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Electronic Supplementary Information

Mobility and Versatility of the Liquid Bismuth Promoter in the Working Iron Catalysts for Light Olefin Synthesis from Syngas

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CNT pretreatment

The treatments of CNT (Iolitec nanomaterial, 95%, outer diameter 20-40 nm) were performed according to our previous literature [1], which was treated with concentrated HNO_3 (68 wt. % HNO_3) for 14h at 140 °C under reflux. The treated samples were then filtered, washed with distilled water and dried in the oven.

Catalyst preparation

CNT-supported iron catalysts were prepared by incipient wetness impregnation of the CNT support with aqueous solutions of iron nitrate ($Fe(NO_3)_3.9H_2O$, Sigma-Aldrich). Bismuth nitrate ($Bi(NO_3)_3.5H_2O$, Sigma-Aldrich) was used for preparation of the Bi-promoted iron catalysts by co-impregnation. The Fe loading was fixed at 10 wt. % and bismuth content was 0.8 wt. % for in-situ XANES and in-situ STEM experiments. The molar ratios of Fe/Bi were 100/2. The catalyst with higher bismuth content (2 wt. %) were used for NAP-XPS. After the impregnation, the samples were dried in an oven at 80 °C for 12 h followed by calcination at 400 °C for 4 h under a flow of nitrogen (50 mL/min). The Bi/CNT (10 wt.%) was also prepared by the same synthesis procedure. The Bi- promoted catalyst was also prepared by mechanical mixing. The Fe/CNT and Bi/CNT samples were mechanically mixed in an agate mortar for 10 min to obtain the same molar ratio with the co-impregnated catalysts. The obtained physical mixtures were denoted as Fe/CNT +Bi/CNT.

Conventional catalyst characterization

The monometallic Fe/CNT iron catalyst and iron catalysts promoted with bismuth were prepared by either impregnation (FeBi/CNT) or mechanical mixing (Fe/CNT+Bi/CNT). The catalysts were first characterized by conventional ex-situ techniques (**Table S1**). The BET surface area of pure CNT was 143 m^2/g. The surface area and porous volume slightly decreased after introduction of iron and promoter. The iron and bismuth contents measured in the catalysts by ICP-OES were close to the inventory. The XRD patterns of the fresh iron catalysts (**Fig. S13**) clearly indicate the presence of mostly Fe_3O_4 magnetite with small amount of hematite (Fe_2O_3) in the calcined catalysts. Calculation using the Scherrer equation indicates similar iron oxide particle size (about 6 nm) in both monometallic and Bi-promoted catalysts. The iron oxide particles sizes measured by XRD are consistent with the results of TEM (**Table S1**). Iron dispersion in the calcined catalysts seems not to be much affected by the Bi promotion.

The H_2-TPR profiles of the iron monometallic and bismuth promoted catalysts (**Fig. S14**) are similar with the previous results observed for iron catalysts[2,3]. They show at least three hydrogen consumption peaks. The low-intense low temperature peaks at 380°C are attributed to the reduction of small amount of hematite present in the catalysts to magnetite [1,3,4], while the unresolved high temperature TPR peaks with the maximum at around 550°C correspond to the reduction of magnetite to wüstite and metallic iron. The Bi promotion results in higher intensity of high temperature TPR peaks compared to the monometallic Fe/CNT catalyst. This suggests that iron reducibility and in particular, reduction of magnetite to wüstite and metallic iron seem to be enhanced by the Bi promotion. The hydrogen consumption increases from 1.82 to 2.49 mmol/g after the promotion with bismuth (**Table S1).** The conclusion about the assignment of the TPR peaks and better reducibility of iron species in the Bi-promoted catalyst is also consistent with the in-situ X-ray diffraction (XRD) patterns measured in 5%H_2/N_2 at different temperatures (**Fig. S15)**. They display XRD peaks attributed to magnetite in the freshly calcined samples. Catalyst reduction in hydrogen leads to the appearance of XRD peaks attributed wüstite (FeO) and metallic iron. The patterns of the Bi promoted catalyst exposed to hydrogen at 300°C exhibit higher intensity of the XRD peaks attributed to metallic iron compared to the monometallic counterpart at the same temperatures. In agreement with TPR, the in-situ XRD results also suggest better reducibility of the Bi-promoted catalyst relative to the monometallic counterpart.

Table S1: Characterization of iron catalysts.

Sample	S_{BET}[a] (m^2/g)	V_{tot}[b] (cm^3/g)	D_{meso}[c] (nm)	D_{Fe}[d] (nm)	D_{Fe}[e] (nm)	Total H_2 Consumption[f] (mmol/g)	Fe content[g] (wt%)	Bi content before reaction[g] (wt%)	Bi content after reaction[g] (wt%)
CNT	143.3	0.55	15.4	-	-	-	-	-	-
Fe/CNT	130.3	0.46	14.1	6.5	6.4	1.82	10.3	-	-
FeBi/CNT	125.7	0.44	12.9	6.1	6.7	2.49	10.6	0.88	0.87
Fe/CNT+Bi/CNT	129.4	0.47	13.6	6.3	6.5	-	10.4	0.90	0.89

[a] BET surface area.
[b] Single point desorption total pore volume of pores, $P/P_0=0.975$.
[c] Pore diameter in the mesoporous region evaluated by the BJH method.
[d] Average particle size of iron oxide (magnetite) measured by XRD
[e] Average particle size of iron oxide by TEM.
[f] Total H_2 consumption and iron reducibility degree from TPR analysis.
[g] Fe, Bi and Pb contents from ICP-OES.

Table S2. Catalytic performances of CNT supported Fe catalysts in FT synthesis measured in the conventional fixed-bed reactor. [a]

Catalyst	P, bar	FTY, 10^{-4} $\mathrm{molg_{Fe}^{-1}s^{-1}}$	CO conv. (%)	CO_2 select. (%)	Hydrocarbon selectivity (%)				$C_{2-4}^{=}$/ C_{2-4}^{o}
					CH_4	$C_{2-4}^{=}$	C_{2-4}^{o}	C_{5+}	
Fe/CNT	10	1.0	37.1	39	32.1	31.4	18.3	18.2	1.72
	1	0.08	2.7	10	33.5	42.2	10.4	13.7	4.01
FeBi/CNT	10	1.6	58.2	46	28.9	40.0	16.8	14.3	2.38
	1	0.4	15.3	31	30.1	62.2	5.1	2.6	12.2
Fe/CNT+Bi/CNT	10	1.3	47.2	44	30.5	36.5	16.9	16.1	2.16
	1	0.3	9.7	29	32.1	54.3	8.8	4.8	6.17
FeNa/CNT	10	1.0	35.8	40	25.4	28.6	13.8	32.2	2.07
FeK/CNT	10	1.2	40.1	43	24.6	35.7	15.9	24.8	2.25

[a] Reaction conditions: $W = 0.2$ g, $H_2/CO = 1$, $T = 350$ °C, GHSV= 4.8 $\mathrm{Lg^{-1}h^{-1}}$ time on stream = 10 h.

