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Direct conversion of methane to higher hydrocarbons via an oxygen free, low-temperature route

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The direct conversion of methane to higher hydrocarbons over a silica-supported Ru catalyst has been investigated via an oxygen free, two-step route. The reaction consists of decomposition of methane over a 3% silica-supported Ru catalyst at temperatures (T_{CH_4}) between 400 and 800 K to produce surface carbonaceous species followed by rehydrogenation of these species to higher hydrocarbons at T_{H_2} of 368 K. It was found that the Ru/SiO$_2$ catalyst exhibits a trend similar to that for single-crystal Ru catalysts. However, the temperature at which a maximum in ethane selectivity occurs shifts toward a higher temperature. It was also found that the ethane yield can be optimized by changing the surface carbon coverage. Under optimum conditions a net ethane yield of about 13–15% has been realized. For this two-step reaction sequence, only a few reaction cycles could be operated without intermediate high temperature rehydrogenation and without significant loss in ethane yield. This is attributed to large amounts of inactive carbon that could not be hydrogenated at 368 K. Higher methane partial pressures were found to be desirable for this reaction. The activity of the catalyst could also be maintained at total pressures up to 10 atm.

Keywords: methane conversion; Ru catalyst; silica support; temperature effects; ethane selectivity; catalyst activity; pressure effects

1. Introduction

Conversion of natural gas (mainly methane) to easily transportable liquid hydrocarbons / oxygenates has acquired immense importance in recent years due to a world-wide surplus of natural gas. During the past decade, special emphasis has been placed on the direct conversion of methane to higher hydrocarbons or oxygenates rather than indirect routes, such as, methane conversion to syngas followed by Fischer–Tropsch (FT) synthesis or methanol synthesis. Two main catalytic routes have been proposed for the direct conversion of methane, viz. oxidative coupling of methane [1–3] and direct partial oxidation of methane to methanol or formaldehyde [4–6]. However, these processes have not yet proved to be commercially attractive [7]. It is, therefore, necessary to explore alternate routes for direct methane conversion.

Due to a positive change in the Gibbs free energy, the direct conversion of methane to ethane is not thermodynamically allowed. In order to circumvent this thermodynamic limitation, recently van Santen and coworkers [8,9] have proposed a two-step, low temperature, oxygen free route for methane conversion. In the first step, the decomposition of methane is carried out at high temperatures (400–800 K) wherein the enthalpy change is positive but the free energy change is negative. The second step involves rehydrogenation of a surface carbonaceous species (formed in step 1) to higher hydrocarbons and is allowed only at low temperatures (350–450 K).

Van Santen and coworkers have reported on the thermodynamics and kinetics of methane decomposition followed by hydrogenation on supported transition metal catalysts [9]. It was suggested that the metal–carbon bond strength is important for such a conversion; a very high metal–carbon bond strength means that the surface carbon cannot be hydrogenated at relative low temperatures, whereas a very low metal–carbon bond strength means that a surface carbonaceous species cannot be formed via methane decomposition. Of the several transition metal catalysts explored, Co and Ru have the optimum metal–carbon bond strength and exhibit the highest activity for the two-step methane conversion process. Van Santen and coworkers have also identified three types of surface carbonaceous species (carbidic, amorphous, and graphitic) formed from methane decomposition on supported Ru and Co catalysts according to their hydrogenation capabilities. It was suggested that a carbidic carbon was likely responsible for the formation of higher hydrocarbons.

A similar two-step route has also been proposed by Amariglio and coworkers [10,11]. These workers have proposed that both reaction steps be carried out at a unique low temperature (350–450 K) under conditions where the formation of higher hydrocarbons is thermodynamically allowed [11]. However, a detailed kinetic study at higher partial pressures of methane and at high total pressures has not yet been reported.

Recently, we reported on the spectroscopic identification of various intermediates present on single-crystal Ru catalysts following methane decomposition [12]. It was found that methylidyne, vinylidene, and graphitic carbonaceous species exist on single-crystal catalysts following methane decomposition. We also reported ethane/propane yields for methane conversion via a two-step process over single-crystal Ru catalysts determined from elevated pressure experiments [13]. These yields correlated well with the hydrocarbon intermediates identified using high resolution electron energy loss spectroscopy (HREELS) [14].

As a final part of this study, we report here the activity/selectivity behavior for the two-step methane conversion process over supported Ru catalysts. We have focussed on kinetic measurements at 1 atm as well as at high pressures (up to 10 atm); this latter pressure regime is important from an industrial point of view. An effort has been made to relate the single-crystal kinetic studies to the activity/selectivity of the supported catalysts.

