = 5 and 1 bar pressure, (**D**) CO_2/C_2H_6 = 5 and 5 bar pressure. Thermodynamic properties from Knacke et al.[1]

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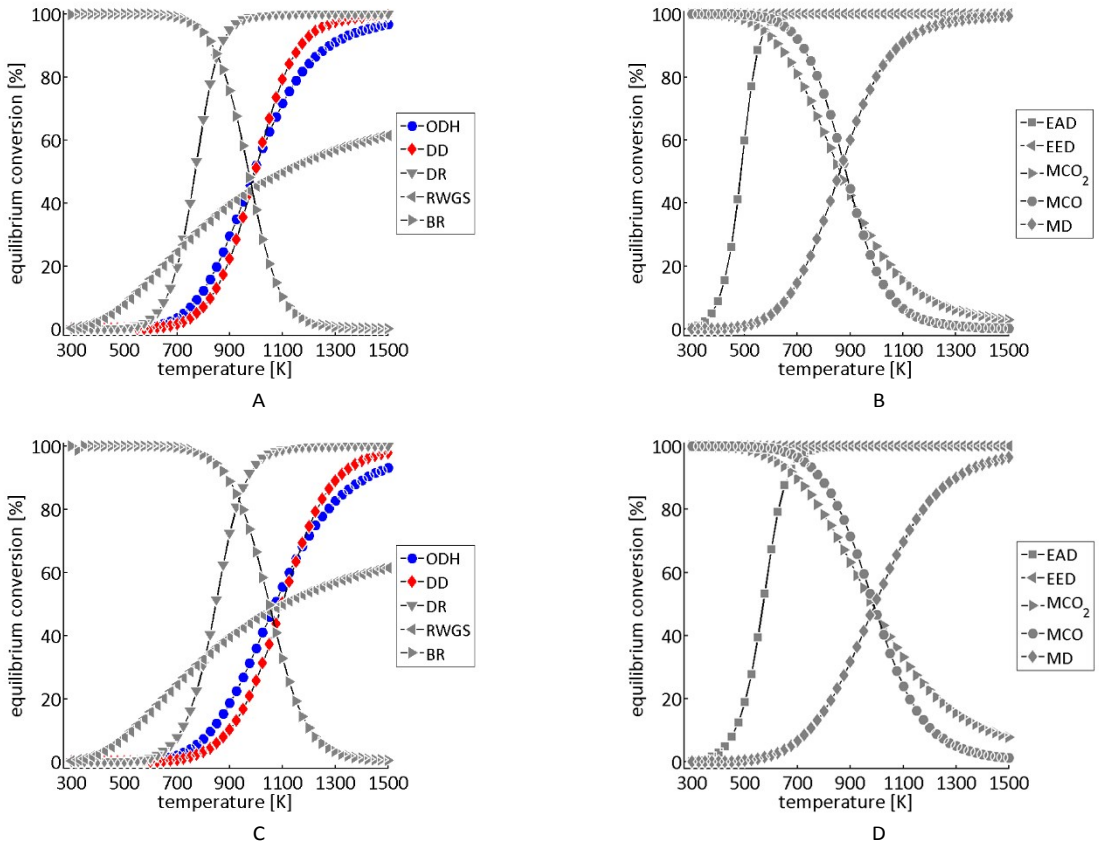
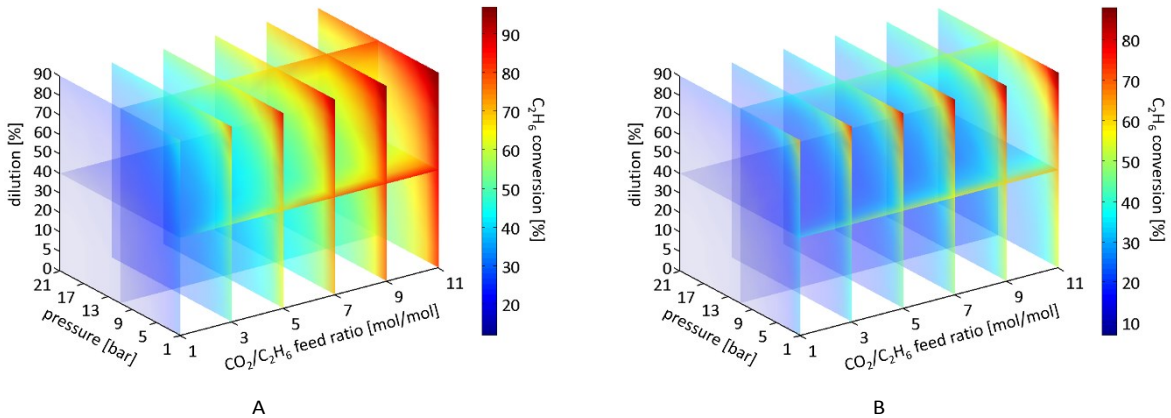
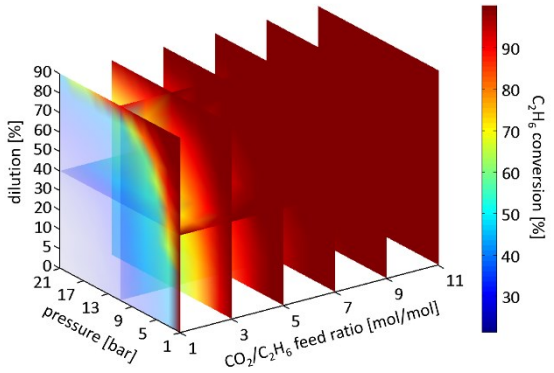


