1	Supporting Information
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3	Influence of the Mn promoter on the composition and activity of the
4	adsorbed phase in the carbon paths of the CO hydrogenation reaction on 20
5	wt% Co/MnOx-Al2O3: An operando-SSITKA and transient kinetic study
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#### 24 MATERIALS AND METHODS

#### 25 S1. H<sub>2</sub>-TIC and H<sub>2</sub>-TPD studies

The transient rate ( $\mu$ mol g<sup>-1</sup> s<sup>-1</sup>) of H<sub>2</sub> chemisorption (R<sub>H<sub>2</sub></sub>) was determined using the following material balance Eq. (S1). The amount of hydrogen chemisorption ( $\mu$ mol H g<sup>-1</sup>) at 100 °C was estimated using Eq. (S2), and assuming a H:Co<sub>s</sub> ratio of 1:1.

30 
$$R_{H_2}(\mu mol g^{-1}s^{-1}) = \frac{F_T}{W} [y_{Kr}(t) - y_{H_2}(t)] - N_T \frac{dy_{H_2}}{dt}$$
 (Eq. S1)

31 
$$N_{\rm H} \,(\mu {\rm mol \ H \ g^{-1}}) = \frac{2 \, F_{\rm T}}{W} \int_{t=0}^{t_{\rm S.S}} [y_{\rm Kr}(t) - y_{\rm H_2}(t)] \,dt$$
 (Eq. S2)

32

In Eqs. (S1) and (S2),  $F_T$  is the total molar flow rate (µmol s<sup>-1</sup>) of the hydrogen gas mixture, W (g) is the mass of catalyst,  $N_T$  (mols) is the total number of moles of gas in the reactor,  $t_{s.s.}$  is the time at which the new steady-state is obtained under the dynamic hydrogen chemisorption conditions,  $y_{Kr}$  is the mole fraction of Kr, and  $y_{H_2}$  is the mol fraction of H<sub>2</sub> gas at the outlet of the CSTR micro-reactor. The accumulation term in Eq. (S1) was found to be very small compared to the other terms.

39

## 40 S2. <sup>12</sup>CO/<sup>13</sup>CO isotopic exchange at 155 °C

The dynamic rate response curve of consumed CO,  $R_{CO}$  (µmol g<sup>-1</sup> s<sup>-1</sup>) and the amount of <sup>12</sup>CO converted into <sup>12</sup>CO<sub>2</sub> at 155 °C during the 1<sup>st</sup> switch were estimated using Eqs. (S3) and (S4), respectively. In the material balance Eq. (S3), the rate of CO(g) accumulation in the CSTR micro-reactor was found to be very small compared with the other terms, thus it was neglected. The amount of <sup>12</sup>CO(g) consumed was estimated after integrating the R<sub>CO</sub>(t) response (Eq. S3), while the amount of adsorbed CO-s (N<sub>CO-s</sub>) is estimated using Eq. (S5).

48 
$$R_{CO}(\mu mol g^{-1}s^{-1}) = \frac{F_T y_{CO}^t}{W} [Z_{Kr}(t) - Z_{CO}(t)]$$
 (Eq. S3)

49 
$$N_{CO_2}(\mu mol g^{-1}) = \frac{F_T}{W} \int_0^{t_{s.s}} [y_{CO_2}(t)] dt$$
 (Eq. S4)

50 
$$N_{CO-s}(\mu mol g^{-1}) = N_{CO} - 2N_{CO_2}$$
 (Eq. S5)

51 In Eq. (S3),  $Z_i$  (i=Kr or CO) is the dimensionless concentration of Kr or CO gas ( $Z_i = y_i/y_{s.s.}$ ), where  $y_{s.s.}$  is the concentration of gaseous species i at steady state (no change 53 in the concentration measured). Thus, at the switch  $Z_i = 0$  and during the switch, 0 < Z54  $\leq 1$ . The parameters  $y_{CO}^f$  (Eq. S3) and  $y_{CO_2}$  (Eq. S4) are the mole fractions of CO in the 55 feed and of the CO<sub>2</sub> in the product stream, respectively.

