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# Deactivation of $Co/\gamma$ -Al<sub>2</sub>O<sub>3</sub> in CO methanation studied by transient isotopic experiments: The effect of Co particle size



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### ABSTRACT

SSITKA coupled with transient isothermal (TIH) and temperature-programmed hydrogenation (TPH) were used to investigate the influence of Co particle size ( $d_{Co} = 11-21$  nm) and time-on-stream, TOS (up to 25 h) on important kinetic parameters of CO methanation at 230 °C on Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. TOF<sub>CO</sub> and TOF<sub>CH4</sub> were independent of  $d_{Co}$  and decreased with TOS. The  $\theta_{CO}$  and  $\theta_{CHx}$  (active CO-s and CH<sub>x</sub>-s) slightly increased with  $d_{Co}$  as opposed to  $\theta_{CxHy}$  (inactive species), which remained practically constant. On the contrary,  $\theta_{CHx}$  and  $\theta_{CxHy}$  largely decreased and increased, respectively, while  $\theta_{CO}$  stayed practically constant with TOS. An inverse D-KIE independent of  $d_{Co}$  was estimated by a novel <sup>13</sup>CO/D<sub>2</sub>-SSITKA experiment, reported for the first time to the best of our knowledge. The reason of catalyst deactivation was the decrease of  $k_{CHx}$  (hydrogenation of -CH<sub>x</sub>) likely because of the influence of -C<sub>x</sub>H<sub>y</sub> on the bonding of active species and on  $\theta_{H}$  (a decrease was determined).

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#### 1. Introduction

The Fischer-Tropsch synthesis (FTS) is an important industrial catalytic reaction that converts a mixture of carbon monoxide and hydrogen (synthesis gas) into liquid hydrocarbons (synthetic fuels) and chemicals. Although FTS reaction has been studied and implemented for many years, due to the complex reaction network [1–3], several fundamental aspects of it have not been explored yet to a great extent. For example, the influence of metal particle size (d<sub>M</sub>, nm) and time-on-stream (TOS) on important intrinsic kinetic and catalyst deactivation parameters, namely: (i) the surface coverage ( $\theta$ ) and site activity (k, s<sup>-1</sup>) related to a given *active* reaction intermediate, and (ii) the surface coverage of *inactive* carbonaceous species formed under FTS and their reactivity in hydrogen at T<sub>FTS</sub> and higher temperatures. Also, how these parameters truly correlate with catalyst's deactivation has little been explored on supported Co FTS catalysts.

Steady-State Isotopic Transient Kinetic Analysis (SSITKA) [4–6] allows to estimate the surface coverage,  $\theta$ , and the mean residence time,  $\tau$  (inversely proportional to the intrinsic reactivity, k) of *ac*-tive reaction intermediates, and of the turnover frequency (TOF<sub>ITK</sub>) of reaction based on the measured concentration of *active* intermediates [6] than on the total metal surface sites (TOF<sub>chem</sub>), the latter

usually measured by XRD, HRTEM and selective hydrogen or CO chemisorption. Also, when SSITKA is combined with a spectroscopic technique (e.g., transmission FTIR or DRIFTS – *operando* methodology), the surface coverage, chemical composition and structure of the *active* reaction intermediates and of the *inactive* (spectator) species can be determined at the same time [4,7,8]. Therefore, SSITKA is considered a very powerful experimental technique for a rigorous investigation of important mechanistic and kinetic parameters of the FTS as already demonstrated in several previous works [3–30].

In principle, the SSITKA technique can be also applied under high-pressure industrial FTS reaction conditions (ca. P = 20 bar). Since C<sub>1</sub> monomers are responsible for chain growth, the nature of elementary reaction steps and sites in the FTS are not expected to change with increasing pressure, and the surface coverage of CO-s is very similar at high P (<30 bar) [31]. For example, at 230 °C, an increase of P<sub>CO</sub> from 1 to 10 bar causes an increase of  $\theta_{CO}$  by only 2.5%. Therefore, SSITKA studies at  $\sim$  1 bar focused on methanation reaction (CO hydrogenation with relatively high selectivity to CH<sub>4</sub>) can also provide very useful mechanistic information which could be extrapolated to practical FTS conditions. In fact, similar trend of results was obtained for SSITKA-FTS studies performed at P = 1 bar and 35 bar [11]. Furthermore, the studies of high-pressure SSITKA on FTS are very limited because of: (i) the proportional consumption of isotope gas at high pressure compared to 1 bar (lower cost), (ii) the requirement of a more complex analytical system (e.g., GC-MS coupled to multiport sampling





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valves, etc), and (iii) the difficulty in interpreting correctly the C<sup>+</sup><sub>2</sub>-hydrocarbons transient response curves due to detainment and readsorption phenomena within the porous system of metal catalyst's support.

The SSITKA technique has been used to investigate FTS with regards to the effect of (i) cobalt particle size [10–12,23], (ii) gas pretreatment conditions [26], (iii) chemical promoters [13], (iv) support modification [10,14,20] and (iv) catalyst deactivation and rejuvenation [15–17]. Furthermore, SSITKA coupled with transient isothermal and temperature-programmed hydrogenation techniques [5,7,18,19,30] has been used to follow the evolution of active intermediates and inactive species formed in methanation reaction over Rh/y-Al<sub>2</sub>O<sub>3</sub>, Rh/MgO and Co/y-Al<sub>2</sub>O<sub>3</sub> catalysts, and relate the information obtained with catalyst's deactivation. Carvalho et al. [15] studied the effect of deactivation of cobalt-based catalysts on the concentration of active sites by using SSITKA and temperature-programmed hydrogenation techniques. The deactivation of catalyst was due to carbon deposition and agglomeration of cobalt nanoparticles (use of TEM), which led to the decrease in the concentration of cobalt active sites (CH<sub>x</sub>-s and CO-s species) and their intrinsic activity. Catalyst rejuvenation in hydrogen, partly restored -CH<sub>x</sub> formation sites, while reversibly adsorbed CO-s remained unaffected [15].

After combining SSITKA with DRIFTS and other transient isothermal and temperature-programmed hydrogenation experiments [7], it was found that *inactive* carbonaceous species (named  $C_{\beta}$ ) formed in FTS (5 vol% CO, H<sub>2</sub>/CO = 2, 230 °C, P = 1.2 bar) over an industrial related 20 wt% Co-0.05 wt% Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst prepared by two different methods was readily hydrogenated at 230 °C ("soft" carbon). The latter type of carbonaceous species was correlated with the catalysts' deactivation behavior under industrial FTS reaction conditions.

The effect of cobalt particle size on the surface mean residence time ( $\tau$ ) of -CH<sub>x</sub> intermediates was reported to decrease significantly with increasing Co particles size, ca. from 2.6 to 6 nm, whereas that of adsorbed CO-s,  $\tau_{CO}$ , to increase [10–12,23]. For Co particles in the 6–16 nm range, the residence time of these active reaction intermediates was found not to depend on particle size. The TOF<sub>chem</sub> of methanation reaction and the surface coverages of -CH<sub>x</sub> and CO-s were reported to decrease for Co particle size below 6 nm, whereas for larger Co particles (6–16 nm), these were found to be practically constant [10,23]. The latter results were interpreted as due to the significant surface coverage of irreversibly adsorbed CO on small (<6 nm) Co particles, result that causes blocking of edge and corner sites, which appear responsible for a higher site activity compared to that of terrace sites [10].

In the present work, we report the evolution (up to 25 h on reaction stream) of the active carbon-containing intermediate species (CO-s and CH<sub>x</sub>-s) found in the carbon-path of methanation reaction (4 vol% CO,  $H_2/CO = 2, 230$  °C, P = 1.2 bar) and that of *in*active carbonaceous species  $(-C_xH_y)$  over two  $Co/\gamma-Al_2O_3$  catalysts with Co mean particle size of 11.4 and 21.3 nm for the first time to the best of our knowledge. Several SSITKA studies reported the role of Co particle size in the 2.6–16 nm range [11,23] and in the 7–40 nm range [10] on kinetic parameters ( $\theta$ , k). These studies, however, did not address the effect of deactivation on these kinetic parameters  $(\theta, \mathbf{k})$ , but also on parameters that implicitly influence deactivation, such as the accumulation of inactive carbonaceous species. Also, the dependence of TOF  $(s^{-1})$  on the Co particle size has been reported in several past works, where TOF was based on the total number of exposed surface Co atoms. In the present work we used also the more correct expression of site activity, that of  $TOF_{ITK}$  (s<sup>-1</sup>), which is based only on the number of surface Co atoms participating in the reaction path of CH<sub>4</sub> formation. This quantity can only be estimated through the measurement of active intermediates participating in the given reaction path via the use of the SSITKA technique, as demonstrated in the present work and others reported earlier [4–8]. We have shown for the first time that  $TOF_{ITK}$  (CH<sub>4</sub>) differs only slightly for supported Co particles of 11 and 21 nm in size.

In addition, a new experimental methodology is proposed for the estimation of the deuterium kinetic isotopic effect based on SSITKA experiments for the first time to the best of our knowledge. Transient isothermal and temperature-programmed hydrogenation experiments were performed to estimate the concentration of inactive - $C_xH_v$  species ( $C_\beta$ ) formed during FTS at 230 °C, which do not lead to CH<sub>4</sub> but are readily hydrogenated at 230 °C in H<sub>2</sub>/He, named "soft carbon". Also, the concentration of refractory carbonaceous species  $(C_{\gamma})$  hydrogenated at T > 230 °C, named "hard carbon" was determined. Complementary characterization techniques, such as powder XRD and H<sub>2</sub>-TPR were conducted for estimating the mean Co particle size and the redox behavior of Co<sub>3</sub>O<sub>4</sub> for the present two  $Co/\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts (d<sub>Co</sub> = 11.4 and 21.3 nm). Also, transient H<sub>2</sub> chemisorption conducted at 100 °C followed by hydrogen temperature-programmed desorption (H<sub>2</sub>-TPD) techniques were used to address the influence of Co particle size and TOS (before and after 25 h of methanation reaction) on the concentration and quality of hydrogen chemisorption sites of the Co metal surface.

# 2. Experimental

# 2.1. Preparation of x wt% Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts

Alumina-supported cobalt catalysts (x wt% Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, x = 15 and 25) were prepared by the wet impregnation method after using an aqueous solution of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Sigma-Aldrich,  $\geq$  98%). The alumina support (Sigma-Aldrich, activated/acidic, Brockmann I) before impregnation was pretreated at 500 °C for 10 h ( $\beta$  = 5 °C/min) in ambient air. The impregnated catalysts were then dried at 120 °C overnight and calcined at 300 °C for 12 h in ambient air. The calcined catalysts were then reduced in H<sub>2</sub> gas flow (1 bar) at 450 °C for 10 h (1 °C/min from 30 to 450 °C). The catalysts after cooling to 30 °C were passivated in 1 vol% O<sub>2</sub>/He at 30 °C for 2 h. The passivated powder catalyst samples used in the catalytic and transient kinetic studies after sieved to the 63–106 µm size were reduced in H<sub>2</sub> (1 bar) gas flow at 425 °C for 2 h. Internal and external mass transport resistances were proved to be absent according to the procedures reported elsewhere [32].

#### 2.2. Catalysts characterization

2.2.1. Textural, structural and redox properties of  $Co/\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts Powder XRD patterns of x wt%  $Co/\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts were recorded using a Shimadzu 6000 series diffractometer (CuKa radiation,  $\lambda = 1.5418$  Å). The specific surface area (SSA, m<sup>2</sup> g<sub>cat</sub><sup>-1</sup>; BET method) was estimated after N<sub>2</sub> adsorption/desorption isotherm measurements at 77 K (Micromeritics apparatus, Gemini model). Prior to SSA measurements, the catalyst sample was degassed at 300 °C for 4 h in  $N_2$  gas-flow to remove adsorbed atmospheric water and most of CO2. Hydrogen temperature-programmed reduction (H<sub>2</sub>-TPR) traces were obtained using 0.3 g of catalyst sample, which was placed in a quartz microreactor, the exit of which was connected to a mass spectrometer (Balzers, Omnistar 1–300 amu) for on-line gas analysis. Prior to H<sub>2</sub>-TPR, the sample was pretreated in 20 vol% O<sub>2</sub>/He at 300 °C for 2 h and then cooled to room T. The gas flow was then switched to He for 15 min and then to 4.93 vol%  $H_2/He$  (50 NmL min<sup>-1</sup>), while at the same time the temperature of the catalyst was increased from room T to 800 °C ( $\beta$  = 30 °C min<sup>-1</sup>). The H<sub>2</sub> (m/z = 2) and H<sub>2</sub>O (m/z = 18) signals in the mass spectrometer were continuously monitored to follow the kinetics of reduction of  $Co_3O_4$  in the x wt%  $Co/\gamma$ -Al<sub>2</sub>O<sub>3</sub>

(x = 15 and 25) solids. The H<sub>2</sub>-TPR traces (concentration vs T profiles) recorded were converted to reduction rate,  $R_{H2}$  (µmol  $g_{cat}^{-1}$  min<sup>-1</sup>) vs temperature profiles, after calibration of the H<sub>2</sub> MS signal (m/z = 2) with a standard gas mixture (0.95 vol% H<sub>2</sub>/He), and using the appropriate material balance for an open gas-flow reactor.

# 2.2.2. Hydrogen transient isothermal chemisorption ( $H_2$ -TIC) and temperature-programmed desorption (TPD) studies

Hydrogen transient isothermal chemisorption (H<sub>2</sub>-TIC) at 100 °C, followed by temperature-programmed desorption (H<sub>2</sub>-TPD) experiments, were used to address the influence of Co particle size and reaction conditions (before and after 25 h of methanation reaction) on the concentration and quality of hydrogen chemisorption sites on the present Co surfaces. A 0.42-g sample of 15 wt% Co/  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and 0.25-g sample of 25 wt% Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> were first reduced at 425 °C for 2 h and then purged with He gas. The temperature was subsequently increased to 600 °C in He gas flow to desorb any H<sub>2</sub> that might have been spilled over the support (until the H<sub>2</sub> MS signal reached the background value). The temperature of the reactor was decreased to 100 °C in He gas flow and the step gas switch He  $\rightarrow$  0.5%H<sub>2</sub>/5%Ar/He (50 NmL min<sup>-1</sup>, t) at 100 °C was performed. After 5 min of chemisorption, no further hydrogen was consumed (chemisorption equilibrium was reached). The catalyst temperature was then decreased to 30 °C in the 0.5%H<sub>2</sub>/5%Ar/ He gas mixture, and left for additional 5 min. The catalyst sample was then purged in He (50 NmL min<sup>-1</sup>) for 5 min and the temperature was subsequently increased to 600 °C ( $\beta$  = 30°C min<sup>-1</sup>). The Ar (m/z = 40) and H<sub>2</sub> (m/z = 2) MS signals were continuously monitored with online mass spectrometer (Balzers, Omnistar 1-300 amu) during the H<sub>2</sub>-TIC, while only the H<sub>2</sub>-MS signal was monitored during TPD. The H<sub>2</sub>-MS signal was calibrated against a standard 0.95 vol% H<sub>2</sub>/He gas mixture. The amount of hydrogen chemisorption estimated from H<sub>2</sub>-TIC was compared with that estimated from H<sub>2</sub>-TPD. A H:Co<sub>s</sub> of 1:1 stoichiometry of adsorption was assumed. The rate of  $H_2$  chemisorption (µmol  $g_{cat}^{-1} s^{-1}$ ) was estimated using the following Eq. (1) for an open gas-flow reactor:

$$\mathbf{R}_{H_2} = \frac{\mathbf{F}_{T} \mathbf{y}_{H_2}^{i}}{\mathbf{W}} \left[ Z_{Ar}(t) - Z_{H_2}(t) \right] \tag{1}$$

where,  $F_T$  is the total molar flow rate (µmol s<sup>-1</sup>) of 0.5%H<sub>2</sub>/5%Ar/He gas mixture,  $y_{H_2}^f$  is the mole fraction of H<sub>2</sub> in the feed (0.5 vol%), W is the mass of catalyst (g) and Z is the dimensionless concentration of Ar or H<sub>2</sub> gas (Z takes the values between 0 and 1). The accumulation term (Eq. (1)) was found to be negligible compared to the other terms appearing in Eq. (1).

The H<sub>2</sub>-TIC experiment conducted after 25 h of methanation reaction was as follows. After methanation reaction, the reactor was purged with He for 5 min, and then an 8 vol% H<sub>2</sub>/Ar (50 NmL min<sup>-1</sup>) gas treatment for 10 min at 230 °C was performed followed by temperature-programmed hydrogenation (TPH, up to 600 °C; 10 °C/min) to remove inactive carbonaceous species as detailed in Section 2.3.4. At the end of TPH, the catalyst was kept in H<sub>2</sub>/Ar for additional 10 min and then purged in He and cooled to 425 °C. The feed to the reactor was then switched to pure H<sub>2</sub> and left for 30 min (hydrogen reduction step), followed by He purge and thermal treatment at exactly the same way as described above for the case of H<sub>2</sub>-TIC of the fresh sample.

