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Effect of H_2 partial pressure on surface reaction parameters during CO hydrogenation on Ru-promoted silica-supported Co catalysts

Joongjai Panpranot,[a] James G. Goodwin Jr.,[a,*] and Abdelhamid Sayari[b]

[a] Department of Chemical Engineering, Clemson University, Clemson, SC 29634, USA
[b] Center for Catalysis Research and Innovation, Department of Chemistry, University of Ottawa, Ottawa, ON, Canada

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Abstract

Steady-state isotopic transient kinetic analysis (SSITKA), one of the most powerful techniques for the investigation of surface reactions, was used to study the effect of hydrogen partial pressure on the fundamental surface reaction parameters for methanation on ordered mesoporous silica (MCM-41) and amorphous SiO_2-supported CoRu catalysts. The abundances, coverages, and lifetimes of surface intermediates of the reaction were measured under reaction conditions and their dependence upon hydrogen partial pressure was determined. Although absolute hydrogen coverage under reaction conditions is not measurable due to the hydrogen isotope effect, relative hydrogen surface concentration as a function of P_{H_2} could be estimated from SSITKA parameters. Increasing the hydrogen partial pressure at a constant reaction temperature of 220 °C not only caused the expected increase in the relative surface concentration of hydrogen but also increased the abundance of surface methane intermediates (N_M), possibly due to increased hydrogenation. The impact of P_{H_2} on N_M for MCM-41-supported CoRu catalysts was similar to that for SiO_2-supported ones, showing an approximately twofold increase in N_M as P_{H_2} increased from 0.23 to 1.71 bar. The relative concentration of surface hydrogen, however, increased fourfold. The abundance of surface methane intermediates and the surface coverages were significantly higher for the MCM-41-supported CoRu catalysts. The average surface reaction residence time of the methane intermediates (τ_M) consistently decreased with increasing hydrogen partial pressure due to the fact that the pseudo first order rate constant ($1/\tau_M$) contains the hydrogen surface concentration term. There was no difference, however, in the intrinsic site activity since the average surface reaction residence times of methane intermediates (τ_M) for SiO_2- and MCM-41-supported CoRu catalysts were essentially identical for a given partial pressure of hydrogen, regardless of Co loading. This also indicates that the type of silica support used (amorphous SiO_2 or MCM-41) did not have an impact on surface hydrogen concentration, contrary to the case for H_2 chemisorption at 100 °C. The increase in rate with increasing hydrogen partial pressure resulted due to the increase in methane surface intermediates and, more importantly, the increase in hydrogen surface concentration.

Keywords: Mesoporous silica; MCM-41; Cobalt catalysts; Ru promotion; CO hydrogenation; Steady-state isotopic transient kinetics analysis (SSITKA); Isotopic tracing; Hydrogen surface concentration

1. Introduction

For high-surface-area heterogeneous catalysts, steady-state isotopic transient kinetic analysis (SSITKA), developed in the late 1970s [1–4], is one of the most powerful surface kinetic techniques capable of assessing surface reaction parameters in situ. With SSITKA, the catalyst is kept under steady-state conditions and an isotopic transient is introduced by abruptly replacing one isotopically labeled reactant by another. In addition to maintaining isothermal and isobaric reaction conditions, the reactant and product concentrations and flow rates remain undisturbed during the step change. Thus, in the absence of isotopic mass effects, steady-state reaction conditions are maintained during the induced transient. From SSITKA, the abundance of surface intermediates and intrinsic activity can be determined. The methodology used has been described extensively by Shannon and Goodwin [4]. This technique has been widely used to study methane formation on Fischer–Tropsch catalysts [5–7]. Methanation has proven to be an ideal system for isotropic transient kinetic investigations due to the simple molecules involved, which are easy to trace by mass spectrometry [8–10].

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[*] Corresponding author.
E-mail address: james.goodwin@ces.clemson.edu (J.G. Goodwin).

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Several groups have studied the effects of reaction conditions during CO hydrogenation on different supported Co catalysts using SSITKA. For example, Hassen et al. [11] studied the effect of water on the Fischer–Tropsch synthesis over Co/Al_2O_3 catalysts. The SSITKA results showed a decrease in the number of active surface sites and no change in the specific site activity. Van Dijk et al. [12] used the SSITKA technique in combination with a GC-MS to obtain mechanistic information about the Fischer–Tropsch synthesis over cobalt-based catalysts. Mims and McCandlish [13] studied the rate of hydrocarbon chain growth in Fischer–Tropsch reaction on Co/SiO_2 catalysts using isotopic switching at high pressure and were able to conclude that little of the active carbon on the surface was in the form of hydrocarbon chains.

In CO hydrogenation, hydrogen partial pressure plays a very important role since the reaction is often ca. first order in hydrogen. The impact of hydrogen partial pressure on the fundamental surface reaction parameters for methanation was first studied by SSITKA for a SiO_2-supported Ru catalyst [10]. The relative coverage of hydrogen was found to increase with increasing hydrogen partial pressure. An increase in the surface methane intermediates with increasing hydrogen partial pressure was also observed; however, the surface coverage of methane intermediates was a complicated function of hydrogen partial pressure, temperature, and deactivation.

