Electronic Supplementary Material (ESI) for ChemComm.

Supporting information

Selectivity shift from paraffins to α-olefins in low temperature Fischer-Tropsch synthesis in the presence of carboxylic acids

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Preparation of catalysts

Alumina-supported cobalt catalyst containing 25 wt% Co and 0.1 wt% Pt were prepared via two-step aqueous incipient wetness co-impregnation of Puralox SCCA-5/170 γ-alumina (S_{BET} = 165 m^2/g, pore diameter of 8.3 nm and pore volume of 0. 477 cm^3/g, Sasol) with solutions of cobalt(II) nitrate ($Co(NO_3)_2$ $6H_2O$) and tetraammineplatinum(II) nitrate ($Pt(NH_3)_4(NO_3)_2$). After impregnation, the catalyst was dried in air flow at 373 K and then calcined at 773 K for 5 h with the temperature ramp of 1 K/min.

Catalyst characterization

X-ray powder diffraction (XRD) analysis was carried out on a Rigaku Ultima IV diffractometer (Japan). The diffraction angles were scanned from 10 to 80° (2θ) with a speed of 5º/min. CuK_{α} radiation (λ = 0.15406 nm) generated at 40 kV and 30 mA was used as the X-ray source.

Thermogravimetric (TG) analysis was performed in air flow on a SDT-Q600 apparatus. The samples were heated from 30 to 800 °C at a heating rate of 10 °C /min. The air flow rate was 100 ml/min.

Infrared spectra of the pellets with KBr have been registered using Nicolet IS50 FT-IR.

Catalytic tests

Carbon monoxide hydrogenation was carried out on the REALCAT platform in a Flowrence® high-throughput unit (Avantium) equipped with 16 parallel milli-fixed-bed reactors (d=2 mm) operating at a pressure of 20 bar, H_2/CO= 2 molar ratio, T=220 ºC and GHSV from 13 -54 Lh^{-1} g_{cat}^{-1}. The molar ratio of acid to CO 0.25 and 0.12 has been used during the test.

The catalyst loading was 100 mg per reactor. Prior to the catalytic test all the samples were activated in a flow of hydrogen at atmospheric pressure during 10 h at 400 °C. During the activation step, the temperature ramp was 3 °C/min. After the reduction, the catalysts were cooled down to 180 °C and a flow of premixed syngas was gradually introduced to the catalysts. When pressure attained pressure of the reaction, the temperature was slowly increased to the temperature of the reaction. The reaction has been conducted for 60 h at different GHSV of syngas. The reaction has been conducted in 3 steps: catalytic test without addition of acid for 12 h, test in the presence of acid flow 30 h and the last step without addition of acid. Gaseous reaction products were analyzed by on-line gas chromatography. Analysis of permanent gases was performed using a Molecular Sieve column and a thermal conductivity detector. C_1-C_4 hydrocarbons were separated in a PPQ column and analyzed by a thermoconductivity detector. C_5-C_{12} hydrocarbons were analyzed using CP-Sil5 column and a flame-ionization detector. High-molecular-weight products were collected at atmospheric pressure in vials heated at 80 °C and analyzed by SIMDIS technique. The carbon monoxide contained 5 % of helium, which was used as an internal standard for calculating carbon monoxide conversion. The catalytic test with labelled acid has been performed by taking samples of gas phase and subsequent analysis in Shimadzu GCMS-QP2010 SE. The product selectivity (S) was reported as the percentage of CO converted into a given product and expressed on carbon basis.

The hydrogenation of octene or octylacetate has been tested separately by addition of 5 mmol/h of octene or octylacetate to 20 mg of reduced catalyst at 220 °C under 20 bar at hydrogen flow 6 ml/min and CO flow 2 ml/min.

