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

Supporting Information:

CO_2 hydrogenation using bifunctional catalysts based on K-promoted iron oxide and zeolite: Influence of the zeolite structure and crystal size

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Supplementary Figures:

Figure S1: FT-IR spectra of acid zeolites BEA(10), n-BEA(10), MFI(10), MFI(30 and n-MFI(30) in the –OH vibration region (left) and in the adsorbed pyridine region after pyridine adsorption and desorption at 250°C (right).

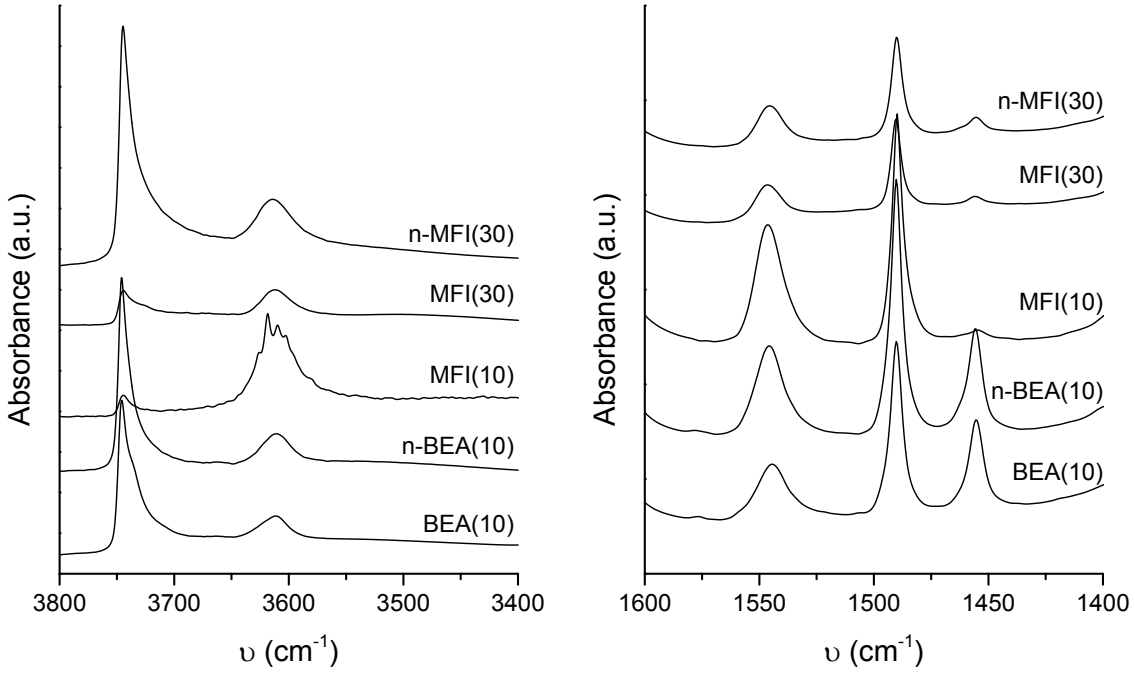


Figure S2: Temperature-programmed desorption of ammonia of the calcined CHA(10) and n-CHA(10)

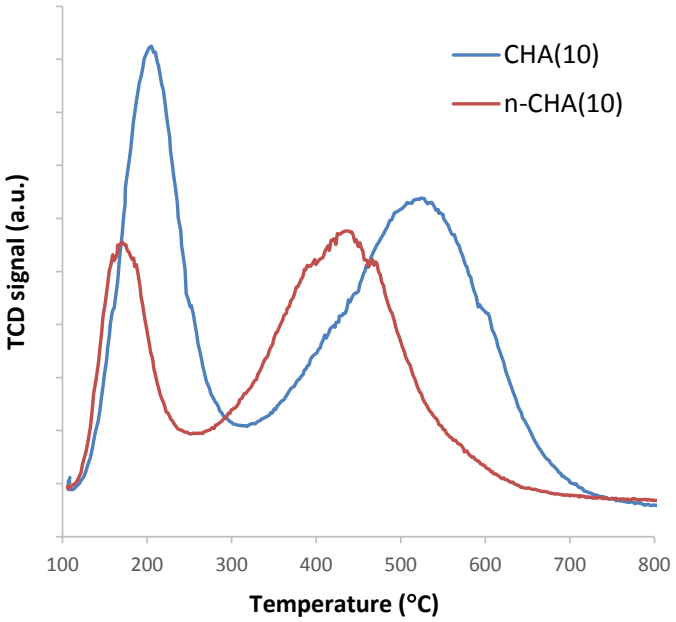


Figure S3: PXRD patterns of the K-promoted iron catalyst fresh, reduced and recovered after reaction.