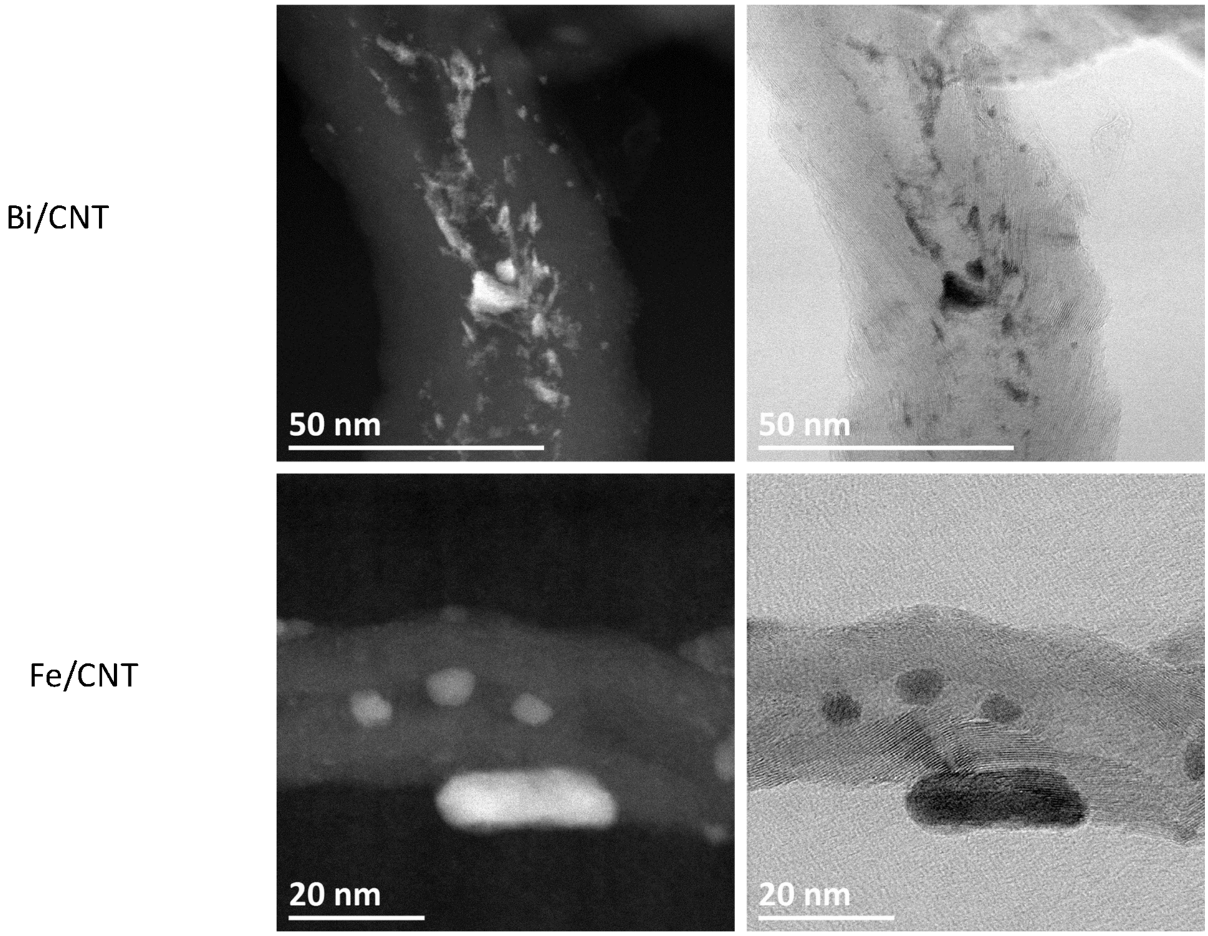


Fig. S1: Ex-situ HAADF (left) and BF (right) STEM images of the fresh Bi/CNT and Fe/CNT samples

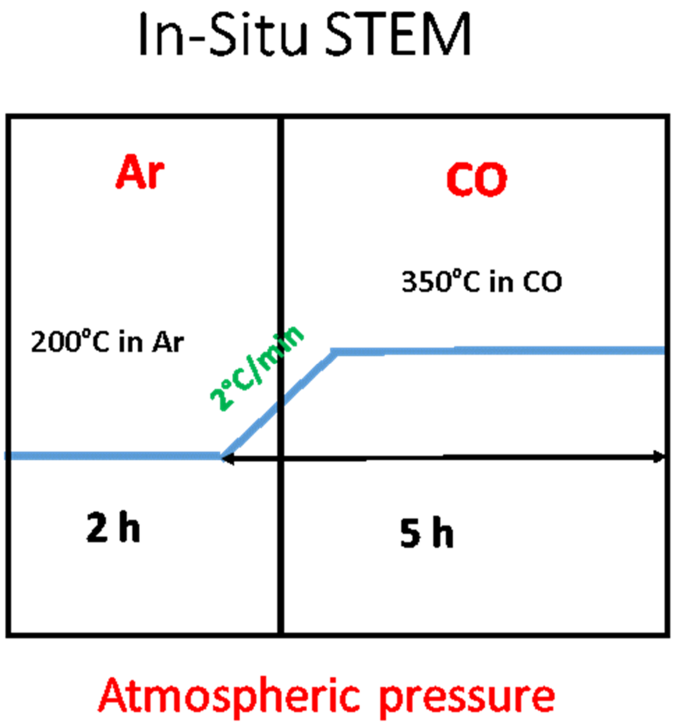
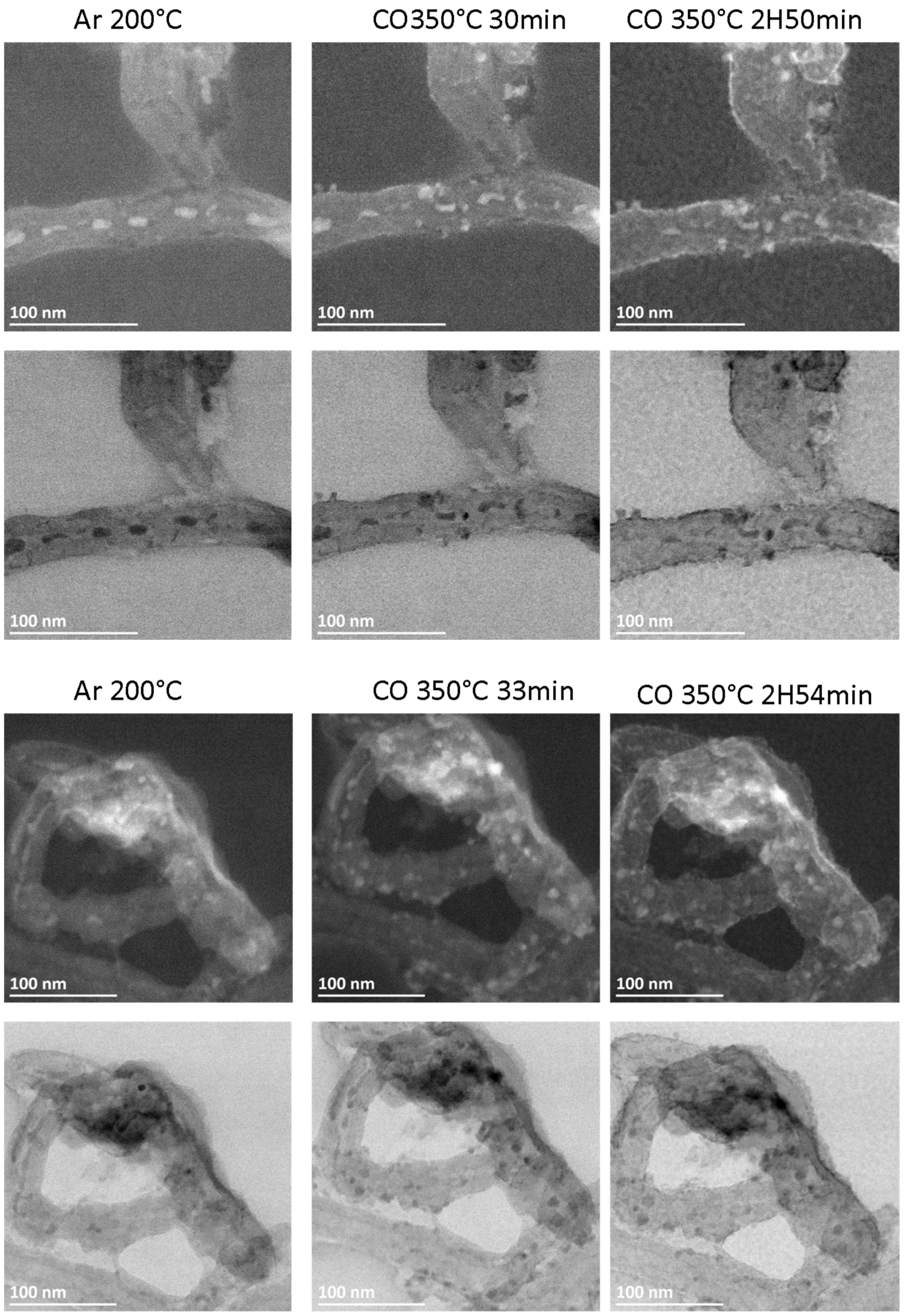