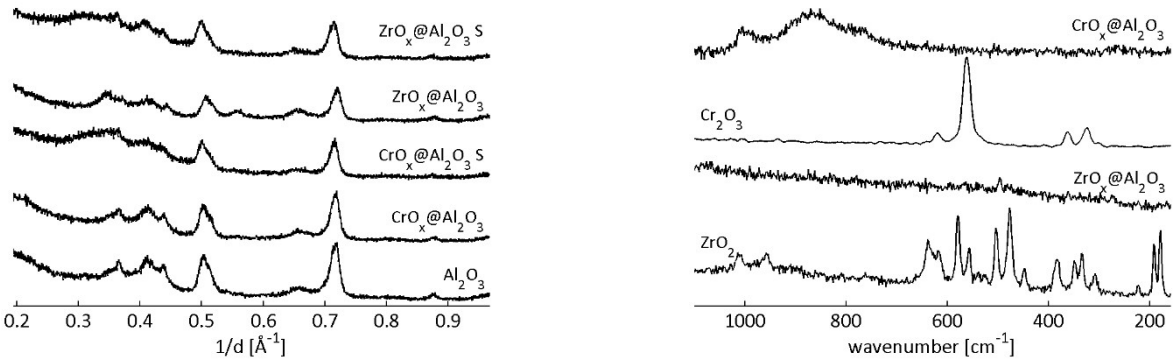
Fig. S2: Equilibrium conversions of CO_2-ODH, direct dehydrogenation of ethane (DD), dry reforming of ethane (DR), reverse water gas shift (RWGS) and the Boudouard reaction (BR) at stochiometric feed composition as a function of temperature at 1 bar (**A**) and 5 bar (**C**). Equilibrium conversions of ethane decomposition (EAD), ethylene decomposition (EED), CO_2 methantion (MCO_2), CO methanation (MCO) and methane decomposition (MD) at stochiometric feed composition as a function of temperature at 1 bar (**B**) and 5 bar (**D**). Thermodynamic properties from Knacke et al.[1]





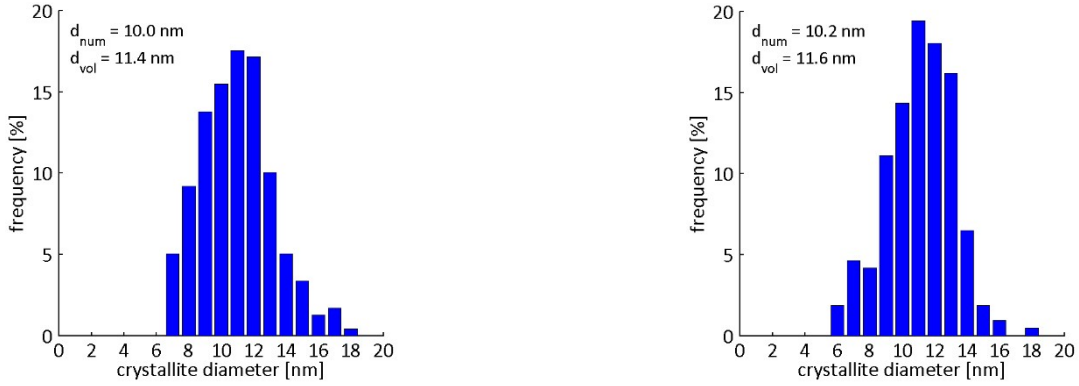
C

Fig. S3: Effect of pressure, feed composition and dilution on C_2H_6 equilibrium conversion at 873K in the CO_2-ODH (**A**), direct dehydrogenation (DD) (**B**) and dry reforming of ethane (DR) (**C**). Thermodynamic properties from Knacke et al.[1]

