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Two-Step Homologation of Methane on Supported Co Catalysts

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Methane homologation has been investigated over Co/SiO_2 catalysts at a CH_4 activation temperature of 450°C. At this temperature, the total moles of CH_x ($x = 0, 1, 2, 3$) accumulated on the catalyst surface was significantly greater than the moles of surface Co, and the 3% C_{2+} yield/site obtained from hydrogenation of the CH_x species at 100°C was significantly higher than the $<1\%$ reported in previous studies. However, a significant fraction of the CH_4 produced inactive carbon and this led to catalyst deactivation during repeated cycling. C_{2+} selectivity decreased when the deposit was aged at either 450 or 100°C and when the activation temperature decreased. These trends were related to changes in the H content of the CH_x species, with $x = 1$ giving the highest C_{2+} selectivity. Generation of C_{2+} products in the second step by isothermal (100°C) reaction in Ar instead of H_2 demonstrated that C–C bond formation occurred after activation, whereas the presence of H_2 facilitated hydrogenation and hydrogenolysis of C–C surface species, thereby decreasing C_{2+} selectivity in comparison with Ar. © 1999 Academic Press

INTRODUCTION

In the two-step CH_4 homologation reaction (1–4), CH_4 is initially activated on a transition metal catalyst at high temperature and low H_2 partial pressure, generating H_2 and surface CH_x species, with $x = 0, 1, 2,$ or 3. Subsequently, the CH_x species are hydrogenated at low temperature and high H_2 partial pressure to yield CH_4 and higher hydrocarbons such as C_2H_6 and C_3H_8, herein referred to collectively as C_{2+} products.

In previous studies, CH_4 activation was performed over supported group VIII metal catalysts either at high temperature (300–430°C) in a dilute stream of CH_4 (2, 5), or with short pulses of CH_4 introduced to the feed gas (6), or at temperatures below 300°C (3). In each case the moles of CH_4 reacted per mole of surface metal atoms was less than one; i.e., the (nominal) coverage of the metal by CH_x species was <1. The C_{2+} yield/site, defined as the moles of C_{2+} product per mole of surface metal, reported in these studies was less than 1% (2, 5, 7).

Three different types of surface carbonaceous species have been identified on the catalyst following CH_4 activation using temperature-programmed surface reaction (TPSR) in H_2 (2). The relative amount of each species depends on the metal coverage and only the most reactive species produce C_{2+} in the isothermal hydrogenation step. Exposure of the carbonaceous species to high temperature results in an "aging" phenomenon by which active carbonaceous species transform to less active species (1, 8). Hence the type, amount, thermal history, and age of the carbonaceous deposit influence the C_{2+} yield.

One possible approach to increasing C_{2+} yield is to increase the surface concentration of the most active carbonaceous species. The objective of the present study was to determine if this may be achieved by increasing the concentration of CH_4 in the feed and reacting more CH_4 during the activation step. The present authors recently proposed a kinetic model for CH_4 decomposition over Co catalysts under conditions of high CH_4 concentration in the feed and high activation temperature (450°C) (9). Under these conditions, the rate of CH_4 decomposition (reported per mole of surface Co available initially) increased to a maximum within the first 30 s of CH_4 exposure, followed by a rapid decline to a steady, nonzero decomposition rate within 1 min. The decomposition rate continued at this level and after 2 min reaction, the CH_x species had an average H content corresponding to $x \approx 1$. The observed CH_4 decomposition kinetics were well described by a model that included migration of the CH_x species from the Co surface to the support that allowed CH_4 decomposition to continue beyond a nominal monolayer coverage of the Co by CH_x.

In the present study, the relative amount and reactivity of the different surface carbon species that result from the decomposition of CH_4 at 450°C are examined. The effect of aging of the carbonaceous deposit on reactivity and the effect of operating conditions are reported. Furthermore, in previous studies, C_{2+} and CH_4 were produced by isothermal hydrogenation in the second step but the significance of the reaction medium (H_2) used in this step has not been addressed (1, 2, 5, 6, 10–12). In the present work, the isothermal step is carried out using different gases in an attempt to examine this issue.