In this investigation, we compared the effect of hydrogen partial pressure on the fundamental surface reaction parameters governing methanation on different silica-supported CoRu catalysts (CoRu/MCM-41 and $CoRu/SiO_2$). Pure silica MCM-41-supported CoRu catalysts have been shown to have higher CO hydrogenation activities than amorphous SiO_2-supported ones due to having higher concentrations of active sites rather than higher intrinsic activities [14]. This is in good agreement with results in the literature showing CO hydrogenation on cobalt catalysts to be a structure-insensitive reaction, with turnover frequency independent of cobalt dispersion [15,16]. CoRu/MCM-41 catalysts having high loadings of Co have also been found to exhibit evidence for hydrogen chemisorption suppression at 100 °C [17], the normal temperature for this measurement on Co. This is contrary to what was found for $CoRu/SiO_2$. It was desired to determine, using SSITKA, how hydrogen partial pressure impacts the difference in activity and if there is a support effect on hydrogen surface concentration under reaction conditions.

2. Experimental

2.1. Catalyst preparation

The pure silica MCM-41 was prepared as reported elsewhere [18] using the gel composition $(1.0\ SiO_2):(0.33\ TMAOH):(0.17\ NH_4OH):(17\ H_2O)$, where TMAOH denotes tetramethylammonium hydroxide. Cab-O-Sil silica (40 g, from Cabot Corp.) was mixed manually with 67 g of water. Then 68.2 g of 25% TMAOH aqueous solution (Aldrich) was added under vigorous magnetic stirring. Another mixture, composed of 40.5 g of cetyltrimethylammonium bromide (CTMABr) (Aldrich), 72 g of water, and 13 g of concentrated ammonia (BDH), was prepared during stirring. Both of these mixtures were transferred into a teflon-lined autoclave, stirred for 30 min, then heated statically at 70 °C for 3 days, and then at 130 °C for 1 day. The obtained solid material was filtered, washed with water, and dried at 60 °C. The sample was then calcined in flowing nitrogen up to 550 °C (1–2 °C/min), and then in air at the same temperature for 5 h. The obtained MCM-41 had a surface area of ca. 1226 m^2/g, pore volume of ca. 0.85 cm^3/g, and an average pore diameter of 2.8 nm. The conventional amorphous silica (SiO_2) used was silica grade 952 obtained from Grace–Davison (surface area ca. 293 m^2/g, pore volume ca. 1.78 cm^3/g, and average pore diameter 23.7 nm).

Ru-promoted Co catalysts were prepared by incipient wetness impregnation of the supports (MCM-41 and SiO_2) with aqueous cobalt nitrate (J.T. Baker, Inc.) and ruthenium nitrosyl nitrate (STREM Chemicals) solutions to yield 5 or 14 wt.% Co and 0.5 wt.% Ru on the supports. The catalysts were dried overnight in an oven at 120 °C and calcined at 300 °C in an air flow for 2 h. 5CoRu/M1 and 14CoRu/M1 are used to refer to MCM-41-supported CoRu catalysts with 5 and 14 wt.% Co, respectively. 5CoRu/S and 14CoRu/S refer to SiO_2-supported CoRu catalysts with 5 and 14 wt.% Co, respectively.

2.2. Catalyst characterization

Elemental analysis using inductively coupled plasma (ICP) spectroscopy was carried out by Galbraith Laboratories, Inc., in order to determine the final loadings of Co and Ru. BET surface area, pore volume, average pore diameter, and pore size distribution of the catalysts were determined by N_2 physisorption at 77 K using a Micromeritics ASAP 2010 automated system. Each sample was degassed at 10^{-6} mm Hg in the Micromeritics system at 200 °C for 4 h prior to N_2 physisorption. Static H_2 chemisorption on the reduced cobalt catalyst samples at 100 °C was also performed with the Micromeritics system using the procedure described by Reuel and Bartholomew [19]. Prior to H_2 chemisorption, the catalysts were evacuated to 10^{-6} mm Hg at 100 °C for 15 min, reduced in flowing H_2 (50 cc/min) at 100 °C for 15 min, reduced in flowing H_2 at 350 °C for 10 h after ramping up at a rate of 1 °C/min, and then evacuated at 10^{-6} mm Hg and 350 °C for 90 min to desorb any hydrogen. The number of exposed metal atoms on the surface was calculated by extrapolating the total adsorption isotherm to zero pressure and assuming coverage of one H atom per Co^0 atom exposed on the surface.