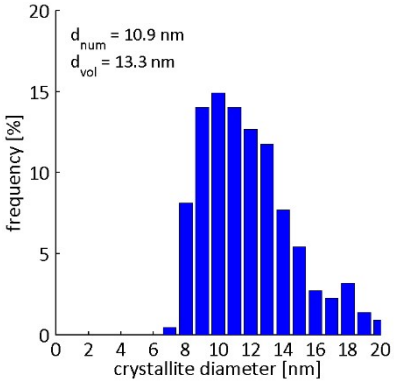


A B

Fig. S4: (**A**) XRD patterns of Al_2O_3, $CrO_x@Al_2O_3$ and $ZrO_x@Al_2O_3$ after synthesis and after reduction and exposure to ODH conditions for 24 hours (spent samples indicated by suffix S). (**B**) Raman spectra of $CrO_x@Al_2O_3$ and $ZrO_x@Al_2O_3$ as well as bulk Cr_2O_3 and ZrO_2. Spectra are stacked for clarity.



A B



C

Fig. S5: TEM derived nanoparticle size distributions of freshly prepared bimetallic oxide materials Fe1Ni1 (A), Fe3Ni1 (B) and Fe5Ni1 (C) as well as number averaged (d_{num}) and volume averaged (d_{vol}) nanoparticle size.

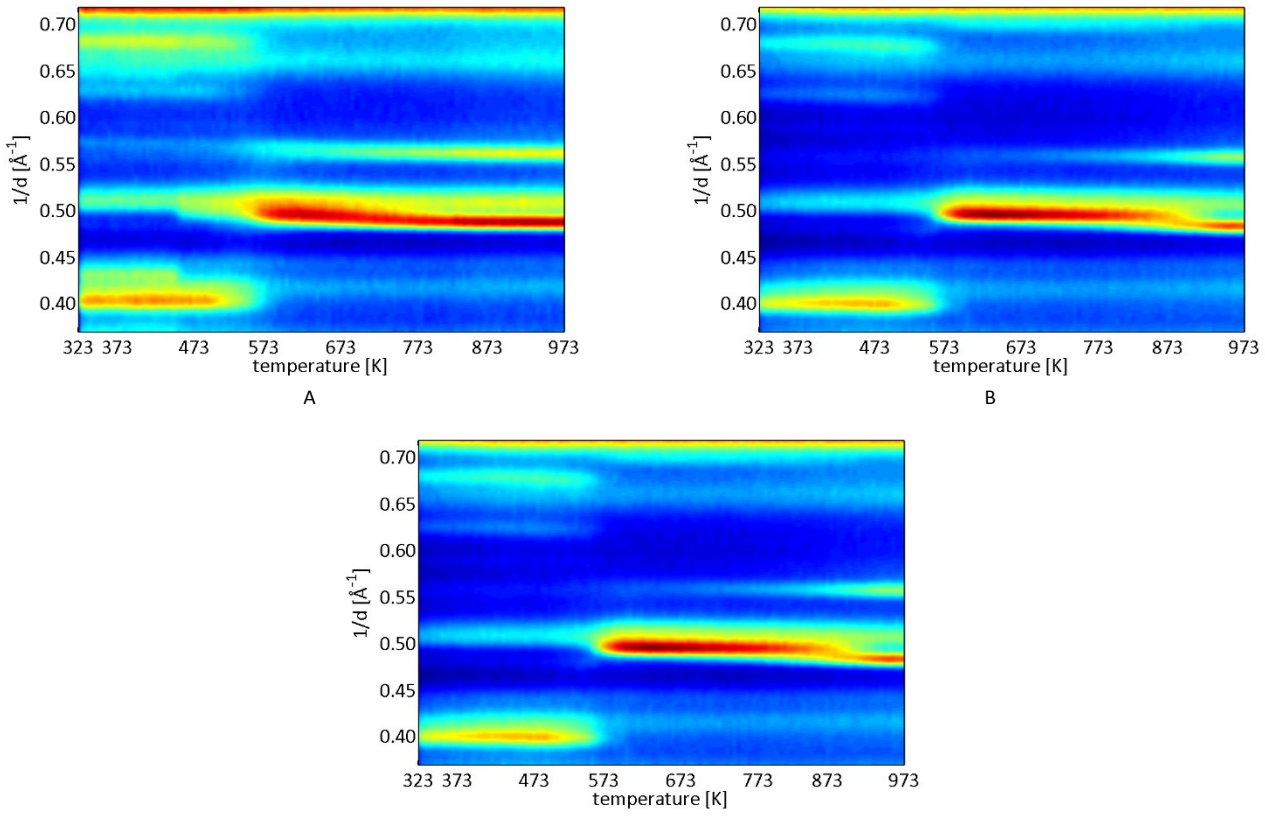


Fig. S6: Top view of in situ XRD patterns and evolution of Fe and Ni phases during the reduction of Fe1Ni1 (**A**) Fe3Ni1 (**B**) and Fe5Ni1 (**C**) supported on ZrO_x@Al_2O_3 as function of temperature in a 5 vol. % H_2 in N_2 gas stream.