2. Experimental

2.1. CATALYSTS

A 3 wt% Ru supported on SiO_2 (Cab-O-Sil, HS5, Cabot Corp., surface area = 300 m^2/g) catalyst was prepared using standard incipient wetness impregnation techniques starting from ruthenium nitrosyl nitrate (99.999% pure, Alfa Chemicals). A nitrate percursor was preferred over a chloride precursor, since it is known that chlorine cannot be completely removed from the catalysts after reduction between 500 and 750 K [15,16]. The catalyst was dried overnight at 80°C, ground to a powder and reduced at 700 K for 12 h in pure hydrogen.

2.2. CATALYST CHARACTERIZATION

The Ru surface area was measured using standard hydrogen chemisorption techniques [17]. The catalyst was reduced in situ for 14 h at 700 K prior to the adsorption measurements. The system was evacuated, first at the reduction temperature for 4 h, and then while cooling to room temperature. Adsorption isotherms were obtained at room temperature with pressures varying from 60 to 400 Torr. In order to account for the reversible H_2 chemisorption, the system was evacuated at room temperature for 2 min and adsorption isotherms were obtained in the pressure range of 60–400 Torr [17].

TEM micrographs of the silica-supported Ru catalyst were obtained using a high resolution Jeol 2010 instrument. The catalyst powder was mounted on a 200 mesh Cu grid by simple dusting. Several bright field TEM micrographs of different portions of the sample were obtained at magnifications up to 1 000 000. An average particle size was determined from these micrographs.

XRD data of the catalyst were obtained with a Scintag diffractometer using Cu Kα radiation. No peaks corresponding to Ru could be detected indicating that either the particle size is less than 50 Å (detection limit of the instrument) or the loading is too low for detection.

2.3. REACTION SYSTEM

A typical microreactor flow system was used to study the activity/selectivity of the supported catalysts. The flow rates of the gases (H_2, He, and 5% CH_4-in-He) were controlled by mass flow meters (Brooks, model 5850). A premixed, diluted mixture of methane in helium was allowed to flow through the reactor by switching a three-way valve located just above the reactor. The amount of methane added to the system could be controlled by varying either the concentration of methane or the time for which methane was admitted in the system.

Provisions were also made to carry out reactions at high pressures. For this purpose, a back pressure regulator (Mity-Mite, model S-90W) was provided down stream of the reaction system. Typically, a ceramic reactor (1/4 inch in diameter and 8 inch high) was used for the atmospheric pressure experiments, whereas a stainless steel reactor (1/4 inch in diameter, 12 inch high) was used for the high pressure experiments. The reactor was heated using either a wound filament (ceramic reactor) or a tube furnace (stainless steel reactor). The temperature was controlled (±1 K, computer controlled, home built) using a thermocouple located inside the reactor.

2.4. GASES

All gases used (5% CH_4-in-He, He, and H_2) were bought from Matheson and were of ultra-high purity (UHP) grade (<0.5 ppm of hydrocarbons).

2.5. REACTION PROCEDURE AND PRODUCT ANALYSIS

Due to the inherent unsteady nature of the reaction (two steps; viz. methane decomposition at 500–800 K, followed by hydrogenation at 360–380 K), it is important to account for all the carbon fed to the system. For this purpose, knowledge of the total amount of carbon retained on the catalyst during the decomposition step and the amounts of hydrocarbons formed during the hydrogenation step is imperative. The procedure used in a typical experiment was as follows. A dilute mixture of methane in He (0.3–5%) was allowed to flow over a catalyst bed (0.3 g in most cases) held at temperatures ranging from 500 to 800 K for a specific time interval (0.5–5 min) and at a GHSV between 6000 and 12000 h^{-1}. The total amount of methane retained on the surface of the catalyst was determined by monitoring the effluent concentration of methane using a flame ionization detector. Thus, the methane conversion, defined as the percentage of methane retained on the catalyst, could be calculated.

The reactor was then rapidly cooled below 150°C to avoid "aging" of the carbonaceous species formed during methane decomposition. The surface carbonaceous species were hydrogenated at temperatures ranging from 350 to 380 K using pure hydrogen (15–20 cm^3/min). Since the concentration of the products changes with time, small portions of the effluent stream were trapped (using a multi-position Valco sampling valve) at various time intervals for further analysis. The concentrations of methane and ethane/propane were then determined by injecting these aliquots into a GC (Carle, series 400) equipped with a Porapak

Q column and a flame ionization detector. The total amounts of methane and ethane/propane formed during hydrogenation were determined from the concentration–time curves and the hydrogen flow rate. One such data set is illustrated in fig. 1. Thus, the ethane selectivity, defined as 2×moles of ethane/total moles of product (i.e., on a C-atom basis), could be determined. The amounts of propane formed were, at best, an order of magnitude lower than ethane and hence are not reported here.

A simple mass balance yielded the amount of "inactive carbon", i.e., carbon that could not be hydrogenated at temperatures less than 380 K.