2.3. Reaction system

A schematic representation of the SSITKA system can be found in Ref. [20]. The reaction was carried out in a quartz microreactor with an ID of 4 mm. A thermocouple was installed on the top of the catalyst bed. A pneumatic valve, operated electrically, was used for the switch between feed streams containing different isotopically labeled reactant species (^{12}CO vs ^{13}CO). The stream not going to the reactor was directly vented. The pressure was maintained constant in the two streams being switched by two back-pressure regulators. The holdup of gas in the entire system was minimized. The lines of the outlet streams were heated to 180 °C in order to avoid the possibility of heavy product deposition and blockage of the tubing. All the gases used for this study were of ultrahigh purity grade. The on-line analytical part of the system consisted of a gas chromatograph (Varian CP-3800) and a quadruple mass spectrometer (Pfeiffer Vacuum). In the GC the products were separated by a 6-ft, Porapaq Q column (Alltech) and detected with a flame ionization detector (FID). The mass spectrometer was equipped with a high-speed data-acquisition system interfaced to a personal computer using Balzers Quadstar 422 v 6.0 software (Balzers Instruments).

2.4. Kinetic measurements

Rate measurements of methanation were made using ca. 20 mg of the catalyst loaded into the microreactor. Before each experiment, the catalyst was reduced in flowing hydrogen (50 cm^3/min) by ramping at 1 °C/min to 350 °C and holding for 10 h at this temperature. After reduction, the catalyst bed temperature was lowered to 220 °C, the desired reaction temperature. The reaction mixture was then introduced into the reactor. The feed (32 cm^3/min) consisted of a constant 2 cm^3/min of CO and 4, 10, 20, or 30 cm^3/min of H_2, with the balance being helium. The total pressure was maintained at 1.82 bar. Specific activities were determined in terms of rate of CO hydrogenation per gram of catalyst and TOF_H of CO hydrogenation based on H_2 chemisorption. A time-on-stream (TOS) study was performed in order to observe the possible impact of reaction conditions on the deactivation process. CO conversion was calculated based on all the carbonaceous products determined by GC, which included methane as well as some small amounts of higher hydrocarbons.

Steady-state isotopic transients were taken by switching between two feed streams where the only difference was the isotopic composition of CO: one stream containing $^{12}CO/Ar$ and the other ^{13}CO. A trace of argon (5%) was present in the ^{12}CO stream in order to measure the gas-phase holdup of the entire reaction system. The isotopic switch did not disrupt steady-state reaction. The time for the passage of the transients through the system was about 13–14 s. The method used to calculate SSITKA parameters (average surface reaction residence time and concentration of surface reaction intermediates) has been described extensively by Shannon and Goodwin [4].

3. Results and discussion

3.1. Properties of MCM-41 and SiO_2-supported CoRu catalysts

Table 1 gives the characteristics of the catalysts studied. The BET surface areas of the MCM-41-supported CoRu catalysts were found to be significantly higher than those of the SiO_2-supported ones as a result of the significant difference in surface areas of the original support materials. The BET surface area, the pore volume, and the average pore diameter decreased when Co loading increased from 5 to 14 wt.%. However, the decrease was found to be more significant in the case of the MCM-41-supported catalysts.

The hydrogen chemisorption results were used to determine the average Co^0 particle size and the amount of surface-exposed Co^0. For catalysts with 5 wt.% Co loading, CoRu supported on MCM-41 had higher hydrogen chemisorption, a smaller average Co metal particle size, and higher %Co dispersion. However, with 14 wt.% Co load-

Table 1
Properties of MCM-41- and SiO_2-supported CoRu catalysts [17]

Catalyst	Co[a] (wt.%)	BET surface area[b] (m^2/g)	Pore volume[b] (cm^3/g)	Avg. pore diameter[b] (nm)	Co red. during TPR (%)		Total H_2 chemisorption[b] (μmol H_2/g cat.)	d_p[d] (nm)	Co[e] dispersion (%)
					30–800 °C[c]	30–400 °C[c]			
5CoRu/S	4.3	264	1.49	22.6	68	68	35.7	6.7	9.8
5CoRu/M1	4.6	987	0.6	2.4	63	57	49.1	4.3	12.7
14CoRu/S	14.2	219	1.23	22.6	70	58	92.6	7.2	7.7
14CoRu/M1	14.4	650	0.34	2.1	69	38	58.7	7.6	4.8

[a] ICP results. Error = ±5% of measurement.

[b] Error = ±5% of measurements.

[c] Correlates to percentage of metal reduced during standard reduction procedure (ramp 1 °C/min to 350 °C, hold for 10 h) [21].

[d] Based on the reduced Co from TPR data, assuming $H/Co_s = 1$ and $d_p = 5/[(\text{metal surface area/g reduced Co}) \cdot \text{Co density}]$. Exposed surface area of $1\ Co_s = 6.62\ Å^2$.

[e] Based on total cobalt and H_2 chemisorption: H/Co_{total}.

ing, CoRu supported on MCM-41 had much lower hydrogen chemisorption, larger average metal particle size, and lower %Co dispersion.