Table S1. Results of catalytic tests without and in the presence of carboxylic acids (T=220 ºC,

Flow, mmol/h·g		Acid transformation		CO transformation											
CO	Acid	Conv., %	Selectivity to alcohol, %	Conv., %	Selectivity, C at. %										
					CH_4	C_2-C_4			C_5-C_{12}			C_{13}-C_{25}			C_{25}+
						olef	par	*ratio*	olef	par	*ratio*	olef	par	*ratio*	
no acid addition															
50	-	-	-	82	5	3	2	*1.5*	5	12	*0.4*	-	38	*0*	35
100	-	-	-	49	6	4	2	*2*	7	14	*0.5*	-	35	*0*	32
200	-	-	-	24	10	5	2	*2.5*	12	13	*0.9*	-	32	*0*	26
Acetic acid															
50	12	14	86	32	6	5	3	*1.6*	17	13	*1.3*	**9**	15	*0.6*	32
100	25	11	90	22	5	5	3	*1.6*	18	14	*1.3*	**12**	15	*0.8*	28
100	12	5	95	25	6	5	3	*1.6*	15	11	*1.4*	**7**	21	*0.4*	32
100	-*	-	-	18	8	5	3	*1.6*	14	11	*1.3*	-	35	-	24
Butyric acid															
50	12	5	79	27	6	5	3	*1.6*	**14**	11	*1.3*	**8**	14	*0.6*	39
100	25	3	80	16	7	5	3	*1.6*	**16**	11	*1.5*	**9**	12	*0.8*	37

* - addition of acid has been switched off

p=20 bar, H_2/CO =2, GHSV=13-54 L/g_{cat}·h)

Flow, mmol/h·g		Conversion of acetic acid, %	Selectivity, %			
			Ethanol	Hydrocarbons		
H_2	Acid			C_2	C_4	C_6
200	25	27	83	6	3	2

Table S2. Results of hydrogenation of acetic acid over Co/Al_2O_3 catalyst (T=220 ºC, p=20 bar)