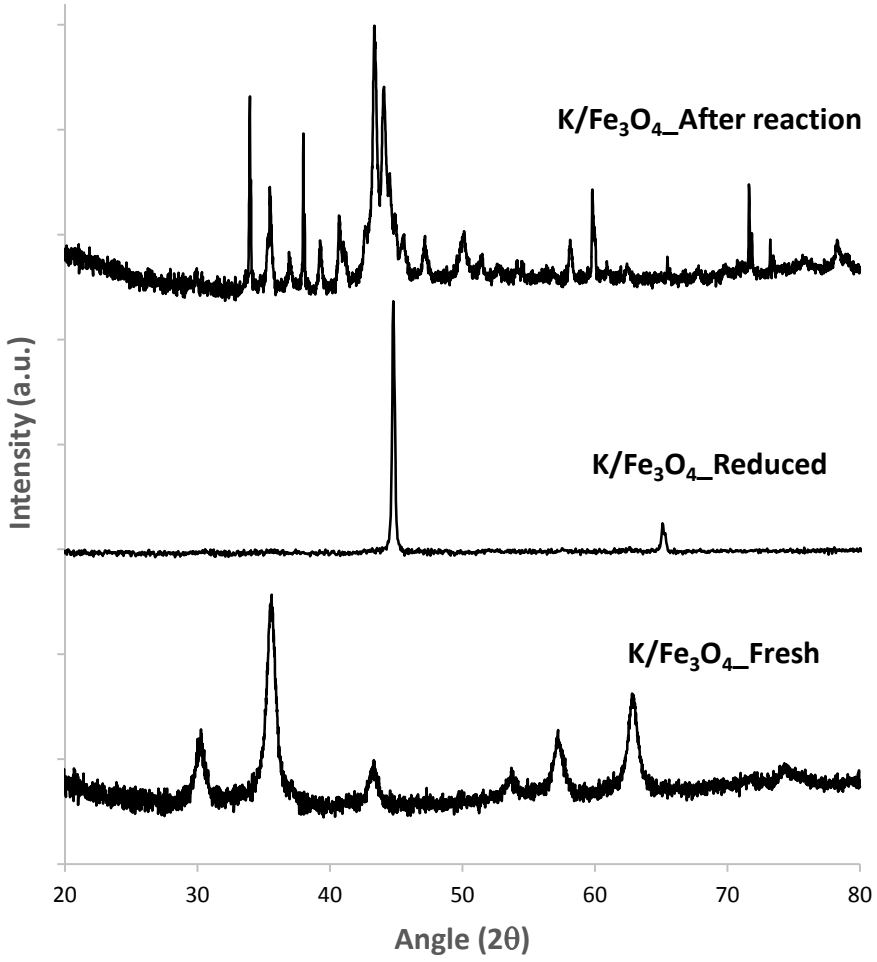


Figure S4: (a,b) FE-SEM images of K/Fe_3O_4 catalyst. (c,d,e) FE-SEM micrograph of K/Fe_3O_4 catalyst and its corresponding EDS elemental mapping for Fe (d) and K (e).