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EXPERIMENTAL

Two different batches of supported Co catalysts were prepared by incipient wetness impregnation of precalcined (25 h at 500°C) silica gel (Grade 62, Aldrich) with $Co(NO_3)_2 \cdot 6H_2O$. Catalyst series A was vacuum-dried at 100°C for 37 h after impregnation and then calcined for 10 min at 450°C. Catalyst series B was simply dried for at least 10 days at 110°C after impregnation. The catalysts were then reduced by temperature-programmed reduction (TPR) in a 60 ml/min flow of 20% H_2/80% Ar using a temperature ramp of 10°C/min up to the maximum temperature of 450°C. Catalyst properties including extent of reduction of cobalt oxides to zero-valent Co and metal dispersion were determined by powder X-ray diffraction (XRD), TPR, and Co reoxidation procedures, details of which have been reported previously (9).

The reactor setup consisted of multiport feed gas selection valves, mass flow controllers, and a fixed-bed microreactor loaded with 0.5 g of catalyst. The U-tube quartz microreactor with an in-bed thermowell and fused silica catalyst support was heated using a temperature-controlled furnace. The reactor product analysis section comprised a thermal conductivity detector (TCD), a quadrupole mass spectrometer (QMS), and a gas chromatograph (GC) equipped with a 10-loop sampling valve and a flame ionization detector (FID).

The two-step homologation reaction sequence was sometimes followed by two additional reaction steps to ensure complete recovery of the carbon deposited during the CH_4 activation step. The full sequence of steps proceeded as follows: After reduction of the catalyst and Ar purge of the reactor, CH_4 was activated (or decomposed) on the reduced Co–SiO_2 catalyst by exposing the catalyst to a 54 ml/min flow of 5% CH_4/95% Ar at 450°C for a period of 1 to 7 min. The reactor effluent was monitored with the QMS during this activation step. After rapid cooling to 100°C in <30 s and purging in 54 ml/min of Ar for 5 min, the carbonaceous deposit was aged for approximately 20 min in static Ar (the aging time for the carbonaceous deposit). The resulting carbonaceous species were then hydrogenated isothermally at 100°C to complete the two-step reaction cycle, producing higher hydrocarbons and CH_4. The Ar purge was designed to remove any residual CH_4 from the reactor following activation so that an accurate measure of CH_4 and C_{2+} production in the subsequent isothermal hydrogenation could be made. Although it is possible that some hydrocarbons were removed from the catalyst during this Ar purge, monitoring this step by QMS showed insignificant amounts of C_{2+}. To ensure complete recovery of the carbon deposited in the activation step, a TPSR with H_2 and a temperature-programmed oxidation (TPO) followed.

Details of the experimental setup, catalyst reduction, and CH_4 activation steps have been reported previously (9). In the isothermal hydrogenation step, the catalyst was exposed to 11 ml/min H_2 at 100°C for 10 min. The reaction products were monitored with the QMS and nine gas samples of the reactor effluent were taken in 1-min intervals using the GC multiloop automatic sampling valve. The GC analysis was done using the FID and a 5 ft (1.5 m) × $\frac{1}{8}$ in. (3.2 mm) 60/80 Carbosieve G packed column (Supelco Canada Ltd) with 30 ml/min of UHP-grade He carrier gas for separation of CH_4, C_2H_4, C_2H_6, C_3H_6, and C_3H_8. The gas chromatograph was calibrated regularly with an analyzed calibration gas mixture (Praxair).

The isothermal hydrogenation was followed by the TPSR in H_2 to quantify the amount and reactivity of the less active carbon species. For the TPSR, 11 ml/min of H_2 flowed through the reactor while the reactor temperature was increased from 30 to 700°C at 15°C/min. The reaction products were monitored with the calibrated QMS.

TPO was used to quantify the carbon species that did not react with H_2. After the TPSR in H_2, the reactor was cooled and flushed in He. The catalyst was then exposed to a flow of 11 ml/min O_2 (UHP, Praxair) while the reactor temperature was increased from 40 to 700°C at 15°C/min. CO_2 production was monitored with the QMS.

RESULTS

1. Carbon Recovery

Figure 1 shows the profiles of CH_4, C_2H_4, and C_2H_6 production as a function of time during isothermal hydrogenation, after a 2-min activation of 5% CH_4/Ar at 450°C over