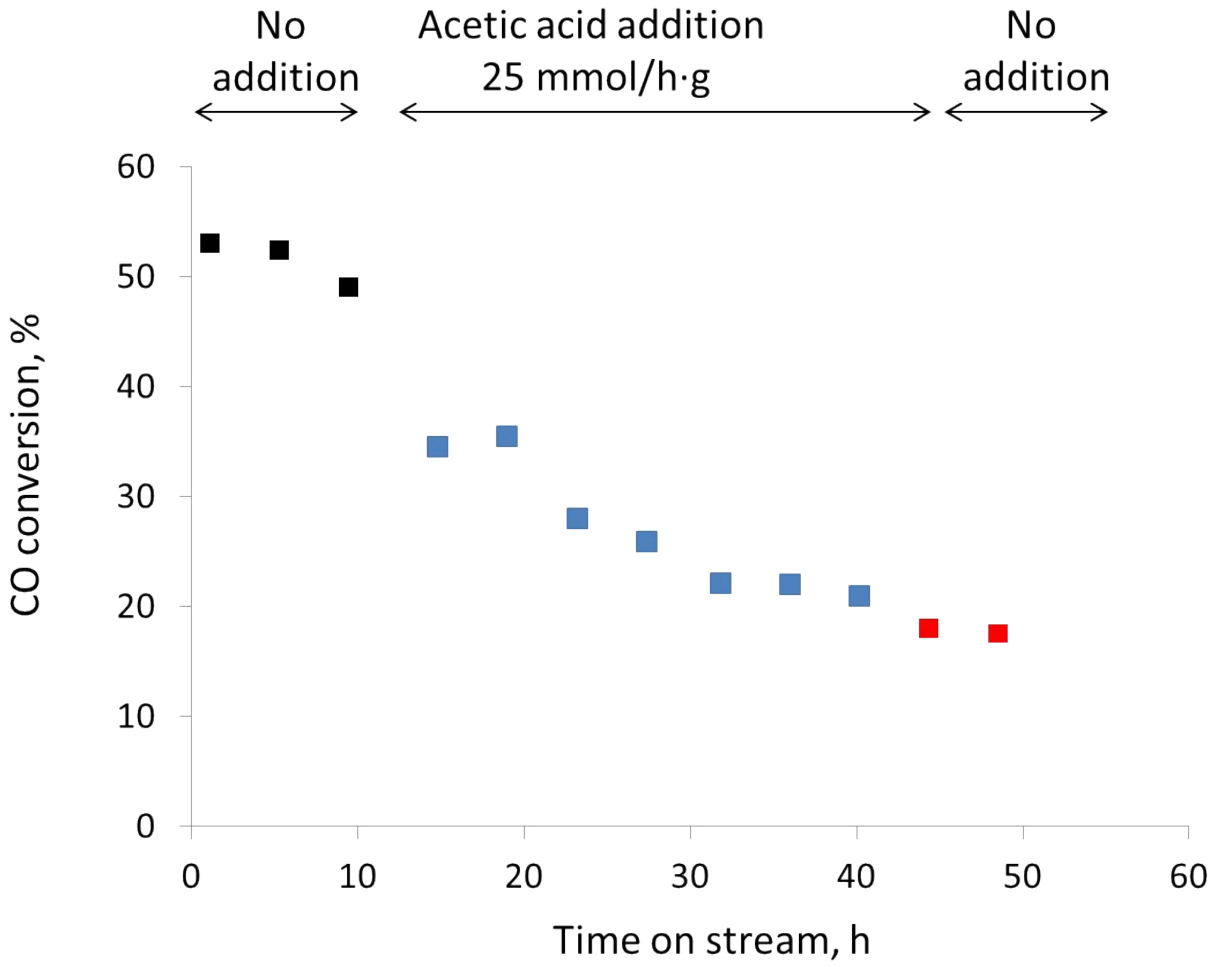

Figure S1. Effect of acetic acid addition on the CO conversion as a function of time. Reaction conditions: p= 20 bar, H_2/CO=2, GHSV =6.7 $Lg^{-1}h^{-1}$.