56 During the 1<sup>st</sup> switch, He  $\rightarrow$  <sup>12</sup>CO/x%H<sub>2</sub>/Kr/He, the amount of <sup>12</sup>CO(g) consumed 57 describes the adsorbed <sup>12</sup>CO-s and the corresponding CO<sub>2</sub>(g) formation primarily via 58 the Boudouard reaction (Eq. S6). The possibility of adsorbed formate (HCOO) 59 production cannot be excluded (Eq. S7) but its decomposition at 155 °C to CO<sub>2</sub> and H<sub>2</sub> 60 must be excluded; no H<sub>2</sub> signal was detected in the gas analysis performed by online 61 mass spectrometer.

$$62 \quad 2 \operatorname{CO}_{s_1} \leftrightarrow \operatorname{CO}_2(g) + \operatorname{C}_{s_1} + s_1 \tag{Eq. S6}$$

63 
$$\operatorname{CO}_{s_1} + \operatorname{OH}_{s_2} \leftrightarrow \operatorname{HCOO}_{s_2} + s_1 \to \operatorname{CO}_2(g) + \frac{1}{2}\operatorname{H}_2(g)$$
 (Eq. S7)

In Eqs. S6-S7,  $s_1$  refers to a Co site, and  $s_2$  refers to an alumina support site. The amount of **reversibly chemisorbed CO-s** at 155 °C was estimated during the 2<sup>nd</sup> switch: 5 vol%  $^{12}CO/x \text{ vol}\% \text{H}_2/2 \text{ vol}\% \text{ Kr/He} \rightarrow ^{13}CO/x \text{ vol}\% \text{ H}_2/\text{He}$  (x=0, 5 and 10) and after using similar relationships as for the 1<sup>st</sup> switch (Eqs. S3-S5), where now the <sup>13</sup>CO and <sup>13</sup>CO<sub>2</sub> transient response curves are used.

69 In an effort to clarify whether formate is produced in a reversible step as shown in Eq. (S7), the same transient <sup>12</sup>CO/<sup>13</sup>CO isotopic experiment was conducted in the 70 DRIFTS reactor cell. IR spectra were recorded after 15 min in <sup>12</sup>CO/x vol% H<sub>2</sub>/He and 71 72 15 min after the switch to the equivalent <sup>13</sup>CO/x vol% H<sub>2</sub>/He isotopic gas mixture. The absence of a *red shift* in the IR bands of (O<sup>13</sup>CO)<sub>asym</sub> and (O<sup>13</sup>CO)<sub>sym</sub> associated with 73 the formate species (~ 1595 and 1380 cm<sup>-1</sup>) would imply that Eq. (S7) is not valid, so 74 75 the reaction step of formate mut be treated as irreversible. In the opposite scenario 76 where a red shift in the IR bands of formate appears, then Eq. (S7) (formation step only) must be valid. Under the <sup>13</sup>CO/x vol% H<sub>2</sub>/He isotopic gas mixture, <sup>13</sup>CO will be 77

consumed (i) to replace reversibly adsorbed <sup>12</sup>CO-s on Co and Mn-promoted Co 78 surfaces, (ii) to replace reversibly adsorbed H<sup>12</sup>COO for H<sup>13</sup>COO via Eq. 7, considering 79 that the concentration of surface formate production reached a steady-state after 15 min 80 gas treatment in <sup>12</sup>CO/x vol% H<sub>2</sub>/He gas mixture (1<sup>st</sup> switch). During the 1<sup>st</sup> switch, 81 consumption of  ${}^{12}CO(g)$  is due to (i) the formation of  $CO_2(g)$  – Boudouard rxn, (ii) 82 83 adsorption of CO-s, (iii) and formation of adsorbed formate (HCOO) species, either reversible, irreversible or both. Always the consumption of  ${}^{12}CO(g)$  will be larger than 84 that of  ${}^{13}CO(g)$ . Material balances allow to estimate the amount of irreversible CO 85

86

#### 87 S3. SSITKA studies

88 The following material balances were used to estimate the concentration ( $\mu$ mol g<sup>-1</sup>) 89 and surface coverage ( $\theta$ ) of adsorbed CO-s and active -CH<sub>x</sub> species formed under CO 90 hydrogenation reaction at 230 °C after applying the SSITKA technique.