Fig. S2: Temperature program used in the in-situ STEM experiments with the FeBi/CNT and Fe/CNT+Bi/CNT samples


Ar 200°C
CO350°C 30min
CO 350°C 2H50min
100 nm
Ar 200°C
CO 350°C 33min
CO 350°C 2H54min
100 nm

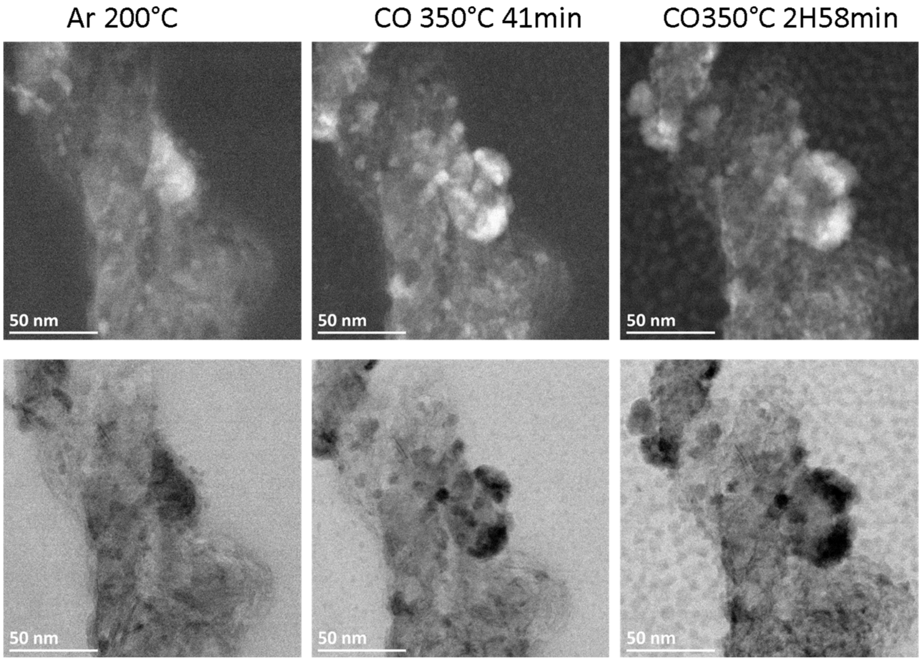
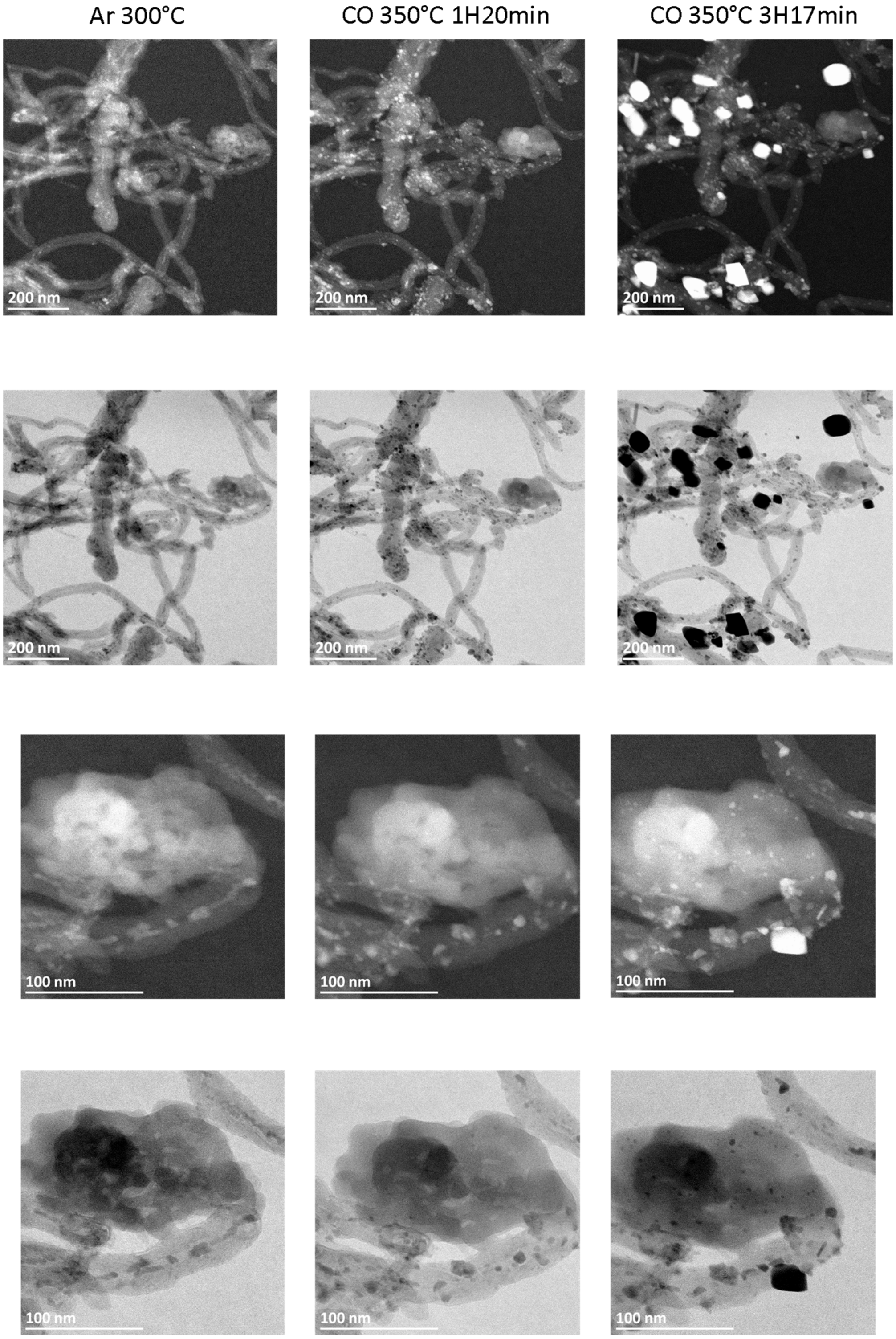


Fig. S3: In-situ HAADF and BF STEM images of the Fe/CNT+Bi/CNT catalyst measured in different zones in the presence of argon, CO and syngas at high temperatures. The temperature procedure is shown in **Fig. S2**.