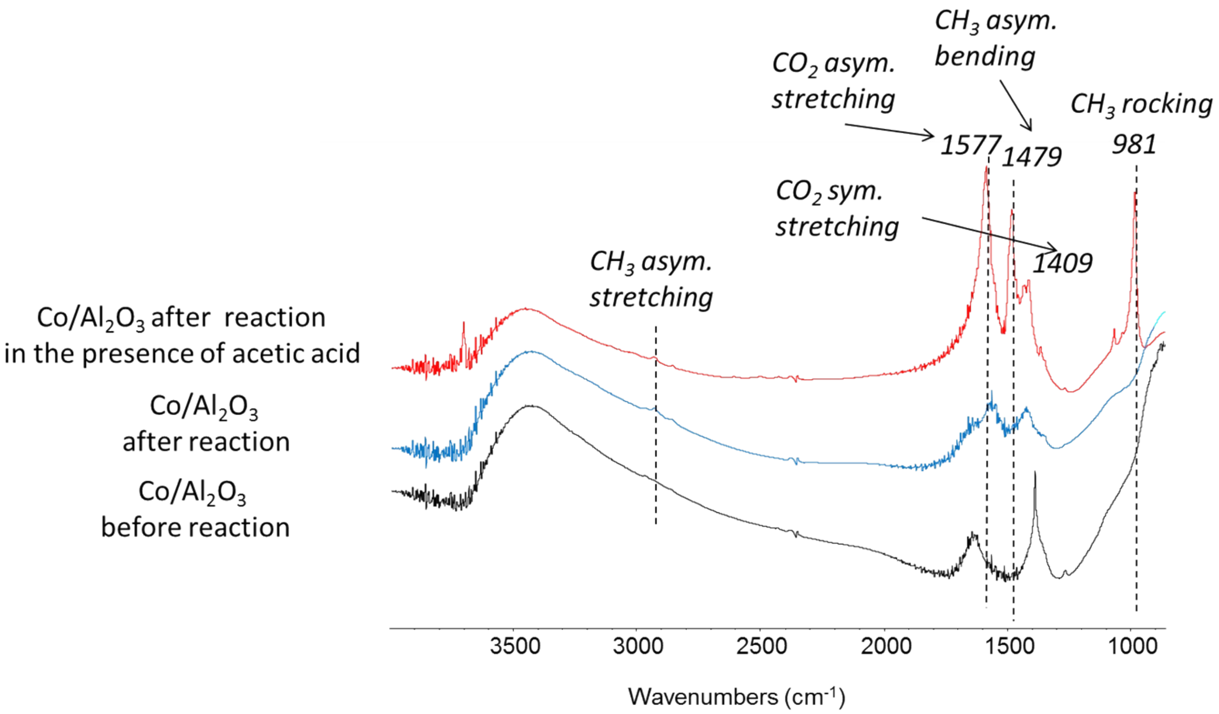

Figure S2. FTIR spectra of the catalyst before and after FT synthesis in the presence of acetic acid . *Reference: Zh. Nickolov, G. Georgieva, D. Stoilovab, I. Ivanova, Journal of Molecular Structure 354 (1995) 119-125.*

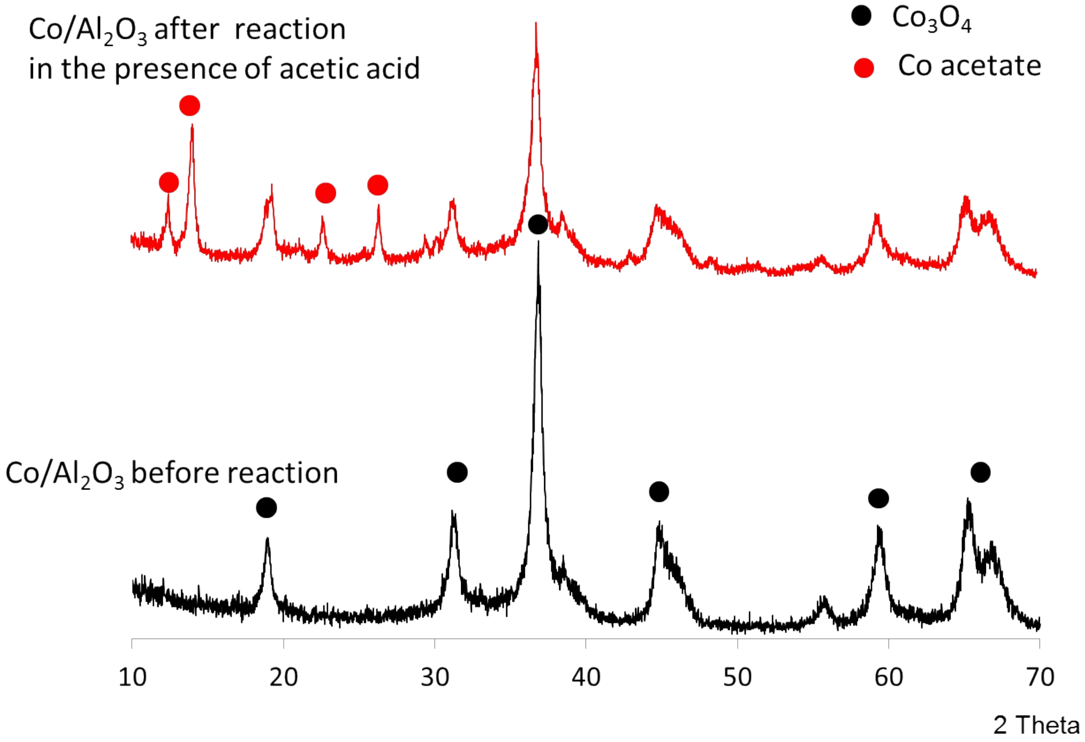

Figure S3. XRD of the catalyst before and after FT synthesis in the presence of acetic acid.