91 
$$N_{CO}(\mu mol g^{-1}) = \frac{F_T y_{CO}^t (1 - X_{CO})}{W} \int_0^{t_{s.s}} [Z_{Kr}(t) - Z_{^{13}CO}(t)] dt$$
 (Eq. S8)

92 
$$N_{CHx}(\mu mol g^{-1}) = \frac{F_T y_{^{13}CH_4}}{W} \int_0^{t_{s.s}} [Z_{^{13}CO}(t) - Z_{^{13}CH_4}(t)] dt$$
 (Eq. S9)

93 
$$\theta_i = \frac{N_i}{N_{Co,surf}} (i = CO, CH_x)$$
 (Eq. S10)

94 where  $y_{13CH_4}$  is the mole fraction of <sup>13</sup>CH<sub>4</sub> at steady-state reaction conditions.

95

### 96 S4. TIH and TPH following SSITKA

97 Conversion of the MS signals (m/z) of 15 and 17 into concentration of  ${}^{12}$ CH<sub>4</sub> and 98  ${}^{13}$ CH<sub>4</sub>, respectively, and estimation of their quantities (µmol g<sup>-1</sup>) and respective surface 99 coverages ( $\theta$ ) were made by using certified calibration gas mixtures (1.04 vol% 100  ${}^{12}$ CH<sub>4</sub>/He and 2.1 vol%  ${}^{13}$ CH<sub>4</sub>/He, respectively) and material balances (Eqs. S11-S13). 101 It is important to mention that after the TIH and TPH steps, the catalyst sample used 102 displayed very similar catalytic activity in CO hydrogenation at 230 °C when compared 103 with that obtained before applying the TIH/TPH.

104 
$$R_{i}(\mu mol g^{-1} s^{-1}) = \frac{F_{T}}{W} y_{i}(t)$$
 (Eq. S11)  
105  $N_{i}(\mu mol g^{-1}) = \frac{F_{T}}{W} \int_{t=0}^{t^{3.5}} y_{i}(t) dt$  (Eq. S12)  
106  $\theta_{i} = \frac{N_{i}}{N_{Co,surf}}$ ; (i = <sup>12</sup>CH<sub>4</sub>, <sup>13</sup>CH<sub>4</sub>) (Eq. S13)  
107  
108 **RESULTS**

# 109 S5. HRTEM, SAED and EDX studies on 20 wt% Co/x wt% Mn-Al<sub>2</sub>O<sub>3</sub>



- 113 Figure S1. HRTEM images of unpromoted Co/γ-Al<sub>2</sub>O<sub>3</sub> catalyst at 10-nm (A) and 5-
- 114 nm (B) scale magnifications with d-spacing of 0.5741 nm.





**Figure S2:** EDX analysis conducted over the Mn-promoted  $Co/\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts (A)

- Mn/Co = 0.011, (B) Mn/Co = 0.111 and (C) Mn/Co = 0.268.



**Figure S3.** High-resolution transmission electron microscopy (HRTEM) images of a Mn-promoted  $Co/\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst with a Mn/Co molar ratio of 0.111 are presented at magnifications of 10 nm (A) and 5 nm (B). The d-spacings observed in these images are 0.2366 nm and 0.2042 nm, respectively.



132 Figure S4. HRTEM images of Mn-promoted Co/γ-Al<sub>2</sub>O<sub>3</sub> catalyst with Mn/Co molar

- 133 ratio of 0.268 at 10-nm (B) scale magnifications with d-spacing of 0.4052 nm.