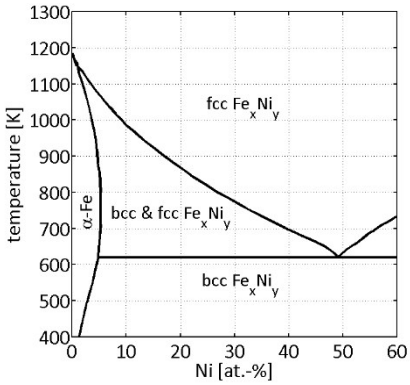


Fig. S7: Fe-Ni phase diagram as function of temperature and Fe:Ni ratio as reported by Predel.[2]

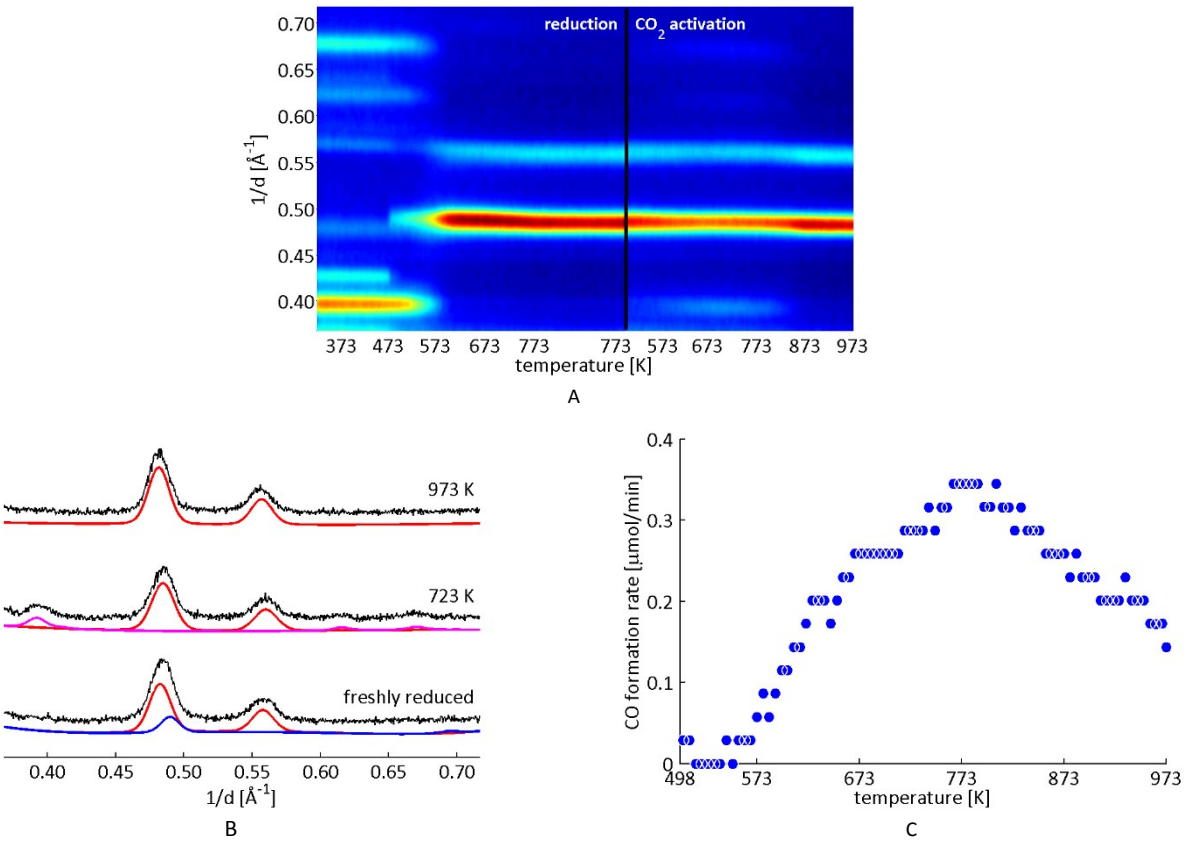


Fig. S8: (**A**) Top view of situ XRD study of CO_2 activation of KIT-6 supported Fe1N1. Reduction at 873 K for 5 h and 1 K/min in 5 vol.-% H_2/N_2 (left of the black divider line). The sample is subsequently cooled to 323 K in inert and heated at 1 K/min in 1 vol% CO_2/N_2 to 973 K. For clarity only the data above 498 K is shown (right of black divider line). (**B**) Selected diffraction patterns (from bottom to top: freshly reduced, at 723 and 973 K under a flow of 1 vol.-% CO_2/N_2) and calculated diffraction patterns for bcc NiFe (blue), fcc NiFe (red) and $Fe_2Ni_1O_4$ (magenta). Experimental and modelled patterns are stacked for clarity. For quantitative analysis see table 3. (**C**) CO evolution as function of temperature in the CO_2 activation step measured in a parallel experiment in a fixed bed reactor.

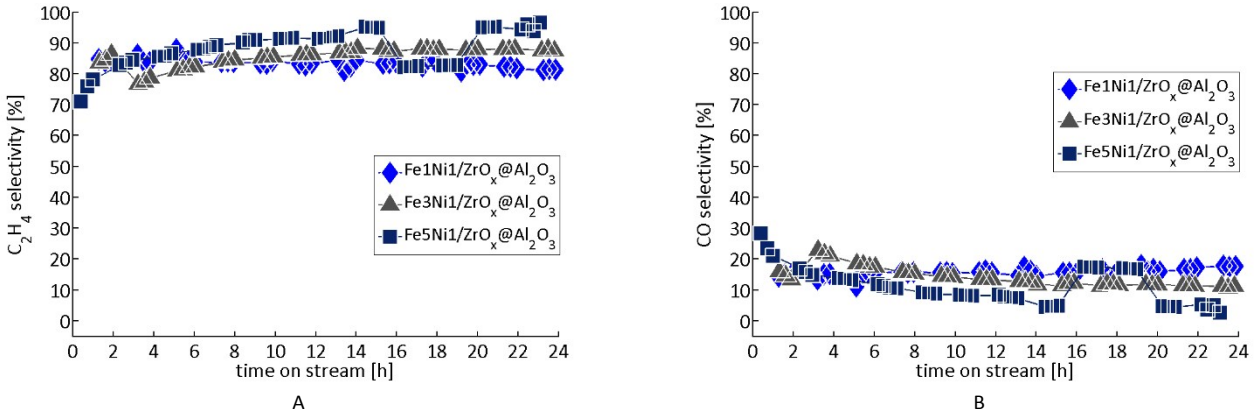