# 2.3. Transient isotopic experiments

# 2.3.1. Steady-state isotopic transient kinetic analysis with mass spectrometry (SSITKA-MS)

The experimental apparatus for the application of Steady-State Isotopic Transient Kinetic Analysis (SSITKA-MS and SSITKA- DRIFTS) was previously described in [4,9]. SSITKA-mass spectrometry (SSITKA-MS) experiments were performed to follow the carbon-path of CO methanation reaction at 230 °C based on the step-gas switch 4 vol%  $^{12}$ CO/8 vol% H<sub>2</sub>/Ar ( $\Delta$ t)  $\rightarrow$  4 vol%  $^{13}$ -CO/8 vol%  $H_2/1$  vol% Kr/Ar (t). The mass of the catalyst, ca. 0.4-g 15 wt% Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and 0.3-g 25 wt% Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and the total volume flow rate (50 NmL min<sup>-1</sup>) were adjusted to keep the CO conversion below 15% and in the absence of any external mass transport resistance. After a given time-on-stream,  $\Delta t (0.5-25 h)$ , the SSITKA step-gas switch was performed and the mass numbers,  $m/z = 15 ({}^{12}CH_4), 17 ({}^{13}CH_4), 18 (H_2O), 29 ({}^{13}CO) and 84 (Kr) were$ continuously monitored by on line mass spectrometry (Balzers, Omnistar 1–300 amu). For the accurate analysis of <sup>13</sup>CH<sub>4</sub> signal, the contribution of any additional  $H_2O(m/z = 17)$  signal to that formed during the <sup>12</sup>CO/H<sub>2</sub> reaction (before the <sup>13</sup>CO/H<sub>2</sub> gas switch) was considered (e.g., the case of very small amounts of water in the gas lines). The above-mentioned SSITKA step-gas switch was repeated twice to check the reproducibility of the SSITKA experiment.

The concentration of reversibly adsorbed CO-s and *active* -CH<sub>x</sub> reaction intermediates, leading to the CH<sub>4</sub> formation, N<sub>CO</sub> and N<sub>CHx</sub> (µmol  $g_{cat}^{-1}$ ), respectively, and their respective surface coverage,  $\theta$ , were estimated using the following Eqs. (2) - (4):

$$N_{CO} = \frac{F_T y_{CO}^r (1 - X_{CO})}{W} \int_0^{t_{ss}} [Z_{Kr}(t) - Z_{13CO}(t)] dt$$
(2)

$$N_{CH_x} = \frac{F_T y_{13CH_4}}{W} \int_0^{t_{ss}} \left[ Z_{13CO}(t) - Z_{13CH_4}(t) \right] dt \tag{3}$$

$$\theta_{i} = \frac{N_{i}}{N_{\text{Co,surf}}} (i = CH_{x}, \text{CO})$$
(4)

where,  $F_T$  is the feed molar flow rate (µmol s<sup>-1</sup>);  $y_{CO}^f$  is the mole fraction of CO in the feed;  $X_{CO}$  is the CO conversion (%) at steadystate; W is the mass of catalyst (g);  $y_{13CH4}$  is the mole fraction of <sup>13</sup>CH<sub>4</sub> at the exit stream of the reactor (new steady-state in <sup>13</sup>CO/ H<sub>2</sub>);  $t_{ss}$  is the time at which the new steady-state is reached under the <sup>13</sup>CO/H<sub>2</sub> gas mixture;  $N_{Co,surf}$  is the total number of surface Co per gram of catalyst (µmol  $g_{cat}^{-1}$ ) estimated on the basis of the dispersion and loading values of Co metal in the Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts (see Eqs. S1 and S2, ESI), and Z<sub>i</sub> is the dimensionless concentration of a given gas-phase species i defined by the following Eq. (5) [4]:

$$Z_i(t) = \frac{y_i(t)}{y_i^{s.s.}} \tag{5}$$

where,  $y_i^{s.s.}$  and  $y_i(t)$  are the mole fraction of gas i at steady-state and at time t, respectively, after the SSITKA step-gas switch. Thus,  $Z_i$  of the non-isotopic gas i at t = 0 (isotopic switch) is equal to 1.0 and at t  $\rightarrow$  t<sub>s.s.</sub> (new steady-state under the isotopic feed gas composition),  $Z_i$  (t)  $\rightarrow$  0. Also, the following relationship applies [4], where  $Z_{i^*}(t)$ refers to the *isotopic* gas i.

$$Z_i(t) + Z_{i^*}(t) = 1(0 \le t \le t_{s.s.})$$
(6)

It is important to mention that the CO conversion (X<sub>CO</sub>, %) used in Eq. (2) accounts for the <sup>13</sup>CO consumed to form the various carbon-containing gas products. Otherwise, the concentration of CO-s (N<sub>CO</sub>, µmol g<sup>-1</sup>) would be overestimated. Eq. (3) considers that the rate of exchange of <sup>12</sup>CO-s with <sup>13</sup>CO(g) is much faster than the rate of exchange of <sup>12</sup>CH<sub>x</sub>-s with <sup>13</sup>CH<sub>x</sub>-s, result which applies in the present work (see Section 3.3). The mean surface residence times of CH<sub>x</sub>-s and CO-s,  $\tau_{CHx}$  (s) and  $\tau_{CO}$  (s), respectively, were estimated using Eqs. (7) and (8), respectively:

$$\tau_{CH_x} = \int_0^{t_{SS}} \left[ Z_{13CO}(t) - Z_{13CH_4}(t) \right] dt \tag{7}$$

$$\tau_{CO} = \int_{0}^{t_{SS}} [Z_{Kr}(t) - Z_{13CO}(t)] dt$$
(8)

The TOF<sub>CH4</sub>, TOF<sub>CO</sub>, TOF<sub>CH4</sub>, <sub>ITK</sub> and TOF<sub>CO</sub>, <sub>ITK</sub>  $(s^{-1})$  were estimated under steady-state CO methanation reaction conditions, before the SSITKA step-gas switch (under  $^{12}CO/H_2$ ) via Eqs. (9)-(12)). The total number of surface Co atoms per mass of catalyst  $(N_{Co,surf}, \mu mol g_{cat}^{-1})$  was estimated based on powder XRD (Eq. S1 and S2, ESI), thus the  $TOF_{CH4,XRD}$  (Eq. (9)) and  $TOF_{CO,XRD}$  (s<sup>-1</sup>), Eq. (10)). H<sub>2</sub> chemisorption was used to estimate the number of Co surface atoms ( $\mu$ mol g<sub>cat</sub><sup>-1</sup>) that accommodate H-s, thus the  $TOF_{CH4,chem}$  (Eq. (9)) and  $TOF_{CO,chem}$ ,  $s^{-1}$  (Eq. (10)). The  $TOF_{CH4, ITK}$ (Eq. (11)) and TOF<sub>CO. ITK</sub>,  $s^{-1}$  (Eq. (12)) were estimated based on the sum of the concentrations of the active CH<sub>x</sub>-s (N<sub>CHx</sub>, µmol g<sub>cat</sub>  $^1)$  and CO (N<sub>CO</sub>, µmol  $g_{cat}^{-1})$  intermediates measured by the SSITKA experiment (Eqs. (2)-(3)). In Eqs. (9)-(12), the steady-state rate  $r_i$ (i = CO or CH<sub>4</sub>) is given in units of  $\mu$ mol  $g_{cat}^{-1}$  s<sup>-1</sup>. It should be noted that  $TOF_{CO, ITK}$  is overestimated (Eq. (12)) since the concentration of active carbonaceous species (N<sub>C2+</sub>, µmol/g) leading to C<sub>2+</sub> - hydrocarbons were not measured. However, TOF<sub>CO, ITK</sub> is a better estimate of turnover rate than  $TOF_{CO}$  (Eq. (10)) based on the total number of surface Co atoms. The concentration of H-s, N<sub>H</sub> (µmol/ g) under FTS reaction conditions is very difficult to be experimentally determined, and this issue is also discussed in Section 4.6.

$$TOF_{CH_4} = \frac{1}{N_{Co,surf}} = k_{CH_x} \theta_H \theta_{CHx}$$

$$k_{eff} = k_{CH_x} \theta_H = \frac{TOF_{CH_4}}{\theta_{CHx}} = \frac{1}{\tau_{CHx}}$$
(9)

$$TOF_{CO} = \frac{r_{CO}}{N_{Co,surf}}$$
(10)

$$\text{TOF}_{\text{CH}_{4,\text{ITK}}} = \frac{r_{\text{CH}_4}}{N_{\text{CO}} + N_{\text{CH}_x}} \tag{11}$$

$$TOF_{CO,TTK} = \frac{r_{CO}}{N_{CO} + N_{CH_x}}$$
(12)

In Eq. (9),  $k_{CHx} (s^{-1})$  is the intrinsic rate constant of  $-CH_x$  hydrogenation to methane, and  $k_{eff}$  is the effective rate constant  $(s^{-1})$  described in Eq. (9). The relationship of  $TOF_{CH4} (s^{-1})$  given by Eq. (9) considers that the hydrogenation of  $-CH_x$  or  $-CH_xO$  intermediate is the rate-determining step (RDS) of methanation reaction.

# 2.3.2. Steady-state isotopic transient kinetic analysis with DRIFTS (SSITKA-DRIFTS)

DRIFTS spectra were recorded before and after the SSITKA step-gas switch 4 vol% <sup>12</sup>CO/8 vol% H<sub>2</sub>/Ar (230 °C, 6 h)  $\rightarrow$  4 vol% <sup>13</sup>CO/8 vol% H<sub>2</sub>/Ar (5 min), where a Perkin-Elmer Frontier FT-IR spectrometer (256 scans per spectrum, resolution of 4  $cm^{-1}$ , scan speed of 2 cm/s) equipped with a high-temperature/high-pressure temperature controllable DRIFTS cell (Harrick, Praying Mantis) were used. The catalyst sample (~80 mg) in a very fine powder form was placed firmly into the ceramic cup of the DRIFTS cell and reduced in H<sub>2</sub> (1 bar) at 425 °C for 2 h. The catalyst sample was then cooled in H<sub>2</sub> gas-flow to 230 °C, which was then switched to Ar and the spectrum of the solid was recorded at 230 °C. The latter spectrum was subtracted from the spectrum of the solid recorded under the isotopic or non-isotopic gas mixture at 230 °C. Deconvolution and curve fitting procedures of DRIFTS spectra were performed considering Gaussian peaks. A blank experiment was performed in order to estimate the ratio of the band areas of the two gas-phase CO absorption bands (R and Q branches of gas-phase CO) due to some observed overlapping of the gaseous CO (Q branch, 2116 cm<sup>-1</sup>) with the high-frequency linear adsorbed CO formed on the Co surface. This information was used later in the deconvolution procedure of the CO-DRIFTS spectra. More precisely, a gas mixture of 4 %CO/Ar was passed through the KBr sample (dry powder) at 230 °C and the spectrum was recorded. From this blank experiment, the Area(R)/Area(Q) ratio was found to be 1.46, where R (centered at 2182 cm<sup>-1</sup>) and Q (centered at 2116 cm<sup>-1</sup>) are the IR absorption branches of gas-phase CO. During deconvolution of the whole CO IR band (including gas-phase CO), the ratio of Area (R)/Area(Q), the position of maximum absorbance and the FWHM of gas-phase CO IR bands remained constant. DRIFTS spectra when necessary were smoothed to remove high frequency noise and further analyzed using the software Spectrum10 for Windows.

#### 2.3.3. Deuterium kinetic isotopic effect (D-KIE)

A novel methodology of SSITKA gas switches <sup>12</sup>CO/H<sub>2</sub>/Ar (230 °C,  $\Delta t$ )  $\rightarrow {}^{13}$ CO/H<sub>2</sub>/Kr/Ar (10 min)  $\rightarrow {}^{12}$ CO/H<sub>2</sub>/Ar (10 min)  $\rightarrow {}^{13}$ CO/D<sub>2</sub>/Kr/ Ar (10 min) conducted at 230 °C over the Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts was designed and performed for the first time to the best of our knowledge, in an effort to measure the D-KIE. The CO conversion was 4% for the catalyst with Co particle size of 11.4 nm and 3.5% for the catalyst with Coparticle size of 21.3 nm after 6 h in TOS. During the first SSITKA switch, the carbon-path of methane formation was traced via the <sup>13</sup>CH<sub>4</sub> transient recorded (<sup>12</sup>C is replaced by <sup>13</sup>C in all the active carbon-containing intermediates formed in the path of CH<sub>4</sub> production). The second SSITKA switch served as to bring back the catalyst adsorbed phase with the various carbon-containing active reaction intermediates labelled <sup>12</sup>C. The third SSITKA switch served as to trace both the C-path and H-path of methanation reaction via the <sup>13</sup>CD<sub>4</sub> transient response recorded. By comparing the <sup>13</sup>CH<sub>4</sub> transient during the first SSITKA switch with that of <sup>13</sup>CD<sub>4</sub> obtained during the third SSITKA switch, the following important mechanistic information can be obtained:

- (i) Possible delay between the Z(<sup>13</sup>CH<sub>4</sub>) and Z(<sup>13</sup>CD<sub>4</sub>) transient response curves suggests the existence of a D-kinetic isotopic effect, where identical transient curves signifies the absence of D-KIE.
- (ii) The KIE for the reaction path of methane formation can be estimated according to the following Eq. (13):

$$\begin{aligned} \text{KIE} &= \frac{r_{\text{CH}_4}}{r_{\text{CD}_4}} = \frac{\text{TOF}_{\text{CH}_4} N_{\text{Co,surf}}}{\text{TOF}_{\text{CD}_4} N_{\text{Co,surf}}} = \frac{k_{\text{eff},\text{CH}_4} \theta_{\text{CH}_x}}{k_{\text{eff},\text{CD}_4} \theta_{\text{CD}_x}} = \frac{\tau_{\text{CD}_4}}{\tau_{\text{CH}_4}} \\ &= \frac{\int_0^{\text{tss}} [Z_{13\text{CO}}(t) - Z_{13\text{CD}4}(t)] \text{d}t}{\int_0^{\text{tss}} [Z_{13\text{CO}}(t) - Z_{13\text{CH}4}(t)] \text{d}t} \end{aligned}$$
(13)

In the derivation of Eq. (13), it is considered that one of the hydrogenation steps of  $-CH_x$  or  $-CH_xO$  intermediates is the ratedetermining step (RDS) for the methanation reaction, and also that  $\theta_H$  and  $\theta_D$  established under  $^{12}CO/H_2$  and  $^{13}CO/D_2$  stay practically the same, as well as the  $\theta_{CHx}$  and  $\theta_{CDx}$ . In fact, for the present supported Co surface, Shafer et al. [33] reported that  $\theta_H \sim \theta_D$  on the Co metal surface of 15% Co/SiO<sub>2</sub> and 25% Co/Al<sub>2</sub>O<sub>3</sub> after treatment with 50%H<sub>2</sub>/50%D<sub>2</sub> for 48 h at 350 °C. The authors concluded that no preferential partitioning of H or D occurs on these Co surfaces, and the *inverse* D-KIE found during CO/H<sub>2</sub> reaction is not affected by preferential isotopic partitioning on the Co metal surface.

According to Eq. (13), the D-KIE is simply the ratio of the surface mean residence times of <sup>13</sup>CD<sub>4</sub> and <sup>13</sup>CH<sub>4</sub> measured via the dimensionless concentration (Z) responses of <sup>13</sup>CO, <sup>13</sup>CD<sub>4</sub> and <sup>13</sup>CH<sub>4</sub> (see Eq. (7)). The construction of these responses *requires no calibration* of the corresponding MS signals, as opposed to the case where steady-state kinetic rates of CD<sub>4</sub> and CH<sub>4</sub> must be estimated via the calibration of the signal from the gas analyzer used (e.g. MS, GC or FTIR) [34]. Also, this SSITKA step-gas switches methodology allows within ~ 15 min of experimentation time to obtain the necessary  $\tau_{CH4}$  and  $\tau_{CD4}$  parameters required for the estimation of D-KIE (see Fig. 8). An alternative SSITKA step-gas switch <sup>12</sup>CO/H<sub>2</sub>/Ar  $\rightarrow$  <sup>12</sup>CO/D<sub>2</sub>/Kr/ Ar (H-path) that enables to follow the evolution of <sup>12</sup>CD<sub>4</sub> (*m*/*z* = 20) would have been difficult to measure with a quadrupole mass spectrometer, because of the large contribution expected by the presence of D<sub>2</sub>O (*m*/*z* = 20) transient, and likely of H/D exhange reactions of H<sub>2</sub>O and DHO with –OD groups (formed by the exchange of –OH with HD and D<sub>2</sub> during the SSITKA switch). Similar to these difficulties in following the H-path of methanation, we have recently reported an alternative experimental methodology (use of D<sub>2</sub> in a series of transient experiments) for the approximate estimation of the concentration of active H-containing species formed in the H-path of the WGS reaction over various supported Pt catalysts [8,35].