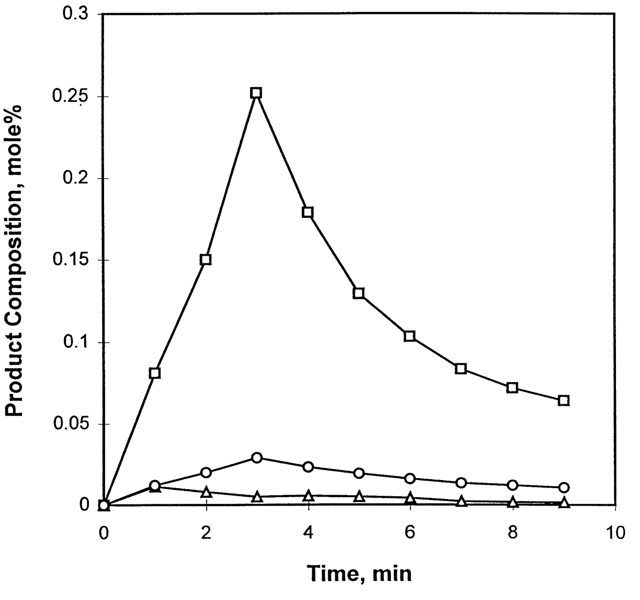

FIG. 1. Profiles of CH_4 (□), C_2H_6 (○), and C_2H_4 (△) production as a function of isothermal hydrogenation at 100°C in 11 ml/min H_2 flow over the A-series 12% Co–SiO_2 catalyst after 2 min activation with 5% CH_4/Ar mixture at 450°C.

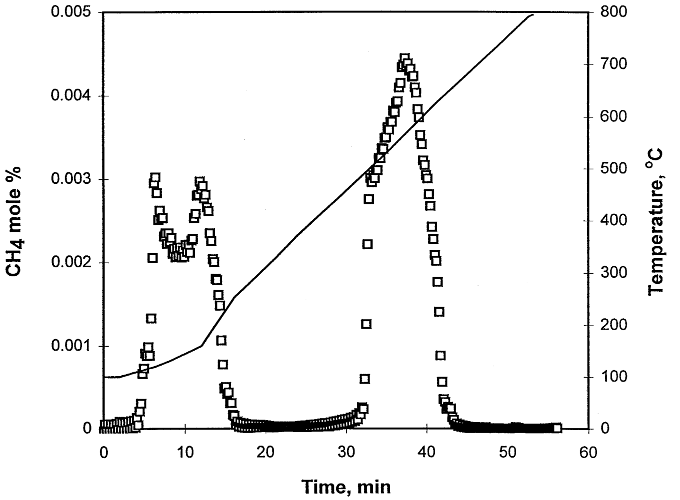

FIG. 2. Profiles of CH_4 production (□) and temperature (—) as a function of time in temperature-programmed surface reaction (TPSR) in 11 ml/min of H_2 flow on A-series 12% Co–SiO_2 catalyst. Activation of CH_4 (2 min flow of 5% CH_4/Ar mixture at 450°C) followed by 10 min isothermal hydrogenation at 100°C.

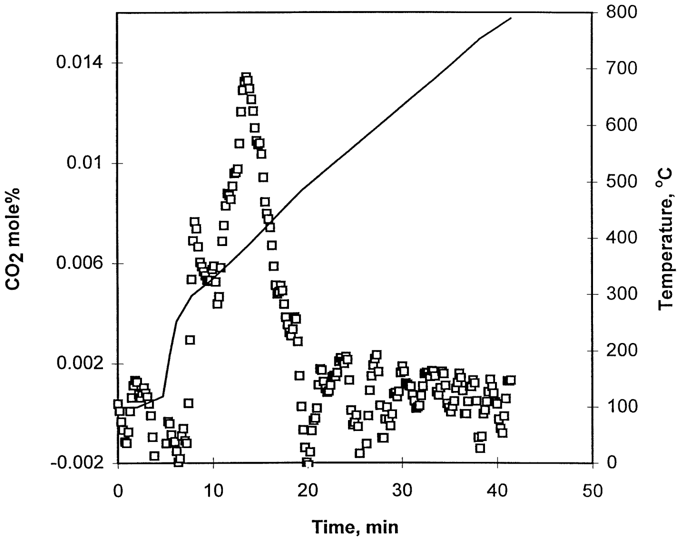

FIG. 3. Profiles of CO_2 production (□) and temperature (—) as a function of time during temperature-programmed oxidation (TPO) in 11 ml/min of O_2 flow on A-series 12% Co–SiO_2 catalyst. Activation: 2 min flow of 5% CH_4/Ar mixture at 450°C.

the A-series 12% Co–SiO_2 catalyst. The total number of moles of each hydrocarbon and the carbon selectivity to C_{2+} products were calculated by numerical integration of the production profiles. TPSR in H_2 followed the 10-min isothermal hydrogenation, with CH_4 being the only significant product. Figure 2 shows that two peaks occurred in CH_4 production: one at about 200°C and the other at 540°C. Hence, in terms of reactivity to H_2, three types of carbon deposit were identified. Previous studies have classified these species as C_α, C_β, and C_γ, in order of their decreasing reactivity to H_2 (2), and a similar classification is valid here.

