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Relationships between oxygenate and hydrocarbon formation during CO hydrogenation on Rh/SiO_2: Use of multiproduct SSITKA

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ABSTRACT

In the present research, the mechanism of C_1 and C_2 hydrocarbon and oxygenate formation during CO hydrogenation on Rh/SiO_2 were for the first time investigated in detail using multiproduct SSITKA (steady-state isotopic transient kinetic analysis). This was also the first effort to explore at the site level the relationship between similar products [e.g., EtOH (ethanol) vs. AcH (acetaldehyde)] on Rh/SiO_2. A fixed-bed differential reactor was used for CO hydrogenation and SSITKA at 250 °C and 1.8 atm. The selectivity to CH_4 was higher than any other product, but the surface reaction residence time for CH_4 formation was not the shortest among all the products. The surface reaction residence time for C_2 hydrocarbons was longer than that for any other product (C_1–C_2). Even though the selectivities to AcH and EtOH were similar, their surface reaction residence times differed significantly. Based on the SSITKA results, MeOH and CH_4 appear to be produced on completely different active sites. Moreover, C_2 hydrocarbons do not appear to be formed from adsorbed AcH. It is likely, however, that all C_2 products share at least one intermediate with CH_4, but none with MeOH. Several recently proposed pathways for EtOH and AcH formation are presented and compared to our results. The secondary reaction of AcH to form EtOH on the same sites does not appear to be a dominant pathway for EtOH formation. However, the precise mechanism for EtOH formation still needs further investigation.

1. Introduction

Ethanol (EtOH) synthesized from syngas derived from natural gas [1], coal [2] or biomass [3] can be used as an additive to gasoline or as an easily transportable and storable source of hydrogen. Compared to gasoline alone, the use of ethanol with gasoline offers several advantages such less pollution and more efficient combustion due to its chemical properties. The incentive for incorporating ethanol in liquid fuels also lies in the general acceptance of new gasoline regulations with more restrictions. Accordingly, much recent research and development in syngas conversion have dealt with ethanol synthesis.

Rh-based catalysts have been found to be the most efficient catalysts for the synthesis of C_{2+} oxygenates due to the unique carbon monoxide adsorption behavior on Rh [4–7]. Understanding the mechanism of CO hydrogenation is essential for better catalyst design that could lead to commercialization of a selective ethanol synthesis process. Even though Fischer–Tropsch synthesis (FTS) has been widely studied since 1923 [8], there is still controversy in the literature about the mechanism for CO hydrogenation due to its complexity. For instance, one controversy is whether C–O bond cleavage occurs during CO hydrogenation via direct dissociation (carbide mechanism) [9–15] or via a hydrogen-assisted process [16–32]. Recently, Choi and Liu [32] focused on EtOH synthesis from CO and H_2 on Rh (1 1 1) using density functional theory (DFT) and found that the optimal reaction pathway for the formation of methanol (MeOH) goes through H insertion into adsorbed –CO species, while the formation of CH_4 favors H-assisted CO dissociation through the bond rupture of –CH_3O species into –CH_3 and –O. However, to the contrary, in another recent work, Mei et al. [33] still preferred the carbide model to explain using a DFT approach the mechanism for CO hydrogenation on a quasi-(1 1 1) surface facet on a 1 nm in diameter Rh_{50} cluster.

Steady-state isotopic transient kinetic analysis (SSITKA) is a powerful tool to evaluate concentration of intermediates, site activity, site heterogeneity and surface reaction mechanism [34]. This technique was developed first by Biloen [35], Bennett [36] and Happel [37] in late 1970s and early 1980s. SSITKA involves a switch from an unlabeled reactant to an isotopically labeled one at steady state of the reaction, the detection of the resulting isotopic transients in the products by mass spectroscopy (MS) and an analysis of these transients to determine surface reaction kinetic parameters. Because of its wide applicability and relatively low cost, SSITKA has now been used by a significant number of researchers. For CO hydrogenation, SSITKA has been employed to better probe the surface reaction parameters on various catalysts including are based on Fe [38–42], Pd [43–46], Co [40,41,47–49],

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Ni [50,51], Ru [52–54] and Rh [55–64]. However, for Rh-based catalysts, there are few detailed studies reported on different product formation at the site level.

The objective of this study was to better understand the mechanism of formation of different products on Rh/SiO_2 at the site level by the application of SSITKA. For this study, 1.5 wt% Rh/SiO_2 was prepared and used as the catalyst for two reasons:

(a) Low amounts of Rh (i.e., 1.5 wt%) supported on SiO_2 produce highly dispersed Rh that is representative of the Rh clusters used in theoretical modeling work.
(b) Rh-based catalysts supported on SiO_2 have shown reasonable selectivities for both hydrocarbons and oxygenates during CO hydrogenation [65–67].

2. Experiments

2.1. Catalyst preparation

Since the Rh/SiO_2 catalyst used in this study was the same as that used in a previous study, a detailed description of catalyst preparation can be found in an earlier paper [68]. Silica gel (99.95%, Alfa Aesar) was first grounded and sieved to 30–50 mesh, washed with boiled distilled water for three times and subsequently calcined in air at 500 °C for 4 h before being used as the support. $Rh(NO_3)_3$ hydrate (Rh ~ 36 wt%, Fluka) was used as purchased. An aqueous solution of $Rh(NO_3)_3$ hydrate was added dropwise to the silica gel until incipient wetness. The catalyst precursor was dried at 90 °C for 4 h and then at 120 °C overnight before being calcined in air at 500 °C for 4 h to remove nitrogenous residues from the precursors. Rh content was kept at 1.5 wt% based on the support weight.

2.2. CO hydrogenation

The reaction system setup is shown in Fig. 1. CO hydrogenation was carried out in a fixed-bed differential reactor (316 stainless steel) with length ~300 mm and internal diameter ~5 mm. Catalyst and inert (α-Al_2O_3) were mixed and loaded between quartz wool plugs placed in the middle of the reactor with a thermocouple close to the catalyst bed.