During the <sup>13</sup>CO/D<sub>2</sub>/Kr/Ar step-gas switch, the mass numbers 21 (<sup>13</sup>CD<sub>4</sub>), 17 (<sup>13</sup>CH<sub>4</sub>), 18 (H<sub>2</sub>O), 29 (<sup>13</sup>CO) and 84 (Kr) were continuously monitored by *online* mass spectrometer. The recording of <sup>13</sup>CD<sub>4</sub> transient response at m/z = 21 provides the means to follow the exchange of <sup>12</sup>CH<sub>x</sub>-s with <sup>13</sup>CD<sub>x</sub>-s without any overlapping with signals associated with other <sup>13</sup>C- and D-labelled methanes. No possible exhange of <sup>13</sup>CD<sub>4</sub> with -OH groups mainly present on the alumina support was found as described in Section 3.3.2. The deuterium kinetic isotopic effect (D-KIE) was estimated for both the CO conversion rate (r<sub>CO</sub> (CO-H<sub>2</sub>) / r<sub>CO</sub> (CO-D<sub>2</sub>)) and the CH<sub>4</sub> formation rate via Eq. (13).

# 2.3.4. Transient isothermal (TIH) and temperature programmed hydrogenation (TPH)

The concentration of inactive (spectator) adsorbed carboncontaining species formed under <sup>12</sup>CO/H<sub>2</sub> at 230 °C for a given TOS was estimated according to similar experiments reported earlier [5,7,18,19]. After the  ${}^{12}CO/H_2/Ar$  ( $\Delta t$ )  $\rightarrow$   ${}^{13}CO/H_2/Kr/Ar$ (10 min) step-gas switch, the feed to the reactor was switched to Ar gas for 4 min, followed by a switch to 8 vol% H<sub>2</sub>/Ar (50 NmL min<sup>-1</sup>) for 10 min at 230 °C (Transient Isothermal Hydrogenation, TIH). At the end of this gas switch, the temperature was increased to 600 °C ( $\beta$  = 10 °C min<sup>-1</sup>) to carry out a temperatureprogrammed hydrogenation (TPH) experiment. The mass numbers 15 (<sup>12</sup>CH<sub>4</sub>), 17 (<sup>13</sup>CH<sub>4</sub>), 18 (H<sub>2</sub>O) and 84 (Kr) were continuously monitored by online mass spectrometer. TIH and TPH experiments were performed after different TOS (0.5–25 h) in CO/H<sub>2</sub> to investigate the effect of TOS on the concentration of *inactive* carbonaceous species formed. After conducting the TIH and TPH experiments, the activity of the catalyst in methanation reaction was found to remain practically the same. For example, the CO conversion was 6.5% after 2 h TOS over the catalyst with Co particle size of 11.4 nm, where after the TIH/TPH followed by 2 h of reaction time in CO/H<sub>2</sub>, a CO conversion of 6.2% was estimated.

### 3. Results

#### 3.1. Catalysts characterization

3.1.1. Textural, structural and redox properties of  $Co/\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts The powder XRD patterns, mean primary crystallite sizes of  $Co_3O_4$  (d<sub>Co3O4</sub>, nm) and Co (d<sub>Co</sub>, nm), Co dispersion (D, %) and the specific surface area (SSA, m<sup>2</sup> g<sup>-1</sup><sub>cat</sub>) of the x wt% Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (x = 15 and 25) catalysts are all provided in Fig. S1 and Table S1 (ESI). The mean particle size of Co was found to be 11.4 and 21.3 nm for 15 and 25 wt% Co supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, respectively. Based on the shape and position of the H<sub>2</sub>-TPR traces of calcined Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts depicted in Fig. S2 (ESI), the effect of Co particle size (11.4 – 21.3 nm) on the reduction behavior of Co<sub>3</sub>O<sub>4</sub> should be considered practically small. 3.1.2. Transient isothermal hydrogen chemisorption and temperatureprogrammed desorption (TPD) studies

Fig. 1a shows the effect of Co particle size (7.7 - 21.3 nm) on the rate of H<sub>2</sub> chemisorption per exposed surface cobalt atom (mol H<sub>2</sub>/mol Co<sub>s</sub>/s) performed at 100 °C and calculated via Eq. (1) for the Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts (fresh samples). The data for the catalyst with Co particle size of 7.7 nm were obtained from Ref. [7] for comparison. It is obvious that as the Co particle increases from 7.7 to 21.3 nm, the maximum rate of hydrogen chemisorption increases, indicating that the rate of dissociative chemisorption of H<sub>2</sub> on the Co surface depends on the Co particle size. Fig. 1b shows the dependence of surface coverage of H ( $\theta_{\text{H}}$ ) on the Co particle size for the given chemisorption conditions applied. It is seen that  $\theta_{\text{H}}$  for Co particles in the 7.7–11.4 nm range is very similar, ca. 0.24–0.26, while for larger Co particles (ca. 21.3 nm),  $\theta_{\text{H}}$  becomes almost twice (~0.5).

Fig. 1c presents the effect of TOS on the rate of H<sub>2</sub> chemisorption (fresh vs. used (25 h in FTS)) for the catalyst with d<sub>Co</sub> = 21.3 nm. After 25 h in CO/H<sub>2</sub>, the number of sites that are capable for hydrogen chemisorption is decreased. In particular, the amount of hydrogen chemisorption for the fresh sample (before reaction) was 95.1 µmol H g<sub>cat</sub><sup>-1</sup> ( $\theta_{\rm H}$  = 0.50), while for the used sample was 70.2 µmol H g<sub>cat</sub><sup>-1</sup> ( $\theta_{\rm H}$  = 0.37). Similar results were obtained for the Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst with d<sub>Co</sub> = 11.4 nm, as shown in Fig. S3 (ESI), where N<sub>H</sub> = 51.9 µmol H g<sub>cat</sub><sup>-1</sup> ( $\theta_{\rm H}$  = 0.24) for the fresh sample and N<sub>H</sub> = 31.2 µmol H g<sub>cat</sub><sup>-1</sup> ( $\theta_{\rm H}$  = 0.14) for the used sample. These important results will be discussed later with regards to the intrinsic reasons of catalyst deactivation (see Section 4.6).

Fig. 2a presents the effect of Co particle size (7.7 – 21.3 nm) on the H<sub>2</sub> desorption rate ( $\mu$ mol g<sub>cat</sub><sup>-1</sup> s<sup>-1</sup>) over Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> fresh catalysts (before reaction), while Table 1 provides the peak maximum desorption temperature and the amount of desorbed hydrogen ( $N_{H}$ , µmol  $g_{cat}^{-1}$ ) for each desorption state (after deconvolution). The deconvolution performed does not entail an accurate estimation of the existing distribution of different types of Co surface sites in each catalyst (Fig. 2d) but rather provides a comparison on the basis of the binding strength between Co and adsorbed H ( $E_{Co-H}$ , kcal mol<sup>-1</sup>). All catalysts present four main hydrogen desorption peaks (chemisorption states). It is obvious that desorption peaks shifted to lower temperatures with increasing Co particle size, indicating the formation of a weaker Co-H bonding on the large Co particles. The ratio of surface coverage of weakly bound H (T < 200 °C) to the strongly bound H (T > 200 °C) was found to be 2.3, 1.5 and 0.7 for Co particles 7.7, 11.4 and 21.3 nm, respectively (Table 1). These results demonstrate that large Co particles possess larger concentration of sites which accommodate strongly bound hydrogen compared to the small particles (Table 1).

Fig. 2b and c shows the effect of TOS on the rate of H<sub>2</sub> desorption (fresh and used (25 h in FTS) catalyst) for Co particle sizes of 11.4 and 21.3 nm. The amount of desorbed hydrogen was found to be lower after FTS reaction (Table 1), in agreement with Fig. 1c. Small differences between the amounts of chemisorbed and desorbed hydrogen are due to the purge of reactor with He gas at 30 °C before the start of TPD run. After FTS reaction, the surface coverage of strongly bound H (T > 200 °C) decreases by a factor of 4.5 and 1.5 for the Co particles of 11.4 and 21.3 nm in size, respectively. The concentration of strongly bound H is significantly decreased for the small Co particles (Fig. 2b and Table 1) after reaction. For the weakly bound H. their concentration decreases by a factor of  $\sim 1.7$  and  $\sim 1.2$  for the Co particles of 11.4 and 21.3 nm in size, respectively. These results illustrate that after reaction, the concentration of sites that accommodate strongly bound H is reduced, especially for the small Co particles.



**Fig. 1.** Effect of Co particle size (7.7 – 21.3 nm) on (a) the rate of H<sub>2</sub> chemisorption per exposed surface cobalt atom at 100 °C, and (b) the surface coverage of H ( $\theta_{H}$ ) for the fresh Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst (before reaction). The data for the catalyst with Co particle size of 7.7 nm were obtained from Ref. [7]. (c) Effect of TOS in FTS on the rate of H<sub>2</sub> chemisorption per exposed surface cobalt over the fresh and used (25 h) 25 wt% Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst (d<sub>co</sub> = 21.3 nm).

# 3.2. Catalytic performance of $Co/\gamma$ -Al<sub>2</sub>O<sub>3</sub> in methanation reaction

Fig. 3a shows the CH<sub>4</sub> production rate,  $r_{CH4}$  (µmol  $g_{cat}^{-1} s^{-1}$ ) measured in CO/H<sub>2</sub> at 230 °C with time-on-stream, TOS (up to 25 h) for the two alumina-supported cobalt catalysts of 11.4 and 21.3 nm Co particle size. It is seen that the CH<sub>4</sub> production rate drops significantly with TOS. In particular, after 6 h and 25 h of reaction, the CH<sub>4</sub> production rate decreases by a factor of 2.1 and 6.9, respectively, after comparison with the initial rate (measured after 30 min on stream) for the catalyst with  $d_{Co}$  = 21.4 nm. After ~ 5 h and up to 25 h in CO/H<sub>2</sub>, the Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with the larger Co particle size (21.4 nm) presents higher CH<sub>4</sub> production rates than the catalyst with smaller Co particle size (11.3 nm). A very similar trend is also observed for the CO consumption rate, r<sub>co</sub>  $(\mu mol g_{cat}^{-1} s^{-1})$  as shown in Fig. 3b. In particular,  $r_{CO}$  decreases by a factor of 8 after 25 h in TOS. The methane selectivity (%) for the present catalytic system and reaction conditions was in the 62–72% range (Fig. 3c). It is obvious that methane selectivity is only slightly affected by TOS as opposed to the rate of methanation reaction and CO conversion to CH<sub>4</sub> and C<sub>2+</sub>-hydrocarbons.

# 3.3. SSITKA-Mass spectrometry studies

# 3.3.1. Carbon-path

SSITKA experiments (see Section 2.3.1) were conducted at different TOS, namely: 0.5, 1, 2, 4, 6, 8 and 25 h. Fig. S4 (ESI) presents

original transient response curves of MS signals for H<sub>2</sub>O (*m*/*z* = 18), <sup>13</sup>CO (*m*/*z* = 29), <sup>13</sup>CH<sub>4</sub> (*m*/*z* = 17), <sup>12</sup>CH<sub>4</sub> (*m*/*z* = 15) and Kr (*m*/*z* = 84) during the SSITKA step-gas switch <sup>12</sup>CO/H<sub>2</sub>/Ar (0.5 h, 230 °C)  $\rightarrow$  <sup>13</sup>CO/H<sub>2</sub>/Kr/Ar (t). It should be stated here that the correct performance of a SSITKA experiment should reveal the following features: (i) the quantities (Z<sub>13CO</sub> + Z<sub>12CO</sub>) and (Z<sub>13CH4</sub> + Z<sub>12CH4</sub>) should be equal to one *at any time* during the SSITKA step-gas switch, and in addition, the two isotopic dimensionless concentrations Z<sub>i</sub>(t) and Z<sub>i</sub>·(t) should cross each other at Z = 0.5 [4,8,9]; (ii) the concentration of H<sub>2</sub>O, which is a product of the FTS reaction, should remain stable during the SSITKA switch since the partial pressures of both CO and H<sub>2</sub>, the reaction temperature and the space velocity are kept constant. The above described features were fully satisfied in all the SSITKA experiments conducted in this work.

Fig. 4 shows normalized concentration (Z) response curves of Kr (tracer gas), <sup>13</sup>CO and <sup>13</sup>CH<sub>4</sub> obtained during the SSITKA step-gas switch at 230 °C over the Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst with Co particle size of 21.3 nm. The <sup>13</sup>CO(g) transient response curve lags behind that of Kr tracer as the result of a measurable concentration of *reversibly adsorbed CO-s* formed during the applied FTS reaction conditions. The <sup>13</sup>CH<sub>4</sub> (g) transient response curve lags behind that of <sup>13</sup>CO (g), and this feature is due to the fact that <sup>13</sup>C passes through the various kinds of *active* carbon-containing adsorbed reaction intermediates (e.g., CH<sub>x</sub> and/or -CH<sub>x</sub>O) following the pool of adsorbed CO-s before forming <sup>13</sup>CH<sub>4</sub>(g). For example, reversibly adsorbed



**Fig. 2.** Rates of  $H_2$  desorption ( $\mu$ mol  $g_{cat}^{-1} s^{-1}$ ) over Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts. (a) Effect of Co particle size (7.7 – 21.3 nm) before reaction; data for catalyst with Co particle size of 7.7 nm were obtained from Ref. [7]). Effect of TOS on the rate of  $H_2$  desorption (fresh and used (25 h in FTS) catalyst) for Co particle size of (b) 11.4 nm and (c) 21.3 nm. (d) Deconvoluted  $H_2$ -TPD trace of fresh Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst with  $d_{co}$  = 21.3 nm.

#### Table 1

Peak maximum desorption temperature ( $T_{M}$ ,  $^{\circ}C$ ) and amount of desorbed hydrogen,  $N_H$  (µmol H  $g_{-1}^{-1}$ ) for each of the deconvoluted peaks of H<sub>2</sub>-TPD traces obtained over Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts with Co particle size ( $d_{Co}$ , nm) in the 7.7–21.3 nm range, for the fresh and used (25 h in FTS) catalysts. The ratio of the surface coverage of weakly to strongly bound H ( $\theta_{H(T<200^{\circ}C)})/\theta_{H(T>200^{\circ}C)}$ ) is provided.

dCo, nm	1st peak		2nd peak		3rd peak		4th peak		N <sub>H, total,</sub> μmol H σ <sup>-1</sup> .	$\theta_{H(T<200^{\circ}C)}/$
	T <sub>M</sub> °C	N <sub>H,</sub> μmol H g <sup>-1</sup> <sub>cat</sub>	T <sub>M</sub> °C	N <sub>H,</sub> μmol H g <sup>-1</sup> <sub>cat</sub>	T <sub>M</sub> °C	N <sub>H,</sub> µmol H g <sup>-1</sup> <sub>cat</sub>	T <sub>M</sub> °C	N <sub>H,</sub> µmol H g <sup>-1</sup> <sub>cat</sub>	•• &cat	ЧH(1>200 С)
7.7- Fresh	111	$28.0(0.07)^{a}$	176	46.3(0.11)	237	20.1(0.05)	286	11.9(0.03)	106.3(0.23)	2.3
11.4- Fresh	99	12.2(0.06)	131	17.9(0.08)	245	17.5(0.08)	334	2.4(0.01)	50.0(0.23)	1.5
11.4-Used	100	1.4(0.006)	146	15.4(0.07)	240	3.7(0.02)	-		20.5(0.09)	3.8
21.3- Fresh	98	15.8(0.08)	128	17.4(0.09)	187	13.7(0.07)	265	32.5(0.17)	79.4(0.41)	0.7
21.3-Used	95	10.4(0.054)	133	16.1(0.084)	206	11.9(0.062)	282	19.3(0.10)	57.7(0.30)	0.8

<sup>a</sup> The surface coverage of H ( $\theta_{\rm H}$ ) is given in parentheses.

CO-s is hydrogenated in two steps to form HCOH-s, followed by its dissociation to CH-s and OH-s [2,36–39]. The CH-s intermediate formed is then hydrogenated to form CH<sub>4</sub>(g). A blank experiment was performed using an empty reactor (no catalyst in place, only quartz wool of equivalent volume as of the catalyst powder), where the transient response curves of dimensionless concentration (Z) of Kr and <sup>13</sup>CO were identical after the SSITKA switch. This means that the difference in position between Z(Kr) and Z(<sup>13</sup>CO) in Fig. 4 with the catalyst in place is due only to the catalytic effect mentioned above.