3. Results and discussion

3.1. CATALYST CHARACTERIZATION

The dispersions based on irreversible and total hydrogen chemisorption were calculated in a manner similar to that suggested by Yang and Goodwin [17] as 28 and 16%, respectively. The average particle size was calculated from the irreversible hydrogen chemisorption as 60 Å based on an average area of 0.0817 nm^2 per Ru atom and assuming the particle to be cubic with five sides exposed.

TEM micrographs showed more or less spherical particles uniformly distributed on the support. The average particle size was estimated as 50 Å, which is in agreement with the particle size estimated by hydrogen chemisorption and by XRD analysis.

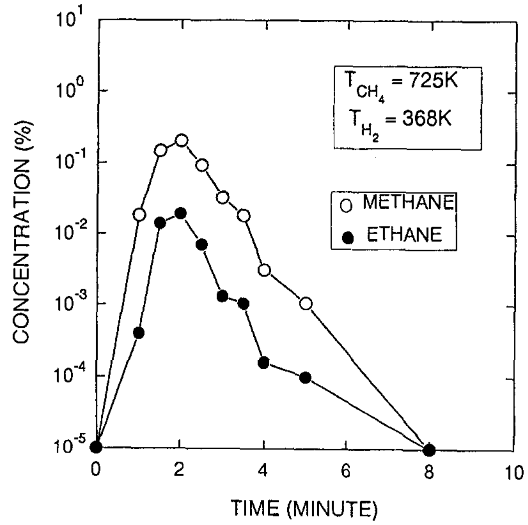

Fig. 1. Concentration of methane and ethane versus time during the hydrogenation of surface carbon at 368 K (step 2) after methane decomposition at 725 K over a 3% Ru/SiO$_2$ catalyst.

3.2. REACTION STUDIES

3.2.1. Effect of methane decomposition temperature

For the 3% Ru/SiO_2 catalyst, the results indicate that the ethane yield (defined as moles of ethane/site) increased initially with an increase in temperature from 550 to 725 K (see fig. 2). A further increase in temperature, however, led to a decrease in the ethane yield. This trend is consistent with that observed for reaction over single-crystal Ru catalysts at elevated pressures [13], which exhibited a maximum at around 500–600 K and is also shown in fig. 2 for comparison purposes. The temperature at which the maximum occurs for supported Ru, however, appears to be shifted to a higher temperature. In order to explain this behavior a close examination of the methane conversion, ethane selectivity, and the percentage of decomposed carbon hydrogenated at lower temperatures is necessary (see table 1).

The methane conversion (defined as percent methane decomposed) increased monotonically with temperature. This is consistent with the trend observed by van Santen and coworkers [9] over Ru/SiO_2, and Wu et al. [13] over single crystal Ru catalysts. Wu et al. have also identified surface carbonaceous species formed on methane decomposition using HREELS as: methylidyne (CH), vinylidene (CCH_2), and ethylidyne (CCH_3) [12] (for details on structure, bonding geometry, and assignment of these species see ref. [12] and references therein). Methylidyne and vinylidene intermediates were suggested to be precursors for the formation of higher hydrocarbons at methane decomposition temperatures as low as 450 K [14]. However, at temperatures between 400 and 600 K, the supported catalysts did

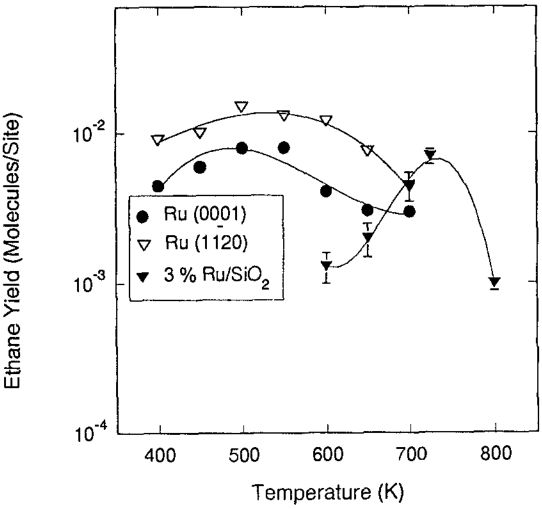

Fig. 2. Comparison of the ethane yield for single-crystal (ref. [5]) and supported Ru catalysts (conditions used were: $GHSV_{CH_4} = 6000\ h^{-1}$, total methane input= 4.8 μmol, $T_{H_2} = 368$ K, $GHSV_{H_2} = 2000\ h^{-1}$).