Molecular sieve traps (Alltech) were used to remove H_2O, and a CO purifier (Swagelok) was applied to the flow from the CO cylinder to remove CO_2 and any carbonyls. A Varian 3380 GC equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD) was used to analyze the reaction rate and product distribution. A Restek RT-QPLOT column (30 m, 0.53 mm ID) connecting with the FID was capable of separating C_1–C_7 hydrocarbons and oxygenates, while another Restek packed column (80/100, 6ft) connecting with the TCD was used to separate CO and other inorganic gases.

Prior to reaction, the catalyst was reduced at 500 °C (ramped to temperature at 5 °C/min) under 30 mL/min hydrogen for 1 h. After reduction, the reaction was carried out at 250 °C and a pressure of 1.8 atm. The total flow rate of the reaction mixture was kept constant at 30 mL/min with 9 mL/min of 95% CO + 5% Ar, 18 mL/min of H_2 and 3 mL/min of He to obtain a H_2:CO ratio of 2:1, which is favorable for EtOH production [69]. The reaction conversion was always kept at less than 5% to avoid mass or heat transfer effects. Even though the selectivities for oxygenates, especially for EtOH, may not be as great as those at more optimum conditions (e.g., lower reaction temperature), these reaction conditions were chosen to maximize yields of C_1–C_2 products, especially the C_2 oxygenates, so that they could be detected by MS. The reaction rates were observed to be independent of total flow rate (25–100 mL/min) and particle size of the catalyst (18–100 mesh), indicating no external/internal mass transfer limitations. The apparent activation energy (25–28 kcal/mol) and the good linearity of Arrhenius Plots further indicated that there were no mass or heat transfer limitations under the reaction conditions used.

2.3. SSITKA

An isotopic switch was carried out after reaction steady-state was reached (after 15 h). A switch between 95% ^{12}CO + 5% Ar and ^{13}CO was made using a Valco 2-position valve with an electric actuator without disturbing any other reaction conditions. The 5% Ar in the ^{12}CO flow was used as an inert tracer to determine the gas phase holdup time. Two back pressure regulators in the system were used to minimize pressure disturbance while switching. A Valco 34-port valve was employed to collect 16 samples during the 10-min period of the isotopic transients after switching. The collected effluent samples were injected separately into another Restek RT-QPLOT column in the GC with 30 mL/min H_2 as the carrier gas. The products were separated by the column and then fed into a hydrogenolysis/hydrogenation reactor (containing 5 g of 5% Pt/Al_2O_3) with the source of H_2 being the carrier gas. This reactor was maintained at 400 °C in order to convert hydrocarbons and oxygenates totally to methane. The resulting product CH_4 was subsequently fed into an MS (Pfeiffer Vacuum) for analysis. The MS was equipped with a high-speed data-acquisition system interfaced to a computer using Balzers Quadstar 422 v 6.0 software. The isotopic concentration measured by the MS was able to be used with the time for the collection of each sample in the 34-port valve, and the identity of the compound separated by the GC sent to the hydrogenolysis reactor to construct the isotopic transients for the various products. An example of the normalized transients for ^{12}C in CH_4, C_2H_n, MeOH, AcH, EtOH and ^{13}C in CH_4 obtained by switching from ^{12}CO to ^{13}CO is given in Fig. 2. It would be meaningful to study C_2H_4 and C_2H_6 separately, but in our SSITKA study, C_2H_6 was the predominant C_2 hydrocarbon formed (>90% based on GC analysis). Thus, the amount of C_2H_4 was too small for isotopic tracing analysis.

Surface kinetic parameters including the average surface residence times and surface concentrations of intermediates for CH_4, C_2H_n, MeOH, AcH and EtOH were determined from the isotopic transient curves using SSITKA data analysis software [34,70]. The difference in area under the normalized transient curves of a particular species (i) and the inert tracer (Ar) gives the average surface reaction residence time (τ_i). The concentration of active surface intermediates for a particular product can be calculated by $N_i = \text{Rate}_i * \tau_i$ [34,71].

It is worth noting that different from most other SSITKA studies (e.g., methanation) where the isotopic transient response is traced directly and continually by MS, this work adopted a 34-port autosampling valve to collect samples and a GC to separate different products before MS analysis. An important advantage of this methodology, used among the first by Bennett and co-workers [50,51], is that the surface parameters of various hydrocarbon products instead one product (i.e., CH_4 in methanation studies) can be determined without the common MS analysis problem caused by fragmentation and overlapping of different products. Thus, the term “multiproduct SSITKA” is used in this study to emphasize this approach.

3. Results

Table 1 shows the surface kinetic parameters for different products on varying amounts of the Rh/SiO_2 catalyst. The % CO conversions were all under differential conditions (<5%), and the selectivities for different products were constant regardless of