At the same time, the  ${}^{13}CH_4$  and  ${}^{13}CO$  transient response curves required longer time to reach the new steady-state (under  ${}^{13}CO/H_2$ ) when the SSITKA switch was performed after 25 h in CO/H<sub>2</sub>

reaction, to be compared to those recorded after 0.5 h in TOS (compare Fig. 4a and b). This behaviour could be understood if the rate constant of hydrogenation of the active  $-CH_x$  species that lead to  $CH_4$  ( $k_{CHx}$ ,  $s^{-1}$ ) becomes smaller and/or its surface coverage increases with increasing TOS (see Eq. (2)). It should be also noted that the time delay appeared between the <sup>13</sup>CO and Kr response curves decreases with increasing TOS (Fig. 4c), while at the same time the <sup>13</sup>CO response takes a bit longer time to reach the new steady-state (Z = 1) as also observed in the <sup>13</sup>CH<sub>4</sub> response curves (compare Fig. 4a and b).

Fig. 5 shows the surface coverage of CH<sub>x</sub>,  $\theta_{CHx}$  (Fig. 5a) and CO,  $\theta_{CO}$  (Fig. 5b) estimated using Eqs. (2)-(4) as a function of TOS and Co particle size (11.4 vs. 21.3 nm) over the Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst.



**Fig. 3.** (a) CH<sub>4</sub> production rate,  $r_{CH4}$  (µmol  $g_{cat}^{-1}$  s<sup>-1</sup>); (b) CO consumption rate,  $r_{CO}$  (µmol  $g_{cat}^{-1}$  s<sup>-1</sup>) and (c) CH<sub>4</sub> selectivity (%) over Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts (d<sub>Co</sub> = 11.4 and 21.3 nm) as a function of TOS (h). Reaction conditions: P ~ 1.2 bar, T = 230 °C, 4 vol% CO and H<sub>2</sub>/CO = 2; Amount of catalyst used: 15 wt% Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, W = 0.4 g; 25 wt% Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, W = 0.3 g.

The  $\theta_{CO}$  and  $\theta_{CHx}$  values are found to increase with increasing Co particle size (Fig. 5a, b) for any TOS, whereas the surface coverage of CH<sub>x</sub> ( $\theta_{CHx}$ ) decreases significantly with increasing TOS, while that of  $\theta_{CO}$  stays practically constant for both cobalt particle sizes. It is noted at this point that the  $\theta_{CHx}$  and  $\theta_{CO}$  values reported in this work are in the range of those reported by den Breejen et al. [11] and Vada et al. [20].

The mean surface residence time of active  $CH_x, \tau_{CHx}$  and that of CO,  $\tau_{CO}$  were estimated using Eqs. (7)-(8) and the obtained results are shown in Fig. 6. The  $\tau_{CHx}$  (s) steadily increases with increasing TOS (0.5 – 25 h) and appears to be practically independent of the Co particle size (Fig. 6a). The inverse of  $\tau_{CHx}$  provides the effective rate constant,  $k_{eff}$  (Eq. (9), Fig. 6c). Knowledge of  $\theta_{H}$  would allow to estimate the intrinsic rate constant, k<sub>CHx</sub>, associated with the ratedeterming step (RDS). The  $k_{\text{CHx}}$  refers to an average site activity of all  $CH_x$  intermediates (e.g.,  $-CH_x$ , -COH, -HCOH-), which are sequencially hydrogenated to finally form CH<sub>4</sub>(g). In contrast, the  $\tau_{CO}$  (s) is rather not influenced (<10% differences) by either TOS or Co particle size (Fig. 6b). The results of  $\tau_{CO}$  show that the active Co sites which accommodate molecularly adsorbed CO and are found in the carbon-path of CH<sub>4</sub> and C<sub>2+</sub>-hydrocarbons formation were slighlty only affected by TOS, whereas those accomodating the -CH<sub>x</sub> active intermediates are largely influenced by TOS (Fig. 6a, c). More precisely, the intrinsic rate constant of  $CH_x$  ( $k_{CHx}$ ) hydrogenation to  $CH_4$  and/or  $\theta_H$  must decrease with TOS (see Fig. 6c,  $k_{eff} = 1/\tau_{CHx}$ ;  $k_{eff} = k_{CHx} \theta_H$ ) since  $k_{eff}$  decreases.

Table 2 shows  $TOF_{CH4}$  and  $TOF_{CO}(s^{-1})$  values estimated after 2 h and 25 h in CO/H<sub>2</sub> based on Eqs. (9)-(12). The total amount of surface Co sites per mass of catalyst (N<sub>Co, surf</sub>, µmol g<sup>-1</sup><sub>cat</sub>) was estimated based on the Co dispersion obtained from XRD data (use of Eqs. S1 and S2 in ESI;  $TOF_{CH4,XRD}$  and  $TOF_{CO,XRD}$ ,  $s^{-1}$ ), the amount of surface Co able to chemisorb hydrogen in the 25-100 °C range was obtained by H<sub>2</sub> chemisorption/TPD (Section 3.1.2, TOF<sub>CH4,chem</sub> and  $TOF_{CO,chem}$ ,  $s^{-1}$ ) and the amount of surface Co accommodating the active CO-s and CH<sub>x</sub>-s was obtained based directly on the SSITKA experiments (Fig. 7a, b;  $TOF_{CH4, ITK}$  and  $TOF_{CO, ITK}$ ,  $s^{-1}$ ). For example, in the case of  $Co/\gamma$ -Al<sub>2</sub>O<sub>3</sub> with d<sub>Co</sub> = 21.3 nm, the total amount of surface Co was found to be 190.9  $\mu$ mol  $g_{cat}^{-1}$ , the amount of surface Co able to chemisorb hydrogen 79.4  $\mu$ mol g<sub>cat</sub><sup>-1</sup>, and the amount of surface Co accommodating the active CO-s and CH<sub>x</sub>-s, 55  $\mu$ mol g<sub>cat</sub><sup>-1</sup> (Fig. 7b). The values of TOF<sub>XRD</sub> are significantly lower than those of  $\text{TOF}_{\text{chem}}$  and  $\text{TOF}_{\text{ITK}}$ , because Eq. S1 (ESI) assumes that all Co is reduced, result that may not be correct [40], and participate in the FTS reaction.

The *number* of surface cobalt atoms per mass of catalyst for estimating TOF ( $s^{-1}$ ) could also be considered those measured via H<sub>2</sub>chemisorption, but still this value would not be representative of the true number of cobalt sites that participate in the reaction path of FTS reaction. It should be mentioned here that the exposed Co surface atoms under FTS reaction conditions may decrease with TOS due to some oxidation or sintering of cobalt [41]. Therefore, the number of cobalt surface atoms estimated via H<sub>2</sub>-



**Fig. 4.** Transient response curves of dimensionless concentration (Z) of Kr,  ${}^{13}$ CO and  ${}^{13}$ CH<sub>4</sub> obtained during the SSITKA step-gas switch at 230 °C over the Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst (d<sub>Co</sub> = 21.3 nm) for (a) 0.5 h and (b) 25 h in TOS. (c) Transient response curves of dimensionless concentration Z<sup>13</sup>CO obtained during the SSITKA step-gas switch performed after 0.5 and 25 h in 4%<sup>12</sup>CO/8%H<sub>2</sub>/88%Ar gas mixture; Amount of catalyst used: 15 wt% Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, W = 0.4 g; 25 wt% Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, W = 0.3 g.



**Fig. 5.** Surface coverage of *active* CH<sub>x</sub>,  $\theta_{CHx}$  (a) and adsorbed CO,  $\theta_{CO}$  (b) as a function of TOS and Co particle size ( $d_{Co}$  = 11.4 vs 21.3 nm) over Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts. Amount of catalyst used: 15 wt% Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, W = 0.4 g; 25 wt% Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, W = 0.3 g.

chemisorption on fresh samples would apparently lead to an underestimation of true TOF values as suggested in Section 3.1.2.

The most appropriate way to estimate the TOF of the present methanation reaction is to consider the surface cobalt atoms that participate in the reaction pathway. In the present work, the *active*  reaction intermediates CO-s and  $CH_x$ -s ( $N_{CO}$  and  $N_{CHx}$ ) were estimated. Other *active* reaction intermediate that participate in the CH<sub>4</sub> formation is adsorbed atomic hydrogen, H-s. As will be shown in Section 3.4, the fact that *inactive* species (e.g.,  $C_xH_y$ , named  $C_\beta$  and  $C_\gamma$ ) accumulate on the Co surface at the present reaction con-



**Fig. 6.** Mean surface residence time of CH<sub>x</sub>,  $\tau_{CHx}$  (a), CO,  $\tau_{CO}$  (b) and effective rate constant of CH<sub>x</sub> (k<sub>eff</sub>) (c) as a function of TOS and Co particle size (d<sub>Co</sub> = 11.4 vs 21.3 nm) over the Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts. Amount of catalyst used: 15 wt% Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, W = 0.4 g; 25 wt% Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, W = 0.3 g.

#### Table 2

TOF<sub>CH4 or CO, XRD</sub> (s<sup>-1</sup>) based on the dispersion of Co estimated from XRD, TOF<sub>CH4 or CO, chem</sub> (s<sup>-1</sup>) based on H<sub>2</sub> chemisorption (25–100 °C) and TOF<sub>CH4 or CO, ITK</sub> (s<sup>-1</sup>) based on the surface concentration of *active* CO-s and CH<sub>x</sub>-s intermediates (N<sub>CO</sub> and N<sub>CHx</sub>, µmol  $g_{c1}^{-1}$ ) measured during SSITKA as a function of Co particle size and TOS (2 h vs 25 h).

d <sub>Co</sub> (nm)	TOS (h)	$\begin{array}{c} \text{TOF}_{\text{CH4,XRD}} \\ (s^{-1}) \times 10^3 \end{array}$	$\begin{array}{c} TOF_{CH4,chem} \\ (s^{-1}) \times 10^3 \end{array}$	$\begin{array}{c} \text{TOF}_{\text{CH4, ITK}} \\ (s^{-1}) \times 10^3 \end{array}$	$\begin{array}{c} \text{TOF}_{\text{CO,XRD}} \\ (s^{-1}) \times 10^3 \end{array}$	$\begin{array}{c} TOF_{CO,chem} \\ (s^{-1}) \times 10^3 \end{array}$	$\begin{array}{l} \text{TOF}_{\text{CO, ITK}} \\ (s^{-1}) \times 10^3 \end{array}$
11.4	2	0.7	3.1	3.2	1.0	4.4	4.5
	25	0.1	0.4	0.5	0.1	0.6	0.7
21.3	2	0.8	2.0	2.9	1.3	3.1	4.5
	25	0.2	0.4	0.6	0.2	0.6	0.9

ditions, and according to their surface coverage estimated, the  $\theta_{\rm H}$  is expected to be rather very small. Also, according to the H<sub>2</sub>-TIC results reported in Table 1 and Fig. 1,  $\theta_{\rm H}$  is in the range of 0.1– 0.3 for the used catalysts when H<sub>2</sub> chemisorption was conducted in the 25–100 °C range. It is expected that at 230 °C,  $\theta_H$  would take lower values. An attempt to measure  $\theta_H$  by  $H_2/D_2$  transient isotopic experiments would not be successful because of the exchange of D<sub>2</sub> with –OH groups on the surface of alumina support [42]. Thus, the number of active sites related to the methanation reaction (N<sub>CO</sub> +-N<sub>CHx</sub>) must be considered close to the true number of active sites at the operating reaction conditions. It should be noted that this estimation assumes a stoichiometry of 1:1 for Co<sub>s</sub> - CO and Co<sub>s</sub> - CH<sub>x</sub>, which is essentially valid. According to SSITKA-DRIFTS results (Fig. 12 and Fig. S5) and other reported DRIFTS spectra [7,31,43,44], only the linear-type of adsorbed CO on Co surface was observed.

The concentration of active CH<sub>x</sub>-s and CO-s participating in the methanation reaction and the sum of the two (total) as measured by SSITKA experiments (Fig. 5), along with the  $TOF_{ITK}$  (s<sup>-1</sup>) vs TOS (0.5 - 25 h) are plotted in Fig. 7 for the two Co particles (11.4 and 21.3 nm). It is illustrated that the amount of active CH<sub>x</sub> (N<sub>CHx</sub>,  $\mu$ mol  $g_{cat}^{-1}$ ) decreases by 4 and 2.9 times (Fig. 7a,b), while TOF<sub>CH4. ITK</sub> decreases by 9.5 and 6.2 times (Fig. 7c) for Co particles of 11.4 and 21.3 nm in size, respectively, with increasing TOS from 0.5 to 25 h. At the same time, the effective rate constant  $(k_{eff})$  estimated by SSITKA experiments as well (Fig. 6c) decreases approximately by 2.5 times with increasing TOS for both catalysts. Thus, the decrease of TOF<sub>CH4, ITK</sub> is due to the decrease of both  $k_{eff}$  and  $N_{CHx}$  (or  $\theta_{CHx}$ ); TOF<sub>CH4</sub> =  $k_{eff} \theta_{CHx}$ . The decrease of  $k_{eff}$  (= $k_{CHx} \theta_{H}$ ) shows in turn that the intrinsic rate constant of  $CH_x$   $(k_{CHx})$  and/or  $\theta_{\rm H}$  decrease with TOS. The amount of CO-s ( $N_{CO}$ ,  $\mu$ mol  $g_{cat}^{-1}$ ) is approximately constant with TOS (Fig. 7a, b), while TOF<sub>CO. ITK</sub> decreases by 9.8 and 7.2 times



**Fig. 7.** Concentration of active reaction intermediates  $N_{CO}$  and  $N_{CHx}$  (µmol  $g_{c1}^{-1}$ ) estimated from SSITKA experiments for (a)  $d_{Co}$  = 11.4 nm and (b)  $d_{Co}$  = 21.3 nm. (c) TOF<sub>CO, TTK</sub> and TOF<sub>CH4, TTK</sub> values estimated based on the sum of the concentrations of *active* CH<sub>x</sub>-s and CO-s intermediates measured by SSITKA over Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts ( $d_{Co}$  = 11.4 and 21.3 nm) as a function of TOS. Reaction conditions: P ~ 1.2 bar, T = 230 °C, 4 vol% CO and H<sub>2</sub>/CO = 2; Amount of catalyst used: 15 wt% Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, W = 0.4 g; 25 wt% Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, W = 0.3 g.

for Co particles of 11.4 and 21.3 nm in size, respectively, with increasing TOS (0.5 to 25 h, Fig. 7c). These results show that coadsorb species may affect the binding strength of CO-s with cobalt surface sites and/or the reactivity of CH<sub>x</sub>-s for CH<sub>4</sub> and higher hydrocarbons (S<sub>C2+</sub> ~ 30–35%). In the case where the TOF<sub>ITK</sub> would be calculated including  $\theta_{\rm H}$  (CO-s, CH<sub>x</sub>-s and H-s), the obtained values would be slightly lower, but TOF<sub>ITK</sub> would still decrease with increasing TOS, since  $\theta_{\rm H}$  is expected to decrease with TOS based on the present H<sub>2</sub>-chemisortpion results (Fig. 1c, 2b, 2c and Table 1). Small or no differences were found for the TOF<sub>CO</sub> and TOF<sub>CH4</sub> at a given TOS (Table 2 and Fig. 7c) with increasing Co particle size (11.4 vs. 21.3 nm), and this result is in agreement with literature [45,46].

# 3.3.2. C-path and H-path of methanation reaction

Fig. 8 shows the transient response curves of normalized concentrations (Z) of Kr,  ${}^{13}CH_4$  and  ${}^{13}CD_4$  recorded during the 2nd and 4th step-gas switch of the following sequence of SSITKA switches  ${}^{12}CO/H_2/Ar$  (230 °C, 6 h)  $\rightarrow {}^{13}CO/H_2/Kr/Ar$  (10 min)  $\rightarrow {}^{12}CO/H_2/Ar$  (10 min)  $\rightarrow {}^{13}CO/D_2/Kr/Ar$  (10 min) performed at 230 °C over the Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst (d<sub>Co</sub> = 21.3 nm) as detailed in Section 2.3.3. A similar experiment was also performed over the catalyst with the smaller Co particle size of 11.4 nm. For both catalysts the same (within experimental error) Z<sub>CO</sub>(t) transient response curves were obtained during the  ${}^{13}CO/H_2$ -SSITKA and  ${}^{13}CO/D_2$ -SSITKA (not presented), result which indicates that the



**Fig. 8.** Dimensionless concentration (Z) transient response curves of Kr,  ${}^{13}$ CH<sub>4</sub> and  ${}^{13}$ CD<sub>4</sub> obtained during  ${}^{13}$ CO/H<sub>2</sub>-SSITKA and  ${}^{13}$ CO/D<sub>2</sub>-SSITKA at 230 °C over the 25 wt % Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with d<sub>Co</sub> = 21.3 nm and after 6 h in 4%CO/8%H<sub>2</sub>/He. Amount of catalyst used: 0.3 g.

kinetics of  ${}^{12}$ CO-s/ ${}^{13}$ CO(g) exchange is not influenced by the presence of H-s or D-s on the cobalt surface.