Table 1
Activity/selectivity for methane conversion on Ru/SiO_2 catalyst (methane concentration = 0.3%, total methane input = 4.8 μmol, $GHSV_{CH_4}$ = 6000 h^{-1}, T_{H_2} = 368 K, $GHSV_{H_2}$ = 2000 h^{-1})

Decomp. temp. (K)	Methane conversion[a] (%)	Ethane selectivity[b] (%)	Ethane yield × 10^3 (mol/site)	Methane hydrogenated at 368 K (%)
600	54 ± 3	6.0 ± 1	1.3	25 ± 5
650	68	7.4	2.0	38
700	80	10.2	4.5	38
725	100	14.0	7.4	40
800	100	9.6	1.0	25

[a] Defined as percentage of carbon retained on the catalyst.
[b] Defined as moles of carbon incorporated in ethane/total moles of carbon hydrogenated.

not show significant activity for ethane formation in spite of the fact that some methane was retained on the catalyst (not shown in table 1). Unlike the single crystal catalysts, the supported catalysts consist of different types of sites (low and high coordination), which likely exhibit different activities to methane decomposition. It is also likely that certain highly active sites preferentially adsorb methane, leading to intermediates similar to those observed over single-crystal catalysts, but which then rapidly transform to "inactive" carbon. This inactive carbon cannot be hydrogenated at lower temperatures. Further evidence for the formation of inactive carbon comes from the fact that only 30–50% of the carbon decomposed was hydrogenated in the second step at 368 K regardless of the decomposition temperature. Van Santen and coworkers [8,9] have also reported that at 725 K only about 50% of the carbon can be hydrogenated. Kuijpers et al. [18] have reported that methane decomposition on silica-supported Ni catalysts is more efficient on small particles, which contain more sites of lower coordination, than on large particles.

Van Santen and coworkers have also stressed the importance of rapid cooling to avoid aging of the carbonaceous species that can lead to inactive carbon. However, despite rapid cooling of the catalyst after the methane decomposition, some transformation of the active species to inactive carbon is unavoidable. Once the highly active centers are covered (and poisoned), additional surface carbon species lead to the formation of ethane, resulting in higher ethane yields at the higher temperatures. At temperatures >725 K, however, the inactive carbon is probably formed even on sites of high coordination resulting in lower ethane yield. This is consistent with the formation of an inactive, graphite-like carbon on single-crystal Ru catalysts at $T > 750$ K [12].

In general, the ethane yield also correlates well (same order of magnitude) with that for the single-crystal Ru catalysts. This correlation is indeed remarkable given the uncertainty in the determination of the number of sites on the supported catalysts.

3.2.2. Effect of carbon coverage

Displayed in fig. 3 are the methane conversion, ethane selectivity, and ethane yield as a function of surface carbon coverage. The surface carbon coverage was changed by varying the adsorption time at 725 K and a methane concentration of 0.3%. A methane decomposition temperature of 725 K was chosen since this temperature exhibited a maximum in ethane selectivity in the experiments described above. This temperature also coincides with the experiments of van Santen and coworkers [9]. The surface carbon coverage was calculated assuming a stoichiometry of one carbon atom per surface Ru atom. It should be noted that although such an assumption may not be entirely valid, especially at the higher carbon coverages, it is appropriate for a qualitative analysis. For a methane decomposition temperature of 725 K, the ethane selectivity initially increased with an increase in the carbon coverage with a maximum (~ 18%) at around 40% coverage (see fig. 3b). A further increase in the carbon coverage led to a drop in the ethane selectivity. The net ethane yield, however, is determined not only by the selectivity to