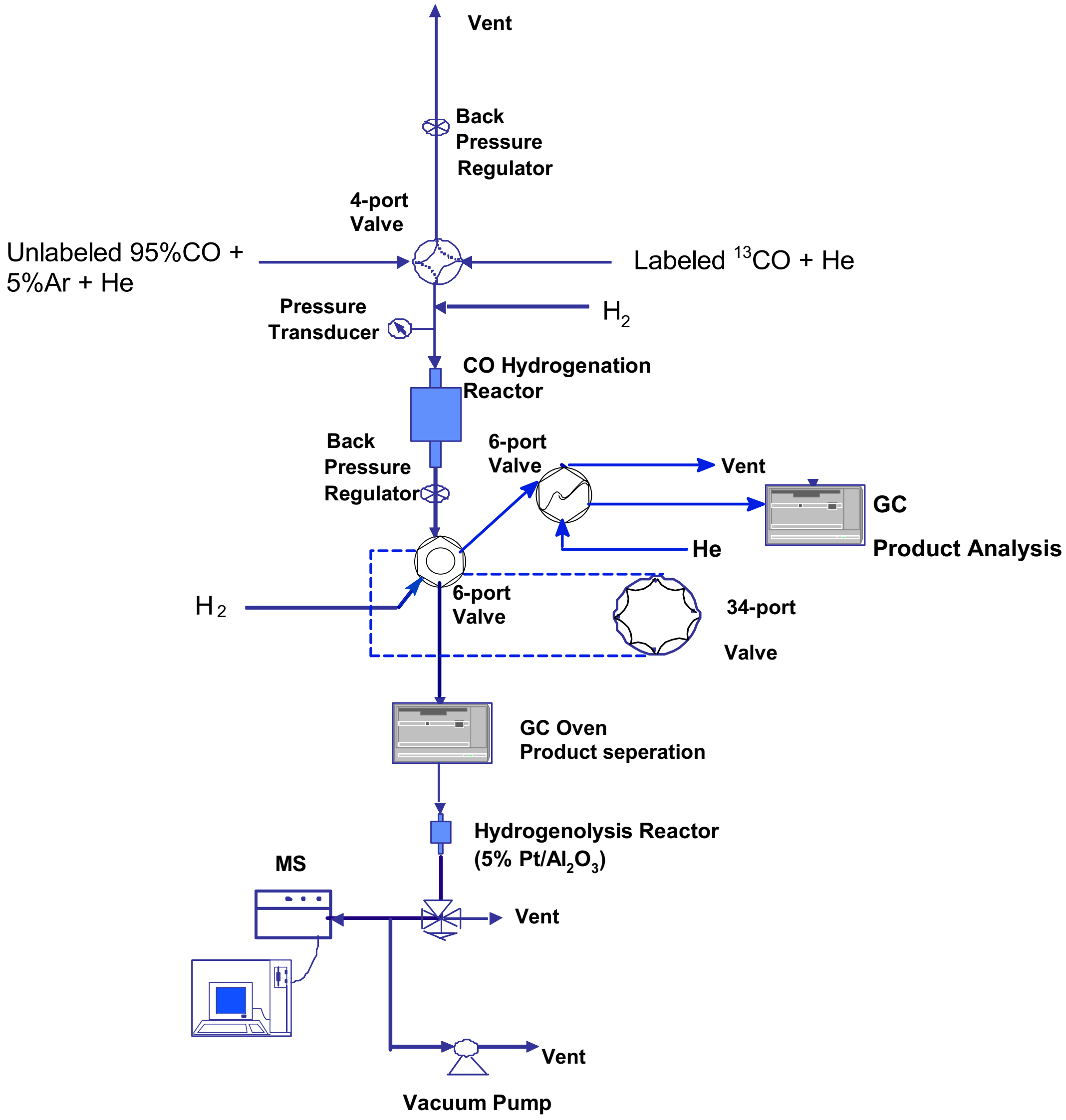

Fig. 1. The reaction system setup for multiproduct SSITKA.

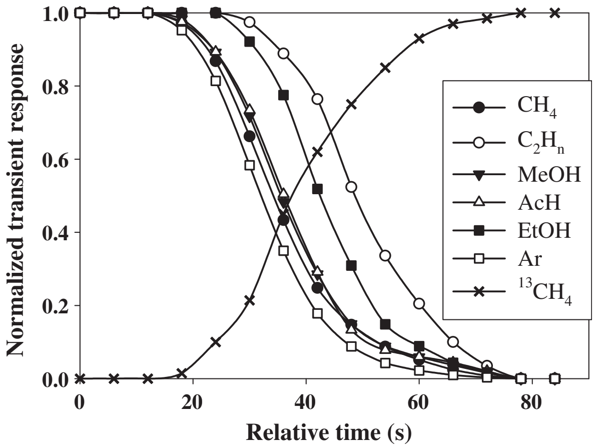

Fig. 2. Typical normalized transient responses for ^{12}C in CH_4, C_2H_n, MeOH, AcH, EtOH, ^{13}C in CH_4 and for Ar during steady-state reaction on Rh/SiO_2.

the amount of catalyst being used. However, the average surface reaction residence times [calculated as the area between the normalized transient curves of a particular species (i) and the inert tracer (Ar)] of MeOH and AcH (acetaldehyde) changed with the amount of the catalyst being used, while the residence times for all the other products were not affected. This was due to the ease of readsorption of these products and the resulting chromatographic effect [45]. To clarify, Fig. 3 shows how the average surface reaction residence times for MeOH and AcH change with the amount of Rh/SiO_2 catalyst used in our study. When the catalyst amount changed from 0.2 to 1.0 g, the average surface reaction residence times for MeOH and AcH formation increased linearly, from 2.7 to 4.2 s and from 2.6 to 4.0 s, respectively. Thus, contrary for other products, readsorption of MeOH and AcH on Rh/SiO_2 could not be ignored and had to be addressed before the surface reaction residence times could be evaluated, otherwise both TOF based on these values (TOF_{ITK}) and the number of active surface intermediates/sites involved in their synthesis would be underestimated and overestimated, respectively. This was accomplished by extrapolating the residence times determined for different amounts of catalyst to 0 g of catalyst, i.e., an infinitely thin bed [46]. By extrapolating the trend line to 0 g catalyst, the surface residence times for MeOH and AcH formation on the surface were determined to both be approximately 2.3 s.