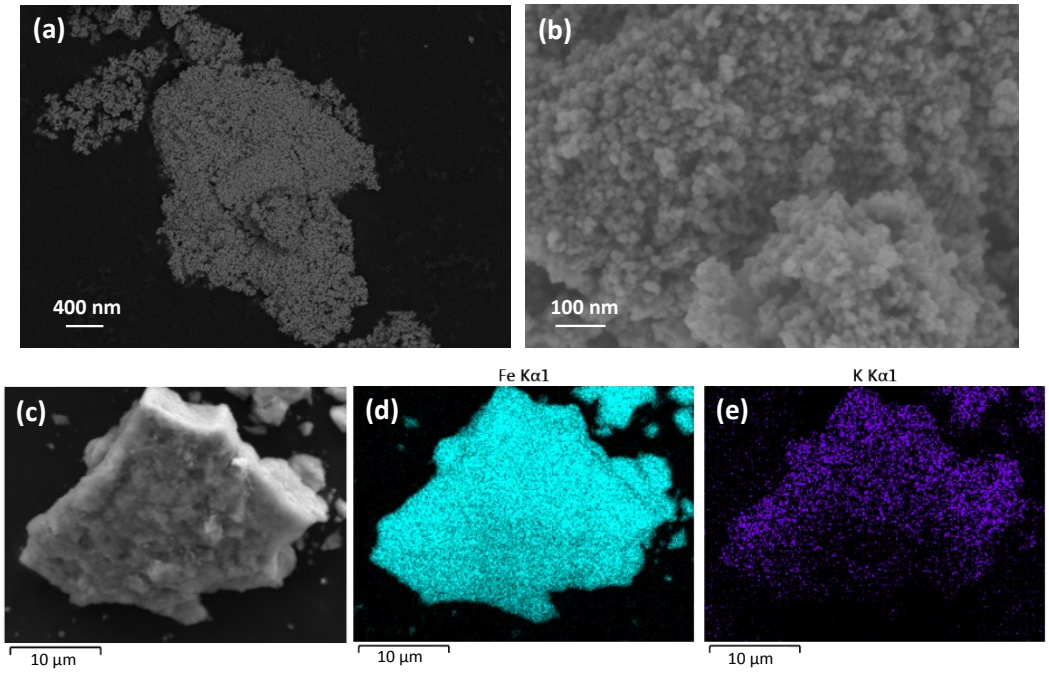
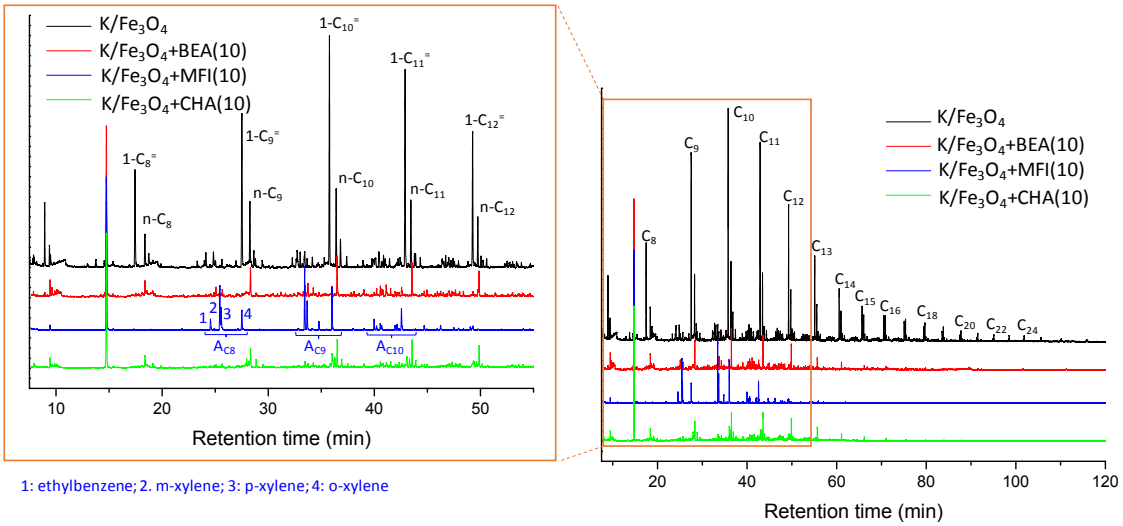


Figure S5: Product distribution within the condensed liquid fraction observed by GC-MS using K/Fe_3O_4 and combination of K/Fe_3O_4 with BEA(10), MFI(10) and CHA(10).



1: ethylbenzene; 2. m-xylene; 3: p-xylene; 4: o-xylene

Figure S6: Evolution of C_1-C_4 product selectivities with TOS catalyzed by K/Fe_3O_4 (a) and combination of K/Fe_3O_4 with BEA(10) (b), MFI(10) (c) and CHA(10) (d). Reaction conditions: 0.5 g K/Fe_3O_4, 0.5 g zeolite (if required), T=320°C, P=25 bar, H_2/CO_2 = 6 mol/mol, total flow = 142 ml/min (100 H_2/8 N_2/ 34 CO_2), WHSV=7 h^{-1} (referred to Fe_3O_4)

