Enhanced C_2 Yields from Methane Oxidative Coupling by Means of a Separative Chemical Reactor

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Of the processes for converting natural gas into a more useful chemical feedstock, the oxidative coupling of methane to form ethane and ethylene (C_2) has perhaps been the most intensively investigated in recent years, but it has proved extremely difficult to obtain C_2 yields in excess of 20 to 25%. Methane oxidative coupling was carried out in a separative chemical reactor that simulated a countercurrent chromatographic moving-bed. This reaction gives 65% methane conversion, 80% C_2 selectivity, and a C_2 yield slightly better than 50% with Sm_2O_3 catalyst at ~1000 K.

The metal oxide–catalyzed reaction of methane (CH_4) in the presence of oxygen (O_2) to form ethane (C_2H_6) and ethylene (C_2H_4) has received much attention (*1–3*), primarily because of interest in converting abundant natural gas reserves to more useful feedstocks (*4, 5*). Although many catalysts exhibit selectivity for the C_2 hydrocarbons (*6–8*), the less than stoichiometric O_2/CH_4 ratios necessary to minimize complete oxidation cause small CH_4 conversions and modest C_2 yields. The C_2 yields are typically ~20% for the most active and selective catalysts (*7*), and the feasibility of commercialization is marginal. We report that a simulated countercurrent moving-bed chromatographic reactor (SCMCR) (*9*) significantly increases the conversion of CH_4 and the yield of C_2 products in comparison with the performance attainable in fixed bed or fluidized bed reactors. With a Sm_2O_3 catalyst at temperatures near 1000 K, CH_4 conversion exceeds 60% and the C_2 selectivity is 80 to 90%, corresponding to C_2 yields of >50%. Optimization could lead to further improvements in yields.

The rapid separation of O_2, CH_4, and C_2 products that occurs in the SCMCR is the key to this process. When reaction products can be separated from one another or from the reactants, such as by distilling off a volatile product, the chemical equilibrium composition can be continuously shifted so as to obtain virtually complete conversion in equilibrium-limited reactions. Similarly, the separation that occurs when chemical reactions are carried out in chromatographic columns can be exploited to increase reactant conversions beyond the thermodynamic equilibrium limit that exists in well-mixed reactors (*10*). Furthermore, if relative motion between the chromatographic bed and the reactant inlet can be achieved, as with the rotating cylindrical annulus (*11*) and the countercurrent moving bed (*12*), the conventional column operation that uses a pulsed input and a low duty cycle can be transformed into a continuous flow process that is desirable for chemical processing.

The oxidative coupling reaction is not equilibrium limited, but it is a low-conversion process if further oxidation of the desired products, C_2H_4 and C_2H_6, as well as complete oxidation of CH_4, is to be minimized. Reaction chromatography can be used to separate O_2 and CH_4 from the C_2 products, suppressing their oxidation. It can also permit more extensive CH_4 contact with the catalyst, increasing the conversion. Finally, it produces a C_2 product stream free not only of O_2 but also of CH_4. We report here experiments demonstrating that the SCMCR can accomplish the required separation and can also enhance CH_4 conversion.

To understand the operation of the SCMCR, it is convenient to first describe the countercurrent moving bed. The countercurrent moving bed may be visualized as a vertical column in which granular solids (a mixture of catalyst and adsorbent) flow slowly downward against a countercurrent stream of inert carrier fluid. A stationary inlet partway along the column permits a feed stream to be introduced. The solids and carrier flow speeds can be arranged so that relatively weakly adsorbed species move upward with the carrier and relatively strongly adsorbed species move downward with the solid. Removal of product streams near the top and bottom permits binary separations by continuous chromatography in the case of no catalyst, or, if a catalyst is present, separation of reactants and products in a continuous reaction chromatograph.

In the SCMCR, countercurrency is simulated by replacing the flow of solids past a stationary feedport that characterizes the countercurrent moving-bed reactor (*12*) with motion of the feed stream past a fixed bed by shifting it sequentially through a series of inlets located along the bed (*9*). The reactant is introduced at the first inlet for a predetermined length of time, then is advanced to the next for an equal interval, then to the next, and so on. When the feedpoint has progressed to the end it is returned to the starting position and the process is repeated. The movement of the feed and the product positions in the direction of fluid flow simulates discretized motion of the solids in the opposite direction. If the bed consists of a mixture of chromatographic stationary phase and catalyst, then reaction and separation occur simultaneously, with the switching interval selected such that weakly adsorbed species move ahead of the feed position and more strongly adsorbed species lag behind. The SCMCR may also be configured as several shorter columns connected in series, each column corresponding to the section between each inlet and outlet of the SCMCR described in (*9*). A modification of the latter configuration was used in this work.