Table 1
The surface reaction kinetic parameters for CO hydrogenation on the nonpromoted Rh/SiO_2 catalyst.[a]

Product[h]	Rate[b] (μmol of C/g/s)	%C Selectivity [c]	τ_i[d] (s)	$TOF_{ITK,\,i}$[e] (s^{-1})	N_i[f] (μmol of C/g)
0.2 g Rh/SiO_2[i]					
CH_4	0.076	64.0	2.7	0.37	0.20
C_2H_n[g]	0.011	9.7	14.9	0.07	0.17
MeOH	0.001	0.5	2.7	0.37	0.00
AcH	0.005	4.2	2.6	0.38	0.01
EtOH	0.006	5.1	10.3	0.10	0.06
0.6 g Rh/SiO_2[j]					
CH_4	0.069	64.0	2.8	0.35	0.20
C_2H_n[g]	0.011	9.8	14.8	0.07	0.16
MeOH	0.001	0.5	3.6	0.28	0.00
AcH	0.005	4.7	3.6	0.28	0.02
EtOH	0.005	5.0	10.3	0.10	0.06
1.0 g Rh/SiO_2[k]					
CH_4	0.073	70.0	3.1	0.32	0.22
C_2H_n[g]	0.009	8.9	13.6	0.07	0.13
MeOH	0.001	0.6	4.2	0.24	0.00
AcH	0.003	3.2	4.0	0.25	0.01
EtOH	0.005	4.5	10.6	0.09	0.05

[a] Reaction was carried out at 250 °C; $P = 1.8$ atm, flow rate = 30 mL/min (H_2:He:CO = 6:1:3). The measurements reported were done after 15 h of reaction when steady state was reached. All reactions were carried out at differential conversions with % CO conversion <5%.

[b] Steady-state rate.

[c] Carbon selectivity = $n_i C_i / \sum n_i C_i$.

[d] Surface residence time of intermediates.

[e] $TOF_{ITK,\,i} = 1/\tau_i$.

[f] $N_i = Rate_i * \tau_i$.

[g] Hydrocarbons with 2 carbons.

[h] Experimental errors of all the results for CH_4 and C_2H_n are ± 5%; experimental errors of all the results for MeOH and AcH are ±12%; experimental errors of all the results for EtOH are ±8%.

[i] 0.2 g catalyst was used with 2.8 g α-Al_2O_3 dilution.

[j] 0.6 g catalyst was used with 2.4 g α-Al_2O_3 dilution.

[k] 1.0 g catalyst was used with 2 g α-Al_2O_3 dilution.

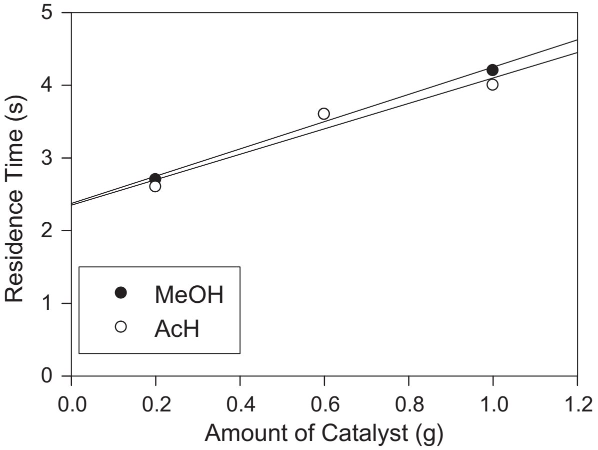

Fig. 3. The change in surface residence times for MeOH and AcH formation with different amounts of Rh/SiO_2 catalyst.

With respect to the surface reaction residence time for each individual product, the residence time for C_2H_n was the longest among all the C_1–C_2 hydrocarbon and oxygenate products. The surface reaction residence time for MeOH was somewhat shorter than that for CH_4, but the selectivity to CH_4 was more than 100 times than that for MeOH. The concentration of intermediates for EtOH was larger than that for AcH, but the turnover frequency (TOF_{ITK}) of sites based on SSITKA ($TOF_{ITK,\,i} = 1/\tau_i$) for AcH formation was higher than that for EtOH formation. It is interesting to note that the residence time for MeOH was about the same as AcH, while the selectivity for AcH was around an order of magnitude greater than that for MeOH.

4. Discussion

4.1. Relationship between selectivity and surface reaction residence time

One advantage of SSITKA is that it can provide the surface reaction residence time and the concentration of active intermediates on the surface without having to know the details of the reaction mechanism. However, with these parameters, a proposed mechanism should be able to be after disproved or substantiated. Before analysis and discussion of the detailed mechanism of CO hydrogenation on Rh/SiO_2 based on the SSITKA, it is useful to present some basic definitions and parameter relationships.

In terms of measured rate of reaction,

$$R_i = \frac{1}{\tau_i} N_i,$$

where R_i represents the reaction rate to produce the specific product i, and N_i represents the amount of active intermediates (in terms of carbon atoms) on the surface that leads to product i [71]. In the case of SSITKA of CO hydrogenation, these parameters can be determined for any reactant or product molecules containing carbon (since carbon is isotopically traced). N_i is closely related to the number of active sites on the catalyst surface at any time used for product i formation [71]. Residence time of a product, τ_i (the average surface reaction residence time to form i), is equal to the sum of all the reaction residence times for the intermediates leading to that particular product i.

If two products share any intermediates (and hence also the same type of sites), the ratio between their selectivities (S_i) should be related to the inverse of the τ_is. For example, if

$\tau_1 > \tau_2$,

then it must be that

$N_1 < N_2$,

due to the probability that more active intermediates will form product 2 due to its faster formation rate (smaller τ_i) than will form product 1. Thus, since both $N_1 < N_2$ and $(1/\tau_1) < (1/\tau_2)$,

$$(1/\tau_1) \times N_1 < (1/\tau_2) \times N_2.$$

And, by definition,

$R_1 < R_2$.

Thus,

$S_1 < S_2$.

So, in summary, if two products share any carbon-containing intermediates, if $\tau_1 > \tau_2$, then $S_1 < S_2$. If not, they do not share any intermediates in their many formation routes, unless somehow secondary reaction could decrease the amount of product 2 detected.