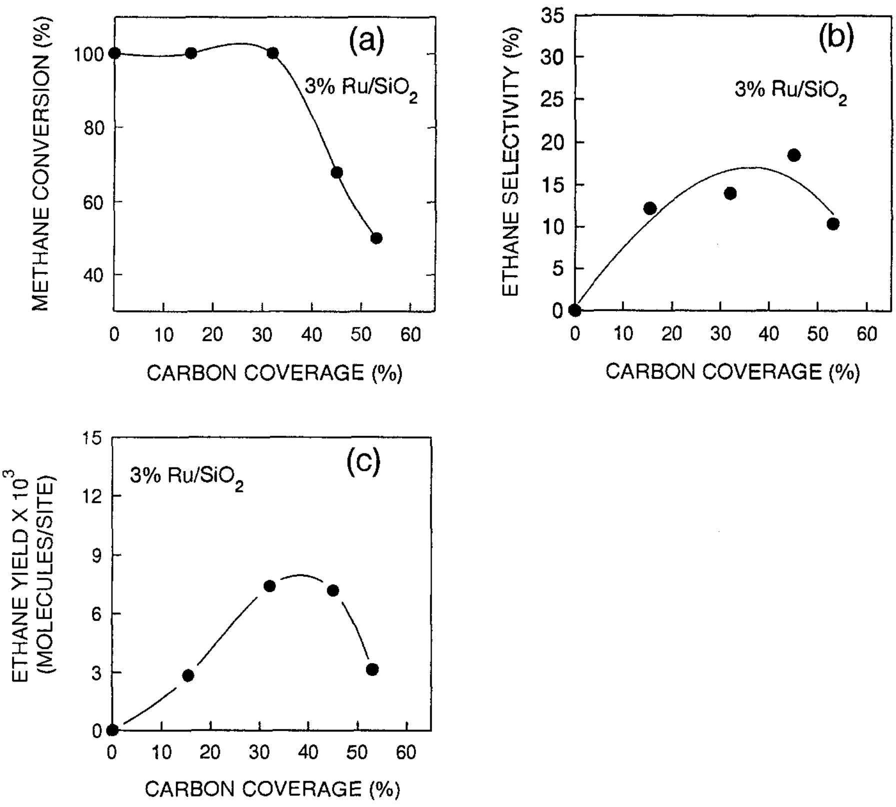

Fig. 3. Effect of change in carbon coverage on the activity/selectivity for methane conversion over a 3% Ru/SiO_2 catalyst: (a) methane conversion versus carbon coverage; (b) ethane selectivity versus carbon coverage; (c) ethane yield versus carbon coverage (conditions used were: $T_{CH_4} = 725$ K, $GHSV_{CH_4} = 6000\ h^{-1}$, total methane input = 4.8 μmol, $T_{H_2} = 368$ K, $GHSV_{H_2} = 2000\ h^{-1}$).

ethane but also by the amount of carbon retained on the catalyst during the decomposition step. The percentage of methane decomposed decreased with an increase in the carbon coverage (see fig. 3a). The optimum ethane yield was found to be around 30–35% carbon coverage as shown in fig. 3c. A similar behavior was observed by van Santen and coworkers over Ru/SiO_2 catalysts [9]. They also reported the identification of three types of surface carbonaceous species formed upon methane decomposition depending on their hydrogenation capabilities; viz. C_α (active "carbidic" carbon), C_β (amorphous carbon), and C_γ (inactive "graphitic carbon) by analogy with the CO hydrogenation studies of Bell and coworkers [19,20]. At low coverages, the chain growth probability is low. With an increase in carbon coverage, the inactive carbon forms, C_β and C_γ, increase at the expense of the active carbon (C_α). This leads to the observed "volcano"-type behavior as a function of carbon coverage. In our experiments, the increase in the amount of inactive carbon with an increase in the surface carbon coverage was evident from the lower percentage of hydrocarbons (~ 10%) hydrogenated at 368 K at relatively high carbon coverages.

3.2.3. *Effect of multiple reaction cycles*

It was shown earlier that only approximately 30–50% of the carbon decomposed can be hydrogenated at 368 K. From an industrial point of view, it is important to determine the lifetime and regeneration capabilities of the catalyst.

Fig. 4 shows the number of decomposition–hydrogenation cycles that can be performed without intermediate rehydrogenation. It was found that at 700 K, after approximately three cycles without intermediate hydrogenation, the activity decreased as indicated by a decrease in both the ethane yield (see fig. 4a) and the methane conversion (see fig. 4b). At higher temperatures, however, the activity decreased more rapidly than at lower temperatures. It should be noted that the

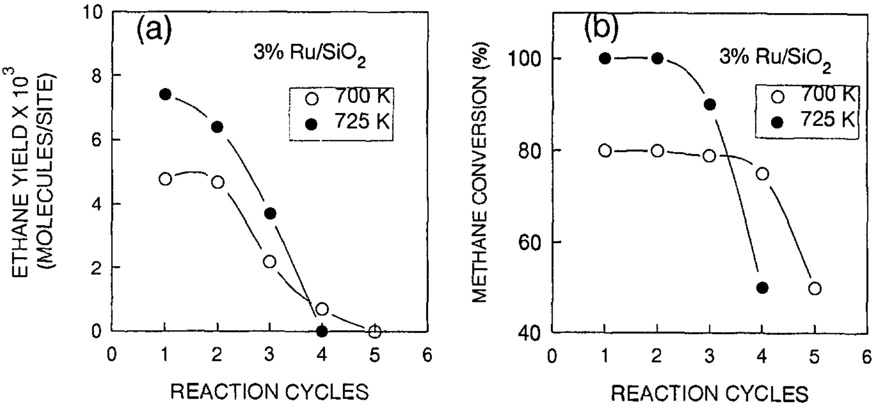

Fig. 4. Effect of number of reaction cycles for methane conversion over a 3% Ru/SiO_2 catalyst: (a) ethane yield; (b) methane conversion (conditions used were: $GHSV_{CH_4} = 6000\ h^{-1}$, total methane input = 4.8 µmol, $T_{H_2} = 368$ K, $GHSV_{H_2} = 2000\ h^{-1}$).

activity can be recovered completely after rehydrogenation at 700 K for 4 h. These results suggest that the build-up of the inactive carbon is important and that high-temperature rehydrogenation is necessary after a few reaction cycles. More importantly, it seems that the inactive carbon, at least in part, spills over onto the support or is present in the form of long carbon chains as has been proposed for FT synthesis [20–22]. Partial evidence for this was derived from the pulse experiments which show that even after pulsing several small aliquots of methane (total equivalent to two monolayers) over the catalysts, the conversion per pulse was significant. In other words, the catalyst surface could not be "saturated", indicating that some carbon does spill over onto the support.