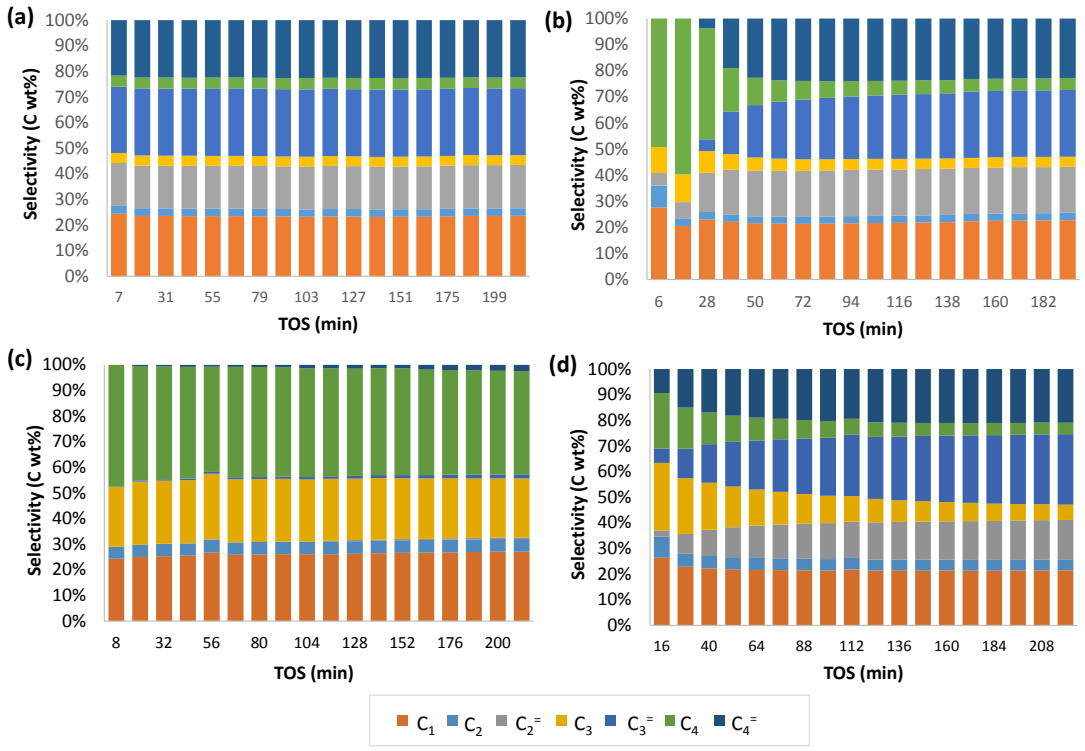


Figure S7: Olefin to paraffin ratios in C_2-C_4 (a) and olefin yields (b) under steady-state conditions obtained with catalyst K/Fe_3O_4 and combination of K/Fe_3O_4 with BEA(10), MFI(10) and CHA(10). Reaction conditions: 0.5 g K/Fe_3O_4, 0.5 g zeolite (if required), T=320°C, P=25 bar, H_2/CO_2 = 6 mol/mol, total flow = 142 ml/min (100 H_2/8 N_2/ 34 CO_2), WHSV=7 h^{-1} (referred to Fe_3O_4)

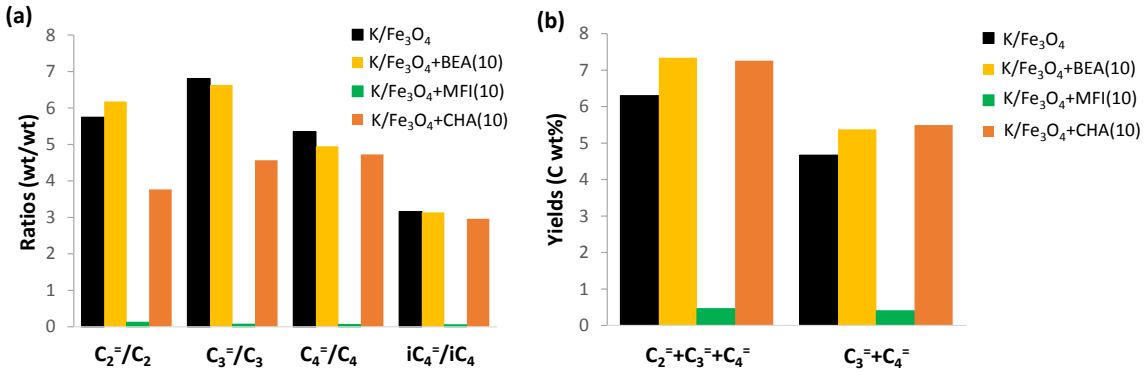
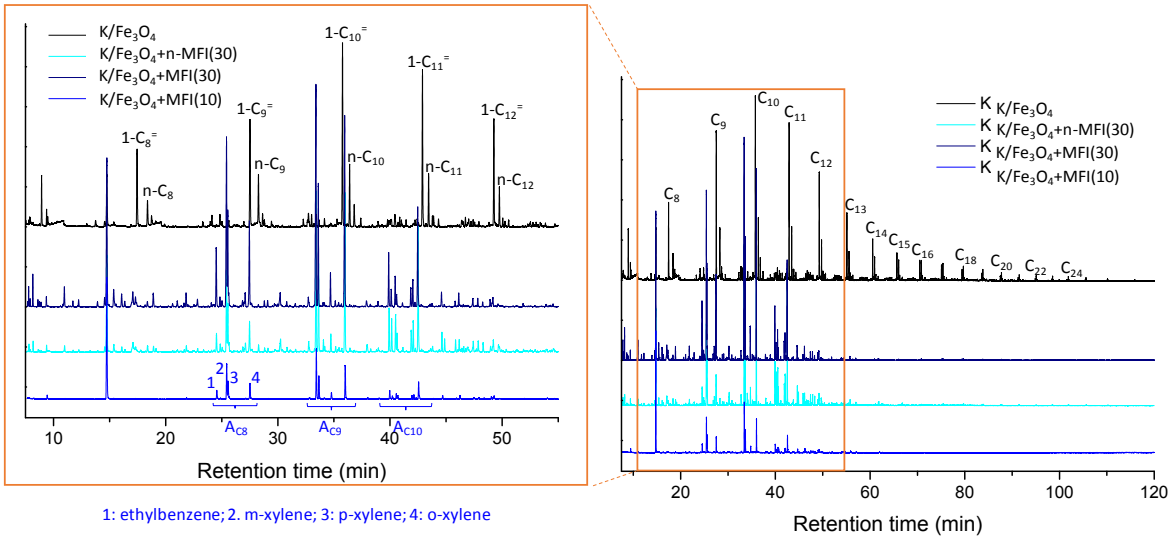