TPO was the final step in accounting for all the carbon deposited during CH_4 activation and Fig. 3 shows the CO_2 generated during TPO. Integration of this profile yielded the amount of inactive carbon not removed by TPSR in H_2. During TPO, the mass numbers 18, 31, and 28 corresponding to H_2O, CH_3OH, and CO were also monitored. H_2O showed a distinct peak due to oxidation of hydrogen adsorbed on the catalyst and this corresponded to the rapid initial increase in reactor temperature shown in Fig. 3. There was no evidence for CH_3OH or CO production.

Table 1 compares the amounts of deposited and recovered carbon from each reaction step over the 12% Co/SiO_2 catalyst. About 10% of the deposited carbon was recovered by isothermal hydrogenation, 60% by TPSR in H_2, and most importantly approximately 30% was inactive toward hydrogenation and was recovered only by TPO. The average error between the moles of CH_4 reacted in the activation step and the moles of carbon recovered, based on a number of repeated experiments (not shown), was ±20%. In previous studies (2, 5, 13–15), the amount of carbon recovered from the isothermal hydrogenation and TPSR was assumed to equal the carbon deposited in the activation step. Table 1 shows that under the conditions of the present study, a significant fraction of the deposited carbon was inactive toward hydrogen. Product yield data are therefore based on the total moles of carbon deposited in the activation step and not on the carbon recovered in the isothermal and TPSR hydrogenations.

TABLE 1

Carbon Recovery after CH_4 Activation at 450°C for 2 min Using the 12% Co–SiO_2 A-Series Catalyst

Reaction sequence	Complete cycle[a]	Complete cycle excluding hydrogenations[b]
CH_4 activation		
CH_4 reacted at 450°C for 2 min (μmol CH_4 converted)	61	63
Carbon recovery		
Isothermal hydrogenation at 100°C		
C recovered as $CH_4 + C_{2+}$ (μmol)	5	—
TPSR in H_2		
C recovered as CH_4 (μmol)	29	—
TPO		
C recovered as CO_2 (μmol)	15	65
Total C recovered (μmol)	49	65
Error (%)[c]	−20	+3

[a] The complete cycle consisted of activation at 450°C, isothermal hydrogenation at 100°C, TPSR in H_2, and TPO.

[b] The isothermal hydrogenation and TPSR in H_2 were omitted from this experiment.

[c] Difference between C recovered and CH_4 reacted, expressed as a percentage of the CH_4 reacted.

TABLE 2

Effect of Catalyst Metal Loading on Hydrogenation of Carbonaceous Deposit over the Co–SiO_2 A-Series Catalyst[a]

Catalyst loading (wt%)	12	5	2
Extent of reduction (mol%)	85	76	42
Co dispersion (%)	5.6	5.1	5.3
CH_4 activation			
μmol CH_4/μmol Co	1.3	2.0	2.3
x of CH_x	0.9	1.3	1.6
Isothermal hydrogenation			
C_{2+} selectivity (mol%)	8	5	2
C_{2+} yield/site (mol C_{2+}/mol Co %)	0.5	0.4	0.1
C recovered in isothermal and TPSR hydrogenation (%)	29	21	12

[a] Reaction conditions: CH_4 activation at 450°C for 2 min, isothermal hydrogenation at 100°C, and TPSR in H_2.

2. *Effect of Catalyst Metal Loading*

Table 2 summarizes the properties of the Co/SiO_2 catalysts with 2, 5, and 12 wt% Co loading, examined in the present study (9). As Co loading decreased the extent of reduction decreased but the dispersion of the reduced Co was approximately the same for all three catalysts. This trend suggests an increased metal–support interaction with decreased metal loading that decreased the extent of reduction. The data in Table 2 also show that CH_4 consumption during 2 min activation at 450°C increased as the metal loading decreased. The kinetic model for CH_4 decomposition developed previously (9) assumed that the increased CH_4 consumption was a consequence of increased migration of CH_x surface species from Co to the catalyst support, which in turn resulted from a stronger metal–support interaction.

