Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

In situ XAFS study on the formation process of cobalt carbide under Fischer-Tropsch reaction

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Table S1. Co K-edge EXAFS curves fitting parameters in syngas1 process:

Sample	**Shell**	**N**	**R(Å)**	**ΔE_0 (eV)**	**$\Delta\sigma^2*10^3$ (Å^2)**
Co_3O_4	Co-O	4.0	1.91	-8.3	2.1
	Co-Co	12.0	3.04	9.5	9.2
	Co-O	5.0	3.44	-8.3	3.2
H_2-145min	Co-O	1.9	2.12	2.8	5.8
	Co-Co	9.6	2.49	1.4	9.8
	Co-Co	4.6	3.05	1.4	3.1
Syngas1-90	Co-C	0.6	1.91	10.0	6.1
	Co-Co	5.4	2.52	0.5	8.6
	Co-Co	1.5	2.70	0.5	15.6
	Co-Co	0.7	2.90	0.5	9.8
Syngas1-148min	Co-C	1.2	1.91	-10.0	6.31
	Co-Co	1.0	2.52	-9.5	4.47
	Co-Co	1.6	2.72	-9.5	8.34
	Co-Co	2.2	2.98	-9.5	6.06
Syngas1-224min	Co-C	1.8	1.90	-5.6	4.00
	Co-Co	0.7	2.51	-5.6	6.54
	Co-Co	3.4	2.63	-5.6	6.54
	Co-Co	2.6	2.79	-5.6	6.54
	Co-Co	1.2	3.00	-5.6	6.54

$\Delta k = 3.0 – 12.0 Å^{-1}$, $\Delta r = 1.0 – 3.0$ Å.

N, coordination number; R, distance between absorber and backscatter atoms; ΔE_0, inner potential correction;σ^2, Debye-Waller factor to account for both thermal and structural disorders;

The obtained S_0^2 of Co foil was 0.90 and it was fixed in the subsequent fitting of Co K-edge data for the catalyst.

Table S2. Co K-edge EXAFS curves fitting parameters in syngas2 process:

Sample	**Shell**	**N**	**R(Å)**	**ΔE_0 (eV)**	**$\Delta\sigma^2*10^3$ (Å^2)**
Co_3O_4	Co-O	4.0	1.91	-8.3	2.1
	Co-Co	12.0	3.04	9.5	9.2
	Co-O	5.0	3.44	-3.3	3.2
H_2-10min	Co-O	6	2.09	-5.0	11.5
	Co-Co	12	3.00	1.4	12.8
syngas2-91min	Co-C/O	4.4	2.12	6.8	13.0
	Co-Co	0.2	2.51	10.0	3.0
	Co-Co	2.4	2.70	10.0	9.8
	Co-Co	6.7	3.15	10.0	5.4
syngas2-176min	Co-C	1.8	1.90	-5.6	4.00
	Co-Co	0.7	2.51	-5.6	6.54
	Co-Co	3.4	2.63	-5.6	6.54
	Co-Co	2.6	2.79	-5.6	6.54
	Co-Co	1.2	3.00	-5.6	6.54

$\Delta k = 3.0 – 12.0 Å^{-1}$, $\Delta r = 1.0 – 3.0$ Å.

N, coordination number; R, distance between absorber and backscatter atoms; ΔE_0, inner potential correction;σ^2, Debye-Waller factor to account for both thermal and structural disorders;

The obtained S_0^2 of Co foil was 0.90 and it was fixed in the subsequent fitting of Co K-edge data for the catalyst.

Table S3. Catalytic evaluation during syngas1 and syngas2 process.

	Reaction time (min)	CO conv. (C%)	CO_2 sele. (C%)	Product distribution				Olefin/Paraffin ratio $C_{2-4}^{=}/C_{2-4}$
				CH_4	C_{2-4}(O&P)	C_{5+}	$C_{2-4}^{=}$	
Syngas1	36	5.65	9.22	4.21	19.18	76.61	18.00	15.3
	67.2	5.11	11.34	3.79	13.98	82.23	13.04	13.8
	97.8	5.32	14.45	4.64	13.33	82.02	12.11	9.8
	129	5.62	18.43	4.87	11.2	83.92	9.85	7.2
	159	5.73	19.89	5.98	11.98	82.04	10.29	6.1
	190.2	5.93	24.60	5.52	10.98	83.51	9.33	5.7
	220.8	6.11	30.82	4.50	10.68	84.82	8.91	5.0
Syngas2	37.2	10.76	14.36	9.64	20.24	70.12	15.77	3.5
	67.8	6.65	13.71	5.16	17.29	77.55	15.31	7.7
	97.8	7.25	16.27	5.56	16.22	78.22	13.91	6.0
	129	11.34	25.78	5.75	13.21	81.05	10.81	4.5
	160.2	13.63	33.56	4.96	10.48	84.56	8.56	4.4
	190.8	15.06	39.15	4.25	9.62	86.13	8.14	5.5