Ar 300°C
CO 350°C 1H20min
CO 350°C 3H17min
200 nm
200 nm
200 nm
200 nm
200 nm
200 nm
100 nm
100 nm
100 nm
100 nm
100 nm
100 nm

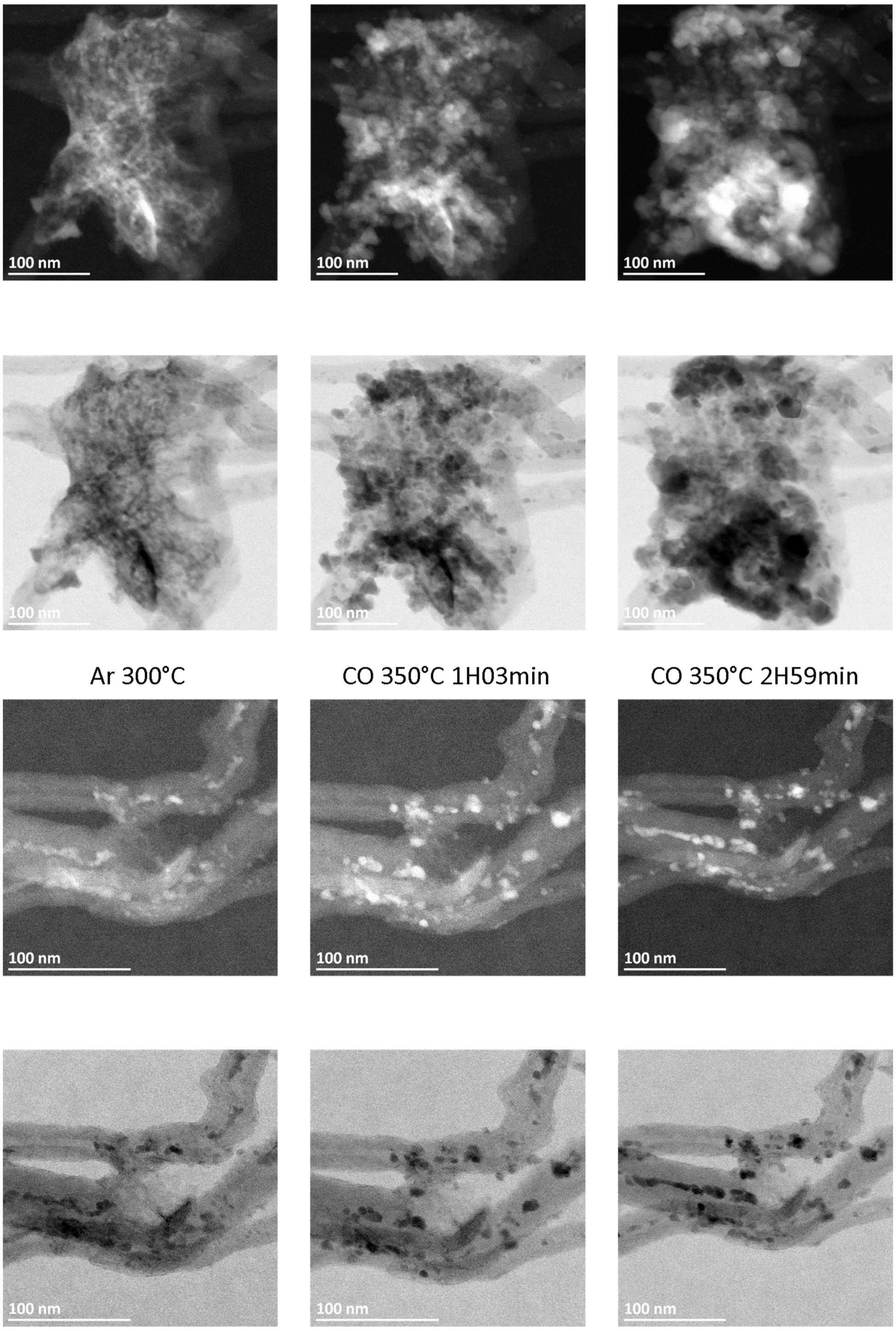


Fig. S4. In-situ HAADF and BF STEM images of the FeBi/CNT catalyst measured in different zones in the presence of argon and CO at high temperatures.

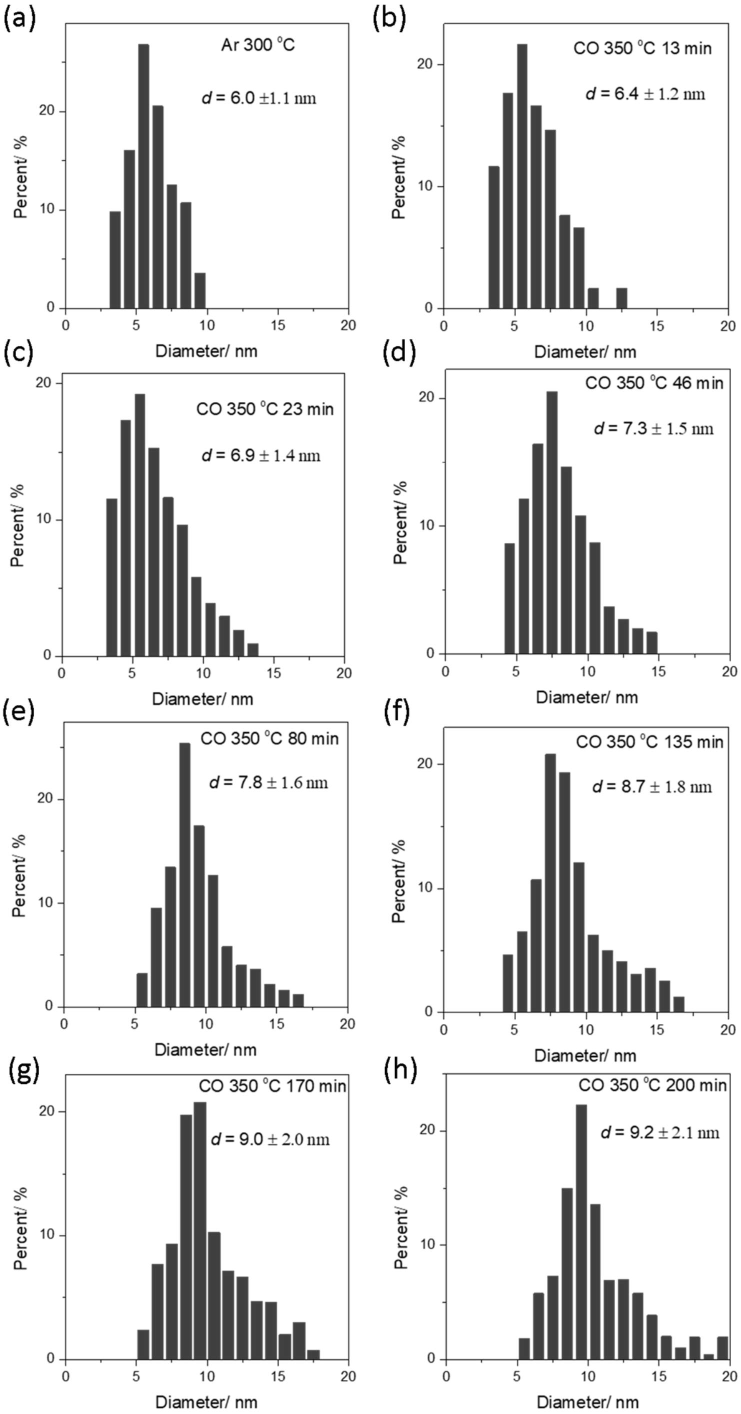


Fig. S5: Particle size distributions calculated from in-situ STEM images as function of time for the activation in CO for FeBi /CNT co-impregnated catalyst.