**Figure S5:** Selected Area Electron Diffraction (SAED) pattern of (A) unpromoted, and

- 139 of Mn-promoted Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts with Mn/Co molar ratio of (B) 0.011, (C) 0.111,
- 140 and (D) 0.268 with their respective d-spacings listed.







**Figure S6:** (A)-(B) H<sub>2</sub> desorption rate ( $\mu$ mol g<sup>-1</sup> s<sup>-1</sup>) obtained during He-TPD, 147 following H<sub>2</sub> chemisorption at 100 °C and cooling in H<sub>2</sub>/He adsorption gas mixture 148 (Section 2.3); (C) Amount of H desorbed in terms of N<sub>H</sub> ( $\mu$ mol H g<sup>-1</sup>) and surface 149 coverage (based on Co surface)  $\theta_{\rm H}$ , as a function of Mn/Co molar ratio.





**Figure S7:** Transient normalized concentration (Z) response curves of Kr, <sup>13</sup>CO, and 169 <sup>12</sup>CO obtained during the SSITKA switch:  $5\%^{12}$ CO/5%H<sub>2</sub>/Ar/He (15 min)  $\rightarrow$ 170  $5\%^{13}$ CO/5%H<sub>2</sub>/1%Kr/Ar/He (t) at 155 °C on the unpromted 20 wt% Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> 171 catalyst.



184 **Figure S8:** (A) In situ DRIFTS spectra recorded on Co/MnO<sub>x</sub>-Al<sub>2</sub>O<sub>3</sub> (Mn/Co=0.111)

after treated in 5%  $^{12}$ CO/5 or 10% H<sub>2</sub>/He at 155 °C for 15 min. (B) The deconvoluted spectrum recorded after 15 min in 5%  $^{12}$ CO/10% H<sub>2</sub>/He. (C) IR spectrum (1700-1300

187 cm<sup>-1</sup>) with its deconvolution recorded after 15 min in  $5\%^{13}$ CO/10%H<sub>2</sub>/He.



188

189 **Figure S9.** Logarithmic plot of  $\theta_{CO}$  versus time (Eq. 4) after conducting the  ${}^{12}CO/{}^{13}CO$ 

190 isotopic switch at 155 °C with 5%CO/He over the 20 wt% Co/MnO<sub>x</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts

191 (Mn/Co=0.0, 0.011, 0.111 and 0.268).

## 192 S8. <sup>13</sup>CO-SSITKA studies

193





Figure S10: Transient normalized concentration (Z) response curves of Kr, <sup>13</sup>CO, <sup>12</sup>CO, <sup>13</sup>CH<sub>4</sub> and <sup>12</sup>CH<sub>4</sub> during the SSITKA switch: 5%<sup>12</sup>CO/10%H<sub>2</sub>/Ar/He (2 h) → 5%<sup>13</sup>CO/10%H<sub>2</sub>/1%Kr/Ar/He (t) at 230 °C on the unpromted 20 wt% Co/γ-Al<sub>2</sub>O<sub>3</sub> (199) catalyst.

200



201

Figure S11: SSITKA transient normalized concentration (Z) response curves of Kr and

 $^{13}$ CO after 5, 10, 30 and 50 h TOS in CO hydrogenation at 230 °C.

204

**Table S1:** SSITKA kinetic parameters obtained for the CO hydrogenation at 230 °C207and various TOS as a function of Mn/Co molar ratio (0 - 0.268) on 20 wt% Co/MnO-208Al<sub>2</sub>O<sub>3</sub> catalysts.