The oxidative coupling reaction requires sufficiently elevated temperatures that mixing the adsorbent and catalyst would be unsatisfactory, because most adsorbents will not maintain structural integrity at the ~900 to 1100 K reaction temperatures, and those that do will not exhibit enough adsorption selectivity for CH_4 and the C_2 products at these temperatures to give a separation. A schematic representation of the four-section SCMCR that was developed to overcome this difficulty is shown in Fig. 1. Each section consists of a 0.64-cm outside diameter (OD) tubular quartz microreactor packed with 70 mg of unpromoted Sm_2O_3 catalyst powder (Aldrich Chemicals), maintained at the reaction temperature in a tube furnace, followed by a 19 cm by 0.64 cm OD Al separation column packed with activated charcoal (Alltech) at 373 K in a gas chromatograph (GC) oven. The separation column is divided into two parts, one 7.6 cm long and one 11.4 cm long. Sm_2O_3 has been reported to be one of the most selective and active of the methane oxidative coupling catalysts (*13*). The tandem column arrangement performs the same reaction-separation function that a single section packed with a mixture of catalyst and adsorbent would.

The atmospheric pressure reactor is fed initially with 18 ml min^{-1} of a CH_4-air mixture ($CH_4/O_2 = 50$) and 100 ml min^{-1} of N_2 carrier gas, measured at ambient temperature. The CH_4 and O_2 that react are replaced by a make-up mixture at 1.4 to 1.7 ml min^{-1} of 2:3 CH_4/O_2 at every feed position advancement thereafter. This was the value calculated to maintain the CH_4/O_2 entering the feed section at 50/1. The 100-ml/min carrier enters the section

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behind feed section, and C_2H_6 and C_2H_4 are removed from the adsorption column that is two sections behind the feed section after traveling only 7.6 cm because the breakthrough time for the full length is about 4 min; otherwise the reactant would overtake it on the next cycle. The detail of the adsorption columns is also shown in Fig. 1, with a sketch of the C_2 (dotted line) and CH_4 (solid line) concentration fronts that move through the adsorption columns. N_2 and O_2 are not separated and fill the entire reactor more or less uniformly. The C_2 concentration in the carrier at the product takeoff is ~1%. Unreacted CH_4 is routed to the next section upon breaking through the full length of the feed section adsorber column, because just before breakthrough the feed position is advanced by switching the make-up feed ahead to the next section. The section ahead of the feed section is purged with N_2 at an elevated flow rate to remove any species that may remain in order to prepare it for becoming the feed section. All section inlet and effluent flows are directed through 0.32-cm OD lines by computer-operated solenoid valves. Reaction product analyses are obtained by automatic sampling analytical gas chromatography. A description of the computer control and the GC has been published (*14*). Some experiments were performed with a tubular quartz microreactor, also packed with 70 mg of catalyst, to compare conventional tubular reactor and SCMCR performance. In experiments with a tubular quartz reactor without catalyst, the oxidation of CH_4 was negligible. The only reaction products detected with a GC were C_2H_6, C_2H_4, CO_2, and CO.

Figure 2 shows the CH_4 conversion and C_2 selectivity obtained from the SCMCR as a function of temperature when the feedstream is shifted from section to section at 28-s intervals. The selectivity and conversion both increase with increasing temperature. The C_2 yield, calculated as the product of conversion and selectivity, increased from ~5% between 823 to 873 K to >50% as the temperature approached 1073 K, where the C_2H_4 to C_2H_6 ratio is ~0.33. This performance can be compared with Fig. 3, showing conversion and selectivity in a single 998 K microreactor as a function of CH_4/O_2 ratio. Here, the selectivity exceeds 90% at high ratios, but the low conversion gives small C_2 yields. At the 50:1 ratio of the SCMCR experiments, the C_2 yield from the microreactor is <3%. This performance is similar to that previously reported for microreactor studies with Sm_2O_3 catalyst (*13*). The SCMCR leads to an improvement in C_2 yield of a factor of >12. The SCMCR performance depended upon the interval between successive switches of feed and the CH_4/O_2 ratio. The values reported here, 28 s and 50:1, respectively, represent optimum SCMCR performance for this catalyst-adsorbent combination.