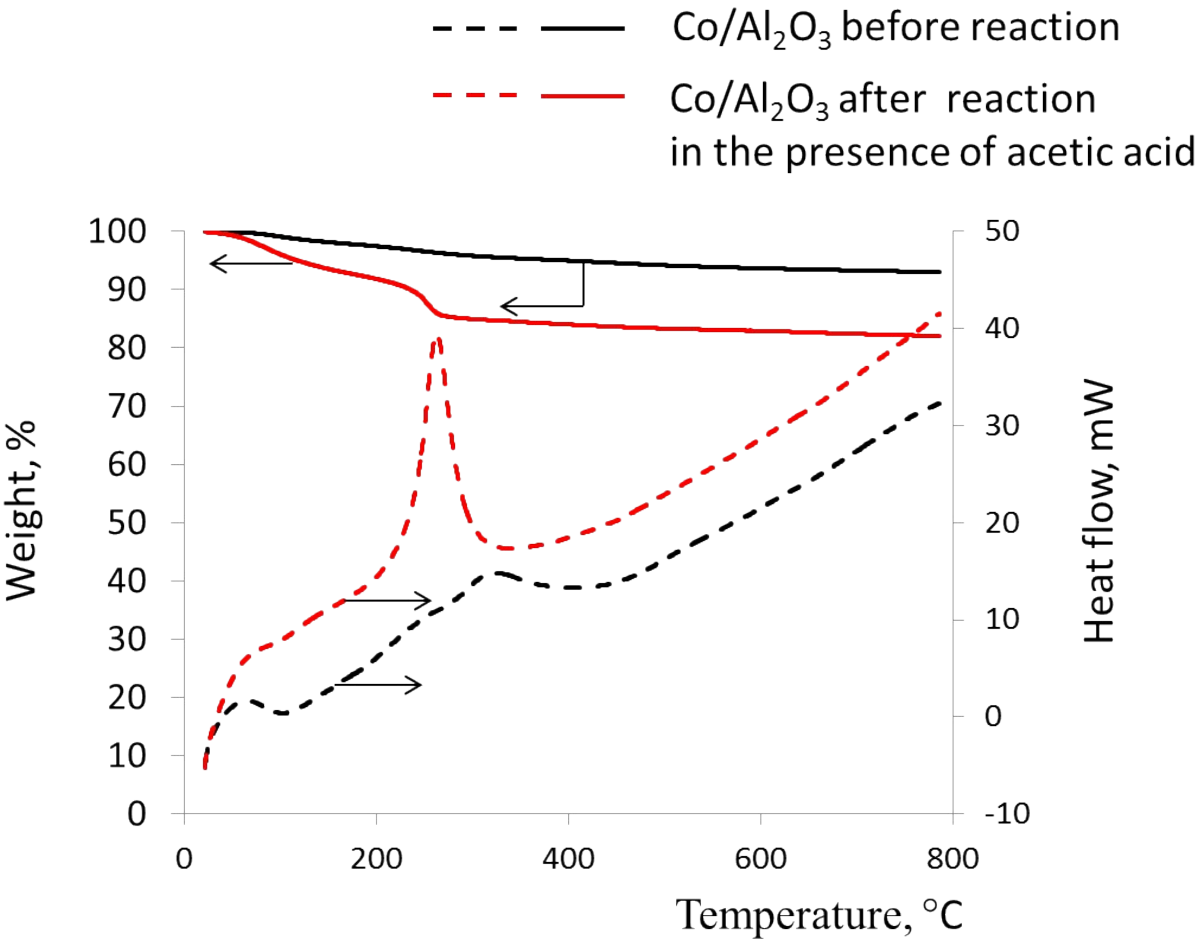

Figure S4. TG analysis of the catalyst before and after FT synthesis in the presence of acetic acid.