Decreasing the metal loading from 12 to 2% Co also increased the H content of the CH_x species from 0.9 to 1.6, whereas the C_{2+} selectivity obtained from the isothermal hydrogenation decreased from 8 to 2%. Hence, although the catalysts with lower loading had higher activity for CH_4 activation, they had lower selectivity for C–C bond formation. Data presented in Table 2 also show that the percentage carbon recovered by the isothermal and TPSR hydrogenation steps decreased with decreased metal loading.

3. *Effect of CH_4 Activation Time and Temperature*

The results presented in Section 2 reported C_{2+} yield following activation of CH_4 under the same reaction conditions. However, the reactivity of the carbonaceous species resulting from the CH_4 activation step is very dependent on the activation conditions. For example, increasing either the duration or the temperature of activation leads to a decrease in the amount of active carbon due to high-temperature aging (1–4). To quantify this effect in the present work, 5% CH_4/Ar was reacted on the A-series 12% Co–SiO_2 catalyst for periods of 1, 2, and 7 min.

The results, reported in Table 3, show that as the activation time increased more CH_4 was reacted and the resulting CH_x species dehydrogenated such that their H content decreased from $x = 1.1$ after 1 min activation to $x = 0$ after 7 min activation. In the subsequent isothermal hydrogenation, the amount of carbon recovered and the selectivity to C_{2+} hydrocarbons also decreased with increased activation time and the total carbon recovered in the form of CH_4 (from TPSR) increased. These data clearly show that high activation temperature and increased activation time result in a loss in reactivity of the CH_x species and lower selectivity and carbon recovery in the isothermal hydrogenation step. These results are indicative of the generation of carbon species with low H content that are less reactive not only for C–C bond formation, but also for hydrogenation to produce CH_4. It is also worth noting that the 163 μmol CH_4 produced during TPSR after 7 min activation and isothermal hydrogenation was more than the 48 μmol surface Co available on the catalyst. This suggests that in TPSR, a large amount of carbon with very low H content residing on the support was also hydrogenated. The mechanism of this phenomenon is not clear but may be related to hydrogen spillover or reverse spillover of CH_x from the support to the Co.

Decreasing the CH_4 activation temperature from 450 to 360°C decreased the moles of CH_4 reacted per mole of Co, but increased the hydrogen content of the carbon deposit as shown by the data in Table 4. In the isothermal hydrogenation step, C_{2+} production decreased from 0.22 μmol for an activation temperature of 450°C to 0.09 μmol for an activation temperature of 360°C. C_{2+} selectivity decreased by a factor of 2 as the activation temperature decreased from 450 to 360°C. In addition, the TPSR data of Table 4

TABLE 3

Effect of Activation Time on the Hydrogenation of the Carbonaceous Deposit over the 12% Co–SiO_2 A-Series Catalyst[a]

	Activation time (min)		
	1	2	7
CH_4 activation			
CH_4 consumed (μmol)	45	61	177
H_2 generated (μmol)	64	94	352
x of surface CH_x	1.1	0.9	0.0
Isothermal hydrogenation			
C_{2+} generated (μmol)	0.24	0.22	0.1
C_{2+} selectivity (%)	7	8	5
C produced (μmol)	7	5	4
TPSR in H_2			
C produced (μmol)	1	29	163

[a] Reaction conditions: CH_4 activation at 450°C, isothermal hydrogenation at 100°C and TPSR in H_2.

TABLE 4

Effect of Activation Temperature on the Hydrogenation of the Carbonaceous Deposit over the 12% Co–SiO_2 A-Series Catalyst[a]

	Activation temperature (°C)		
	360	390	450
CH_4 activation			
CH_4 consumed (μmol)	27	37	61
H_2 generated (μmol)	26	47	94
x of surface CH_x	2.1	1.4	0.9
Isothermal hydrogenation			
C_{2+} generated (μmol)	0.09	0.21	0.22
C_{2+} selectivity (%)	4	7	8
TPSR in H_2			
C produced (μmol)	0.1	0.6	29

[a] Reaction conditions: CH_4 activation for 2 min, isothermal hydrogenation at 100°C, and TPSR in H_2.

show that the amount of CH_4 recovered in the TPSR step decreased as the activation temperature decreased from 450 to 360°C. Hence, higher activation temperature favors higher C_{2+} selectivity in the isothermal hydrogenation since the CH_x species have lower H content, but more inactive carbon is deposited during the CH_4 activation.