Substantial CH_4 conversion could be achieved by using a conventional recycle reactor, but matching the 65% conversion observed in the SCMCR would require a recycle reactor volume 50 to 100 times larger (*15*). In addition to the much larger catalyst inventory required, the increased contacting of the recycled C_2 products with the catalyst would result in lower C_2 yields through oxidation. A significant advantage of the SCMCR over a recycle reactor is the rapid separation of the readily oxidizable C_2s from the oxidant and CH_4 between each reactor-separator section. Furthermore, the adsorption columns provide an energy-efficient separation. Although the cycling of CH_4 around the SCMCR gives it an appearance of a recycle reactor, it is more closely related to the countercurrent moving-bed chromatographic reactor from which it is derived. When viewed simply as a device into which reactants are introduced and from which products are extracted, the performance for the oxidative coupling reaction

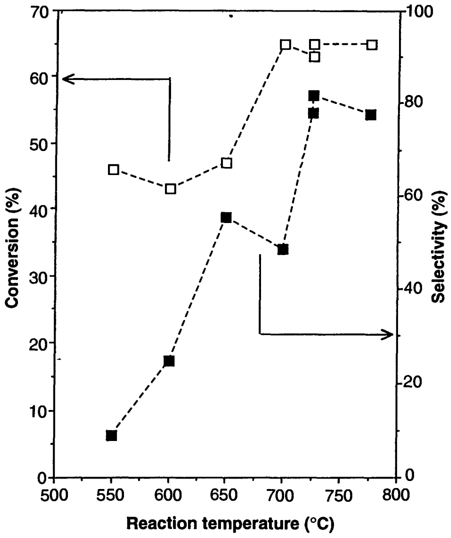

Fig. 2. Simulated countercurrent moving-bed performance showing the dependence of CH_4 conversion and C_2 selectivity on reactor temperature at switching times of 27 and 28 s, and CH_4/O_2 = 50.

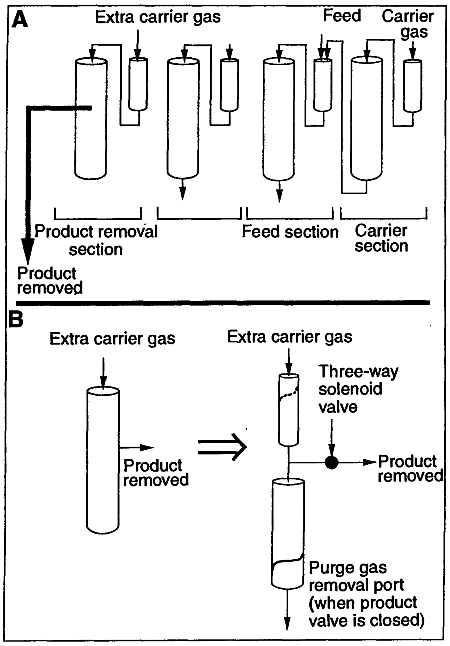

Fig. 1. (**A**) Schematic of the four-section simulated countercurrent moving-bed chromatographic reactor. The small columns contain the Sm_2O_3 catalyst, and the large columns the adsorbent. The N_2 carrier gas is shown entering the first section, and make-up CH_4/O_2 feed the second. Section 3 is isolated, with no flow, while C_2 products are purged from the fourth section by N_2 at a somewhat higher flow rate than the carrier and collected. The effluent from section 2 exits the apparatus until just before the concentration front breaks through, when the feed is advanced to section 3 and the carrier is simultaneously advanced to section 2, sweeping unreacted CH_4 into section 3. At the same time, section 1 becomes the product removal reaction, and section 4 is temporarily isolated. Just before unreacted CH_4 breaks through section 3, all flow positions are advanced one section again, and this process is repeated, cycling the carrier, feed, and product removal positions through the four sections as long as desired. (**B**) Detail of a two-section adsorbent column, indicating intermediate port for removal of C_2s. The dotted line represents a C_2 concentration front, and the solid line represents a CH_4 concentration front. When this is a product removal section, C_2s elute from the shorter column, and when it is a feed section, the CH_4 front moves through the longer column until just before breakthrough, when the feed position is advanced to the next section.

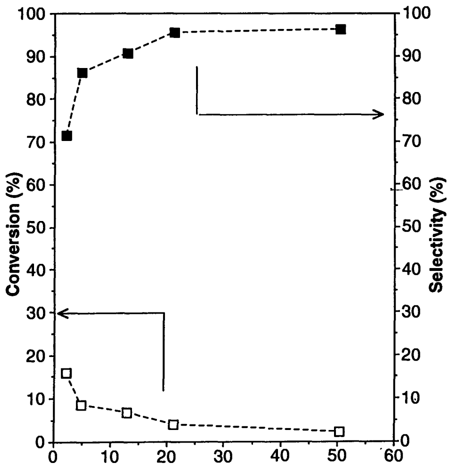

Fig. 3. Dependence of CH_4 conversion and C_2 selectivity on CH_4/O_2 in a microcatalytic fixed bed reactor at 1023 K.

exceeds that previously reported.