4.2. Relationship between CH_4 and MeOH formation

Comparing our results with the mechanism shown in Fig. 4, which is essentially that used by Choi and Liu [32] and Storsaeter et al. [18], the following points can be made:

(a) According to this mechanism, if the surface reaction residence time for CH_4 is larger than that for MeOH, the selectivity to MeOH should be larger than that of CH_4 since they are formed on the same type of site and share at least some intermediates in their formation. However, in our results for Rh/SiO_2, the selectivity to CH_4 was nearly 120 times larger than that for MeOH, but the surface reaction residence time for CH_4 was slightly longer than that for MeOH (2.7 vs. 2.3 s).

(b) The –CH_3OH or/and –CH_3 species on the surface may also take part in other product formations. For instance, if there is a large amount of –CH_3 species that also take part in C_{2+} hydrocarbon or oxygenate formation, then the selectivity to CH_4 should be even lower than expected. However, this is not the case since S_{CH_4} is more than 100 times larger than S_{MeOH}. It was proposed by Takeuchi et al. [72] that EtOH could be formed from MeOH homologation in CO hydrogenation, which could explain low MeOH selectivity and the high selectivity ratio. But there was no dimethyl ether detected in the system to prove the further reaction of MeOH (MeOH homologation or condensation/coupling) on the surface.

(c) If the formation routes of MeOH and CH_4 share at least one common intermediate on the same kind of active sites, it is impossible to explain based on SSITKA data the big difference between selectivities to MeOH and to CH_4 with no such difference between their formation residence times.

Thus, even though the reaction mechanism on Rh(1 1 1) and other metals has been proposed based on theoretical calculation, the modeling work assumed that the same reaction sites were used to produce CH_4 and MeOH. If there were only one kind of reaction sites on Rh/SiO_2, all carbon-containing products would share at least one common intermediate, adsorbed CO. This appears not to be true for CH_4 and MeOH formation on Rh/SiO_2. Thus, it is probable that there is more than one kind of sites on the catalyst surface. The SSITKA results suggest that most of the active sites for MeOH and CH_4 formation are different and indicate that there are many more sites producing CH_4 than sites producing MeOH. As shown in Table 1, the number of intermediates (N_i) on the Rh/SiO_2 catalyst used for CH_4 formation was around 20 μmol/g cat, while for MeOH, it was less than 0.01 μmol/g cat. Thus, the selectivity to CH_4 was much larger than that for MeOH even through the intrinsic rates of formation (inverse residence times) were similar.

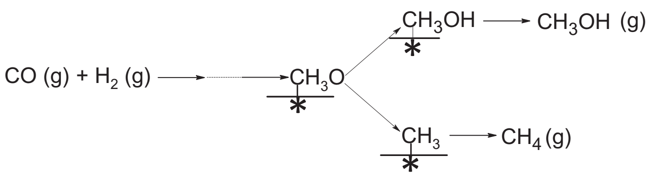

Fig. 4. Recently proposed pathways of MeOH and CH_4 formation during CO hydrogenation (based on Refs. [18,32]).

In short, the assumption of a single type of site would appear to be the most fundamental cause for the failure of the mechanism shown in Fig. 4 to apply to CO hydrogenation on supported Rh or possibly Rh clusters with different crystalline faces, as gleamed from for the formation of CH_4 and MeOH. Different from perhaps Rh(1 1 1), it is reasonable that there would be more than one kind of Rh sites on the Rh/SiO_2 catalyst surface. As a matter of fact, while Yates et al. [73] detected only one single hydrogen desorption peak for Rh(1 1 1) with TPD, in our previous study [74] two hydrogen desorption peaks were detected for Rh/SiO_2, which is similar to the results of Bertucco and Bennett [75] results for a 10% Rh/SiO_2 catalyst. It is well known that besides increasing the dispersion of Rh, a support may interact with Rh due to SMOI, affecting the morphology of the Rh clusters, the oxidation state and stability of reaction intermediates [65,75–80]. Thus, it may be reasonable that Rh/SiO_2 would show different behavior from Rh(1 1 1) in CO hydrogenation. However, Choi and Liu [32] had no experimental selectivity data for comparison when they did their modeling work on Rh(1 1 1).

We, thus, cannot rule out that CH_4 and MeOH may be able to be made on the same sites on Rh(1 1 1). Our conclusions are based and applied only to the system we studied, Rh/SiO_2. However, our results do serve as a caution to using the assumption that CH_4 and MeOH share intermediates, no matter how attractive such a possibility is, for heterogeneous catalyst surfaces.

4.3. Relationship between the formation of C_2 products and C_1 products

Due to the complexity in the chain growth step, there are few detailed studies in the literature regarding the mechanism of C_2 product synthesis, especially for C_2 oxygenates.

Table 1 shows that the selectivity to MeOH was significantly lower than that for any of the C_2 products (AcH, EtOH or C_2H_n) and that the surface reaction residence time for MeOH formation was much shorter. If MeOH and any C_2 products (hydrocarbons and oxygenates) shared an intermediate (–CH_xO), C_2 product selectivity should have been lower than that for MeOH since all of the C_2 products had longer surface reaction residence times than MeOH. Thus, it is unlikely for any of the C_2 products to have shared an intermediate with MeOH on Rh/SiO_2.

On the other hand, the selectivity to CH_4 was higher than that for any of the C_2 products, and the surface reaction residence time for CH_4 was shorter. Thus, the possibility that all C_2 products share intermediates on the same active sites with CH_4 is possible and cannot be excluded.