The reducibilities of all the catalysts during TPR 30–800 °C were not significantly different, ranging from 63 to 70%, and the reducibility went up or remained the same as the loading went from 5 to 14%. In general, CoRu/MCM-41 had lower reducibilities than $CoRu/SiO_2$, due probably to the stronger interaction of Co with the MCM-41 support. During TPR 30–400 °C, lower reducibility at higher Co loading was observed and it was probably related to the fact that (a) there was a difference in concentration of Co nitrate during the impregnation of these two loadings and at higher concentrations of Co nitrate a more acidic solution results that can affect the interaction of Co with the support, and/or (b) more water vapor was produced during reduction of these calcined catalysts from the 14 wt.% Co, resulting in an increase in the interaction of Co with the support, as has been determined previously by us [21,22] and others [23]. This did not result in the formation of additional cobalt silicates (not reducible $\leqslant 800\,^\circ$C) perhaps, but it did result in stronger interaction of Co atoms with the silica support, requiring higher temperatures for reduction. This may have been the cause also for the low H_2 chemisorption on 14CoRu/M1. CoRu/M1 containing 14 wt.% Co has also been shown to have a less uniform metal distribution than $CoRu/SiO_2$, Co being more concentrated toward the outer surface of the support granules [17]. However, as evidenced by SEM and EDX for the same study, the lower the Co loading, the more uniform distribution of Co observed.

The average Co^0 particle size on M1 for all Co loadings was calculated to be larger than the average pore diameter of M1. Part of this was probably due to larger Co^0 particles being on the external surface of the M1 granules. However, overestimation of Co metal particle size is also possibly due to particles being occluded in the pores, blocking some of the surface of the particles from adsorbing hydrogen [24], or a result of H_2 chemisorption suppression. In a previous study of F–T synthesis on CoRu/MCM-41, evidence for H_2 chemisorption suppression was found [17].

3.2. Catalyst activities

CO hydrogenation was carried out at 220 °C and 1.82 bar. The hydrogen partial pressure was varied from 0.23 to 1.71 bar while the CO partial pressure was kept constant at 0.11 bar with helium making up the difference. Table 2 presents the CO conversion, CO hydrogenation rate, methane selectivity, and turnover frequency of the catalysts at different partial pressures of hydrogen. For a given Co loading, MCM-41-supported CoRu catalysts exhibited significantly higher %CO conversions and CO hydrogenation rates than the SiO_2-supported ones for all hydrogen partial pressures used in this study. The methane selectivities, however, were not significantly different. As expected, the CO hydrogenation rate increased with increasing hydrogen partial pressure. The apparent activation energies for CoRu/M1 were found to be 21–24 kcal/mol, which are in line with typical values reported in the literature [10,25]. It can be concluded that there was no effect of diffusion due to MCM-41 structure on the reaction rate. It should be noted that during reaction conditions at the highest concentration of hydrogen, the conversion was much higher than desired in two instances and not exactly differential (for 14CoRu/M1 at $P_{H_2} = 1.14$ and 1.71 bar). The largest steady-state value was 26.1%. However, the other runs had conversions lower than 10%, going down to 1%. This is one of the difficulties in trying to hold as many parameters constant as possible in doing a study over a wide range of catalysts and partial pressures

Table 2
Catalyst activities during CO hydrogenation ($T = 220\,^\circ$C, $P_{total} = 1.82$ bar, and $P_{CO} = 0.11$ bar): effect of H_2 partial pressure

Catalyst	P_{H_2} (bar)	CO conversion[a] (%)		CO hydrogenation rate[a] (μmole CO/g cat. s)		CH_4 selectivity[a]	TOF_H[b] $\times 10^3$ (s^{-1})
		Initial	Steady-state	Initial	Steady-state	(%)	steady-state
5CoRu/S	0.57	1.6	1.1	1.1	0.7	80	10
	1.14	2.8	1.9	2.0	1.3	82	18
	1.71	5.0	3.2	3.5	2.2	85	31
5CoRu/M1	0.57	3.2	2.1	2.2	1.4	80	14
	1.14	6.2	4.5	4.1	3.1	84	32
	1.71	7.7	6.5	5.4	4.5	88	46
14CoRu/S	0.23	2.1	1.4	1.5	1.0	73	5
	0.57	3.6	2.3	2.5	1.6	80	9
	1.14	9.1	5.0	6.3	3.4	80	18
	1.71	12.2	8.4	8.5	5.8	80	31
14CoRu/M1	0.23	5.1	2.9	3.5	2.0	78	17
	0.57	15.9	8.5	11.1	5.9	82	50
	1.14	27.8	17.3	19.4	12.0	84	102
	1.71	46.3	26.1	32.2	18.2	88	153

[a] Error = ±5% of measurement.

[b] Based on total H_2 chemisorption and the CO hydrogenation rate.