Fig. 8 shows that  $Z(^{13}CH_4)$  lags behind the  $Z(^{13}CD_4)$  due to the existence of a deuterium kinetic isotopic effect (D-KIE). The latter

for the CO consumption rate was estimated based on the steadystate rates of CO consumption in  ${}^{12}$ CO/H<sub>2</sub>/Ar and  ${}^{13}$ CO/D<sub>2</sub>/Kr/Ar feed gas mixtures according to Eq. (14):

$$D - KIE = \frac{r_{CO}(CO/H_2)}{r_{CO}(CO/D_2)} = \frac{r_H}{r_D}$$
(14)

when the ratio  $r_H/r_D$  is greater than unity, the KIE is named normal, and if it is less than unity is named inverse [47]. The deviation of KIE from unity is due to the formation or breaking of H-bond(s) of kinetically relevant steps. In the case where the KIE is unity, this means that the  $r_{\rm H}$  is equal to  $r_{\rm D}$  and the kinetically relevant steps do not involve formation or breaking of H-bonds. The D-KIE estimated for the CO consumption rate should reflect the overall D-KIE, from the CO reactant to all the reaction products (e.g. CH<sub>4</sub> and  $C_2^{\dagger}$ ) formed at the conditions of the experiment. The overall D-KIE value was found to be 0.83 and 0.81 for the Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst with Co particle size of 11.4 and 21.3 nm, respectively, indicating the presence of an *inverse* KIE. Thus, one of the following steps might be considered as potential rate-determing step of methanation reaction: (i) the hydrogenation of CO-s to form HCO-s and then HCOH-s, and (ii) one of the sequential hydrogenation steps of CH-s to finally form CH<sub>4</sub>. The value of D-KIE for the CH<sub>4</sub> formation reaction path was estimated via Eq. (13) and was found to be 0.94 and 0.91 (inverse KIE) for the catalysts with Co particle size of 11.4 and 21.3 nm. respectively.

The SSITKA results shown in Fig. 8 and after using Eq. (7) allowed to estimate the surface residence times of CD<sub>4</sub> (91.2 s) and CH<sub>4</sub> (100.2 s), resulting also in k<sub>eff, CD4</sub> ~ 1.1 × 10<sup>-2</sup> s<sup>-1</sup> and k<sub>eff, CH4</sub> ~ 1 × 10<sup>-2</sup> s<sup>-1</sup>, respectively (see Eq. (9)) for d<sub>Co</sub> = 21.3 nm. In the case of d<sub>Co</sub> = 11.3 nm, the  $\tau_{CH4}$ ,  $\tau_{CD4}$ , k<sub>eff, CH4</sub> and k<sub>eff, CD4</sub> were found to be 99.6 s, 93.6 s,  $1.00 \times 10^{-2} s^{-1}$  and  $1.06 \times 10^{-2} s^{-1}$ , respectively.

In order to test that during the  ${}^{13}\text{CO}/\text{D}_2$  gas-switch the  ${}^{13}\text{CD}_4$  transient response is not influenced by exchange reactions of  ${}^{13}\text{CD}_4$  (g) with –OH groups mainly formed on the alumina support and to a much lesser extent on the Co surface, the following sequence of step-gas switches was performed at 230 °C: Ar  $\rightarrow$  8 vol% D<sub>2</sub>/Ar (15 min)  $\rightarrow$  0.14 vol% CH<sub>4</sub>/1 vol% Kr/Ar. The first step-gas switch Ar  $\rightarrow$  8 vol% D<sub>2</sub>/Ar was performed in order to exchange part of the –OH groups of alumina with –OD as shown in Fig. S6 (ESI, transient response of HD(g)). At this step, D-s on the cobalt surface is also expected to be formed. During the 2nd step-gas switch, the transient response curves of Kr and CH<sub>4</sub> (m/ z = 15) were practically identical as shown in Fig. S7 (ESI), illustrating that no exchange of CH<sub>4</sub> with -OD of the alumina and/or D-s on Co surface occurred.

# 3.4. Transient isothermal hydrogenation (TIH) and Temperature-Programmed hydrogenation (TPH) of carbonaceous species

Fig. 9 shows transient response curves of <sup>13</sup>CH<sub>4</sub> and <sup>12</sup>CH<sub>4</sub> formation obtained during isothermal hydrogenation at 230 °C of the surface carbonaceous species formed after 25 h in FT synthesis (see Section 2.3.4) over the Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst with Co particle size of 11.4 nm. The transient response of <sup>13</sup>CH<sub>4</sub> is due to the hydrogenation of reversibly adsorbed CO-s and *active* CH<sub>x</sub>-s (C<sub>α</sub>) formed and which exchanged under the <sup>13</sup>CO-SSITKA step-gas switch. The surface coverage of intermediates leading to <sup>13</sup>CH<sub>4</sub> estimated by the TIH experiment ( $\theta_{13CH4}$ ) should be equal to the sum of the active intermediates estimated by SSITKA ( $\theta_{CO} + \theta_{CHx}$ ). The  $\theta_{13CH4}$  (TIH) was found to be 0.14 and the sum of  $\theta_{CO}$  and  $\theta_{CHx}$ (SSITKA) to be 0.20. This difference is due to some desorption of CO-s occurred during the Ar gas purge before the 8%H<sub>2</sub>/Ar switch (TIH). It should be also noted that the initial sharp peak (spike) of <sup>13</sup>CH<sub>4</sub> response is due to the hydrogenation of the *active* CH<sub>x</sub>-s



**Fig. 9.** <sup>13</sup>CH<sub>4</sub> and <sup>12</sup>CH<sub>4</sub> transient isothermal hydrogenation response curves at 230 °C obtained under 8%H<sub>2</sub>/Ar gas flow following the sequence of step-gas switches: <sup>12</sup>CO/H<sub>2</sub> (25 h)  $\rightarrow$  <sup>13</sup>CO/H<sub>2</sub> (10 min)  $\rightarrow$  Ar (4 min)  $\rightarrow$  H<sub>2</sub>/Ar (t) over 15 wt% Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst (d<sub>Co</sub> = 11.4 nm). Amount of catalyst used: 0.4 g.

and the rest of response (e.g., t > 15 s) is due to the hydrogenation of adsorbed CO-s [5].

The transient response curve of <sup>12</sup>CH<sub>4</sub> is due to the hydrogenation of *inactive*  $C_xH_y$ -s ( $C_\beta$ ) and likely some non-exchangeable adsorbed CO-s formed under FTS reaction conditions. On the basis of SSITKA-DRIFTS results (see Section 3.5), all kinds of linear adsorbed CO-s identified are bound on the surface *reversibly*. Therefore, the <sup>12</sup>CH<sub>4</sub> transient response (Fig. 9) is due to *inactive*  $C_xH_y$ -s ( $C_\beta$ , "soft carbon") species, which are readily hydrogenated to CH<sub>4</sub> at 230 °C in 8% H<sub>2</sub>/Ar gas mixture but not in 4%CO/8%H<sub>2</sub>/Ar. The amount of  $C_\beta$  was found to be 21.5 µmol  $g_{cat}^{-1}$  ( $\theta$  = 0.10) and 26.6 µmol  $g_{cat}^{-1}$  ( $\theta$  = 0.14) after 25 h in TOS for the Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with Co particle size of 11.4 and 21.3 nm, respectively.

Fig. 10 shows transient response curves of <sup>12</sup>CH<sub>4</sub> obtained under temperature-programmed hydrogenation (TPH) following 2 h and 25 h of methanation reaction over the two  $Co/\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts and according to the gas delivery sequence described in Section 2.3.4. The deconvolution of these TPH profiles is shown in Fig. 10b. The resulting four peaks are attributed to different kinds of inactive carbonaceous species,  $C_x H_v$  (named  $C_v$ , "hard carbon") formed on the catalyst surface under reaction conditions and hydrogenated at temperatures higher than 230 °C. Table 3 shows the CH<sub>4</sub> peak maximum temperature (T<sub>max</sub>, °C) and the concentration ( $\mu$ mol g<sup>-1</sup><sub>cat</sub>) of carboneceous species for each of the deconvoluted peaks over the Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts after 2 h and 25 h in  $CO/H_2$ . The amount of *inactive* carbonaceous species  $C_{\gamma}$  was found to be practically the same at a given TOS ( $\theta$  = 0.35 for 2 h and 0.7– 0.74 for 25 h) for both catalysts (Co particle size of 11.4 and 21.3 nm). On the other hand, the catalyst with Co particle size of 21.3 nm shows significantly lower amount of  $C_{\gamma}$  hydrogenated in the 350-550 °C range compared with the catalyst of 11.4 nm Co particle size ( $\theta$  = 0.28 vs. 0.46) after 25 h in TOS. By increasing the TOS from 2 to 25 h, all the CH<sub>4</sub> peak maxima shifted to higher temperatures, indicating the formation of stronger bound  $C_{\gamma}$  species ("hard carbon") with TOS (Table 3). The TIH/TPH experiments following the SSITKA step-gas switch proved to be very informative since they allowed to probe the existence of (i) *inactive*  $-C_xH_y$  species ( $C_{B}$ ) hydrogenated at 230 °C (TIH) in the absence of CO and under conditions of higher surface coverage of hydrogen, and (ii) inactive carbonaceous  $-C_xH_y$  species hydrogenated only at temperatures>230 °C (C<sub>γ</sub>, TPH).

Fig. 11 shows the amount of  ${}^{12}$ CH<sub>4</sub> (µmol g<sup>-1</sup>) measured by TIH (C<sub> $\beta$ </sub>) and TPH (C<sub> $\gamma$ </sub>) as a function of TOS (0.5 – 25 h) over the Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with Co particle size of 11.4 nm. By increasing the TOS, the



**Fig. 10.** (a) <sup>12</sup>CH<sub>4</sub> traces obtained in TPH (up to 600 °C) performed over 15 and 25 wt% Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts (d<sub>co</sub> = 11.4 and 21.3 nm) after 2 h in CO/H<sub>2</sub>. (b) Deconvoluted <sup>12</sup>CH<sub>4</sub>-TPH trace of Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts (d<sub>co</sub> = 11.4 nm) obtained after 2 h in TOS. (c) <sup>12</sup>CH<sub>4</sub> traces obtained in TPH over 15 and 25 wt% Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts (d<sub>co</sub> = 11.4 and 21.3 nm) after 25 h in CO/H<sub>2</sub>.

#### Table 3

 $CH_4$  peak maximum temperature ( $T_M$ ,  $^{o}C$ ) and concentration ( $\mu$ mol  $g_{cat}^{-1}$ ) of several types of inactive carbonaceous species ( $-C_xH_y$ ) formed after deconvolution of TPH traces obtained over  $Co/\gamma$ - $Al_2O_3$  catalysts with Co particle size ( $d_{Co}$ , nm) of 11.4 and 21.3 nm and after 2 h and 25 h in  $CO/H_2$ .

d <sub>co</sub> (nm)	TOS (h)	1st peak		2nd peak		3rd peak		4th peak		Total	
		T <sub>M</sub> (°C)	$N_1 \ (\mu mol \ g^{-1})$	$T_M (^{o}C)$	$N_2 (\mu mol \; g^{-1})$	$T_M (^{o}C)$	$N_3 (\mu mol g^{-1})$	T <sub>M</sub> (°C)	$N_4 (\mu mol \; g^{-1})$	N ( $\mu mol \ g^{-1}$ )	
11.4	2	286	15.0(0.07) <sup>a</sup>	322	26.7(0.12)	372	17.7(0.08)	419	15.1(0.07)	74.5(0.35) <sup>a</sup>	
	25	290	16.2(0.07)	342	36.7(0.17)	398	68.3(0.32)	446	29.8(0.14)	150.8(0.70)	
21.3	2	280	7.9(0.04)	322	33.3(0.17)	374	19.5(0.10)	422	7.4(0.04)	68.1(0.35)	
	25	292	42.1(0.22)	343	45.8(0.24)	385	33.0(0.17)	430	21.3(0.11)	142.2(0.74)	

<sup>a</sup> Number in parentheses refer to surface coverage based on the Co exposed surface atoms determined by powder XRD.

amount of both  $C_{\beta}$  and  $C_{\gamma}$  is significantly increased, where the amount of  $C_{\beta}$  is significantly smaller than that of  $C_{\gamma}$ . It is interesting to note that the surface coverage of all *inactive* carbonaceous species ( $C_{\beta}$  and  $C_{\gamma}$ ) after 25 h in CO/H<sub>2</sub> is significantly larger than the surface coverage of *active* species (SSITKA,  $\theta_{CO}$  and  $\theta_{CHx}$ , Fig. 5). In particular, for the Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with Co particle size of 11.4 nm,  $\theta$  ( $C_{\alpha}$ ) +  $\theta$  ( $C_{\beta}$ ) = 0.80, which is four times larger than the surface coverage of *active*  $C_{\alpha}$  and CO-s ( $\theta$  = 0.20) determined by SSITKA. Similar results were obtained for the larger Co particle size of 21.3 nm ( $\theta$  = 0.27 vs. 0.88). Comparable results were reported also by Happel at al. [48] and Otarod et al. [49].

# 3.5. SSITKA-DRIFTS studies

SSITKA-DRIFTS spectra were recorded after 6 h in  $4\%^{12}$ CO/8%H<sub>2</sub>/ Ar at 230 °C and 10 min in  $4\%^{13}$ CO/8%H<sub>2</sub>/1%Kr/Ar following the SSITKA step-gas switch over the Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst with Co particle size of 21.3 nm. Fig. 12a presents the characteristic IR bands of v(C-H) stretching vibrational mode recorded in the 3000–2800 cm<sup>-1</sup> range. The IR bands centered at 2925 ( $v_1$ ) and 2856 cm<sup>-1</sup> ( $v_2$ ) correspond to the symmetric and asymmetric stretching vibrational modes of methylene (-CH<sub>2</sub>) group, while the IR band at 1460 cm<sup>-1</sup> to the bending vibrational mode of – CH<sub>2</sub> group (Fig. 12a) [30,50]. The small shoulder appeared at 2965 cm<sup>-1</sup> corresponds to the symmetric vibrational mode of methyl (-CH<sub>3</sub>) group [30,50]. As depicted in Fig. 12a, none of the IR bands of -C<sub>x</sub>H<sub>y</sub> intermediate species shows the red isotopic shift, indicating that these species are *inactive*. A large concentration of inactive -C<sub>x</sub>H<sub>y</sub> intermediate species was found (TIH/TPH-MS) with respect to the very small amount of active -CH<sub>x</sub> species was not observed due to the overlapping with the large concentration of inactive -C<sub>x</sub>H<sub>y</sub> species.

Fig. 12b shows SSITKA-DRIFTS spectra recorded in  $^{12}$ CO/H<sub>2</sub> and  $^{13}$ CO/H<sub>2</sub> gas mixtures at 230 °C in the 2250–1800 cm<sup>-1</sup> range. The IR bands at 2182 and 2116 cm<sup>-1</sup>, labeled as 1 and 2, are due to the



**Fig. 11.** Amount of  $^{12}CH_4$  (µmol  $g_{cat}^{-1}$ ) measured by TIH (C<sub> $\beta$ </sub> carbon) and TPH (C<sub> $\gamma$ </sub> carbon) experiments as a function of TOS over the Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst with  $d_{Co}$  = 11.4 nm.

R and Q branches of gas phase <sup>12</sup>CO [51]. The IR bands at 2056, 2033 and 1992 cm<sup>-1</sup> correspond to three linear-type adsorbed CO on a reduced Co surface, while that at 1922 cm<sup>-1</sup> to a bridged-type adsorbed CO [30,31,43,44]. In the case of 15 wt% Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst (d<sub>Co</sub> = 11.4 nm), two linear-type adsorbed CO-s species (2045 and 2002 cm<sup>-1</sup>) and one bridged-type adsorbed CO at 1922 cm<sup>-1</sup> are formed (Fig. S5, ESI). Both catalysts show the

red isotopic shift upon the switch  ${}^{12}\text{CO/H}_2 \rightarrow {}^{13}\text{CO/H}_2$ , which implies that all linear- and bridged-type adsorbed CO-s species are reversibly chemisorbed on the Co surface. It is reported in Fig. 4 that the exchange kinetics of adsorbed  ${}^{12}\text{CO}$  with  ${}^{13}\text{CO}$  is rapid and completed within ~ 130 s. Based on the SSITKA-DRIFTS results (Fig. 12b), it cannot be concluded whether all linear- and bridged-type adsorbed CO-s species participate in the FTS reaction.