3.2.4. *Effect of methane partial pressure*

In order to study the effect of high total pressure (and hence high partial pressure of methane) on the activity/selectivity of the Ru/SiO_2 catalyst, experiments were carried out first at higher partial pressures of methane at a total pressure of 1 atm. As far as possible, the total amount of methane fed to the system as well as the contact time were held approximately constant. This was achieved by exposing the catalysts to a flow of methane for different time periods. Also, the range of partial pressures that could be studied was limited since at very high partial pressures of methane, for a given amount of catalyst and a constant total methane input, the exposure time was unreasonably small.

Results for activity/selectivity of methane decomposition followed by hydrogenation as a function of methane partial pressure are illustrated in fig. 5 and tabulated in table 2. These results indicate that, with an increase in the partial pressure of methane, the methane conversion decreased (see fig. 5). It is known that during

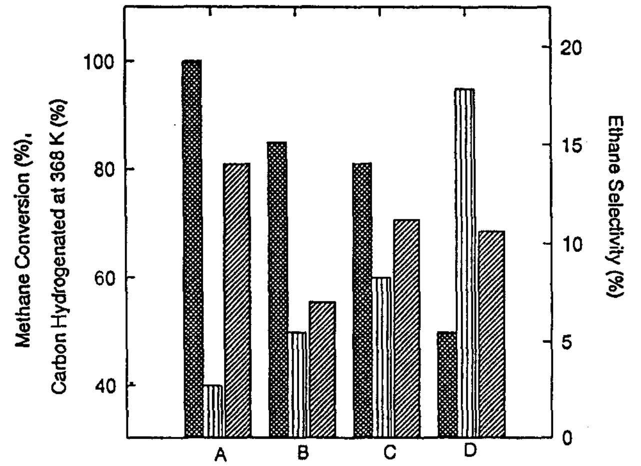

Fig. 5. Effect of partial pressure of methane on the activity/selectivity for methane conversion over a 3% Ru/SiO_2 catalyst (see table 2 for conditions used; (▒) methane conversion, (▨) ethane selectivity, (▥) methane hydrogenated at 368 K, A: $P_{CH_4} = 0.3\%$, B: $P_{CH_4} = 0.6\%$, C: $P_{CH_4} = 1.2\%$, D: $P_{CH_4} = 2.4\%$).

Table 2
Effect of methane partial pressure on the activity/selectivity for methane conversion over Ru/SiO_2 catalyst ($T_{CH_4} = 725$ K, $GHSV_{CH_4} = 6000\ h^{-1}$, total methane input = 4.8 μmol, $T_{H_2} = 368$ K, $GHSV_{H_2} = 2000\ h^{-1}$)

P_{CH_4} (%)	Methane conversion (%)	Ethane selectivity (%)	Methane hydrogenated at 368 K (%)	Ethane yield×10^3 (mol/site)
0.3	100 ± 3	14.0 ± 1	40 ± 5	4.4
0.6	85	8.2	51	5.6
1.2	81	10.6	62	5.7
2.4 [a]	50	10.2	95	9.1

[a] Total methane input = 6 μmol.

methane decomposition, hydrogen is released, and that the amount of hydrogen released varies between 1.4 and 1.7 atoms per molecule of methane [9]. Kuijpers et al. [18] have shown that during methane decomposition over a Ni/SiO_2 catalyst in a continuous flow mode, the surface hydrogen partial pressure is high and the transport of hydrogen is slow at high temperatures between 300 and 500°C. They attributed the low conversion seen in their methane decomposition experiments to high local (surface) hydrogen partial pressures which prevented further decomposition of methane. In the present studies, it is likely that hydrogen transport limitations prevent methane from being chemisorbed. This would result in a fractional order with respect to methane and is consistent with our results. It should be noted that the initial rate of methane chemisorption, i.e., on a clean surface, may indeed show a first-order dependence at low conversions (which implies low H_2 surface coverages). However, such a regime (low methane conversion) was not examined in our experiments.

Another phenomenon that can be explained by the presence of surface hydrogen is the increase in the amount of methane hydrogenated at 368 K (see fig. 5). Higher amounts of available surface hydrogen may lead to a higher H/C ratio in the surface hydrocarbonaceous species. When quenched rapidly, such a species can be more easily hydrogenated at 368 K. Likewise, the ethane selectivity decreased somewhat at higher methane partial pressures. Also consistent with the above are the higher yields of ethane at higher methane decomposition pressures.