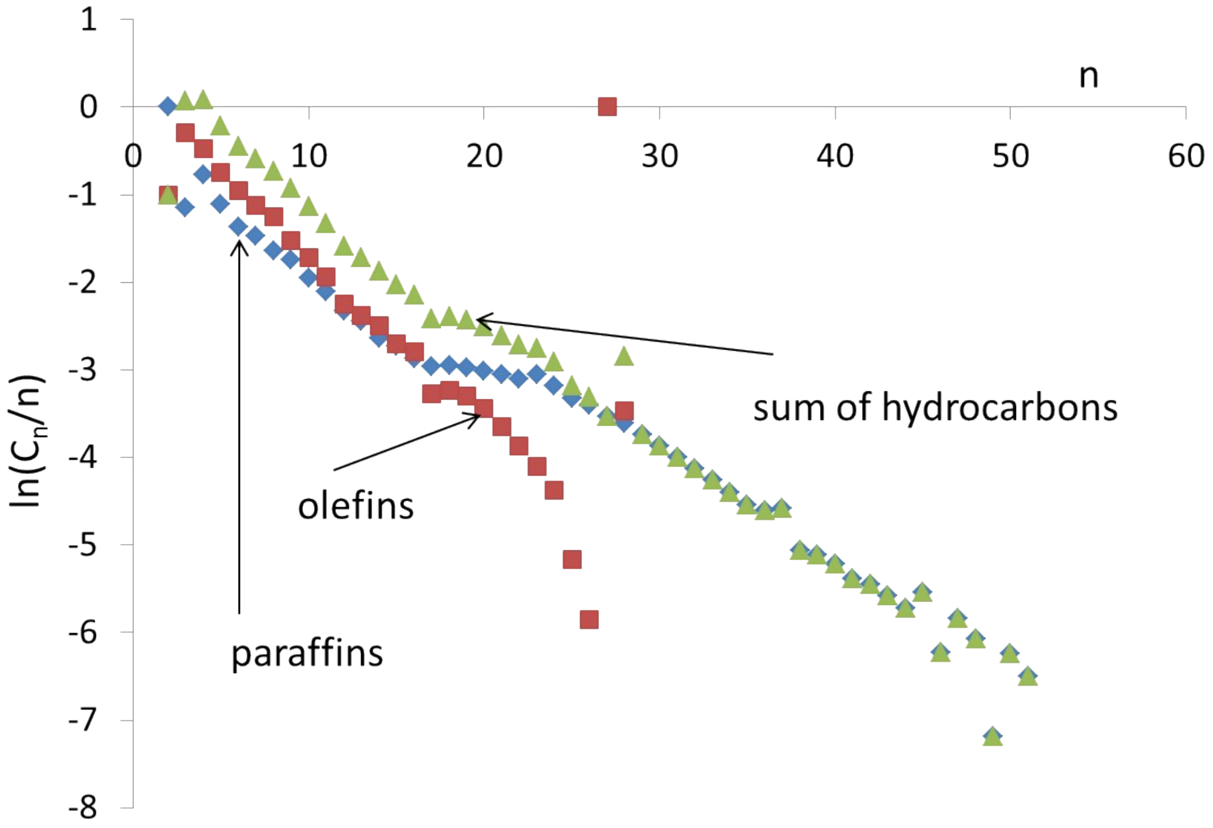

Figure S5. ASF distribution for olefins, paraffins and sum of hydrocarbons for FT synthesis with addition of butyric acids