It is of interest to be mentioned here that only part of adsorbed CO was considered as *active* intermediate in the WGS reaction [52,53] over a supported Pt catalyst based on DRIFTS transient isothermal reaction experiments, where CO-s formed in WGS (CO/H<sub>2</sub>O) was partly reacted off by the following H<sub>2</sub>O/He gas switch. Recent work [7] over Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts has shown two linear-type CO-s of different reactivity in H<sub>2</sub>.

Fig. 12c presents SSITKA-DRIFTS spectra recorded in <sup>12</sup>CO/H<sub>2</sub> and <sup>13</sup>CO/H<sub>2</sub> gas mixtures at 230 °C in the 1700–1300 cm<sup>-1</sup> range, which are associated with the stretching vibrational modes of the O-C-O group of adsorbed carbonate, carboxylate and formate species. The IR bands recorded at 1593 and 1380 cm<sup>-1</sup> are assigned to –OCO- symmetric and antisymmetric vibrational modes of formates on the alumina surface [30,50,54,55]. No formate IR bands were recorded after passing CO/H<sub>2</sub> (4 h) at 230 °C over the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> alone. The IR band at 1593 cm<sup>-1</sup> shows a shoulder at 1640 cm<sup>-1</sup>, which is assigned to adsorbed molecular water [56,57]. After the new steady-state under the isotopic gas mixture was reached, none of the IR bands showed the red isotopic shift, indicating that these species are merely *spectators* for the methanation reaction.



Fig. 12. SSITKA-DRIFTS spectra recorded in the 3000 – 2800 (a), 2250–1800 (b) and 1700–1300 cm<sup>-1</sup> range (c) over the 25 wt% Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (d<sub>co</sub> = 21.3 nm). DRIFTS spectra were recorded after 6 h in 4%<sup>12</sup>CO/8%H<sub>2</sub>/Ar at 230 °C and 10 min after the SSITKA step-gas switch.

# 4. Discussion

The present work has provided new data and insight regarding the influence of some intrinsic kinetic parameters strongly related to the deactivation of  $Co/\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst with mean cobalt particle size of 11 and 21 nm under mainly methanation reaction conditions (4%CO/8%H<sub>2</sub>/He, 230 °C and P  $\sim$  1.2 bar). A new methodology based on the SSITKA technique was presented allowing to estimate the D-KIE for the methanation reaction for the first time to the best of our knowledge. SSITKA-MS followed by transient isothermal and temperature-programmed hydrogenation (TIH/TPH) experiments revealed information about the time evolution (up to 25 h in FTS reaction) of the concentration of three types of carbonaceous species, namely,  $C_{\alpha}$ ,  $C_{\beta}$  and  $C_{\gamma}$  formed on the Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and their dependence on the Co particle size for the first time. The  $C_{\alpha}$  consists of *active* CH<sub>x</sub>-s/CH<sub>x</sub>O-s reaction intermediates formed in the carbon-path of methanation reaction, while  $C_{\beta}$  and  $C_{\gamma}$  are considered spectator (*inactive*) species. Also, the site activity  $(k_{eff}, s^{-1})$  of  $C_{\alpha}$  was followed with TOS based on the SSITKA technique. The effect of TOS on the concentration of hydrogen chemisorption sites as a function of  $d_{Co}$  (nm) was also monitored by transient isothermal chemisorption at 100 °C followed by TPD for the first time as well. All this information provided important fundamental understanding about the origin of deactivation of  $C_0/\gamma$ -Al<sub>2</sub>O<sub>3</sub> during the CO methanation reaction, which might be of industrial interest (Co and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> are important constituents of industrial FTS catalysts). The above outlined main issues of this work and the obtained results are discussed in more detail in the following sections.

#### 4.1. Methanation reaction path through interconnecting -CH<sub>x</sub> pools

The <sup>13</sup>CO-SSITKA (Figs. 4 and 5a) and <sup>12</sup>CH<sub>4</sub>-TIH (Fig. 9) experiments have revealed the presence of two different types of carbonaceous species formed on the catalyst surface under methanation reaction conditions, an active  $C_{\alpha}\left(CH_{x}\right)$  which is in the pathway of  $CH_4$  formation, and an *inactive* one ( $C_\beta$ , "soft carbon") which is not hydrogenated at 230 °C under CO/H<sub>2</sub> but is hydrogenated only when CO is removed from the gas-phase (e.g.,  $CO/H_2/Ar \rightarrow Ar \rightarrow H_2/$ Ar). As presented in Fig. 9 (Section 3.4), the  $^{13}$ CH<sub>4</sub> response is the result of hydrogenation of the *active*  ${}^{13}CH_x$  ( ${}^{13}C_{\alpha}$ , spike, initial transient response) and of adsorbed <sup>13</sup>CO-s. On the other hand, the <sup>12</sup>CH<sub>4</sub> response is due to the hydrogenation of another type of - $C_xH_y$  species, named  $C_\beta$  (Figs. 9 and 12a). As we have recently reported on a similar TIH experiment following the SSITKA stepgas switch over a commercial 20 wt% Co-0.05 wt% Pt/γ-Al<sub>2</sub>O<sub>3</sub> catalyst [7], the chemical structure of  $C_{\beta}$  is that of an hydrocarbon alkyl chain (x > 1, see Fig. 12a). The likelihood that the  ${}^{12}CH_4$ response was the result of hydrogenation of a non-exchangable adsorbed CO-s is fully excluded based on the SSITKA-DRIFTS results presented in Fig. 12b. Also, the concentration of active  $C_{\alpha}$ was found to decrease with increasing TOS (Fig. 5a,  $\theta_{CHx}$ ), whereas that of  $C_{\beta}$  to increase significantly (Fig. 11).

According to the above observations, we propose that the methanation reaction proceeds via two interconnecting pools of carbonaceous species as depicted in Scheme 1. More precisely, CO(g) is reversibly adsorbed on the catalyst surface (CO-s) followed by dissociation via a likely H-assisted CO dissociation mechanism [2,7] to form -CH<sub>x</sub>O (named  $C_{\alpha}$ ) intermediates, which finally lead to methane formation, but also to the  $C_{\beta}$  (- $C_xH_y$ ) carbonaceous species. We propose that part of  $C_{\beta}$  is converted to  $C_{\alpha}$ . As TOS in CO/H<sub>2</sub> increases, the rate of conversion of  $C_{\beta}$  to  $C_{\alpha}$  (active species) decreases due to the decreasing  $\theta_H$  (see Section 3.1.2), and this explains well the build-up of  $C_{\beta}$  on the catalyst surface (Fig. 11) and at the same time the depletion of  $C_{\alpha}$  with TOS (Fig. 5a). The



**Scheme 1.** Carbon pathway from CO(g) to CH<sub>4</sub>(g) through two different types of carbonaceous species ( $C_{\alpha}$  and  $C_{\beta}$ ), where only  $C_{\alpha}$  leads directly to the methane formation.

 $C_{\beta}$  is hydrogenated at 230 °C only when CO is removed from the gas-phase and cobalt surface, and when the surface is rich in adsorbed H-s. Thus, when CO-s is depleted from the cobalt surface, an increased concentration of free cobalt surface sites become available for hydrogen chemisorption necessary for the hydrogenation of C<sub>B</sub>. The latter important information could lead to possible identification of site location(s) of C<sub>B</sub>. Carvalho et al. [15] reported on the deactivation of CoPt/SiO<sub>2</sub> FTS catalyst using also the SSITKA technique along with kinetic modelling of the <sup>12</sup>CO and <sup>12</sup>CH<sub>4</sub>-SSITKA transients. They reported that models which considered the existence of two intermediate carbon pools in the methane reaction path, as those shown in Scheme 1, provided the best fits of expermental data. Thus, the proposed Scheme 1 that explains well the SSITKA/TIH experimental results of this work on Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> finds strong support by similar SSITKA experimental results coupled with kinetic modelling on the CoPt/SiO<sub>2</sub> catalyst [15].

The establishment of the small surface coverage of  $C_{\alpha}$  must depend on the *net rate* of carbon transfer from  $C_{\beta}$  to  $C_{\alpha}$  carboncontaining pools, the rates of carbon transfer from the CO-s pool to the  $C_{\alpha}$  and  $C_{\beta}$  pools, and the rate of CH<sub>4</sub>(g) formation associated with the reactivity of  $C_{\alpha}$ . A similar to Scheme 1 carbon-path for methane formation has also been proposed by Soong et al. [58] after performing SSITKA step-gas switches of varying time ( $\Delta t$ ) in <sup>13</sup>CO/H<sub>2</sub> to explain the observed tailing feature of the <sup>13</sup>CH<sub>4</sub> decay response (step-gas switch from <sup>13</sup>CO/H<sub>2</sub> to <sup>12</sup>CO/H<sub>2</sub>).

Recent DFT calculations [59,60] have shown that -CH<sub>x</sub> monomers formed on Co stepped sites migrate to planar sites, where they can be hydrogenated to CH<sub>4</sub> or stay on the stepped sites, where they contribute to chain growth (C<sup>+</sup><sub>2</sub>-hydrocarbons formation). Thus, the concentration of step-edge and planar sites might affect the relative concentration of active  $C_{\alpha}$  and inactive  $C_{\beta}$ . Furthermore, metal nanoparticles can reconstruct under reaction conditions because of the strong CO adsorption on Co surfaces [44,61]. Surface reconstruction leads to the formation of stepped sites on planar surfaces. The concentration of stepped sites might have increased and that of planar sites decreased with TOS in CO/H<sub>2</sub> at 230 °C. An increasing concentration of stepped sites with TOS could have led to a higher concentration of -CH<sub>x</sub> monomers but the shortage of planar sites led finally to an increasing concentration of *inactive*  $C_{\beta}$  species, in harmony with the experimental observations (Fig. 11).

#### 4.2. Methanation reaction through parallel carbon pathways

SSITKA-DRIFTS results (Figs. 12 and S4) indicated that both Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts with different Co particle size show the red isotopic shift for all linear- and bridged-type adsorbed CO-s. This does not apriori suggest that all types of CO-s species trully participate in the formation of CH<sub>4</sub> and of higher hydrocarbons, as previously mentioned, since the isotopic exchange of <sup>12</sup>CO-s with <sup>13</sup>CO(g) (-Figs. 4 and 12b) can readily occur. Previous DRIFTS transient hydrogenation kinetic studies [7] on the 25 wt% Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst revealed the presence of two linear-type CO-s of different reactivity towards H<sub>2</sub> on the surface of cobalt particles of 7 and 10 nm in size. It was shown that the catalyst with the largest mean Co

particle size favored the population of adsorbed CO-s with different site activity distribution ( $k_{eff}$ ,  $s^{-1} = k_{CHx} \theta_H$ ;  $k_{CHx}$  is the intrinsic rate constant of the hydrogenation step (RDS) of HCO-s) compared to the smaller cobalt particle. More precisely, the ratio value of  $k_{eff}$ 's related to the two linear-type CO-s species was found to be 0.95 and 0.78, respectively, for the smaller and larger Co particle size. We propose that at least two linear-type CO's (CO<sup>A</sup>-s and CO<sup>B</sup>-s) might be considered to had formed as precursors of two parallel carbon paths of methanation reaction, as shown in Scheme 2. In the case that Scheme 2 applies, then the C<sub> $\alpha$ </sub> measured by SSITKA should be the sum of CH<sup>A</sup><sub>x</sub> and CH<sup>B</sup><sub>x</sub>. The proposed Scheme 2 finds also strong support by the SSITKA work of Carvalho et al. [15] on CoPt/SiO<sub>2</sub>.

#### 4.3. Deuterium kinetic isotopic effect (D-KIE)

The present work provided a new experimental methodology for estimating the D-KIE based on the SSITKA technique, where both  $^{13}$ CO and D<sub>2</sub> isotopes were used (see Section 3.3.2, Fig. 8) to follow at the same time the carbon and hydrogen reaction paths for the formation of CH<sub>4</sub>. The advantage of this methodology is that the catalyst surface structure and the composition of the adsorbed phase under both the CO/H<sub>2</sub> and CO/D<sub>2</sub> are investigated within a very short period of time (ca. 10-15 min), thus the CH<sub>4</sub> and CD<sub>4</sub> rates of methanation reaction are free of catalyst structural modification and catalyst deactivation phenomena, which may affect the results. In particular, the CO conversion after 6 h in the CO/H<sub>2</sub> reaction mixture was 3.5%, whereas after 10 min in the isotopic gas mixture, the CO conversion was 3.45%. Furthermore, the analysis provided (Eq. (13)) does not require the use of any calibration gas for isotopes, ca. CD<sub>4</sub>, as this is the case using ordinary MS or GC analysis at steady-state reaction conditions [34].

The overall KIE was estimated under steady-state reaction conditions from CO conversion rate data in  ${}^{12}CO/H_2/Ar$  and  ${}^{12}CO/D_2/Kr/Ar$ , where it was found to be 0.83 and 0.81 for the Co particle size of 11.4 and 21.3 nm, respectively. Experimental data previously reported on Co-based catalysts [50,62,63] showed overall KIE values in the 0.66–0.80 range for cobalt particle sizes in the 4–21 nm range, which also did not affect the kinetically relevant step or the KIE value, in agreement with the present results. The overall KIE is a combination of kinetic and thermodynamic isotope effects according to the following Eq. (15) [38]:

$$\frac{r_{\rm H}}{r_{\rm D}} = \frac{K_2^{\rm H}}{K_2^{\rm D}} \frac{K_3^{\rm H}}{K_3^{\rm D}} \frac{k_4^{\rm H}}{k_4^{\rm D}} \tag{15}$$

where,  $K_2$ ,  $K_3$  and  $k_4$  are the equilibrium constants and rate constant for the elementary RDS step, respectively, of an H-assisted CO dissociation mechanism depicted in Scheme 3:

Ojeda et al. [38] reported *inverse thermodynamic effects* for the H<sub>2</sub> dissociation process ( $K_2^H/K_2^D$  = 0.61) and for the formation of HCO<sup>\*</sup> (step 3 in Scheme 3;  $K_3^H/K_3^D$  = 0.64) but reported *normal* kinetic isotopic effect for the formation of HCOH<sup>\*</sup> (step 5, Scheme 3;  $k_4^H/k_4^D$  = 1.79) on the Co(0001) surface. Thus, for the lat-



# 4.4. Effect of Co particle size on important kinetic parametes $(\theta, k)$

The effect of Co particle size on the site activity of Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst in a quantified manner is apparently different, depending on the type of TOF (s<sup>-1</sup>) used (Table 2). This inherent situation encountered in every catalytic system is the result of the lack of precise knowledge of the number density of active sites participating in the given catalytic cycle operated under reaction conditions. In the present work, the methanation rate is ~ 4.5 times lower when all the exposed Co surface sites are considered participating in the reaction, as opposed to those estimated by SSITKA (N<sub>CHx</sub> and N<sub>CO</sub>). It is true that the TOF<sub>CH4, TTK</sub> and TOF<sub>CO, TTK</sub> values (Table 2) were overestimated since the sites of hydrogen chemisorption were not accounted for. However, this overestimation of TOF of methanation reaction should be considered rather small compared to the case if all Co surface sites were considered.

The TOF<sub>CO, ITK</sub> and TOF<sub>CH4, ITK</sub> and the mean residence times  $\tau_{CO}$ and  $\tau_{\text{CHx}}$  were found to be similar for the two Co particle sizes (Fig. 6a, 7c). These results suggest also that  $k_{eff}$  ( $k_{eff} = k_{CHx} \theta_{H}$ ) values are also similar for the two Co particle sizes (Fig. 6c). Given the large difference in the distribution of H-adsorption sites with Co particle size as reported in Fig. 2 and Table 1, it could be speculated that under FTS reaction conditions the intrinsic k<sub>CHx</sub> might depend on the Co particle size. The lower surface coverage of active -CH<sub>x</sub> and CO-s intermediates on the small Co particle size (11.4 nm) compared to the large one (ca. 21.3 nm) depicted in Fig. 5a and b, respectively, is due to purely kinetic reasons that govern the rates of CO chemisorption, C-O bond dissociation and hydrogenation, but also the rates of  $C_{\beta}$  and  $C_{\gamma}$  formation that could influence (at the local surface environment) the energetics of the relevant steps of methanation, and in turn the surface coverage of active species. For example, an increase in the rate of dissociation of C-O would be expected to lower the surface coverage of CO-s according to the formalism of series of carbon pools describing the methanation reaction mechanism [5,6,8].

The present work provided also very important information on the effect of Co particle size on the surface coverage and reactivity towards hydrogen of the various types of *inactive* (spectator) carbonaceous species accumulated on the catalyst surface. According to the TPH results of Fig. 10 and Table 3, both Co particle sizes appear to form four types of "carbon" of similar reactivity towards hydrogen (similar  $T_M$  values) and surface concentration (e.g.,



**Scheme 2.** Parallel carbon pathways for the conversion of CO(g) to  $CH_4(g)$  through two kinds of adsorbed CO-s having different reactivity ( $k_1$  and  $k_2$ ) [7,15].