The performance of the SCMCR could be improved by using a different catalyst and adsorbent combination. Promoted catalysts (*16*, *17*) and hydrothermally treated lanthanide oxides (*18*) with somewhat better activity and selectivity than unpromoted Sm_2O_3 have been reported. Furthermore, a limitation of the CH_4 conversion in these experiments is the loss of CH_4 from the adsorption columns. The charcoal adsorbent has a heterogeneous surface on which some of the CH_4 is relatively strongly adsorbed, enough so that a portion is not carried forward to undergo further reaction but remains behind as the feed section is advanced. It is then purged away by the carrier gas just before the section in which it resides becomes the feed section once more. Greater CH_4 conversions and higher C_2 yields would be obtained if the CH_4 loss were eliminated. This could be accomplished by using an adsorbent on which CH_4 tailing is reduced, and if necessary by increasing the number of reactor-adsorber sections.

The performance might also be enhanced by working at lower CH_4/O_2 ratios. Microreactor studies showed that at 725°C, the C_2 selectivity only decreased from 97% at $CH_4/O_2 = 50$ to 95% at $CH_4/O_2 = 20$. At smaller ratios, the conversion per pass is expected to be larger, so the C_2 yield in the SCMCR is expected to increase. This effect would be offset somewhat by oxidation of the C_2s.

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Molecular Dynamics Simulations of a Lipid Bilayer and of Hexadecane: An Investigation of Membrane Fluidity

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Molecular dynamics simulations of a fluid-phase dipalmitoyl phosphatidylcholine lipid bilayer in water and of neat hexadecane are reported and compared with nuclear magnetic resonance spin-lattice relaxation and quasi-elastic neutron scattering data. On the 100-picosecond time scale of the present simulations, there is effectively no difference in the reorientational dynamics of the carbons in the membrane interior and in pure hexadecane. Given that the calculated fast reorientational correlation times and the "microscopic" lateral diffusion of the lipids show excellent agreement with the experimental results, it is concluded that the apparently high viscosity of the membrane is more closely related to molecular interactions on the surface rather than in the interior.

Lipid membranes show an almost paradoxical combination of fluidity and rigidity. As noted by Overton (*1*) almost a century ago and by many others since then (*2*), the membrane behaves very much like an oil drop in terms of the solubility and diffusion of small nonpolar molecules. In contrast, the translational diffusion constants of lipids and proteins in membranes are characteristic of media with viscosity over two orders of magnitude higher than that of an oil such as hexadecane (*3*). An understanding of the molecular basis of this behavior is essential for elucidating transport phenomena in membranes. For example, when quinone crosses the bilayer in the oxidation-reduction pathway, is it diffusing in a low- or high-viscosity fluid? To begin to provide the molecular details of diffusion in membranes, we report the results of molecular dynamics (MD) simulations of a dipalmitoyl phosphatidylcholine (DPPC) lipid bilayer in water and of neat hexadecane; both simulations were carried out at the same temperature (50°C) with the use of identical potential energy parameters (*4*), thus enabling straightforward comparisons.

MD studies of monolayers (*5*), bilayers (*6*, *7*), and micelles (*8*) interacting with solvent are relatively recent. This is due in part to the fact that membranes are lyotropic, and the stability of the simulation is sensitive to details of the potential energy parametrization (*5*, *6*). Additionally, and in contrast to the case for proteins and DNA where x-ray structures provide reasonable initial conditions for a simulation (*9*), the biologically active (L_α) phase of lipid bilayers is disordered and information from the crystal (L_c) or gel (L_β) phases is not directly relevant (*10*, *11*). Here initial conditions for the L_α phase bilayer were developed using a mean field approach. In our two-step method, we first generated conformations of individual lipids in a Marcelja mean field (*12*), using a recently developed torsional Monte Carlo procedure (*13*); the parameters of the field were adjusted so that the average orientations were consistent with experimental deuterium order parameters (S_{CD}) (*14*). Second, 72 independent configurations were packed into an L_α phase bilayer-water assembly with appropriate dimensions (*15*). This procedure circumvents the long equilibration time otherwise necessary to obtain a configuration consistent with experimental order parameters and dimensions when starting with more gel-like distributions [for additional details, see (*16*, *17*)].

Figure 1 shows an 8 Å slab from the system at 120 ps (approximately midway through the simulation). The liquid-like nature of the bilayer interior and the solvation of the headgroup and glycerol region are evident. The movement of a selected set of eight lipids (part of one row) over the interval 100 to 190 ps is illustrated in Fig. 2. It is clear that on this time scale the chain dynamics consist primarily of dihedral angle isomerization and other local motions, with little overall rotation or translation of the lipids. We first compare these short-time reorientations with those of hexadecane and with experiment and then proceed to the consideration of molecular translation.

The simulated reorientational correlation functions,

$$\langle P_2[\hat{\mu}(t) \cdot \hat{\mu}(0)]\rangle = \langle \tfrac{3}{2} [\hat{\mu}(t) \cdot \mu(0)]^2 - \tfrac{1}{2}\rangle$$

where P_2 is the second rank Legendre polynomial, $\hat{\mu}$ is a unit vector, and t is time, are shown in Fig. 3 for selected CH vectors of

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