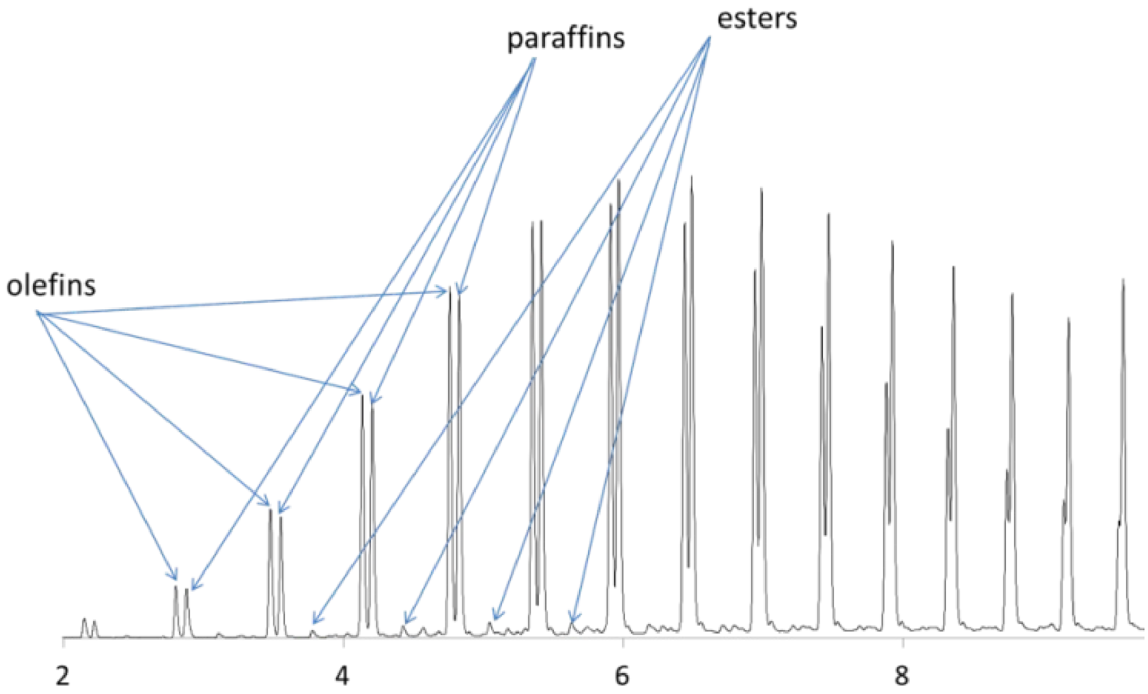

Figure S6. Chromatogram of SimDist analysis with identification of the peaks by GC-MS analysis

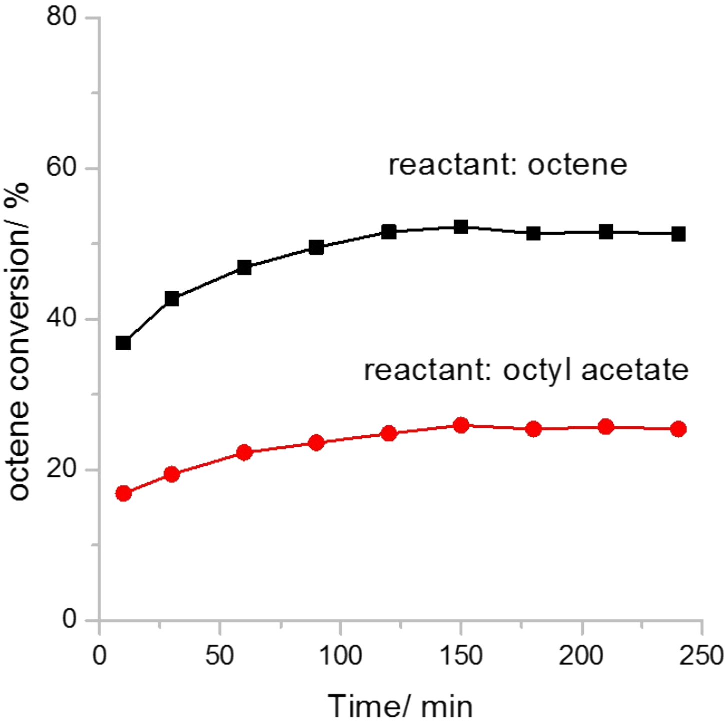

Figure S7. Time on stream for octene and octyl acetate hydrogenation under FT condition. Reaction condition: catalyst 20 mg, H_2 6 ml/min, CO 2 ml/min, P=20 bar, T=220 ^{o}C, octene or octyl acetate rate: 5 mmol/h.