4. Carbon Aging

The above results showed the effect of increased activation time at high temperature. However, in those experiments longer activation time also resulted in higher carbon accumulation on the catalyst. Consequently in this series of experiments, the CH_4 activation time was kept constant and the aging time at 100°C was reduced below the normal 20 min in an attempt to separate the effects of time and temperature on the aging process.

The 12% Co–SiO_2 A-series catalyst used in these experiments was exposed to a 5% CH_4/Ar mixture at 450°C for 2 min. As before the moles of CH_4 converted was greater than the moles of surface Co. The deposit was then aged in a static Ar atmosphere for 5, 10, and 20 min at 100°C and subsequently hydrogenated isothermally at 100°C for 10 min. TPSR and TPO followed the isothermal hydrogenation step.

The data, summarized in Table 5, show that as the age of the carbonaceous deposit increased, the production of both CH_4 and C_{2+} hydrocarbons in the isothermal hydrogenation step decreased, as did the C_{2+} selectivity, indicating that aging decreased C–C bond formation. Interestingly, there was some C_2H_4 production for the shorter aging times which decreased to zero at longer times and a small amount of C_{3+} hydrocarbon was generated in the 5-min aging experiment. Hence as aging time increased the most active carbon, which is capable of multiple C–C bond formation, either underwent C–C bond breakage to generate C_{2+} and eventually CH_4 or further C–C bond formation to produce inactive polycarbon species. Also of note is the fact that by decreasing the aging time from 20 to 5 min the C_{2+} yield per site was increased from 0.9 to 3.2%. The latter yield is approximately three times greater than what has been reported previously (2, 5, 7).

The total amount of carbon recovered in the isothermal hydrogenation step is reported as C_α in Table 5. TPSR after the isothermal hydrogenation showed that the amount of C_β decreased with aging time while the least active form of carbon, C_γ, increased with aging time (for the first 10 min). This suggests that aging results in transformation of C_α to C_β, which in turn can be converted to C_γ. The increasing trend of CO_2 production (from TPO) with aging indicates that the least active C_γ also deactivated to a less active carbon that could be recovered only by TPO.

5. Isothermal Reaction Medium

In the two-step CH_4 homologation, C_{2+} products are generated during the isothermal hydrogenation at low temperature to overcome the thermodynamic barrier to C_{2+} formation at 450°C. However, once C–C bond formation has occurred, the question of whether H_2 is necessary to displace the desired product from the surface has not been addressed. Following the experimental procedures already described, the B-series 8% Co–SiO_2 catalyst was exposed to 5% CH_4/Ar gas at 450°C for 2 min to activate CH_4. After briefly purging the reactor in Ar, the catalyst was exposed to either H_2, Ar, CO_2, or O_2 at 100°C for 10 min. During

TABLE 5

Effect of Carbon Aging at 100°C on the Hydrogenation of the Carbonaceous Deposit over the 12% Co–SiO_2 A-Series Catalyst[a]

	Carbon aging time (min)		
	5	10	20
CH_4 activation			
CH_4 consumed (μmol)	52	51	55
H_2 generated (μmol)	79	78	81
x of surface CH_x	0.95	0.95	1.04
Isothermal hydrogenation			
CH_4 production (μmol)	4.8	3.9	2.8
C_{2+} production (μmol)	0.84	0.74	0.21
C_{2+} yield/site (%)	3.2	3.0	0.9
C_{2+} selectivity (%)	29	27	13
C_2H_4/C_2H_6 product	0.28	0.29	0
C_α production (μmol)	6.6	5.4	3.2
TPSR in H_2			
C_β production (μmol)	6.2	4.3	0.1
C_γ production (μmol)	18.6	19.5	ND[b]
C produced (μmol)	24.8	23.8	ND
TPO			
CO_2 production in TPO (μmol)	11.0	15.3	26.9

[a] Reaction conditions: CH_4 activation at 450°C for 2 min, isothermal hydrogenation at 100°C, TPSR in H_2 and TPO.

[b] Not determined.

this period, nine product gas samples were taken in 1-min intervals via the multiloop sampling valve and stored for later analysis by GC.