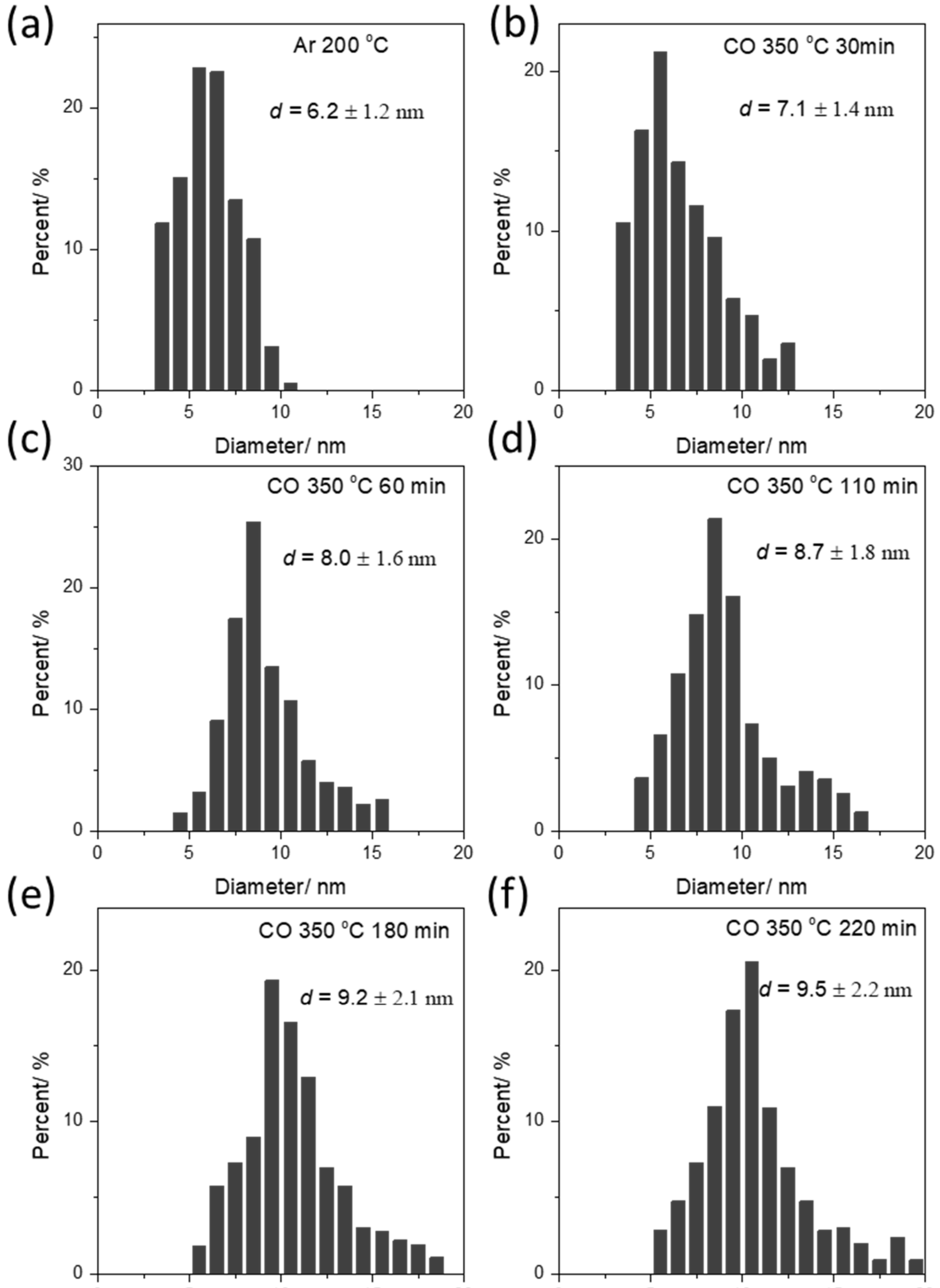


Fig. S6: Particle size distributions calculated from in-situ STEM as function of the time for the activation in CO for Fe/CNT+Bi/CNT prepared by mechanical mixing.

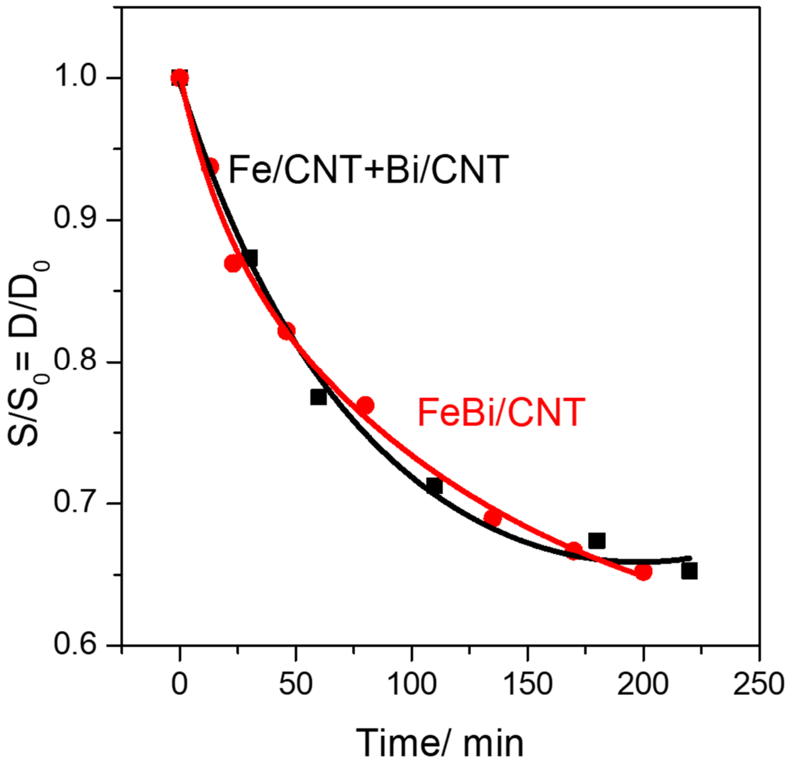


Fig. S7: Normalized surface areas for sintering of FeBi/CNT and Fe/CNT + Bi/CNT mixture catalysts in CO under 350 °C; symbols correspond to experimental data points, the solid curves to calculated data based on second order (m = 2) GPLE kinetics.