Figure S8: Product distribution within the condensed liquid fraction observed by GC-MS using K/Fe_3O_4 and combination of K/Fe_3O_4 with MFI(10), MFI(30) and n-MFI(30)



1: ethylbenzene; 2. m-xylene; 3: p-xylene; 4: o-xylene

Figure S9: CO_2 conversion (a) and overall product selectivity (b) to CO (open symbols) and hydrocarbons (solid symbols) with time-on-stream (TOS) catalyzed by K/Fe_3O_4 and combination of K/Fe_3O_4 with MFI(10), MFI(30) and n-MFI(30). Reaction conditions: 0.5 g K/Fe_3O_4, 0.5 g zeolite (if required), T=320°C, P=25 bar, H_2/CO_2 = 6 mol/mol, total flow = 142 ml/min (100 H_2/8 N_2/ 34 CO_2), WHSV=7 h^{-1} (referred to Fe_3O_4)

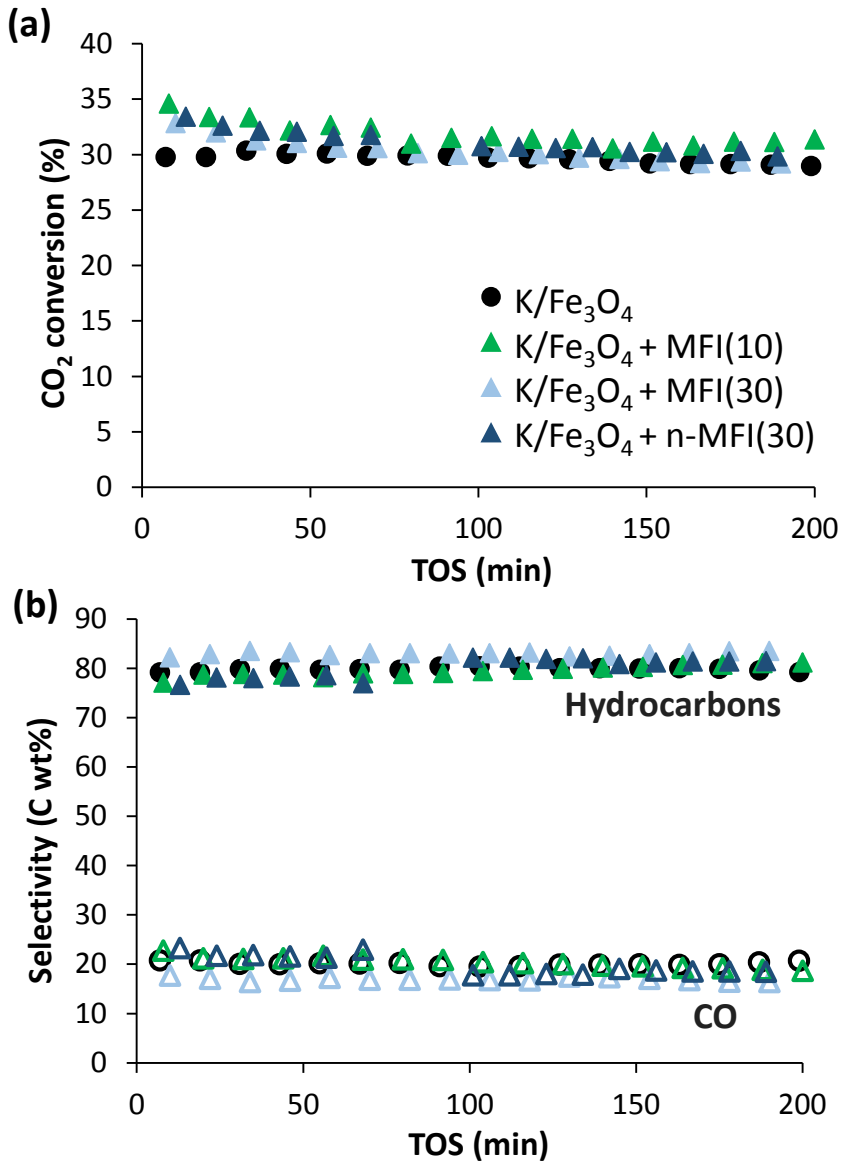