4.4. Relationship of AcH and C_2H_n formation

It is interesting to note that the surface reaction residence time for C_2H_n synthesis was longer than that for any other C_1–C_2 product, while the selectivity for C_2H_n was not the lowest, which sug-

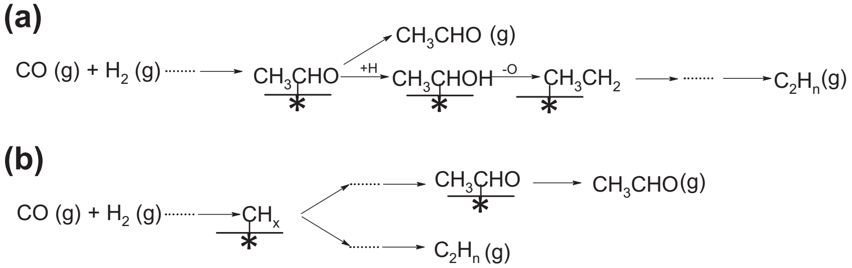

Fig. 5. Recently proposed pathways of AcH and C_2 hydrocarbon formation during CO hydrogenation: (a) from Ref. [18] and (b) from Ref. [33].

gests that the mechanism for C_2H_n synthesis is perhaps more complex than the mechanisms for the other products discussed earlier. Fig. 5 shows two popular mechanisms recently proposed for C_2H_n formation. One is related to AcH formation as an integral part to forming C_2 hydrocarbons [18], as shown in possibility 5a; the other one has AcH and C_2H_n sharing a common $-CH_x$ intermediate, with different chain growth steps to produce AcH or C_2H_n, as shown in possibility 5b [33].

Following the same logical reasoning applied earlier, possibility 5a is not valid for Rh/SiO_2 because $\tau_{C_2H_n}$ was significant longer than τ_{AcH} (14.4 vs. 4.1 s), but $S_{C_2H_n}$ was larger than S_{AcH} (9.5% vs. 4.1%). Possibility 5b is more likely to be true on Rh/SiO_2. The fact that S_{AcH} was lower than expected could be explained by the further reaction of the intermediates to form other products (e.g., $-C_2H_xO$ may be an intermediates for both AcH, EtOH and C_3H_xO formation). However, there have been few studies on the mechanism of C_{2+} hydrocarbon and oxygenate synthesis on Rh-based catalysts so far, and the SSITKA results are not sufficient yet to elucidate the mechanism further.

4.5. Relationship of EtOH and AcH formation

There has been disagreement as to the relationship between AcH and EtOH formation in the literature [6,18,32,33,60,72,81–84]. The SSITKA results obtained in this work, however, can be used to provide more insight regarding the mechanism for the formation of EtOH and AcH.

Fig. 6a and b shows two of the most popular and recently published routes for AcH and EtOH formation during CO hydrogenation. One possibility, 6a, as proposed by Storsaeter et al. [18] and Mei et al. [33], is that some AcH formed on the surface desorbs, while the rest goes through two-step hydrogenation to form EtOH. The other possibility, 6b, as proposed by Choi and Liu [32], is more complex with EtOH and AcH sharing the same intermediates through CH_3CO–, which is then hydrogenated to CH_3CHO– and $CH_3C(OH)$–, precursors for AcH and EtOH, respectively.

If possibility 6a is true, it requires two hydrogenation steps to produce EtOH from AcH. This should result in a higher selectivity to AcH since τ_{AcH} is shorter than τ_{EtOH} ($\tau_{AcH} \approx 2.3$ s, $\tau_{EtOH} \approx 10.4$ s) – but this is contradictory to our reaction results since $S_{AcH} \approx S_{EtOH}$. It might be expected that EtOH could also be produced during the readsorption of AcH, but this does not appear to be the case since τ_{EtOH} did not vary with the amount of the catalyst used, within experimental error. This would have been happened if readsorption and subsequent reaction played a significant role in the formation of EtOH.

Similarly, using the same reasoning, possibility 6b would appear not to be valid for our system either. With certain intermediates shared by both AcH and EtOH, the expected selectivity to AcH should have been larger than that for EtOH because of $\tau_{AcH} < \tau_{EtOH}$. Thus, both possibilities 6a and b can be ruled out with the same reasoning.

However, as is shown in 6c, if adsorbed AcH could further react to form other products, it would be reasonable that the selectivity for AcH was lower than expected, even close to the selectivity for EtOH. However, based on the detailed study of this possibility in Section 4.4, this is also unlikely to happen on Rh/SiO_2.

Thus, none of the popular mechanisms presented recently can explain our SSITKA results for the formation of EtOH and AcH. Although the secondary reaction of AcH to form EtOH by hydrogenation cannot be excluded since it is well known that hydrogenation of AcH can be carried out under mild conditions [83], under

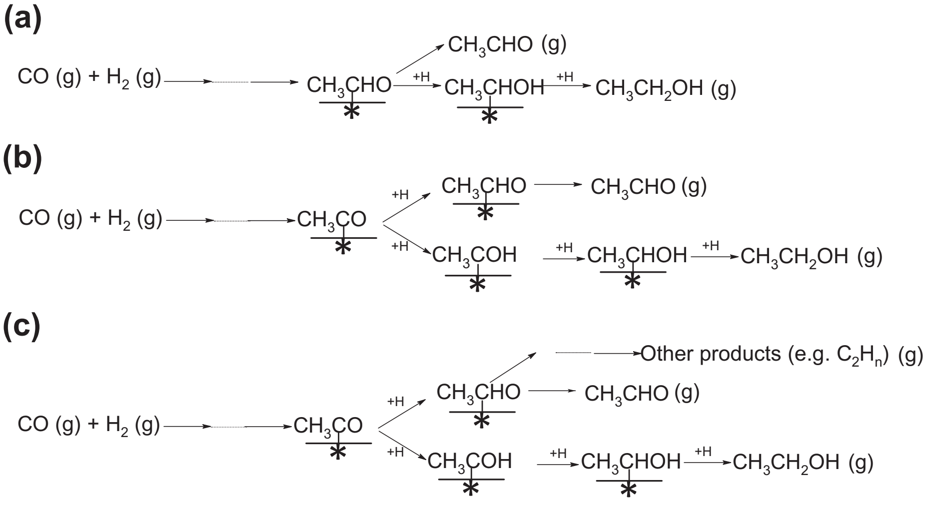

Fig. 6. Recently proposed pathways of AcH and EtOH formation during CO hydrogenation: (a) from Ref. [33], (b) from Ref. [32], and (c) from Ref. [18].

our reaction conditions, the secondary reaction of AcH to form EtOH on the same active Rh sites does not appear to be a dominant pathway for EtOH formation. Thus, it is highly likely that the mechanism for AcH and EtOH formation is much more complex than expected and cannot be resolved based on our results here.