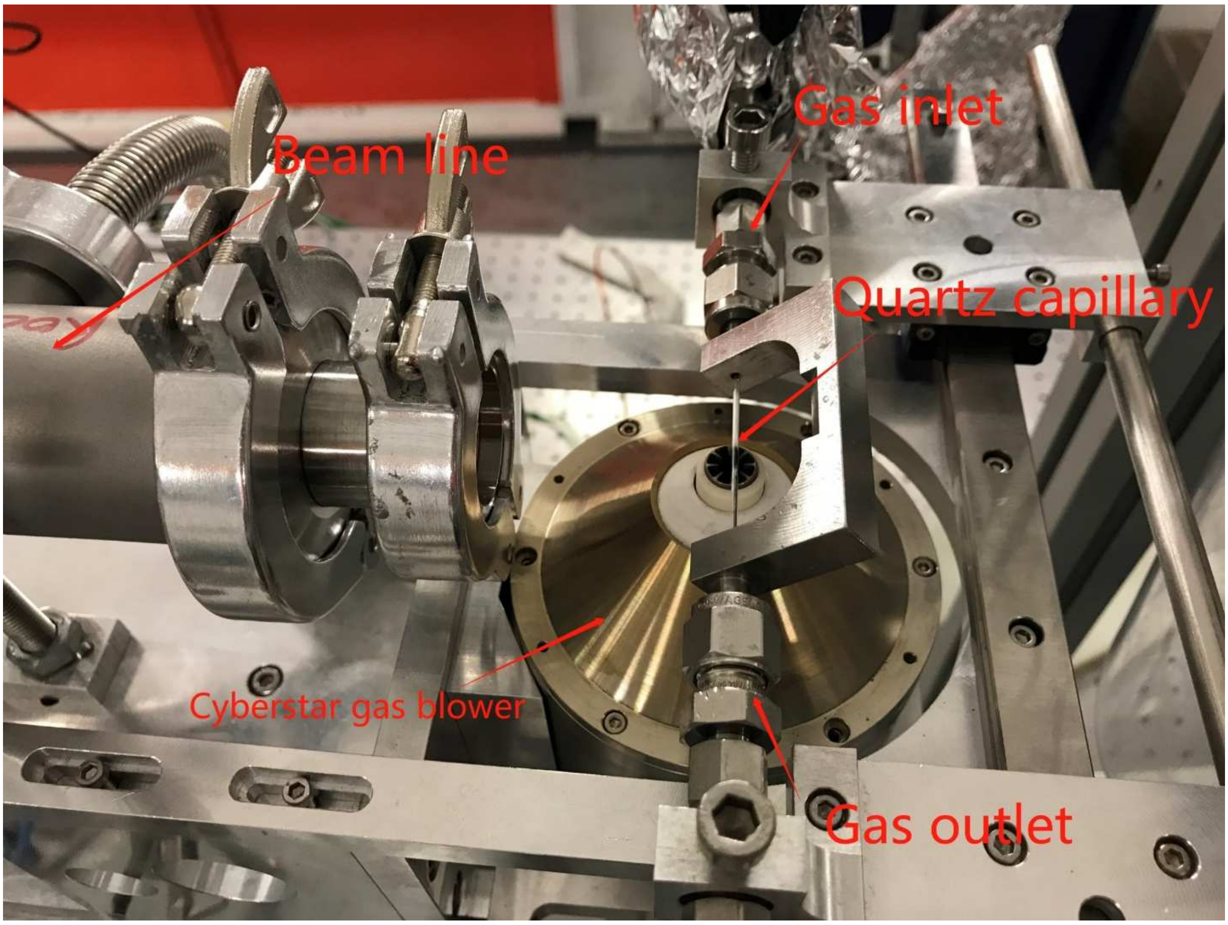


Fig. S8: Capillary reactor used for the in-situ XANES experiments

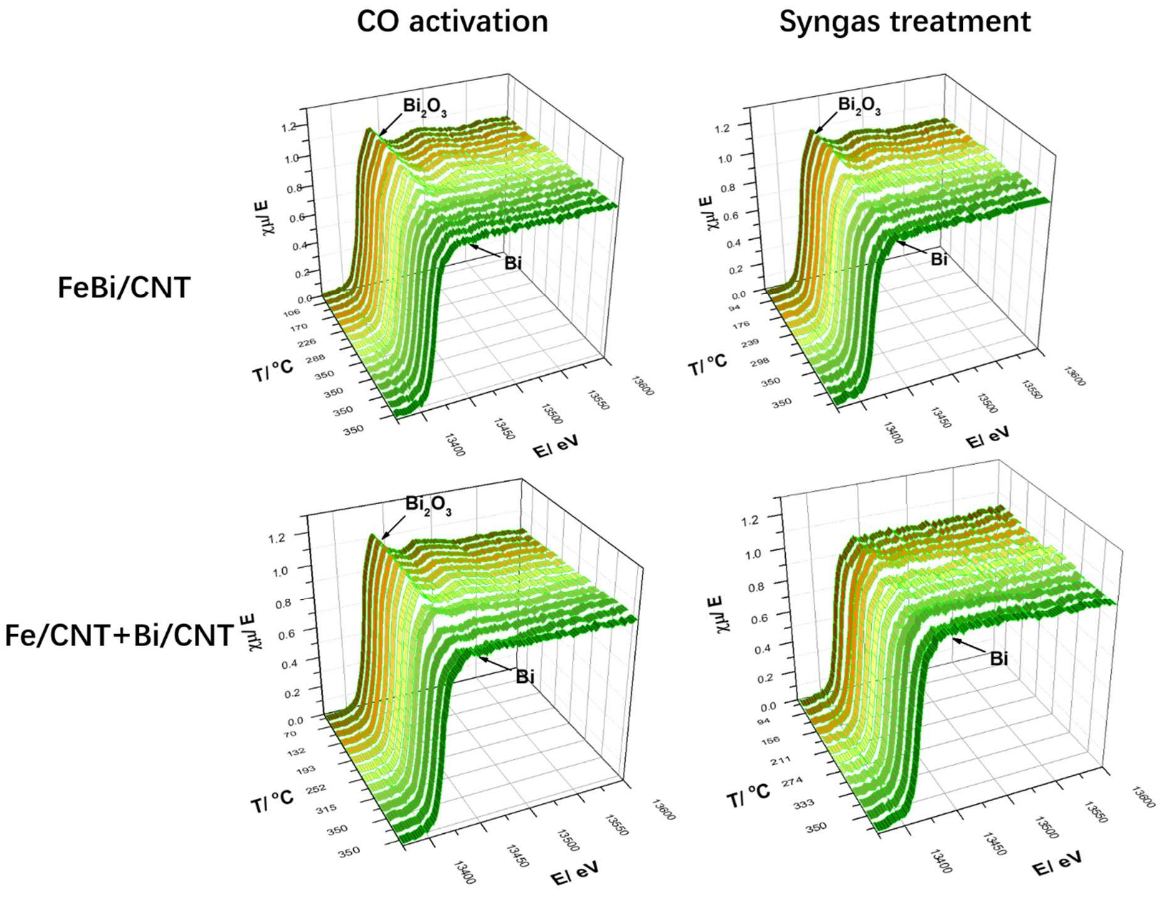


Fig. S9: Bi L3-edge XANES spectra of the temperature-programmed carbonization and reaction of the iron-based catalysts.