Figure S10: Evolution of C_1-C_4 product selectivities with TOS catalyzed by the combination of K/Fe_3O_4 with MFI(30) (a) and n-MFI(30) (b). Reaction conditions: 0.5 g K/Fe_3O_4, 0.5 g zeolite, T=320°C, P=25 bar, H_2/CO_2 = 6 mol/mol, total flow = 142 ml/min (100 H_2/8 N_2/ 34 CO_2), WHSV=7 h^{-1} (referred to Fe_3O_4)

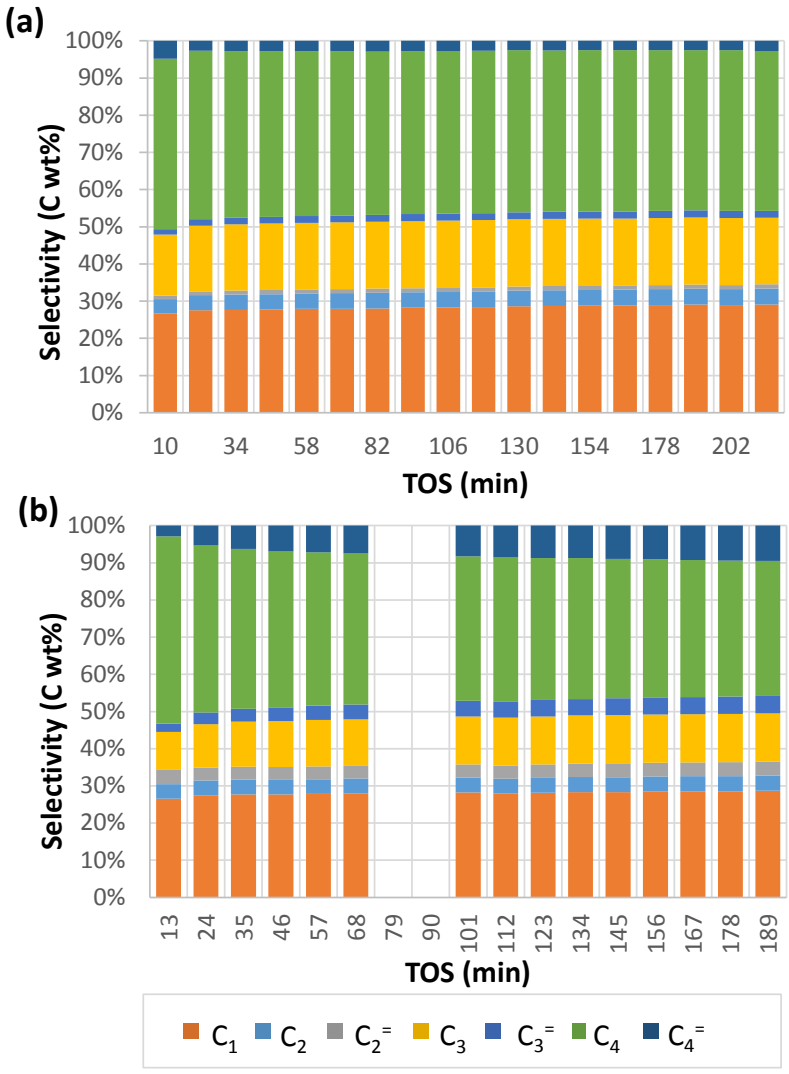


Figure S11: CO_2 conversion (a,c) and overall product selectivity (b,d) to CO (open symbols) and hydrocarbons (solid symbols) with time-on-stream (TOS) catalyzed by K/Fe_3O_4 combined with BEA-type zeolites (a,b) and CHA-type zeolites (c,d). Reaction conditions: 0.5 g K/Fe_3O_4, 0.5 g zeolite (if required), T=320°C, P=25 bar, H_2/CO_2 = 6 mol/mol, total flow = 142 ml/min (100 H_2/8 N_2/ 34 CO_2), WHSV=7 h^{-1} (referred to Fe_3O_4)