 $CO(g) + * \bigoplus CO^{*} (K_{1})$   $H_{2}(g) + 2^{*} \bigoplus 2H^{*} (K_{2})$   $CO^{*} + H^{*} \bigoplus HCO^{*} + * (K_{3})$   $HCO^{*} + H^{*} \longrightarrow *HCOH^{*} (k_{4})$   $*HCOH^{*} \longrightarrow CH^{*} + OH^{*} (k_{5})$ 

**Scheme 3.** Elementary steps of an H-assisted CO dissociation mechanism for the methanation reaction [38].

 $\theta_{CxHy} = 0.35$  for 2 h, Table 3). The catalyst with Co particle size of 11.4 nm shows a higher concentration of carbon formed after 25 h in CO/H<sub>2</sub> and which is hydrogenated in the 350–520 °C range compared to the largest Co particle size (21.3 nm). These results might be linked to the slightly weaker C-O bond strength (Fig. S4, 2045 cm<sup>-1</sup> vs. Fig. 11b, 2056 cm<sup>-1</sup>), thus to a stronger Co<sub>s</sub>-CO bond with increasing TOS for the catalyst with small cobalt particles (ca. 11.4 nm) compared to the larger Co particles. The existence of stronger metal–carbon bonding on the small cobalt particles could lead to the formation of a larger concentration of inactive carbonaceous species (e.g., hydrogenated at temperatures higher than 350 °C) as observed.

### 4.5. Effect of TOS on important kinetic parametes ( $\theta$ , k)

Several causes of deactivation of Co-based catalysts reported might be considered relating to the present work. For example, sintering of Co particles, deposition of inacive carbonaceous species, formation of cobalt carbide, oxidation of cobalt active sites, and formation of cobalt-alumina complexes [6]. Iglesia [46] reported re-oxidation of small Co particles (5–6 nm) by water formed during the FT synthesis due to strong metal-support interactions. Also, it has been reported [41] that oxidation of Co particles during FTS can be excluded for Co particles>6 nm and for CO conversions<60%. Keyvanloo et al. [64] showed that sintering of Co particles with 11– 12 nm in size did not occur after 800 h TOS in FT synthesis. In the present work, the Co particle size was in the 11.4-21.3 nm range, and the CO conversion<15%. Also, the formation of complexes between Co and the alumina support can be excluded due to the low partial pressure of water (4%CO,  $H_2/CO = 2$ ,  $X_{CO} < 15\%$ ). The surface coverage of CO ( $\theta_{CO}$ ) was found to be practically constant with TOS (Fig. 5b), suggesting that catalyst's deactivation is rather unlikely to be due to: (i) sintering of Co particles, (ii) formation of cobalt carbide, (iii) oxidation of cobalt active sites and (iv) formation of cobalt-support complexes, since in these cases,  $\theta_{CO}$  would have been expected to decrease with increasing TOS. Furthermore, it should be noted here that the catalytic activity vs time profiles shown in Fig. 3a,b were very reproducible. After the application of TIH/TPH at several TOS in CO/H<sub>2</sub> (Figs. 9 and 10), the reinitiation of the methanation reaction for the subsequent TOS measurements provided very similar (within 5%) initial reaction rates with those seen at previous TOS measurements.

The amount of active  $CH_x$  (N<sub>CHx</sub>, µmol  $g_{cat}^{-1}$ , Fig. 7a and b) decreases by 4.0 and 2.9 times, the effective rate constant ( $k_{eff}$ ) of active  $CH_x$ -s decreases by 2.5 times (Fig. 6c), while  $TOF_{CH4, TTK}$ by 9.5 and 6.2 times (Fig. 7c) for Co particles of 11.4 and 21.3 nm in size, respectively, with increasing TOS (0.5 to 25 h). Thus, the decrease of  $TOF_{CH4, ITK}$  is due to the decrease of both  $k_{eff}$  and  $N_{CHx}$ (or  $\theta_{CHx}$ ); TOF<sub>CH4</sub> =  $k_{eff} \theta_{CHx}$ . The decrease of  $k_{eff}$  (= $k_{CHx} \theta_{H}$ ) shows in turn that the intrinsic rate constant of CHx (k<sub>CHx</sub>) and/or  $\theta_{\rm H}$ decrease with TOS. It is also likely that the large amount of  $C_{B}$ and  $C_{\gamma}$  that is accumulated on the catalyst surface with TOS (Fig. 11) blocks active sites for H<sub>2</sub> chemisorption, thus, the mean life-time of  $CH_x(\tau_{CHx})$  increases. Strong evidence for the likely deficient in H-s with TOS in CO/H<sub>2</sub> reaction Co surface is provided by the H<sub>2</sub>-TIC/TPD results shown in Figs. 1 and 2 and Table 1. Based on this information, the TOS in CO/H<sub>2</sub> has influenced the concentration and quality of hydrogen chemisorption sites on the Co surface, and in particular those of small Co particles (Fig. 2, Table 1).

On the other hand, the large drop of  $k_{eff}$  ( $k_{CHx}$   $\theta_H$ ) with TOS (Fig. 6c) could suggest that the very likely drop of  $\theta_H$  at 230 °C with increasing TOS may not explain alone the drop of  $k_{eff}$  observed. This means that the decrease in the true site activity, k, of CH<sub>x</sub> towards hydrogenation to CH<sub>4</sub> must also be considered. The surface coverage of active CH<sub>x</sub> ( $\theta_{CHx}$ ) decreases with TOS (Fig. 5a) as opposed to the surface coverage of inactive C<sub>β</sub> and C<sub>γ</sub> (Fig. 11).

Thus, inactive carbon may poison sites at which  $-CH_x$  are formed, thus leading to lower TOF<sub>CH4. ITK</sub> with increasing TOS. According to the work of Pestman et al. [59] and Zijlstra et al. [60],  $-CH_x$ monomers formed on Co stepped surface sites can migrate to planar sites, where they get hydrogenated to CH<sub>4</sub>. By increasing TOS, some  $-CH_x$  on stepped sites might become inactive because of the shortage of planar sites (formation of stepped sites on planar surfaces [44,61]), and this possibility is in line with Scheme 1.

The work of Weststrate and Niemantsverdriet [65] explains the increasing values of  $\tau_{CHx}$  (Fig. 6a) and the decreasing values of k<sub>eff</sub> (Fig. 6c). The authors proposed that -CH<sub>x</sub> intermediates cannot be viewed as adsorbed species on terrace sites because they must react fast. High values of  $\tau_{\text{CHx}}$  are due to the slow hydrogenation of step-bound C-atoms formed by CO dissociation, and their endothermic migration to terrace sites is made irreversible due to the subsequent CO dissociation that blocks -CH<sub>v</sub> reattachment onto the step-edge sites. This slow hydrogenation of -CH<sub>x</sub> species can be seen by the delay of <sup>13</sup>CH<sub>4</sub> transient response to reach the new steady-state after 25 h in CO/H<sub>2</sub> compared to the 0.5-h short TOS (compare Fig. 4a and b). Thus, it is suggested that the main origin of catalyst deactivation for the present  $Co/\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts is the deposition of inactive carbonaceous species identified by TIH/TPH which built up on the catalyst surface (Scheme 1, Fig. 10). The rate of decrease of  $\theta_{\rm H}$  at 230 °C seems to be less important on the rate of catalyst deactivation during the present methanation rection on the Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts (d<sub>Co</sub> = 11 and 23 nm).

The  $\tau_{CO}$  and  $\theta_{CO}$  (or  $N_{CO}$ , µmol  $g_{cat}^{-1}$ ) kinetic parameters were found practically constant with TOS for both Co particle sizes (Fig. 5b, 6b, 7a,b), while TOF<sub>CO, ITK</sub> decreases by 9.8 and 7.2 times for Co particles of 11.4 and 21.3 nm, respectively, with increasing TOS (Fig. 7c). These results show that inactive species (Fig. 11) may affect the binding strength of active CO-s and/or the reactivity of active CH<sub>x</sub>-s towards CH<sub>4</sub> and higher hydrocarbons formation (S<sub>C2+</sub> ~ 30–35%). The SSITKA work coupled with microkinetic modeling of the chain-growth on 17 wt% Co – 0.04 wt% Pt/SiO<sub>2</sub> reported by Chen et al. [3] revealed that the chain-growth rate is limited by the supply of CH<sub>x</sub>-s (C<sub>1</sub> monomers), in harmony with the close resemblance of TOF<sub>ITK</sub>, CH<sub>4</sub> and TOF<sub>ITK</sub>, CO illustrated in Fig. 7c.

It is expected that adsorption of CO(g) should be a fast step, thus, to maintain a constant surface coverage of CO-s with TOS and at the same time to experience drop in the rate of CH<sub>4</sub> formation, the rate of CO-s dissociation should not be considered as the RDS of methanation reaction. Thus, one step from the hydrogenation of  $-COH/-CH_x$  species must be reasonably consider as the rate-determining step (RDS) of reaction. Ojeda et al. [2] showed that H-assisted CO activation occurs on Co surfaces, and the ratelimiting-step of methanation is the hydrogenation of -COH to form the HCOH species.

#### 4.6. Effect of particle size and TOS on H<sub>2</sub> chemisorption

In the present work the effect of Co particle size (7.7 - 21.3 nm) on the transient rate of H<sub>2</sub> chemisorption per exposed cobalt surface atom is reported. The initial rate of H<sub>2</sub> chemisorption (clean Co surface) increases with increasing Co particle size (ca. from 7.7 to 21.3 nm, Fig. 1a). These results agree with the work of Zowtiak and Bartholomew [66] who concluded that the activation barrier for dissociative adsorption of H<sub>2</sub> on cobalt increases with increasing degree of metal-support interactions, which in turn increases with decreasing Co particle size. Thus, the higher activation energy of H<sub>2</sub> adsorption on small Co particles is responsible for the lower transient rates and  $\theta_{\rm H}$  (0.24–0.26) compared to the large Co particles ( $\theta_{\rm H}$  = 0.5, Fig. 1b). Van Helden et al. [67] reported that the presence of defect sites of increasing formation as the Co particle size increases accelerate the adsorption of hydrogen by providing alternative, almost barrierless pathways for adsorption.

These results agree very well with those shown in Fig. 1a, where the initial  $H_2$  chemisorption rate (first 10 s) observed on the large Co particles (ca. 21.3 nm) is larger compared to that on the small Co particles (ca. 7.7 nm).

The H<sub>2</sub> desorption profiles are in very good agreement with those reported by Zowtiak and Bartholomew [66] over the Co/SiO<sub>2</sub> and Co/Al<sub>2</sub>O<sub>3</sub> catalysts, following an activated chemisorption in the 25–200 °C range. The temperature of maximum desorption rate shifted to lower temperatures with increasing Co particle size (Table 1). It has been reported [67] that the presence of defects in high concentrations gives rise to adsorption sites with lower activation energies for desorption. The larger quantity of strongly bound H (high temperature desorption peaks, T > 200 °C) observed in the large Co particles compared to the small ones could be due to the higher number density of stepped Co sites [68].

The effect of TOS (fresh vs 25 h) on the rates of H<sub>2</sub> chemisorption and desorption is depicted in Fig. 1c, 2b, 2c and Table 1. The  $\theta_H$  after 25 h in TOS decreased by 2.4 and 1.4 times for the 11.4 and 21.3 nm in size Co particles, respectively. The initial transient rate of H<sub>2</sub> chemisorption remains the same for the fresh and used catalysts (Fig. 1c and S3), but the transient rate recorded on the used catalyst drops to a larger extent than on the fresh catalyst. This behavior suggests that H-chemisorption sites decrease with TOS in CO/H<sub>2</sub> reaction, and as a result of this, the build-up of inactive C<sub>β</sub> species, as discussed above to a great extent.

# 5. Conclusions

SSITKA-Mass spectrometry (use of <sup>13</sup>CO) coupled with transient isothermal (TIH) and temperature-programmed hydrogenation (TPH) experiments were effectively designed and applied to investigate the influence of Co particle size (11.4 and 21.3 nm) and time-on-steam, TOS (0.5 - 25 h) on important intrinsic kinetic parameters  $(\theta, k)$  that may contribute to the observed deactivation of  $Co/\gamma$ -Al<sub>2</sub>O<sub>3</sub> in the CO methanation reaction (4 vol% CO,  $H_2/CO = 2$ , T = 230 °C and 1.2 bar total pressure). The evaluation with TOS of the surface coverage of *active*  $(-CH_x \text{ or } C_{\alpha})$  and *inactive*  $(-C_xH_y \text{ or } C_\beta \text{ and } C_y)$  carbonaceous species formed under reaction conditions and of the concentration of hydrogen chemisorption sites, revealed that the accumulation of inactive carbonaceous species and to a less extent the depletion of sites for hydrogen chemisorption are the main intrinsic reasons for the drop of initial methanation rate (per gram basis). The  $TOF_{CO}$  and  $TOF_{CH4}$  were found to drop by about five to eight times for the large (21.3 nm) and small (11.4 nm) Co particles supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, respectively, after 25 h in CO/H<sub>2</sub>. The  $C_{\beta}$  and  $C_{\gamma}$  inactive species may had affected the binding strength of co-adsorb active reaction intermediates and/or occupied sites where active species are formed (e.g., adsorbed H-s).

A novel sequence of SSITKA step-gas switches (use of both <sup>13</sup>CO and D<sub>2</sub>) was designed and performed to measure the D-KIE for the methanation reaction path. The results of the present study provided very useful fundamental kinetic information for better understanding of the deactivation of Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> used at high pressure FTS as well, since elementary reaction steps for -CH<sub>x</sub> monomer(s) and relevant sites are not expected to largely change in the 1–10 bar range.

The results of the present work allowed us to propose that CO methanation reaction proceeds through two interconnecting pools of carbonaceous species derived from the dissociation of adsorbed CO-s, where part of the first one,  $-C_xH_y$  ( $C_\beta$ , "soft carbon") feeds the pool of the truly active -CHx ( $C_\alpha$ ) species that forms methane. The rate of transfer of CH<sub>x</sub>-type species from  $C_\beta$  to  $C_\alpha$  decreases with TOS due to the decrease of  $\theta_H$ . It was shown that  $C_\beta$  is readily hydrogenated to CH<sub>4</sub> at 230 °C only when CO-s is removed from

the surface. The surface coverage of stronger bound C<sub> $\gamma$ </sub> ("hard carbon") species hydrogenated at higher temperatures (ca. 350–520 °C) was found not to be influenced by the Co particle size (11.4 – 21.3 nm).

The TOF<sub>CO or CH4</sub> (s<sup>-1</sup>) and  $\tau_{CO \text{ or CH4}}$  (s) were also found not to be influenced by the Co particle size as opposed to the  $\theta_{CO}$  and  $\theta_{CHx}$ , which were found to increase with increasing Co particle size. Lower rates for H<sub>2</sub> chemisorption and smaller  $\theta_H$  was estimated at 100 °C for the small Co particle size of 11.4 nm as opposed to the larger one of 21.4 nm.

The apparent rate constant,  $k_{eff}$  ( $k_{eff} = 1/\tau_{CHx} = k \theta_H \theta_{CHx}$ ),  $\theta_{CHx}$ , TOF<sub>CH4</sub> or <sub>CO</sub> and the CH<sub>4</sub> production rate (µmol/g<sub>cat</sub>/s) were all found to decrease significantly with TOS in CO/H<sub>2</sub>, while  $\theta_{CO}$  and  $\tau_{CO}$  were found practically constant with TOS. Hydrogen chemisorption sites and their binding strength ( $E_{M-H}$ , kcal/mol) distribution were found to be influenced to a larger extent for the small than the large supported Co particles with TOS in CO/H<sub>2</sub> at 230 °C [35].

#### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary material

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#### References

- A.Y. Khodakov, W. Chu, P. Fongarland, Advances in the development of novel cobalt Fischer-Tropsch catalysts for synthesis of long-chain hydrocarbons and clean fuels, Chem. Rev. 107 (2007) 1692–1744.
- [2] M. Ojeda, R. Nabar, A.U. Nilekar, A. Ishikawa, M. Mavrikakis, E. Iglesia, CO activation pathways and the mechanism of Fischer-Tropsch synthesis, J. Catal. 272 (2010) 287–297.
- [3] W. Chen, I.A.W. Filot, R. Pestman, E.J.M. Hensen, Mechanism of cobaltcatalyzed CO hydrogenation: 2, Fischer-Tropsch Synthesis, ACS Catal. 7 (2017) 8061–8071.
- [4] A.M. Efstathiou, J.T. Gleaves, G.S. Yablonsky, in "Characterisation of Solid Materials: From Structure to Surface Reactivity" (M. Che, J.C. Vedrine, Eds.), Ch. 22 – Transient Techniques: Temporary Analysis of Products (TAP) and Steady State Isotopic Transient Kinetic Analysis (SSITKA), Wiley VCH, 2012, pp. 1013– 1073.
- [5] A.M. Efstathiou, C.O. Bennett, The CO/H<sub>2</sub> reaction on Rh/Al<sub>2</sub>O<sub>3</sub>: II. Kinetic study by transient isotopic methods, J. Catal. 120 (1989) 137–156.
- [6] S.L. Shannon, J.G. Goodwin, Characterization of catalytic surface by isotopictransient kinetics during steady-state reaction, Chem. Rev. 95 (1995) 677–695.
- [7] M.A. Vasiliades, C.M. Kalamaras, N.S. Govender, A. Govender, A.M. Efstathiou, The effect of preparation route of commercial Co/γ-Al<sub>2</sub>O<sub>3</sub> catalyst on important Fischer-Tropsch kinetic parameters studied by SSITKA and CO-DRIFTS transient hydrogenation techniques, J. Catal. 379 (2019) 60–77.
- [8] A.M. Efstathiou, Elucidation of mechanistic and kinetic aspects of water-gas shift reaction on supported Pt and Au catalysts via transient isotopic techniques, Catalysis 28 (2016) 175–236.
- [9] A.M. Efstathiou, X.E. Verykios, Transient methods in heterogeneous catalysis: Experimental features and application to study mechanistic aspects of the CH<sub>4</sub>/ O<sub>2</sub> (OCM), NH<sub>3</sub>/O<sub>2</sub> and NO/He reactions, Appl. Catal. A: Gen. 151 (1997) 109– 166.
- [10] B.C. Enger, V. Frøseth, J. Yang, E. Rytter, A. Holmen, SSITKA analysis of CO hydrogenation on Zn modified cobalt catalysts, J. Catal. 297 (2013) 187–192.
- [11] J.P. den Breejen, P.B. Radstake, G.L. Bezemer, J.H. Bitter, V. Frøseth, A. Holmen, K.P. de Jong, On the origin of the cobalt particle size effects in Fischer-Tropsch catalysts, J. Am. Chem. Soc. 131 (2009) 7197–7203.

- [12] J. Yang, V. Frøseth, D. Chen, A. Holmen, Particle size effect for cobalt Fischer-Tropsch catalysts based on in situ CO chemisorption, Surf. Sci. 648 (2016) 67– 73.
- [13] N. Lohitharn, J.G. Goodwin Jr., Effect of K promotion of Fe and FeMn Fischer-Tropsch synthesis catalysts: analysis at the site level using SSITKA, J. Catal. 260 (2008) 7–16.
- [14] B. Jongsomjit, J. Panpranot, J.G. Goodwin Jr., Effect of zirconia-modified alumina on the properties of Co/γ-Al<sub>2</sub>O<sub>3</sub> catalysts, J. Catal. 215 (2003) 66–77.
- [15] A. Carvalho, V.V. Ordomsky, Y. Luo, M. Marinova, A.R. Muniz, N.R. Marcilio, A.Y. Khodakov, Elucidation of deactivation phenomena in cobalt catalyst for Fischer-Tropsch synthesis using SSITKA, J. Catal. 344 (2016) 669–679.
- [16] B. Legras, V.V. Ordomsky, C. Dujardin, M. Virginie, A.Y. Khodakov, Impact and detailed action of sulfur in syngas on methane synthesis on Ni/γ-Al<sub>2</sub>O<sub>3</sub> catalyst, ACS Catal. 4 (2014) 2785–2791.
- [17] M. Rothaemel, K.F. Hanssen, E.A. Blekkan, D. Schanke, A. Holmen, The effect of water on cobalt Fischer-Tropsch catalysts studied by steady-state isotopic transient kinetic analysis (SSITKA), Catal. Today 38 (1997) 79–84.
- [18] A.M. Efstathiou, C.O. Bennett, The CO/H<sub>2</sub> reaction on RhAl<sub>2</sub>O<sub>3</sub>: I. Steady-State and transient kinetics, J. Catal. 120 (1989) 118–136.
- [19] A.M. Efstathiou, The CO/H<sub>2</sub> reaction on Rh/MgO studied by transient isotopic methods, J. Mol. Catal. 67 (1991) 229–249.
- [20] S. Vada, B. Chen, J.G. Goodwin, Isotopic transient study of La promotion of Co/ Al<sub>2</sub>O<sub>3</sub> for CO hydrogenation, J. Catal. 153 (1995) 224–231.
- [21] V. Frøseth, A. Holmen, CO hydrogenation on Co/γ-Al<sub>2</sub>O<sub>3</sub> and CoRe/γ-Al<sub>2</sub>O<sub>3</sub> studied by SSITKA, Top. Catal. 45 (2007) 45–50.
- [22] G.J. Haddad, B. Chen, J.G. Goodwin Jr., Effect of La<sup>3+</sup> promotion of Co/SiO<sub>2</sub> on CO hydrogenation, J. Catal. 161 (1996) 274–281.
- [23] P.B. Radstake, J.P. den Breejen, G.L. Bezemer, J.H. Bitter, K.P. de Jong, V. Frøseth, A. Holmen, On the origin of the cobalt particle size effect in the Fischer-Tropsch synthesis, Stud. Surf. Sci. Catal. 167 (2007) 85–90.
- [24] J. Panpranot, J.G. Goodwin Jr., A. Sayari, CO hydrogenation on Ru-Promoted Co/ MCM-41 catalysts, J. Catal. 211 (2002) 530–539.
- [25] J. Panpranot, J.G. Goodwin Jr., A. Sayari, Effect of H<sub>2</sub> partial pressure on surface reaction parameters during CO hydrogenation on Ru-promoted silicasupported Co catalysts, J. Catal. 213 (2003) 78–85.
- [26] A.R. Belambe, R. Oukaci, J.G. Goodwin Jr., Effect of pretreatment on the activity of a Ru-promoted Co/Al<sub>2</sub>O<sub>3</sub> Fischer-Tropsch catalyst, J. Catal. 166 (1997) 8–15.
- [27] W. Chen, R. Pestman, B. Zijlstra, I.A.W. Filot, E.J.M. Hensen, Mechanism of cobalt-catalyzed CO hydrogenation: 1 Methanation, ACS Catal. 7 (2017) 8050– 8060.
- [28] H.A.J. van Dijk, J.H.B.J. Hoebink, J.C. Schouten, A mechanistic study of the Fischer-Tropsch synthesis using transient isotopic tracing. Part- 1: Model identification and discrimination, Top. Catal. 26 (2003) 111–119.
- [29] B. Zijlstra, R.J.P. Broos, W. Chen, I.A.W. Filot, E.J.M. Hensen, First-principles based microkinetic modeling of transient kinetics of CO hydrogenation on cobalt catalysts, Catal. Today 342 (2020) 131–141.
- [30] A.M. Efstathiou, T. Chafik, D. Bianchi, C.O. Bennett, A transient kinetic study of the CO/H<sub>2</sub> reaction on Rh/Al<sub>2</sub>O<sub>3</sub> using FTIR and mass spectroscopy, J. Catal. 148 (1994) 224–239.
- [31] C.J. Weststrate, J. van de Loosdrecht, J.W. Niemantsverdriet, Spectroscopic insights into cobalt-catalyzed Fischer-Tropsch synthesis: A review of the carbon monoxide interaction with single crystalline surfaces of cobalt, J. Catal. 342 (2016) 1–16.
- [32] C. Perego, S. Peratello, Experimental methods in catalytic kinetics, Catal. Today 52 (1999) 133–145.
- [33] W.D. Shafer, G. Jacobs, B.H. Davis, Fischer-Tropsch synthesis: investigation of the partitioning of dissociated H<sub>2</sub> and D<sub>2</sub> on activated cobalt catalysts, ACS Catal. 2 (2012) 1452–1456.
- [34] M.K. Gnanamani, G. Jacobs, W.D. Shafer, D. Sparks, B.H. Davis, Fischer-tropsch synthesis: deuterium kinetic isotope study for hydrogenation of carbon oxides over cobalt and iron catalysts, Catal. Lett. 1420–1428 (2011).
- [35] A.M. Efstathiou, K.C. Petallidou, Reply to the letter to the editor concerning the comments of Dr. F. Menier to the article Appl. Catal. B: Environ. 136-137 (2013) 225-238, Kalamaras et al., "The effect of La<sup>3+</sup>-doping of CeO<sub>2</sub> support on the water-gas shift reaction mechanism and kinetics over Pt/Ce<sub>1-x</sub>La<sub>x</sub>O<sub>2-s</sub>", Appl. Catal. B: Environ. 152-153 (2014) 439–443.
- [36] B.T. Loveless, C. Buda, M. Neurock, E. Iglesia, CO chemisorption and dissociation at high coverages during CO hydrogenation on Ru catalysts, J. Am. Chem. Soc. 135 (2013) 6107–6121.
- [37] D.D. Hibbitts, B.T. Loveless, M. Neurock, E. Iglesia, Mechanistic role of water on the rate ans selectivity of Fischer-Tropsch synthesis on Ruthenium catalysts, Angew. Chem. Int. Ed. 52 (2013) 12273–12278.
- [38] M. Ojeda, A. Li, R. Nabar, N.U. Nilekar, M. Mavrikakis, E. Iglesia, Kinetically relevant steps and H<sub>2</sub>/D<sub>2</sub> isotope effects in Fischer-Tropsch synthesis on Fe and Co catalysts, J. Phys. Chem. C 114 (2010) 19761–19770.
- [39] D. Hibbitts, E. Dybeck, T. Lawlor, M. Neurock, E. Iglesia, Preferential activation of CO near hydrocarbon chains during Fischer-Tropsch synthesis on Ru, J. Catal. 337 (2016) 91–101.
- [40] A.Y. Khodakov, A.G. Constant, R. Bechara, F. Villain, Pore-size control of cobalt dispersion and reducibility in mesoporous silicas, J. Phys. Chem. B 105 (2001) 9805–9811.
- [41] N.E. Tsakoumis, M. Rønning, Ø. Borg, E. Rytter, A. Holmen, Deactivation of cobalt based Fischer-Tropsch catalysts: A review, Catal. Today 154 (2010) 162–182.

- [42] W.J. Ambs, M.M. Mitchell, Hydrogen spillover on Platinum-Alumina, effect of water, J. Catal. 82 (1983) 226–229.
- [43] A. Paredes-Nunez, D. Lorito, Y. Schuurman, N. Guilhaume, F.C. Meunier, Origin of the poisoning effect of chlorine on the CO hydrogenation activity of alumina-supported cobalt monitored by *operando* FTIR spectroscopy, J. Catal. 329 (2015) 229–236.
- [44] J. Couble, D. Bianchi, Experimental microkinetic approach of the surface reconstruction of cobalt particles in relationship with the CO/H<sub>2</sub> reaction on a reduced 10% Co/Al<sub>2</sub>O<sub>3</sub> catalyst, J. Phys. Chem. C 117 (2013) 14544–14557, and references therein.
- [45] G.L. Bezemer, J.H. Bitter, H.P.C.E. Kuipers, H. Oosterbeek, J.E. Holewijn, X. Xu, F. Kapteijn, A.J. van Dillen, K.P. de Jong, Cobalt particle size effects in the Fischer-Tropsch reaction studies with carbon nanofiber supported catalysts, J. Am. Chem. Soc. 128 (2006) 3956–3964.
- [46] E. Iglesia, Design, synthesis, and use of cobalt-based Fischer-Tropsch synthesis catalysts, Appl. Catal. A: Gen. 161 (1997) 59–78.
- [47] G. Jacobs, B.H. Davis, Applications of isotopic tracers in Fischer-Tropsch synthesis, Catal. Sci. Technol. 4 (2014) 3927–3944.
- [48] J. Happel, H.Y. Cheh, M. Otarod, S. Ozawa, A.J. Severdia, T. Yoshida, F. Fthenakis, Multiple isotope tracing of methanation over nickel catalyst: II. Deuteromethanes tracing, J. Catal. 75 (1982) 314–328.
- [49] M. Otarod, J. Happel, E. Walter, Transient isotopic tracing of methanation kinetics with parallel paths, Appl. Catal. A: Gen. 160 (1997) 3–11.
- [50] S. Krishnamoorthy, M. Tu, M.P. Ojeda, D. Pinna, E. Iglesia, An investigation of the effects of water on rate and selectivity for the Fischer-Tropsch synthesis on cobalt-based catalysts, J. Catal. 211 (2002) 422–433.
- [51] C. Li, Y. Sakata, T. Arai, K. Domen, K.-I. Maruya, T. Onishi, Carbon monoxide and carbon dioxide adsorption on cerium oxide studies by Fourier-transform infrared spectroscopy. Part 1.- Formation of carbonate species on dehydroxylated CeO<sub>2</sub> at room temperature, J. Chem. Soc., Faraday Trans. I 85 (1989) 929–943.
- [52] C.M. Kalamaras, K.C. Petallidou, A.M. Efstathiou, The effect of La<sup>3+</sup>-doping of CeO<sub>2</sub> support on the water-gas shift reaction mechanism and kinetics over Pt/ Ce<sub>1-x</sub>La<sub>x</sub>O<sub>2-5</sub>, Appl. Catal. B: Environ. 136–137 (2013) 225–238.
- [53] K.C. Petallidou, S. Boghosian, A.M. Efstathiou, Low-temperature water-gas shift on Pt/Ce<sub>0.5</sub>La<sub>0.5</sub>O<sub>2-δ</sub>: Effect of support synthesis method, Catal. Today 242 (2015) 153–167.
- [54] G. Busca, J. Lamotte, J.-C. Lavalley, V. Lorenzelli, FT-IR study of the adsorption and transformation of formaldehyde on oxide surfaces, J. Am. Chem. Soc. 109 (1987) 5197–5202.
- [55] D. Lorito, A. Paredes-Nunez, C. Mirodatos, Y. Schuurman, F.C. Meunier, Determination of formate decomposition rates and relation to product formation during CO hydrogenation over supported cobalt, Catal. Today 259 (2015) 192–196.
- [56] B.A. Sexton, Vibrational spectra of water chemisorbed on Platinum (111), Surf. Sci. 94 (1980) 435–445.
- [57] L. Vlaev, D. Damyanov, M.M. Mohamed, Infrared Spectroscopy study of the nature and reactivity of a hydrate coverage on the surface of γ-Al<sub>2</sub>O<sub>3</sub>, Colloids and Surf. 36 (1989) 427–437.
- [58] Y. Soong, K. Krishna, P. Biloen, Catalyst aging studied with isotopic transients: Methanation over Raney nickel, J. Catal. 97 (1986) 330–343.
- [59] R. Pestman, W. Chen, E. Hensen, Insight into the rate-determining step and active sites in the fischer-tropsch reaction over cobalt catalysts, ACS Catal. 9 (2019) 4189–4195.
- [60] B. Zijlstra, R.J.P. Broos, W. Chen, H. Oosterbeek, I.A.W. Filot, E.J.M. Hensen, Coverage effects in CO dissociation on metallic cobalt nanoparticles, ACS Catal. 9 (2019) 7365–7372.
- [61] I.M. Ciobica, R.A. van Santen, P.J. van Berge, J. van de Loosdrecht, Adsorbate induced reconstruction of cobalt surfaces, Surf. Sci. 602 (2008) 17–27.
- [62] J. Yang, E.Z. Tveten, D. Chen, A. Holmen, Understanding the effect of cobalt particle size on Fischer-Tropsch synthesis: surface species and mechanistic studies by SSITKA and kinetic isotopic effect, Langmuir 26 (2010) 16558– 16567.
- [63] W. Ma, W.D. Shafer, M. Martinelli, D.E. Sparks, B.H. Davis, Fischer-Tropsch synthesis: Using deterium tracer coupled with kinetic approch to study the kinetic isotopic effects of iron, cobalt and ruthenium catalysts, Catal. Today 343 (2020) 137–145.
- [64] K. Keyvanloo, M.J. Fisher, W.C. Hecker, R.J. Lancee, G. Jacobs, C.H. Bartholomew, Kinetics of deactivation by carbon of a cobalt Fischer-Tropsch catalyst: effects of CO and H<sub>2</sub> partial pressures, J. Catal. 327 (2015) 33–47.
- [65] C.J. Weststrate, J.W. Niemantsverdriet, Understanding FTS selectivity: the crucial role of surface hydrogen, Faraday Discuss. 197 (2017) 101–116.
- [66] J.M. Zowtiak, C.H. Bartholomew, The kinetics of  $\rm H_2$  adsorption on and desorption from cobalt and the effects of support Thereon, J. Catal. 83 (1983) 107–120.
- [67] P. van Helden, J.-A. van den Berg, C.J. Weststrate, Hydrogen Adsorption on Co surfaces: a density functional theory and temperature programmed desorption study, ACS Catal. 2 (2012) 1097–1107.
- [68] P. van Helden, I.M. Ciobîcă, R.L.J. Coetzer, The size-dependent site composition of FCC cobalt nanocrystals, Catal. Today 261 (2016) 48–59.