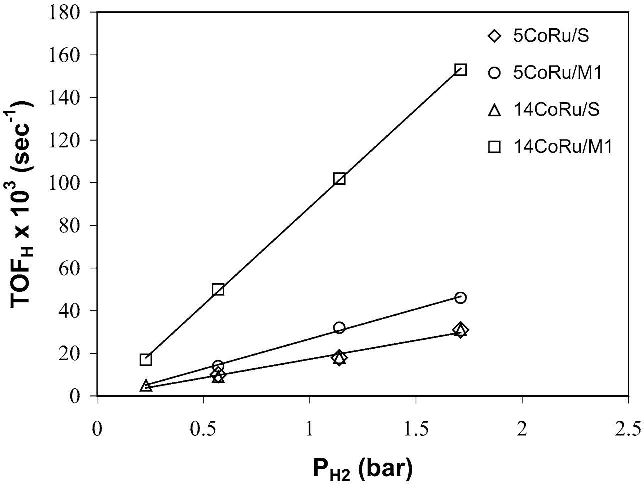

Fig. 1. Variation of overall turnover frequency (TOF_H) with hydrogen partial pressure (based on H_2 chemisorption).

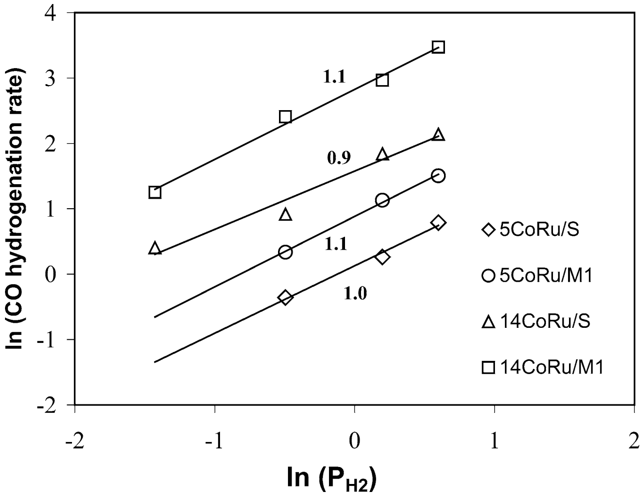

Fig. 2. Hydrogen partial pressure dependency of the CO hydrogenation rate.

of H_2. One must use the two data points at conversions > 10% with some discretion.

TOF_Hs for the catalyst series are plotted as a function of hydrogen partial pressure in Fig. 1. It can be seen that, for any catalyst used in this study, TOF_H increased approximately threefold when hydrogen partial pressure increased from 0.57 to 1.71 bar. For a given hydrogen partial pressure, TOF_H's for the SiO_2-supported CoRu catalysts with different Co loadings were essentially identical. Those of the MCM-41-supported CoRu catalysts were found to be higher. The difference was more significant in the case of 14CoRu/M1, where the TOF_H's were ca. 5 times higher than those of 14CoRu/S. Considering the high reaction rate seen for 14CoRu/M1 but the relatively (for 14 wt.% Co) low amount of H_2 chemisorbed, one is led to conclude that there was probably some sort of H_2 chemisorption suppression for this catalyst [14]. If so, this might explain why TOF_Hs for the MCM-41-supported catalysts calculated based on H_2 chemisorption were so much higher, especially for 14 wt.% Co. Figure 2 shows the hydrogen partial pressure dependency of the CO hydrogenation rates. The order of reaction with respect to hydrogen was calculated to be approximately 1 for all the different catalysts used in this study. These values are in good agreement with typical values reported in the literature [10,26].

3.3. Surface reaction studies using SSITKA

Steady-state isotopic transient kinetic analysis was used in this study in order to investigate in more detail the effect of hydrogen partial pressure on the surface reaction parameters for CO hydrogenation over the different silica-supported CoRu catalysts. A typical set of normalized isotopic transients are shown in Fig. 3. Table 3 gives the values of the surface reaction parameters determined for CO hydrogenation at 220 °C with a constant CO partial pressure of 0.11 bar but different hydrogen partial pressures.

τ_{CO} and N_{CO} represent, respectively, the average surface residence time of CO and the number of CO molecules reversibly adsorbed on the surface at steady state. τ_M and N_M are, respectively, the surface reaction residence time and the concentration of the active surface intermediates of methane. Because CO is a reactant and not all CO flowing through the reactor adsorbs, τ_{CO} is normally more difficult to interpret than the other parameters determined [10]. The methodology used to calculate these parameters using SSITKA can be found in a recent review [4]. Taking into account experimental error, for a given catalyst the average surface residence time and the surface concentration of reversibly adsorbed CO were essentially constant over the whole H_2 partial pressure range (0.23–1.71 bar), indicating little effect of H_2 partial pressure on CO adsorbing and desorbing without reaction. However, an increase in N_{CO}