Fig. S9: Selectivity of bimetallic catalysts supported on $ZrO_x@Al_2O_3$. (**A**) C_2H_4 selectivity of bimetallic catalysts supported on $ZrO_x@Al_2O_3$ and of blank support; (**B**) CO selectivity of bimetallic catalysts supported on $ZrO_x@Al_2O_3$ and of blank support calculated excluding ODH CO formation pathway. In both cases supported Fe1Ni1 – blue diamonds; supported Fe3Ni1 – grey triangles; - supported Fe5Ni1 – dark blue squares.

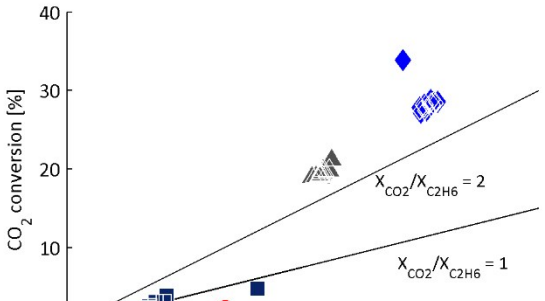


Fig. S10: CO_2 conversion as function of C_2H_6 conversion for FexNiy/CrO_x@Al_2O_3. Ratios of 1 and 2 displayed for clarity. Blank support – red circles; supported Fe1Ni1 – blue diamonds; supported Fe3Ni1 – grey triangles; - supported Fe5Ni1 – dark blue squares.

References

1. O. Knacke, O. Kubaschewski and K. Hesselmann, *Thermochemical properties of inorganic substances*, Springer-Verlag, Berlin, 2nd ed edn., 1991.
2. B. Predel, in *Dy-Er – Fr-Mo*, ed. O. Madelung, Springer Berlin Heidelberg, Berlin, Heidelberg, 1995, DOI: 10.1007/10474837_1321, pp. 1-12.