3.2.5. *Effect of total pressure*

The activity/selectivity behavior of the Ru/SiO_2 catalyst for methane conversion was also tested at high pressures (4 and 10 atm). The results are illustrated in fig. 6 and summarized in table 3. A decrease in the space velocity by virtue of an increase in pressure was partially compensated by deliberately increasing the total mass flow rate. Results indicate that the catalysts exhibited only a slight decrease in the ethane selectivity when the methane decomposition is carried out at 4 atm,

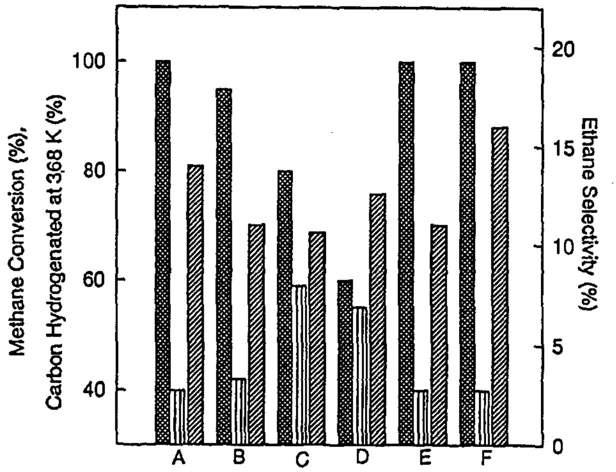

Fig. 6. Effect of total pressure on the activity/selectivity behavior for methane conversion over a 3% Ru/SiO2 catalyst (see table 3 for conditions used; (▩) methane conversion, (▨) ethane selectivity, (▥) methane hydrogenated at 368 K; A: $P_{CH_4} = 1$ atm and $P_{H_2} = 1$ atm, B: $P_{CH_4} = 4$ atm and $P_{H_2} = 1$ atm, C: $P_{CH_4} = 4$ atm and $P_{H_2} = 4$ atm, D: $P_{CH_4} = 10$ atm and $P_{H_2} = 10$ atm, E: $P_{CH_4} = 1$ atm and $P_{H_2} = 10$ atm, F: $P_{CH_4} = 1$ atm and $P_{H_2} = 1$ atm).

and the hydrogenation at 1 atm. This is expected since similar selectivities were observed when the methane partial pressure was increased to 1 atm total pressure. When both methane decomposition and hydrogenation were carried out either at 4 atm or at 10 atm (see figs. 6C and 6D), the activity/selectivity did not change significantly. Unlike the experiments at high methane partial pressures and a total pressure of 1 atm, the amount of methane hydrogenated did not increase significantly. This can be attributed to the lower space velocity in the high pressure experiments, particularly at 10 atm total pressure. Longer contact times may have led to considerable aging of the carbonaceous species, resulting in more inactive carbon and consequently lower ethane yields.

More importantly, higher hydrogen partial pressures did not affect the ethane selectivity significantly. At high hydrogen partial pressures, the rate of hydrogenation of precursors leading to the formation of ethane and methane is high. Also, the hydrogenolysis of ethane to methane is not favorable at high hydrogen partial pressures [23–25]. This is likely why the ethane selectivity decreased only slightly when only the hydrogenation step was carried out at high pressures (see fig. 6E). In any case, the base activity/selectivity (both steps at 1 atm, see fig. 6F) could be easily reproduced after a high temperature hydrogenation, indicating that the catalyst is not significantly poisoned at high pressures.

In summary, experiments at high pressures have indicated that the ethane yield can be reasonably maintained (see table 3). This is important for the commercial applicability of this process.

Table 3
Effect of total pressure on the activity/selectivity for methane conversion over Ru/SiO_2 catalyst (T_{CH_4} = 725 K, total input methane = 4.8 μmol, T_{H_2} = 368 K)

Conditions [a]	Methane conversion (%)	Ethane selectivity (%)	Methane hydrogenated at 368 K	Ethane yield × 10^3 (mol/site)
$P_{CH_4} = 1$ atm, $P_{H_2} = 1$ atm, $GHSV_{CH_4} = 6000\ h^{-1}$	100 ± 3	14.0 ± 1.0	41 ± 5	7.4
$P_{CH_4} = 4$ atm, $P_{H_2} = 1$ atm, $GHSV_{CH_4} = 12000\ h^{-1}$	95 ± 5	11.0	42	6.3
$P_{CH_4} = 4$ atm, $P_{H_2} = 4$ atm, $GHSV_{CH_4} = 12000\ h^{-1}$	80 ± 5	10.6	59	7.4
$P_{CH_4} = 10$ atm, $P_{H_2} = 10$ atm, $GHSV_{CH_4} = 12000\ h^{-1}$	60 ± 5	12.6	55	6.8
$P_{CH_4} = 1$ atm, $P_{H_2} = 10$ atm, $GHSV_{CH_4} = 6000\ h^{-1}$	100 ± 3	11.0	40	5.6
$P_{CH_4} = 1$ atm, $P_{H_2} = 1$ atm, $GHSV_{CH_4} = 6000\ h^{-1}$	100 ± 3	16.0	40	8.2

[a] GHSV at 298 K and 1 atm pressure.