The results of these experiments are summarized in Table 6. CH_4 consumption during activation was very similar for all experiments and in the subsequent isothermal hydrogenation, a small amount of C_{2+} and CH_4, with a C_{2+} carbon selectivity of 13%, was generated. When the isothermal reaction was conducted in the presence of Ar, some CH_4 was generated, but more importantly almost the same amount of C_{2+} was generated as for the isothermal hydrogenation. The carbon selectivity of C_{2+} in the isothermal Ar experiment was about 39% and the carbon recovery was about half that obtained by isothermal hydrogenation. Isothermal reaction in CO_2 also generated some CH_4 and a small amount of C_2H_6. Isothermal reaction with O_2 generated the smallest amount of CH_4 and almost the same quantity of C_{2+} as obtained with CO_2. There was a 5°C temperature rise during the isothermal O_2 flow and product analysis showed some H_2O production. The amount of CO, CH_3OH, or C_2H_5OH was negligible.

6. *Reaction Cycles*

The present study has shown that at high temperature (450°C) a significant fraction of the reacted CH_4 yields inactive carbon species that can be removed from the catalyst only by high-temperature oxidation. In this section, the effect of accumulation of this inactive carbon on the activity of the catalyst in the CH_4 activation step and the subsequent hydrogenation steps (isothermal and TPSR) is reported. Using the A-series 12% Co–SiO_2 catalyst, three cycles of CH_4 activation, isothermal hydrogenation, and TPSR, excluding the TPO step, were completed.

The results, summarized in Table 7, show that as the number of cycles increased, the amount of CH_4 consumed in the activation step decreased, indicative of a gradual loss of activity of the catalyst. Furthermore, increasing the number of cycles from 1 to 3 increased the H content of the CH_x species and decreased the C_{2+} selectivity of the isothermal hydrogenation from 8 to 1%. The buildup of inactive carbon on the catalyst reduced the catalyst activity for CH_4 activation and dehydrogenation of the surface carbon species. Consequently, the H content of the CH_x species increased, resulting in decreased selectivity as the number of cycles increased.

TABLE 6

Effect of the Isothermal Medium on the Product Distribution from the Carbonaceous Deposit over the 8% Co–SiO_2 B-Series Catalyst[a]

	Isothermal medium			
	H_2	Ar	CO_2	O_2
CH_4 activation				
CH_4 consumed (μmol)	55	51	60	55
H_2 generated (μmol)	81	76	86	78
x of surface CH_x	1.0	1.0	1.1	1.1
Isothermal reaction				
CH_4 production (μmol)	2.76	0.87	0.90	0.63
C_{2+} production (μmol)	0.21	0.28	0.04	0.04
C_{2+} selectivity (%)	13	39	8	11

[a] Reaction conditions: CH_4 activation at 450°C for 2 min, isothermal reaction at 100°C, and TPSR in H_2.

TABLE 7

Effect of the Number of Reaction Cycles on the Hydrogenation of the Carbonaceous Deposit over the 12% Co–SiO_2 A-Series Catalyst[a]

	Number of cycles		
	1	2	3
CH_4 activation			
CH_4 consumed (μmol)	61	53	48
H_2 generated (μmol)	94	51	42
x of surface CH_x	0.9	2.1	2.2
Isothermal hydrogenation			
CH_4 production (μmol)	4.9	2.1	1.8
C_{2+} production (μmol)	0.22	0.04	0.01
C_{2+} selectivity (%)	8.2	3.7	1.0
TPSR			
C recovered (μmol)	29	38	36

[a] Reaction conditions: CH_4 activation at 450°C for 2 min, isothermal hydrogenation at 100°C, and TPSR in H_2.

DISCUSSION

The present study has emphasized CH_4 activation at 450°C. At this temperature the number of moles of CH_x accumulated on the catalyst surface was greater than the moles of surface Co. Under these conditions, the C_{2+} yield/site increased from <1% reported in previous studies to approximately 3%, provided the age of the CH_x species was minimized and provided the CH_x species had $x \approx 1$.

Previous reports have concluded that on SiO_2-supported Rh, Co, and Ru catalysts, C–C bond formation is favorable for CH_x species in which the average value of x is about one (2). In addition, computational work, using semiempirical quantum chemistry calculations of the reaction path for C–C bond formation (16), has shown that the combination of threefold-bonded carbon (CH) with CH_2 to form a vinylidene surface species has the lowest activation energy of all possible combinations. This means that the most active CH_x species for C–C bond formation will have an average x value of about one. Results from the present study showing the effect of activation time, temperature, and Co loading are all consistent with this conclusion. For the data presented in Tables 2–4, the C_{2+} selectivity is seen to be greatest when x of the CH_x surface species approaches one.