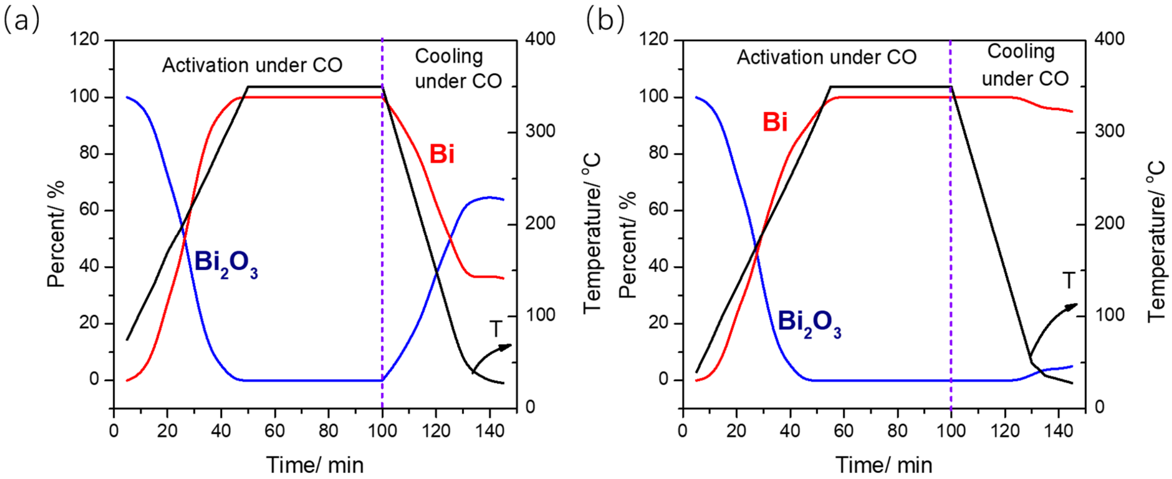


Fig. S10: Linear combination fitting of XANES for bismuth phase evolution during activation and cooling to RT in CO: (a) FeBi/CNT, (b) Fe/CNT+Bi/CNT.

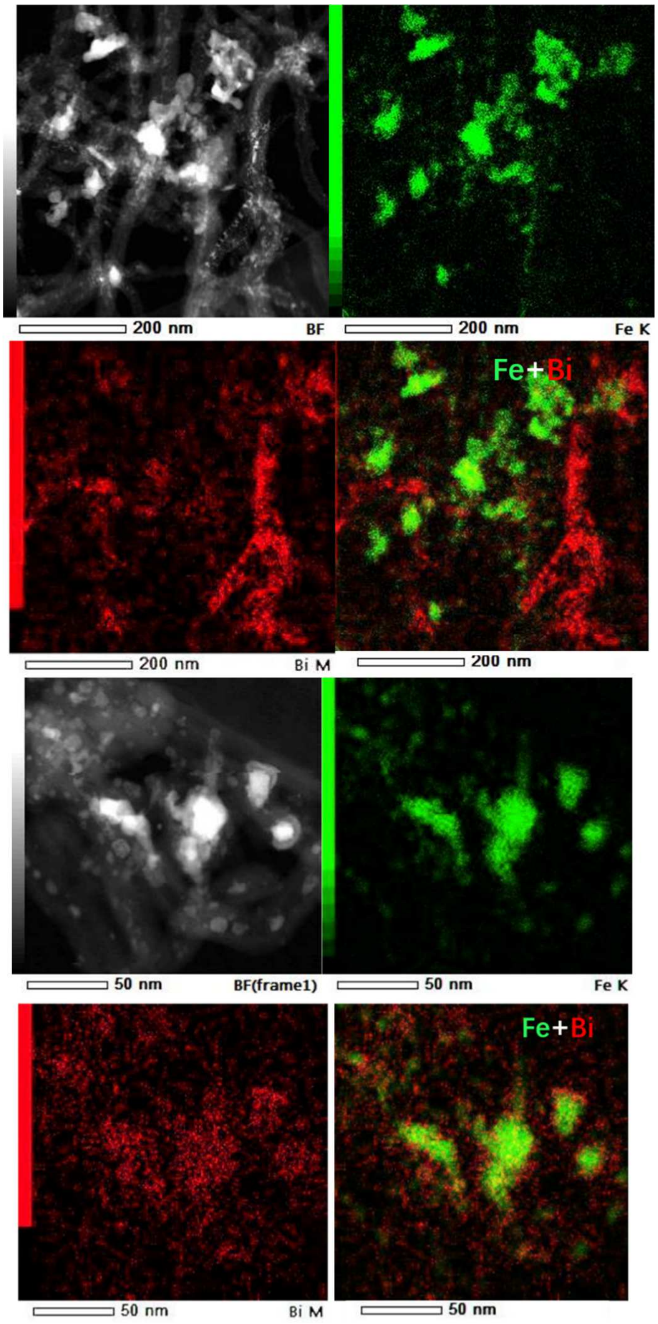


Fig. S11: STEM –EDX images of the fresh (top) and activated (bottom) Fe/CNT+Bi/CNT showing migration of Bi during activation