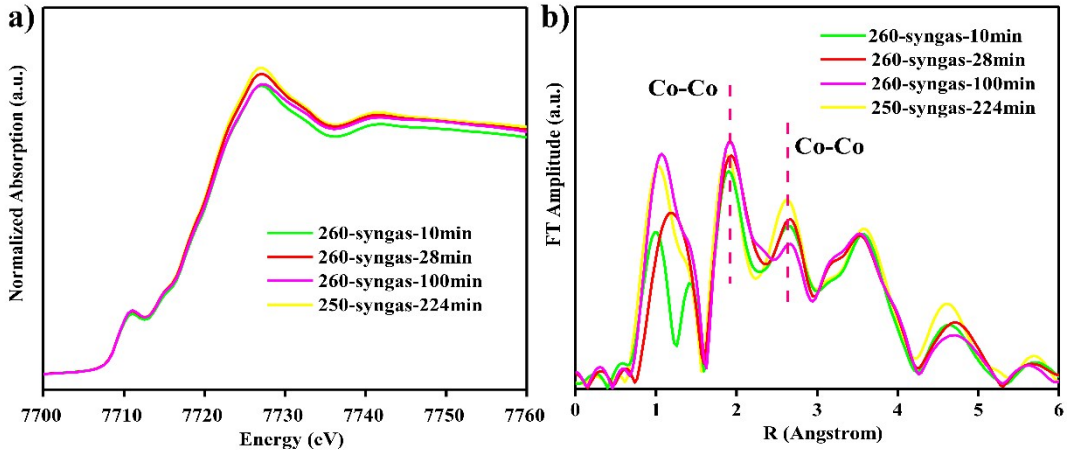

Fig. S1 a) XANES spectra of the change for 250℃ and 260℃; b) Fourier transform spectra for 250℃ and 260℃

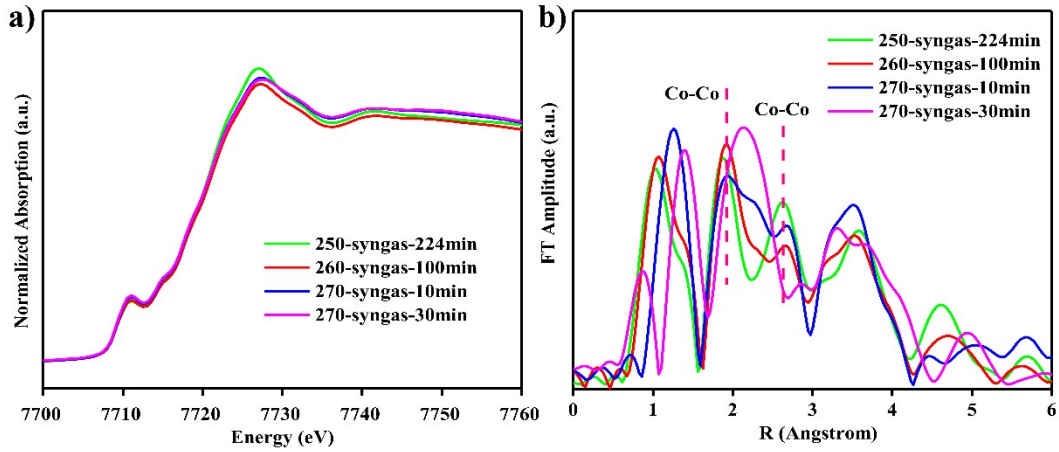

Fig. S2 a) XANES spectra of the change for 250℃, 260℃ and 270℃; b) Fourier transform spectra for 250℃, 260℃ and 270℃