5. Conclusions

In this study, the mechanistic pathways for different product formations in CO hydrogenation on Rh/SiO_2 were for the first time studied at the site level using multicomponent SSITKA. Different from other products, it was found that neither MeOH nor AcH readsorption could be neglected on Rh/SiO_2 and had to be accounted for. It appears likely that, for Rh/SiO_2, MeOH and CH_4 are produced on different kinds of sites. Moreover, the number of sites producing CH_4 on such a catalyst surface is more than 100 times larger than those producing MeOH. It is also unlikely that MeOH shares any intermediates with C_2 products (hydrocarbons and oxygenates). By comparing different currently proposed possibilities for AcH and EtOH formation, it is concluded that the actual mechanism for the formation of these products is complicated and needs further investigation.

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References

[1] J.R. Rostrup-Nielsen, in: J.R. Anderson, M. Boudart (Eds.), Catalysis-Science and Technology, vol. 5, Springer Verlag, Berlin/New York, 1984.
[2] I. Wender, Catal. Rev. Sci. Eng. 14 (1976) 97.
[3] J.J. Spivey, A.A. Egbebi, Chem. Soc. Rev. 36 (2007) 1514.
[4] M. Ichikawa, Bull. Chem. Soc. Jpn. 51 (1978) 2273.
[5] M. Ichikawa, J. Chem. Soc., Chem. Commun. 13 (1978) 566.
[6] R.P. Underwood, A.T. Bell, Appl. Catal. 21 (1986) 157.
[7] R.P. Underwood, A.T. Bell, Appl. Catal. 34 (1987) 289.
[8] F. Fischer, H. Tropsch, Brennst. Chem. 4 (1923).
[9] B. Sarup, B.W. Wojciechowski, Can. J. Chem. Eng. 67 (1989) 620.
[10] B. Sarup, B.W. Wojciechowski, Can. J. Chem. Eng. 67 (1989) 62.
[11] I.C. Yates, C.N. Satterfield, Energy Fuels 5 (1991) 168.
[12] J.M.H. Lo, T. Ziegler, J. Phys. Chem. C 111 (2007) 11012.
[13] G.P. van der Laan, A.A.C.M. Beenackers, Appl. Catal. A: Gen. 193 (2000) 39.
[14] C.S. Kellner, A.T. Bell, J. Catal. 70 (1981) 418.
[15] C.G. Takoudis, Ind. Eng. Chem. Proc. Des. Dev. 23 (1984) 149.
[16] N.V. Pavlenko, Y.I. Pyatnitskii, Theor. Exp. Chem. 33 (1997) 254.
[17] A.I. Tripol'skii, N.V. Pavlenko, G.D. Zakumbaeva, Theor. Exp. Chem. 33 (1997) 165.
[18] S. Storsaeter, D. Chen, A. Holmen, Surf. Sci. 600 (2006) 2051.
[19] O.R. Inderwildi, S.J. Jenkins, D.A. King, J. Phys. Chem. C 112 (2008) 1305.
[20] C. Mazzocchia, P. Gronchi, A. Kaddouri, E. Tempesti, L. Zanderighi, A. Kiennemann, J. Mol. Catal. A: Chem. 165 (2001) 219.
[21] B.H. Davis, Fuel Process. Technol. 71 (2001) 157.
[22] C.F. Huo, Y.W. Li, J.G. Wang, H.J. Jiao, J. Phys. Chem. C 112 (2008) 14108.
[23] M.A. Vannice, J. Catal. 37 (1975) 449.
[24] I.A. Fisher, A.T. Bell, J. Catal. 162 (1996) 54.
[25] K.J. Williams, A.B. Boffa, M. Salmeron, A.T. Bell, G.A. Somorjai, Catal. Lett. 9 (1991) 415.
[26] G.A. Huff, C.N. Satterfield, Ind. Eng. Chem. Proc. Des. Dev. 23 (1984) 696.
[27] Y. Mori, T. Mori, T. Hattori, Y. Murakami, Appl. Catal. 66 (1990) 59.
[28] E. Shustorovich, A.T. Bell, J. Catal. 113 (1988) 341.
[29] Y. Mori, T. Mori, T. Hattori, Y. Murakami, Appl. Catal. 55 (1989) 225.
[30] S. Shetty, A.P.J. Jansen, R.A. van Santen, J. Am. Chem. Soc. 131 (2009) 12874.
[31] M.K. Zhuo, K.F. Tan, A. Borgna, M. Saeys, J. Phys. Chem. C 113 (2009) 8357.
[32] Y. Choi, P. Liu, J. Am. Chem. Soc. 131 (2009) 13054.
[33] D. Mei, R. Rousseau, S.M. Kathmann, V.-A. Glezakou, M.H. Engelhard, W. Jiang, C. Wang, M.A. Gerber, J.F. White, D.J. Stevens, J. Catal. 271 (2010) 325.
[34] S.L. Shannon, J.G. Goodwin Jr., Chem. Rev. 95 (1995) 677.