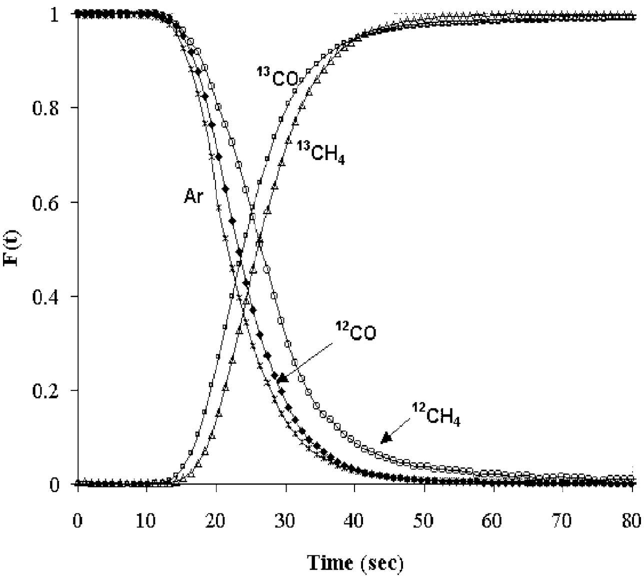

Fig. 3. Typical normalized isotopic-transient responses during methanation at 220 °C and 1.8 atm.

Table 3
SSITKA results at steady state during CO hydrogenation ($T = 220\,°\mathrm{C}$, $P_{\mathrm{total}} = 1.82$ bar, and $P_{\mathrm{CO}} = 0.11$ bar)

Catalyst	$P_{\mathrm{H_2}}$ (bar)	$\mathrm{TOF_H}$[a] $\times 10^3$ ($\mathrm{s^{-1}}$)	τ_{CO}[b] (s)	N_{CO}[c] (μmole/g cat.)	τ_{M}[b] (s)	N_{M}[d] (μmole/g cat.)	θ_{M}[e]	k_{M}[f] ($\mathrm{s^{-1}}$)
5CoRu/S	0.57	10	0.7	33	7.3	4.1	0.06	0.14
	1.14	18	1.0	40	4.2	4.5	0.06	0.24
	1.71	31	0.9	42	3.1	5.8	0.08	0.32
5CoRu/M1	0.57	14	1.0	39	6.8	7.6	0.08	0.15
	1.14	32	1.2	46	4.4	11.5	0.12	0.23
	1.71	46	1.1	43	3.2	12.7	0.13	0.31
14CoRu/S	0.23	5	1.4	56	12.2	11.0	0.04	0.08
	0.57	9	1.4	55	7.3	11.7	0.05	0.14
	1.14	18	1.4	56	4.4	15.0	0.06	0.23
	1.71	31	1.4	55	3.1	17.7	0.08	0.32
14CoRu/M1	0.23	17	1.5	60	14.8	23.1	0.20	0.07
	0.57	50	1.9	73	6.9	31.8	0.28	0.14
	1.14	102	1.7	67	4.1	41.3	0.35	0.24
	1.71	153	1.8	72	3.1	49.1	0.42	0.32

[a] Based on total H_2 chemisorption and the CO hydrogenation rate.
[b] Error of measurement = ±0.1 s.
[c] Error of measurement = ±3 μmol/g cat.
[d] Error of measurement = ±0.6 μmol/g cat.
[e] θ_{M} is the surface coverage of carbonaceous CH_4 intermediates $= N_{\mathrm{M}}/(\text{total adsorbed H})$.
[f] $k_{\mathrm{M}} = 1/\tau_{\mathrm{M}}$, pseudo-first-order rate constant.

with increasing Co loading from 5 to 14 wt.% was observed, as would be expected for a larger metallic surface area.

The average surface residence time of the methane intermediates (τ_{M}) was found to consistently decrease with increasing hydrogen partial pressure. The impact of nonadsorbing molecules is absent for methane since, in order to be formed, every methane molecule has to have been adsorbed. In addition, readsorption is not a major effect since methane essentially does not readsorb. For a given hydrogen partial pressure, the average surface residence time for methane intermediates (τ_{M}) on all the catalysts were essentially identical, suggesting that there was no difference in the nature of the Co active sites.

For Co catalysts, the hydrogenation of carbonaceous surface intermediates has been widely concluded to be the rate-determining step [27,28]. This step can be written as

$$^*\mathrm{CH}_x + {}^*\mathrm{H} \rightarrow {}^*\mathrm{CH}_{x+1} + {}^*. \tag{1}$$