Catalyst	TOS	N <sub>co</sub>	$ au_{CO}$	N <sub>CHx</sub>	θ <sub>CHx</sub>	$ au_{CHx}$	k <sub>eff</sub> x 10 <sup>2</sup>	ТОF <sub>CH4</sub> х 10 <sup>3</sup>
(Mn/Co)		(µmol g <sup>-1</sup> )	<b>(s)</b>	(µmol g <sup>-1</sup> )		<b>(s)</b>	( <b>s</b> <sup>-1</sup> )	(s <sup>-1</sup> )
0	30 min	57.6	0.18	4.6	0.014	56.0	1.79	2.51
	2 h	78.7	0.24	4.9	0.015	54.3	1.84	2.80
	5 h	80.3	0.25	5.3	0.016	59.5	1.68	2.74
	10 h	72.3	0.22	5.3	0.016	66.4	1.51	2.47
	20 h	48.2	0.15	5.5	0.017	79.5	1.26	2.13
	30 h	64.2	0.2	5.5	0.017	80.6	1.24	2.11
	50 h	65.3	0.2	5.1	0.016	79.8	1.25	1.96
0.011	30 min	110.3	0.34	3.2	0.009	29.3	3.41	3.38
	2 h	55.6	0.17	3.1	0.009	33.4	3.00	2.80
	5 h	41.2	0.13	4.3	0.013	53.5	1.87	2.48
	10 h	79.7	0.24	5.1	0.016	76.2	1.31	2.04
	20 h	50.9	0.16	5.6	0.017	72.6	1.38	2.36
	30 h	44.9	0.14	6.8	0.021	81.2	1.23	2.55
	50 h	65.5	0.2	8.1	0.025	108.8	0.92	2.27
0.111	30 min	121.4	0.38	6.4	0.02	39.3	2.54	5.16
	2 h	116.6	0.37	5.3	0.016	38.0	2.63	4.38
	5 h	108.9	0.34	5.9	0.019	48.0	2.08	3.87
	10 h	110.9	0.35	7.1	0.022	70.1	1.43	3.2
	20 h	64.3	0.20	7.2	0.023	71.7	1.39	3.17
	30 h	92.4	0.29	7.3	0.023	85.9	1.16	2.66
	50 h	67.9	0.21	7.6	0.024	120.7	0.83	1.98

0.268	30 min	67.5	0.25	6.1	0.023	57.6	1.74	3.97
	2 h	62.0	0.23	4.7	0.017	58.3	1.71	3.00
	5 h	66.4	0.25	6.0	0.023	68.7	1.45	3.28
	10 h	61.1	0.23	4.8	0.018	76.4	1.31	2.37
	20 h	55.2	0.21	6.4	0.024	92.8	1.09	2.57
	30 h	60.8	0.23	6.5	0.024	88.5	1.13	2.73
	50 h	61.6	0.23	5.6	0.017	96.7	1.03	1.77



Figure S12: Logarithmic plots of the  $(1-Z^{13}CH_4)$  function vs time (SSITKA switch after 50 h TOS in CO hydrogenation) as a function of Mn/Co ratio (0.0-0.268) for the 20 wt% Co/x wt% Mn-Al<sub>2</sub>O<sub>3</sub> catalysts. Feed: 5%CO/10%H<sub>2</sub>/He; T=230 °C, P = 1.2 bar.







Figure S13: ASF plots of the product distribution: olefins (A), paraffins (B), and total

hydrocarbons (olefins+paraffins) (C)) as a function of Mn/Co molar ratio.





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**Figure S14:** (A) DRIFTS spectra recorded in the CO-IR region at 230 °C in Ar and 50% H<sub>2</sub>/Ar gas flow, and (B) deconvolution of the IR band of adsorbed CO-s recorded after 3 min in Ar gas flow (marked Ar (0 s)) over the unpromoted Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst.



253

**Figure S15:** Plots of  $\ln[\alpha]$  versus time (s) in 50%H<sub>2</sub>/Ar gas stream for the hydrogenation at 230 °C of (A) L<sub>I</sub> and (B) L<sub>II</sub> adsorbed CO-s, as a function of Mn/Co molar ratio.

- 257
- 258
- 259