3.3. FURTHER COMMENTS ON THE ACTIVITY/SELECTIVITY AND YIELD FOR METHANE POLYMERIZATION OVER Ru CATALYSTS

A fundamental understanding on the nature of the sites responsible for hydrocarbon formation would be useful in improving the activity/selectivity for the two-step methane conversion.

Qualitatively, it was found that the single-crystal Ru catalysts and the supported Ru catalyst exhibit similar behavior. This means that relatively high coordination Ru sites are important in methane activation. However, supported Ru catalysts also consist of low coordination edge and corner sites. These sites are even more active for methane decomposition and are probably responsible for graphite-like carbon formation. This is consistent with the results reported by Kuijpers et al. [18], where small Ni particles were shown to be more efficient for methane decomposition on silica-supported Ni catalysts than large Ni particles. Trevor et al. [26] have also shown that methane decomposition is most efficient on 2–5-atom clusters of Pt. Recently, we have shown that more open Ru sites are slightly more active for methane decomposition than closely packed Ru sites [13]. This means that, although low coordination sites may be preferable for efficient methane decomposition, formation of inactive carbon on such sites may be unavoidable. The formation of graphitic carbon on the low coordination sites limits the recyclability of the catalysts, i.e., an intermediate reduction step is necessary in order to reactivate the catalyst. On the other hand, larger particle sizes would mean less efficient use of an expensive nobel metal catalyst. Attempts are being made to improve the catalyst performance by poisoning the highly active sites using dopants like sulfur or copper.

In any methane conversion process the yield of higher hydrocarbons is important. Van Santen and coworkers have reported a maximum C_{2+} yield (defined as conversion × selectivity) of about 13%. The methane conversion in such a case was essentially 100%. It should be noted that this conversion was achieved only at low concentrations of methane. On the other hand, Amariglio and coworkers [10,11] have reported very low yields for methane conversion over silica-supported Pt, Ru, and Co catalysts at temperatures between 400 and 550 K where the yields were expressed on a total in-coming carbon basis. If expressed on similar basis, the maximum C_{2+} yield that was achieved in our experiments was around 13–15% (see table 1), in excellent agreement with van Santen and coworkers' results [9]. However, it is the C_{2+} production, i.e., ethane/propane produced per site (defined as yield in this paper), that is a more useful basis for comparison. This method is similar to space-time yield (STY) in continuous flow systems. If expressed in terms of molecules of ethane/site, the yields reported by van Santen and coworkers [9], Amarliglio and coworkers [10,11] and from our results are of the order of 0.01. These are in excellent agreement with the yields for the single-crystal Ru catalysts [13]. For a given catalyst, the ethane yield can be optimized by controlling the surface carbon coverage. We have demonstrated that ethane yield can be improved somewhat by operating at higher partial pressures of methane. Also, the ethane yield can be maintained even at total pressures of around 10 atm, which is important from an industrial point of view.

Perhaps the most important practical information that can be realized is the number of decomposition–hydrogenation cycles that are possible without intermediate rehydrogenation. Indeed, the formation of inactive carbon is a problem and only a few such cycles are possible.

One of the major disadvantages from an industrial point of view of the two-step methane conversion process is heat transfer from the high and low temperature steps. Also, reactor design challenges in terms of short contact times in such a two-step process are yet to be explored. On the other hand, this process offers distinct advantages in savings with respect to capital and operating costs for the production of either oxygen/chlorine in other direct conversion processes, or a syngas for indirect methane conversion processes.

4. Conclusions

A two-step, oxygen free route was investigated for the conversion of methane to higher hydrocarbons. Methane was first decomposed over silica-supported Ru catalysts at higher temperatures (500–800 K) and the carbonaceous species so formed were rehydrogenated at temperatures between 350 and 380 K. The ethane yield was consistent with that observed over single-crystal Ru catalysts. A significant portion of methane, however, was found to form inactive carbon and could not be hydrogenated at 368 K. It was found that the ethane yield is a function of surface carbon coverage. Under optimum conditions, an ethane yield of about 14%, which corresponds to about 0.0074 molecules/site, could be achieved. This ethane yield is in close agreement with that measured for single-crystal Ru catalysts.

It was found that only a few cycles of methane decomposition followed by rehydrogenation could be performed without significant loss in the ethane yield; a high temperature reduction step is necessary to retrieve the complete activity of the catalyst. Results for methane decomposition followed by hydrogenation at high pressures indicated that activity/selectivity decreases only slightly at high pressures. It is suggested that although low coordination Ru sites are desirable for efficient methane decomposition, formation of inactive carbon on these sites can pose problems

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