Thus, the rate of methane formation can be expressed in terms of its rate-determining step as

$$R_{\mathrm{M}} = k \cdot N_{\mathrm{H}} \cdot N_{\mathrm{M}}, \tag{2}$$

where N_{H} is the surface concentration of hydrogen. Since

$$\tau_{\mathrm{M}} = \frac{N_{\mathrm{M}}}{R_{\mathrm{M}}}, \tag{3}$$

the relationship between τ_{M}, the intrinsic rate constant k, and the concentration of surface hydrogen is

$$\frac{1}{\tau_{\mathrm{M}}} = k \cdot N_{\mathrm{H}} = k_{\mathrm{M}}, \tag{4}$$

where k_{M} is a pseudo-first-order rate constant. However, it includes the hydrogen surface concentration dependence. The decrease in τ_{M} with an increase in hydrogen partial pressure confirms this dependence of τ_{M} on N_{H}. A measure of the relative variation in the surface concentration of hydrogen can be determined by dividing $1/\tau_{\mathrm{M}}$ for a given hydrogen partial pressure by the value for it at a reference hydrogen partial pressure,

$$\frac{(1/\tau_{\mathrm{M}})}{(1/\tau_{\mathrm{M}})_{\mathrm{ref.}}} = \frac{(k \cdot N_{\mathrm{H}})}{(k \cdot N_{\mathrm{H}})_{\mathrm{ref.}}} = \frac{N_{\mathrm{H}}}{N_{\mathrm{H,ref.}}}. \tag{5}$$

$N_{\mathrm{H}}/N_{\mathrm{H,ref.}}$ is presented in Table 4, where $N_{\mathrm{H}}/N_{\mathrm{H,ref.}}$ represents the relative surface concentration of hydrogen on the catalyst referenced to a hydrogen partial pressure of 0.57 bar. Figure 4 shows the plots for the effect of H_2 partial pressure on the relative surface concentration of hydrogen of SiO_2- and MCM-41-supported CoRu catalysts. The results for the 5 wt.% Co catalysts at low hydrogen partial pressure are not given due to the very low activities exhibited which made it difficult to perform isotopic tracing. It can be seen in Fig. 4 that the relative hydrogen surface concentrations were identical within experimental error for all the catalysts at a given partial pressure of hydrogen. It can also be concluded

Table 4
Effect of $P_{\mathrm{H_2}}$ on the relative hydrogen surface concentration at steady-state during CO hydrogenation ($T = 220\,°\mathrm{C}$, $P_{\mathrm{total}} = 1.82$ bar, and $P_{\mathrm{CO}} = 0.11$ bar)

$P_{\mathrm{H_2}}$	$N_{\mathrm{H}}/N_{\mathrm{H,0.57\ bar}}$			
(bar)	5CoRu/S	5CoRu/M1	14CoRu/S	14CoRu/M1
0.23	–	–	0.60	0.47
0.57	1.00	1.00	1.00	1.00
1.14	1.74	1.55	1.66	1.68
1.71	2.35	2.13	2.35	2.23

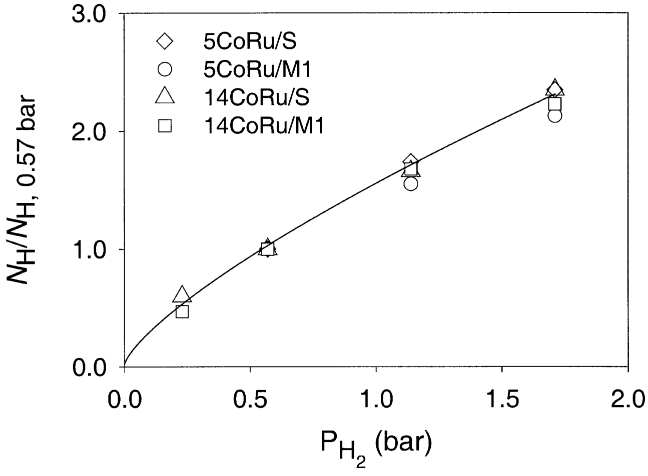

Fig. 4. Effect of hydrogen partial pressure on the relative surface concentration of hydrogen.

that excess water present during the higher conversions on the more active catalysts, such as 14CoRu/M1, did not have any significant impact on the surface concentration of hydrogen.

There was an apparent increase in the surface abundance of methane intermediates (N_M), with increasing hydrogen partial pressure, possibly due to increased hydrogenation. It should be noted that the increase in N_M was not due just to an increase in selectivity for CH_4. Figure 5 shows the effect of H_2 partial pressure on the surface concentration of methane intermediates for the SiO_2- and MCM-41-supported CoRu catalysts. The impact of H_2 partial pressure on the relative surface concentrations of methane intermediates on SiO_2- and MCM-41-supported CoRu catalysts was similar, as evidenced by an approximately twofold increase in N_M as H_2 partial pressure increased from 0.23 to 1.71 bar. However, compared to 14CoRu/S, 14CoRu/M1 had a much higher number of methane surface intermediates (N_M).