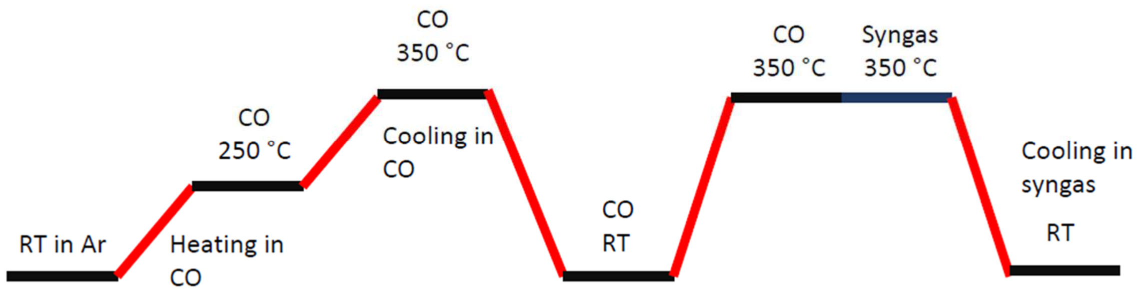


Fig. S12: Temperature procedure used in the NAP-XPS experiments

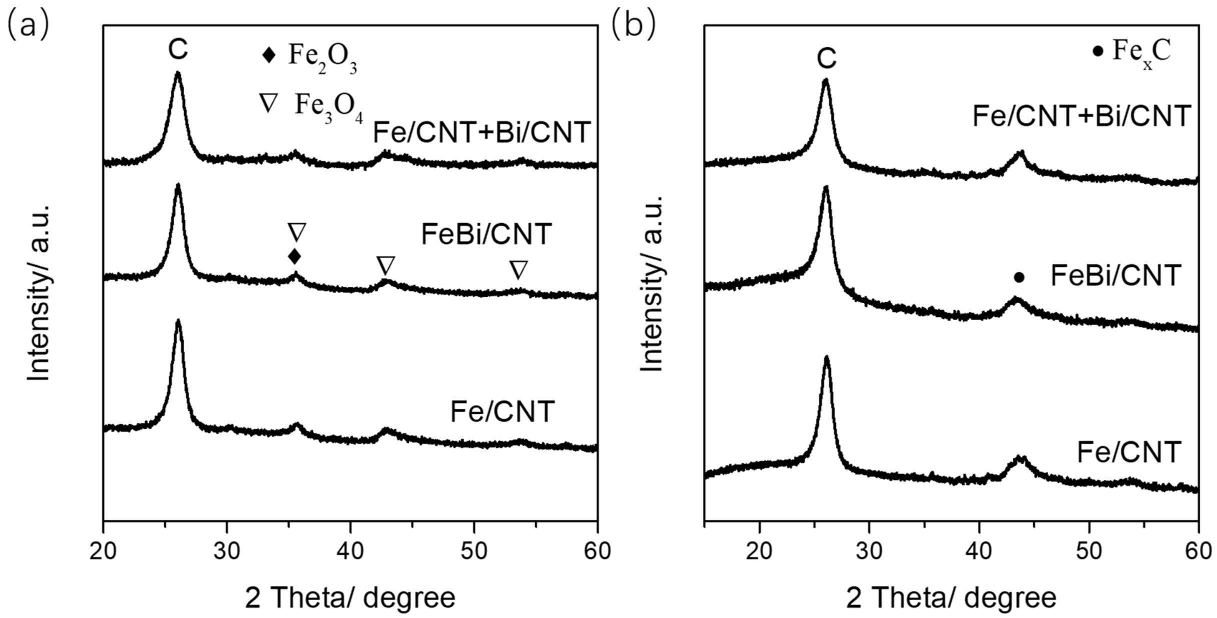


Fig. S13: XRD patterns of the iron-based catalysts: (a) fresh catalysts, (b) spent catalysts.

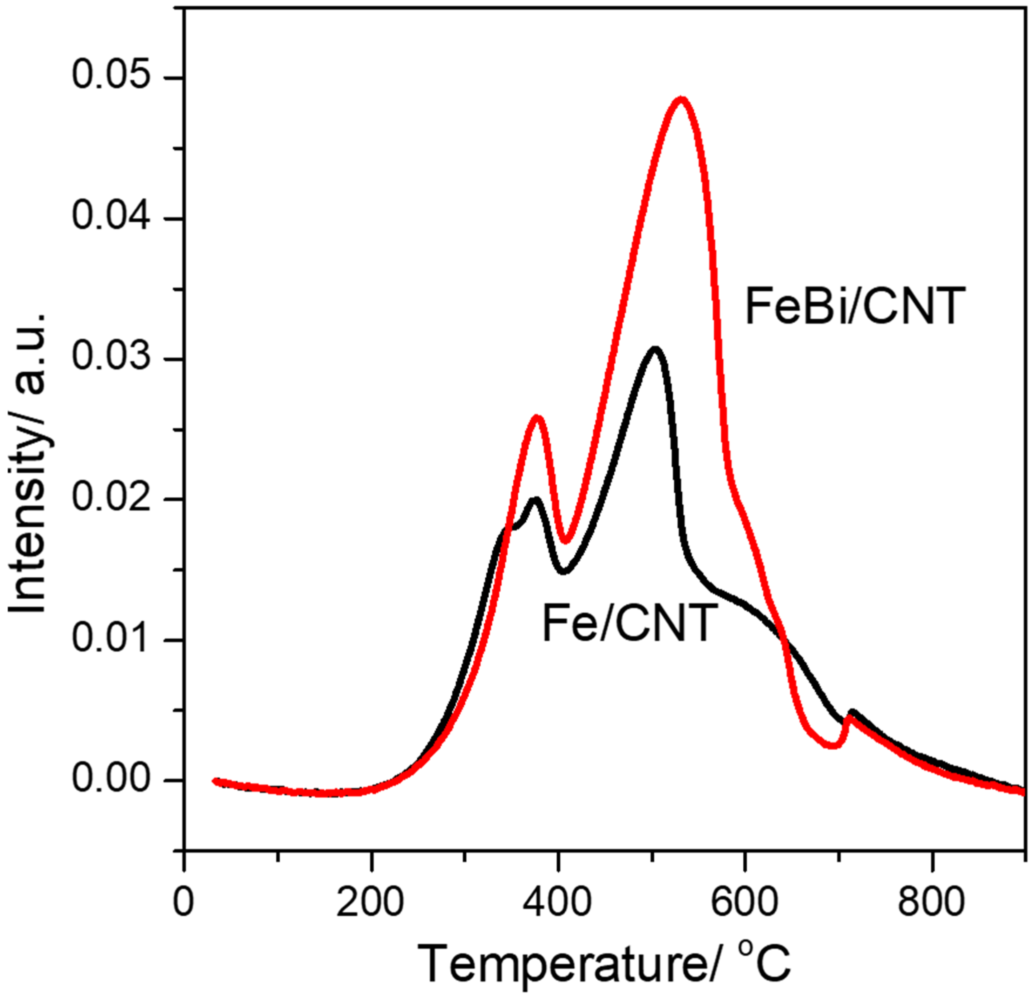


Fig. S14: H_2-TPR profiles of the iron-based catalysts.

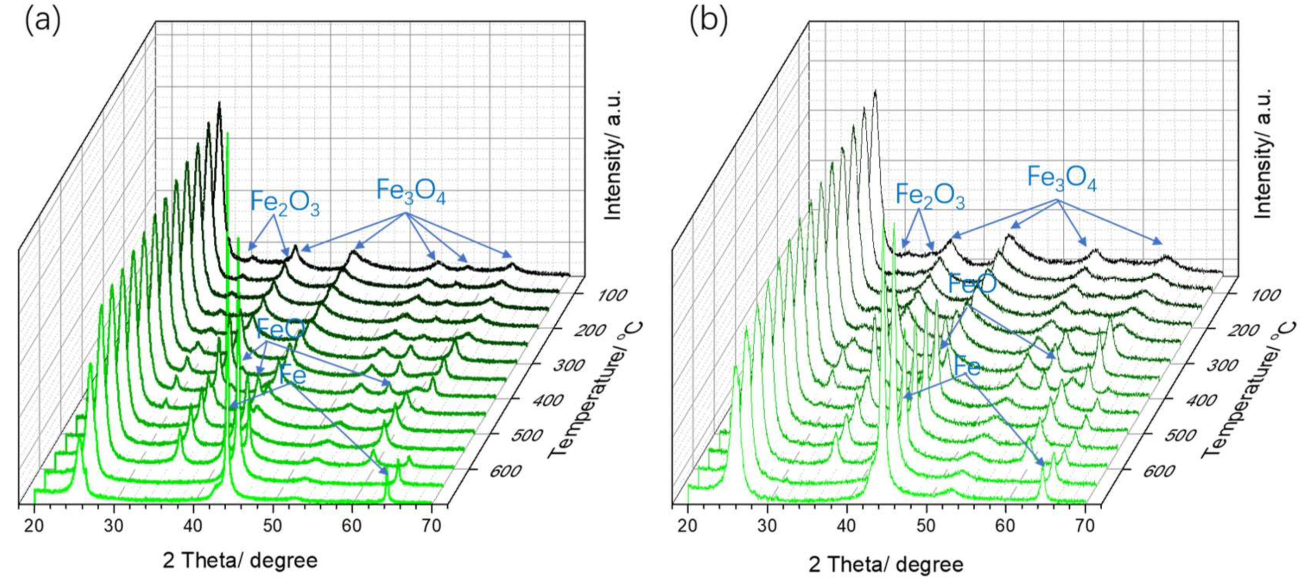


Fig. S15: In-situ XRD profiles of the iron-based catalysts (5%H_2/N_2): (a) Fe/CNT, (b) FeBi/CNT.

Reference

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