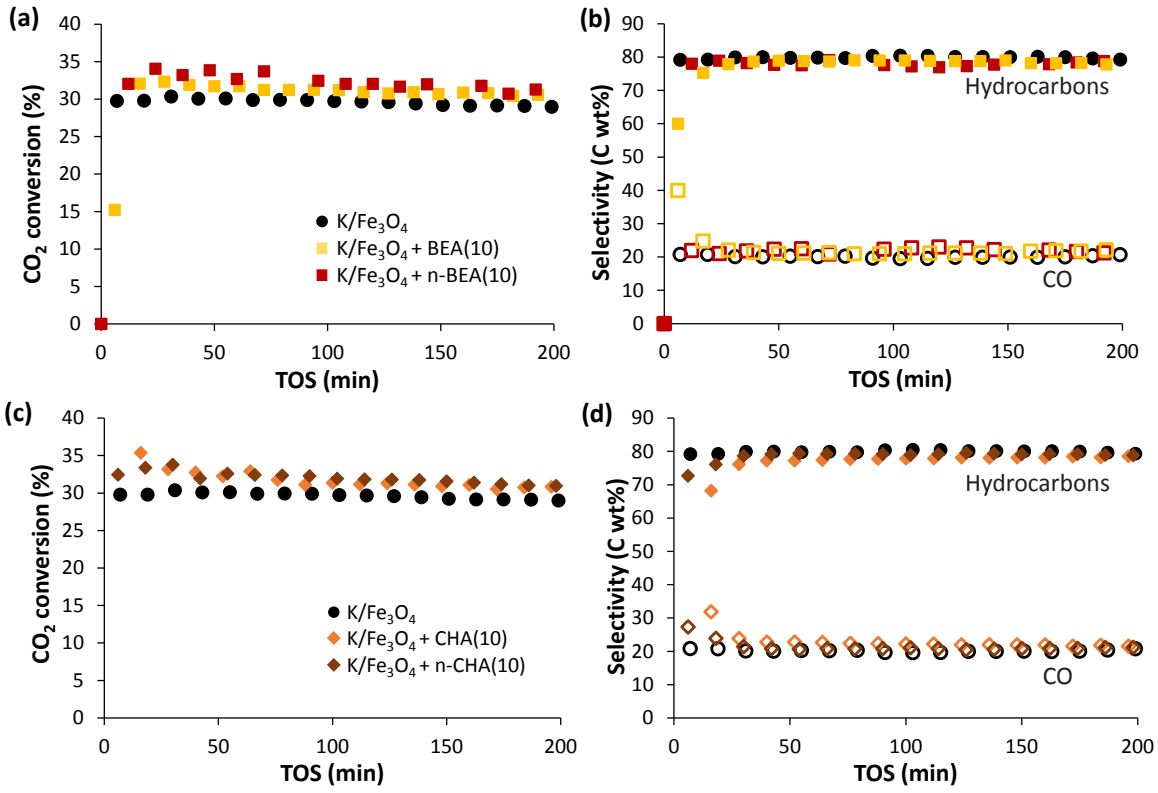
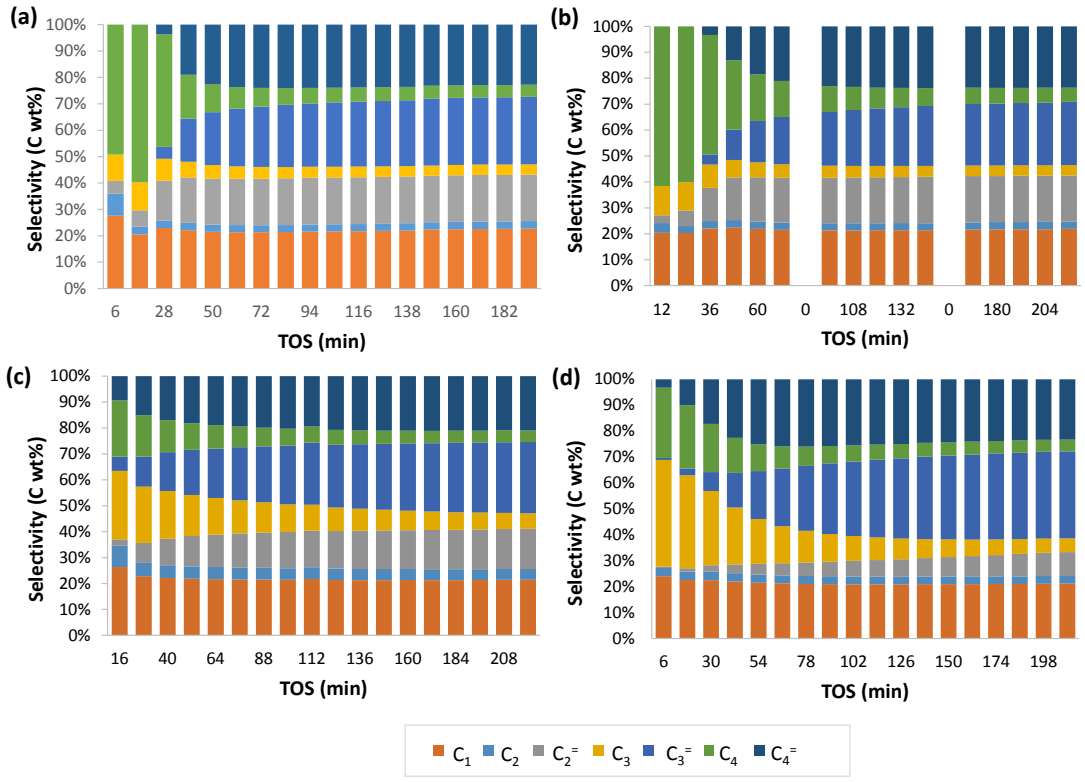