[35] P. Biloen, J. Mol. Catal. 21 (1983) 17.
[36] C.O. Bennett, ACS Symp. Ser. 178 (1982) 1.
[37] J. Happel, Chem. Eng. Sci. 33 (1978) 1567.
[38] N. Lohitharn, J.G. Goodwin Jr., J. Catal. 257 (2008) 142.
[39] K. Sudsakorn, J.G. Goodwin, A.A. Adeyiga, J. Catal. 213 (2003) 204.
[40] C.A. Mims, L.E. Mccandlish, J. Am. Chem. Soc. 107 (1985) 696.
[41] C.A. Mims, L.E. Mccandlish, J. Phys. Chem. 91 (1987) 929.
[42] D.M. Stockwell, D. Bianchi, C.O. Bennett, J. Catal. 113 (1988) 13.
[43] S.H. Ali, J.G. Goodwin Jr., J. Catal. 176 (1998) 3.
[44] S.H. Ali, J.G. Goodwin Jr., J. Catal. 171 (1997) 333.
[45] S.H. Ali, J.G. Goodwin Jr., J. Catal. 171 (1997) 339.
[46] S.H. Ali, J.G. Goodwin Jr., J. Catal. 170 (1997) 265.
[47] S. Vada, B. Chen, J.G. Goodwin, J. Catal. 153 (1995) 224.
[48] V. Froseth, S. Storsaeter, O. Borg, E.A. Blekkan, M. Ronning, A. Holmen, Appl. Catal. A: Gen. 289 (2005) 10.
[49] C.A. Mims, Catal. Lett. 1 (1988) 293.
[50] D.M. Stockwell, C.O. Bennett, J. Catal. 110 (1988) 354.
[51] D.M. Stockwell, J.S. Chung, C.O. Bennett, J. Catal. 112 (1988) 135.
[52] K.R. Krishna, A.T. Bell, J. Catal. 130 (1991) 597.
[53] P. Winslow, A.T. Bell, J. Catal. 86 (1984) 158.
[54] T.E. Hoost, J.G. Goodwin Jr., J. Catal. 137 (1992) 22.
[55] A.M. Efstathiou, T. Chafik, D. Bianchi, C.O. Bennett, J. Catal. 148 (1994) 224.
[56] A.M. Efstathiou, T. Chafik, D. Bianchi, C.O. Bennett, J. Catal. 147 (1994) 24.
[57] A.M. Efstathiou, T. Chafik, D. Bianchi, C.O. Bennett, Stud. Surf. Sci. Catal. 75 (1993) 1563.
[58] A.M. Efstathiou, C.O. Bennett, J. Catal. 120 (1989) 137.
[59] A.M. Efstathiou, C.O. Bennett, Chem. Eng. Commun. 83 (1989) 129.
[60] S.D. Jackson, B.J. Brandreth, D. Winstanley, J. Catal. 106 (1987) 464.
[61] T. Koerts, W.J.J. Welters, R.A. Vansanten, J. Catal. 134 (1992) 1.
[62] T. Koerts, R.A. Vansanten, J. Catal. 134 (1992) 13.
[63] S.S.C. Chuang, M.A. Brundage, M.W. Balakos, Appl. Catal. A: Gen. 151 (1997) 333.
[64] A.M. Efstathiou, J. Mol. Catal. 67 (1991) 229.
[65] S.S.C. Chuang, R.W. Stevens Jr., R. Khatri, Top. Catal. 32 (2005) 225.
[66] N.P. Socolova, Colloids Surf. A: Physicochem. Eng. Aspects 239 (2004) 125.
[67] H. Hayashi, M. Kishida, K. Wakabayashi, Catal. Surv. Jpn. 6 (2002) 9.
[68] J. Gao, X. Mo, A.C. Chien, W. Torres, J.G. Goodwin Jr., J. Catal. 262 (2009) 119.
[69] A. Egbebi, J.J. Spivey, Catal. Commun. 9 (2008) 2308.
[70] S. Hammache, J.G. Goodwin Jr., S.L. Shannon, S.Y. Kim, Encyclopedia Surf. Colloid Sci. 1 (2002) 2445.
[71] J.G. Goodwin Jr., S. Kim, W.D. Rhodes, Catalysis 17 (2004) 320.
[72] A. Takeuchi, J.R. Katzer, R.W. Crecely, J. Catal. 82 (1983) 474.
[73] J.T. Yates, P.A. Thiel, W.H. Weinberg, Surf. Sci. 84 (1979) 427.
[74] X. Mo, J. Gao, N. Umnajkaseam, J.G. Goodwin Jr., J. Catal. 267 (2009) 167.
[75] A. Bertucco, C.O. Bennett, Appl. Catal. 35 (1987) 329.
[76] P.R. Watson, G.A. Somorjai, J. Catal. 72 (1981) 347.
[77] A.L. Borer, R. Prins, Stud. Surf. Sci. Catal. 75 (1993) 765.
[78] H. Arakawa, K. Takeuchi, T. Matsuzaki, Y. Sugi, Chem. Lett. 9 (1984) 1607.
[79] M. Ojeda, S. Rojas, M. Boutonnet, F.J. Perez-Alonso, F.J. Garcia-Garcia, J.L.G. Fierro, Appl. Catal. A: Gen. 274 (2004) 33.
[80] H. Kusama, K.K. Bando, K. Okabe, H. Arakawa, Appl. Catal. A: Gen. 197 (2000) 255.
[81] Y. Wang, H.Y. Luo, D.B. Liang, X.H. Bao, J. Catal. 196 (2000) 46.
[82] H. Orita, S. Naito, K. Tamaru, J. Catal. 90 (1984) 183.
[83] R. Burch, M.I. Petch, Appl. Catal. A: Gen. 88 (1992) 61.
[84] M. Ichikawa, T. Fukushima, J. Chem. Soc. Chem. Commun. 6 (1985) 321.