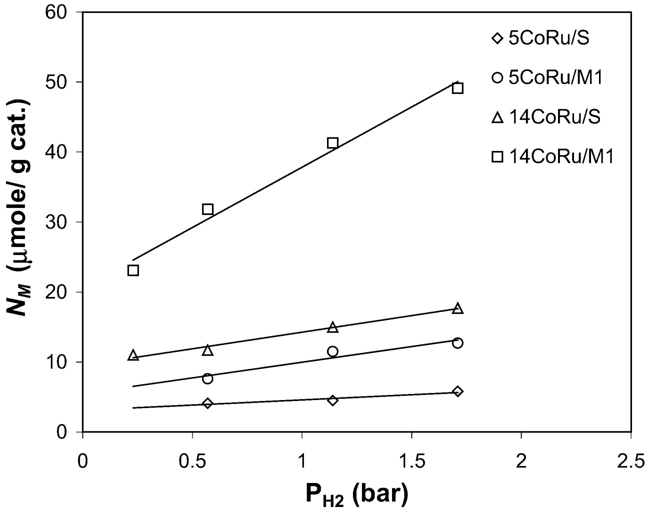

Fig. 5. Effect of hydrogen partial pressure on the surface concentration of methane intermediates.

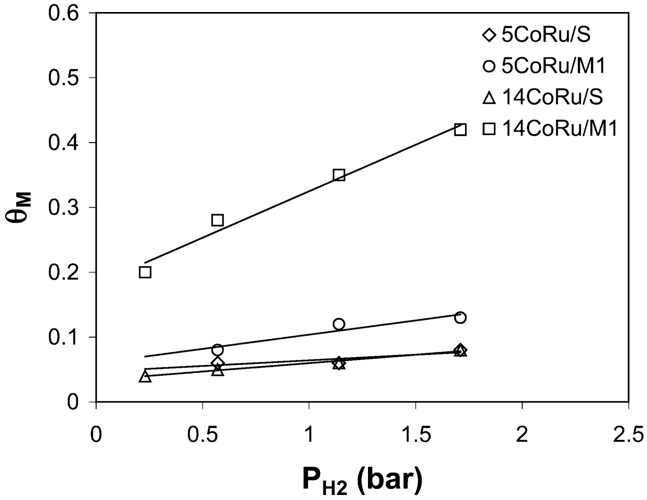

Fig. 6. Effect of hydrogen partial pressure on the surface coverage of methane intermediates.

The effect of hydrogen partial pressure on the surface coverages of methane intermediates (θ_M) is shown in Fig. 6. θ_M increased with increasing hydrogen partial pressure. Except for that of 14CoRu/M1, θ_M was calculated to be in the range of 0.04–0.13, which is typical at under these conditions for SiO_2 - or Al_2O_3-supported Co-based catalysts with ca. 20 wt.% Co loading [19,29]. The surface coverage on 14CoRu/M was found to be much greater and was calculated to be in the range of 0.20–0.42. Since θ_M was calculated based on H_2 chemisorption, it was also probably in error due to possible H_2 chemisorption suppression on 14CoRu/M1. It is known that the number of active intermediates on a Co surface obtained by SSITKA during CO hydrogenation is only a small fraction of the total number of Co metal surface atoms (and hence potential reaction sites) obtained by H_2 chemisorption [30].

Based on the results of this study, the effect of hydrogen partial pressure was similar on the different silica-supported CoRu catalysts. Although suppression of H_2 chemisorption appears to have occurred in the case of MCM-41-supported CoRu catalysts at 100 °C (where H_2 chemisorption was done), especially for high Co loading, it did not appear to have an impact on the effect of hydrogen partial pressure during reaction.

4. Conclusions

Fundamental kinetic measurements under reaction conditions are very useful to describe the surface phenomena occurring during reaction on high surface area heterogeneous catalysts. As indicated by the SSITKA results, the intrinsic site activity and the concentration of surface intermediates for CO hydrogenation are strongly dependent on hydrogen partial pressure. Increasing the hydrogen partial pressure at constant temperature caused an expected increase in the relative surface concentration of hydrogen as well as an increase in the abundance of surface methane intermediates (N_M), possibly due to increased hydrogenation. The average surface residence time of the methane intermediates (τ_M) consistently decreased with increasing hydrogen partial pressure due to its inverse dependence on the surface concentration of hydrogen. Although the cobalt surfaces on MCM-41 are more active than on silica as shown by the higher rates, the impact of hydrogen partial pressure on N_M for MCM-41-supported CoRu catalysts was similar to that for SiO_2-supported ones. However, the abundance of surface methane intermediates and the surface coverages were found to be significantly higher for MCM-41-supported CoRu catalysts than SiO_2-supported ones. It is noted that the type of silica support (amorphous SiO_2 or MCM-41) used did not appear to have a significant impact on relative surface hydrogen concentration nor intrinsic site activity for methanation. Thus, although high loadings of Co in CoRu/MCM-41 catalysts appear to result in hydrogen chemisorption suppression at 100 °C (contrary to the case for $CoRu/SiO_2$), at 220 °C under reaction conditions there was no obvious difference between the catalysts with regards to this. The observed increase in the CO hydrogenation rates with increasing hydrogen partial pressure can be attributed to the increase in the number of active carbon-containing intermediates (as evidenced by an increase in N_M) as well as an increase in the hydrogen surface concentration. The similarity in τ_M during reaction at a given hydrogen partial pressure allows us to conclude that the active sites were identical on the different silica-supported catalysts.

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