Figure S12: Evolution of C_1-C_4 product selectivities with TOS catalyzed by the combination of K/Fe_3O_4 with BEA(10) (a), n-BEA(10) (b), CHA(10) (c) and n-CHA(10). Reaction conditions: 0.5 g K/Fe_3O_4, 0.5 g zeolite, T=320°C, P=25 bar, H_2/CO_2 = 6 mol/mol, total flow = 142 ml/min (100 H_2/8 N_2/ 34 CO_2), WHSV=7 h^{-1} (referred to Fe_3O_4)



Supplementary Tables:

Table S1: Average product distribution achieved using the different catalysts. Reaction conditions: 0.5 g K/Fe_3O_4, 0.5 g zeolite (if required), T=320°C, P=25 bar, H_2/CO_2 = 6 mol/mol, total flow = 142 ml/min (100 H_2/8 N_2/ 34 CO_2), WHSV=7 h^{-1} (referred to Fe_3O_4)

	K/Fe_3O_4	+BEA(10)	+n-BEA(10)	+MFI(10)	+MFI(30)	+n-MFI(30)	+CHA(10)	+n-CHA(10)
Methane	9.2	11.5	12.1	11.5	8.6	10.0	11.9	11.7
Ethane	1.1	1.5	1.6	2.2	1.3	1.4	2.5	1.7
Ethylene	6.5	8.7	8.8	0.1	0.3	1.3	7.2	3.2
Propane	1.5	2.6	3.2	10.6	5.4	4.5	6.1	7.4
Propylene	10.2	10.8	9.8	0.4	0.6	1.5	12.1	13.5
iso-Butane	0.2	4.3	7.7	11.9	8.7	10.2	0.7	1.0
n-Butane	1.5	2.3	2.7	6.7	4.7	4.1	3.4	3.9
t-2-Butene	0.1	4.2	3.7	0.2	0.2	0.7	4.0	4.5
1-Butene	7.8	1.6	1.5	0.0	0.1	0.3	2.0	1.8
iso-Butene	0.6	2.0	2.6	0.3	0.4	1.4	1.6	3.0
c-2-Butene	0.2	2.7	2.5	0.1	0.1	0.4	2.9	3.0
iso-Pentane	0.4	3.5	5.4	9.7	8.4	8.4	0.9	1.1
n-Pentane	1.3	1.8	1.9	3.0	3.1	2.8	1.7	1.7
Pentenes	7.8	7.8	7.5	0.0	0.3	1.9	8.7	9.7
C_6^+	51.5	34.6	29.1	43.2	57.7	51.2	34.3	32.8

Table S2: Average aromatic products' selectivity achieved using the mixture of K/Fe_3O_4 with the different MFI catalysts at steady-state conditions. Reaction conditions: 0.5 g K/Fe_3O_4, 0.5 g zeolite, T=320°C, P=25 bar, H_2/CO_2 = 6 mol/mol, total flow = 142 ml/min (100 H_2/8 N_2/ 34 CO_2), WHSV=7 h^{-1} (referred to Fe_3O_4)

	MFI(10)	MFI(30)	n-MFI(30)
BTX	96.5	84.5	76.1
AC_9	2.3	10.3	12.5
AC_{10}	1.0	4.2	8.5
AC_{11}^+	0.2	1.0	2.9