The value of x calculated for the CH_x species in the present work represents an average value for all the carbonaceous species present on the catalyst. Most previous studies of CH_4 homologation have classified the carbon deposited during CH_4 activation as C_α, C_β, or C_γ, according to the carbon reactivity in H_2, and in the present study a similar classification was valid for most of the carbon. However, a significant portion (about 30%) was unreactive toward H_2, even when the x value of the CH_x species was one. This carbon may arise from the migration of CH_x species from the metal to the support. The migration has also been shown to be important in describing the data in Table 2 and in the kinetic model developed previously for CH_4 activation (9). Accordingly, we have suggested that in the activation step, increased metal–support interactions that result from decreased metal loading give rise to a higher rate of migration of carbon species from the initial activation metal site to the support site (9). However, the possibility of the formation of filamentous carbon during CH_4 activation must also be considered, even when $x = 1$ for the CH_x species. If filamentous carbon were formed, then the Co metal would remain active and hence the moles of CH_x accumulated on the catalyst surface would also be greater than the surface Co. The activation temperature of the present work (450°C) is the lower limit at which the formation of filamentous carbon from CH_4 has been observed previously (17). Also, the formation of filamentous carbon on Co catraysts following CH_4 activation to temperatures of 430°C has not been reported previously (18, 19), even when TEM analysis was carried out on Co catalysts exposed to CH_4 for 1 h (20). Recently, a very detailed model of the kinetics of filament formation was given by Snoeck *et al.* (21, 22). Their data have shown that on Ni catalysts, the rate of carbon formation increases as filaments nucleate but nucleation is a relatively slow process. Once nucleation is complete the rate of CH_4 decomposition reaches a steady value. Furthermore, they have shown that in the absence of H_2 during CH_4 decomposition, the metal surface deactivates due to the formation of "encapsulated carbon" (22). These observations are consistent with the present work where catalyst deactivation was observed during CH_4 activation and in subsequent cycling experiments. Although we cannot exclude the possibility of filament formation, because the CH_4 decomposition occurred over short reaction periods (2 min usually) and since the CH_x analysis has shown that the average hydrogen content of the carbon deposit is not zero, we conclude that under the conditions of the present study, formation of filamentous carbon is less likely than migration of carbon species to the support.

Aging of carbon species is known to reduce C_{2+} selectivity (1–4). The present study has shown that when the amount of CH_x accumulated is greater than the surface Co, a similar aging phenomenon occurs at high temperature. The aging is related to loss of H from the CH_x species (Table 3) which reduces the activity of the carbon species and the C_{2+} selectivity. Also, in previous work (2, 5, 6), it was assumed that fast cooling of the carbon species to about 100°C (the temperature of the isothermal hydrogenation step) after activation prevented deactivation of the carbon species. The results in Table 5 indicate that even at 100°C, there was considerable deactivation of the isothermal hydrogenation step due to aging of the carbonaceous species. The TPO data in Table 5 also show that aging increased the formation of unreactive carbon consistent with increased H loss during aging.

Comparison of the results of the four different reaction media under isothermal conditions showed that H_2 generated the largest amount of CH_4, while H_2 and Ar generated almost the same amount of C_{2+}. These observations suggest that the isothermal medium does not contribute to C–C bond formation and that the homologation products can be released from the catalyst by an inert medium. In the activation step of the above experiments, carbon species with an overall H/C ratio of 1 to 1.1 were deposited on the catalyst. The fact that C_{2+} products with an H/C ratio of 4 to 3 (CH_4, C_2H_6) could be produced by Ar is indicative of C–C bond formation and breakage and hydrogen exchange on the catalyst after activation. In isothermal hydrogenation, hydrogen acts partially as a physical desorbing medium but it also furnishes H for the production of CH_4 and C_2H_6 from adsorbed species. H can also facilitate hydrogenolysis of some of the C–C bonds which are already formed on the surface and this reduces C_{2+} selectivity.

CONCLUSION

The present study has shown that CH_4 activation conducted at 450°C on Co/SiO_2 catalysts results in a maximum C_{2+} yield/site of 3% in the subsequent isothermal (100°C) hydrogenation, provided the CH_x species have $x = 1$. However, a significant fraction of the activated CH_4 produces inactive carbon at 450°C. The trends in C_{2+} selectivity observed under different operating conditions correlated to the H content of the CH_x species, with $x = 1$ giving the highest C_{2+} selectivity. C_{2+} products could be produced in higher selectivity in the second step by isothermal (100°C) reaction in Ar instead of H_2.

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