c^{III} (29). Hence, at a constant driving force, the enthalpy and entropy changes for folding cyt c^{II} are substantially more negative than those for cyt c^{III}.

The topography of the energy surface for folding has important kinetic consequences: a rough surface indicates that the protein has many low-energy nonnative configurations separated by high energy barriers (*1*, *30*). Cyt c^{III} folding has been shown to lead to structures with nonnative His ligands bonded to the Fe center (*3–5*, *24*). These incorrectly folded structures rearrange quite slowly to the native structure. We see no corresponding processes in cyt c^{II}, perhaps because the ferroheme center does not bind a second His ligand as tightly as does a ferriheme. In other words, there may be deeper traps in the cyt c^{III} folding surface.

The complex process of protein folding involves dynamics on time scales that range from picoseconds to minutes. In the picosecond to nanosecond time regime, it is possible to study the motions of amino acid side chains and the folding or unfolding of short peptide segments (*31*). Until very recently, studies of whole-protein folding have been limited to the millisecond and longer time regime, where molten globules collapse to tightly folded structures (*7*). The nanosecond to millisecond gap in measurement times is believed to encompass secondary structure formation and the collapse to compact denatured structures. Rapid initiation of protein folding by electron transfer should be able to bridge this gap.

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19. At higher [GuHCl], our measured k_{f2} values appear to level off, but the uncertainties in these rates are quite large because of the competition from k_o. There has been one report of cyt c^{II} folding measured with stopped-flow methods (*3*). The observed rate constant ($k_f = 1.0 \pm 0.1\ s^{-1}$ at 4.6 M GuHCl and 40°C) agrees quite well with the 1.3 s^{-1} estimated from our data.
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32. We thank G. Mines and S. Lee for technical assistance, M. Gruebele for a preprint of his paper on apomyoglobin, and P. Wolynes for helpful discussions. Supported by the Swedish Natural Science Research Council (T.P.), NIH, NSF, and the Arnold and Mabel Beckman Foundation.

5 December 1995; accepted 29 January 1996

Microsecond Catalytic Partial Oxidation of Alkanes

Duane A. Goetsch and Lanny D. Schmidt*

A single layer of woven platinum–10 percent rhodium gauze was used as a catalyst for the partial oxidation of ethane, propane, *n*-butane, and isobutane. This configuration produced oxygen conversions of equal to or greater than 90 percent and had high selectivity to olefins and oxygenated hydrocarbons at contact times as short as 10 microseconds at atmospheric pressure. This reactor operates by rapid chemical heating (~5 microseconds) followed by rapid quenching to avoid homogeneous reactions, which decompose products. Mixing of the cold unreacted gas passing between the gauze wires with the hot product gas results in rapid quenching (~200 microseconds) of the products from ~800° to ~400°C. The rapid quenching avoids successive homogeneous decomposition reactions of unstable products such as olefins and aldehydes but still allows homogeneous chain reactions that produce these species. The strong variations in products with the feed alkane showed that the reaction pathways operating at $\sim 10^{-5}$ seconds are quite different than those operating at longer residence times. These results could have a significant effect on the direct conversion of alkanes to oxygenates such as formaldehyde.

Catalytic partial oxidation processes offer great potential for the fast, efficient, and economical conversion of light alkanes associated with remote sources of natural gas into more valuable liquid fuels and chemicals. A crucial feature of such processes is the ability to attain high surface reaction rates to minimize contributions from nonselective homogeneous reactions to produce CO_2 and H_2O, thus allowing selective catalytic partial oxidation processes to dominate.

Different catalytic monolith chemical reactor configurations are sketched in Fig. 1. The catalysts could be either metal-coated ceramic monoliths, transition metal oxide coated onto ceramic monoliths, or metal gauzes. Lower activity catalysts typically require the reactants to be preheated to achieve the desired reaction rate; however, preheating the reactants by conventional heat transport through the reactor walls produces significant homogeneous reaction before the reactants contact the catalyst (Fig. 1A).

Previously, we showed that porous α-alumina monoliths coated with Rh (for syngas) (*1*, *2*) or with Pt (for olefins) (*3*) operate autothermally and give essentially complete

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Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455, USA.

*To whom correspondence should be addressed.

conversions of both fuel and O_2 with residence times of $\sim 10^{-3}$ s (Fig. 1B). An essential feature of this configuration is that gases remain at nearly room temperature until they enter the catalyst, which is heated rapidly to ~1000°C by the chemical reactions rather than by the relatively slow transfer of heat through the reactor wall. Because reaction heat is generated directly on the surface of the catalyst, the gas temperature rises from 20° to 1000°C in less than 10^{-4} s. High mass transfer rates within the monolith favor radical termination through surface interactions at the expense of the nonselective homogeneous propagation and chain branching reactions, thus minimizing the contribution of nonselective free radical homogeneous chemistry. However, only small amounts of oxygen-containing products are observed in these experiments because they decompose to yield olefins, CO, and H_2O at high temperatures.

While attempting to construct a chemical preheat system for millisecond partial oxidation on metal oxide ceramic foams (Fig. 1C), we discovered that a single layer of Pt gauze (Fig. 1D) produced high O_2 conversions and very different selectivities than on three-dimensional metal-coated ceramic monoliths or multiple gauzes. Selectivity to partial oxidation products up to 75% has been achieved at contact times as short as $\sim 10^{-5}$ s, with parent olefin, formaldehyde, and acetaldehyde as the most abundant partial oxidation products.

The single layer woven gauze was made of Pt–10% Rh wires (90 μm in diameter and with 81% transparency), such as are used commercially for NH_3 oxidation and for HCN synthesis (4). The single gauze catalyst gives very different results compared with monoliths or multiple gauzes. The contact time over the gauze (wire diameter divided by gas velocity) was varied from 8 to 500 μs.

We observed very different reactivities and selectivities with ethane, propane, butane, and isobutane over the single gauze catalysts (Table 1). Partial oxidation of normal alkanes over an activated gauze catalyst gives nearly complete conversion of the O_2 and high selectivity to partial oxidation products. A comparison of carbon atom selectivities shows that olefin selectivity strongly decreases whereas oxygenate selectivity increases with alkyl chain length when a single gauze is used. At least 40% of the reacted butane is converted to oxygen-containing hydrocarbons, the majority of which are formaldehyde and acetaldehyde. In contrast, either Pt on a ceramic foam monolith or a gauze catalyst give roughly the same amount of partial oxidation products, but these are almost exclusively olefins from cracking reactions, with less than 1% of the organic molecules containing oxygen atoms (5).

Table 1. Effect of chain length on alkane oxidation over a single layer of Pt–10% Rh gauze. The conditions were as follows: superficial velocity, 25 cm/s; pressure, 1.4 atm; C/O = 7; and inlet gas temperature, 25°C.

	Alkane			
	C_2H_6	C_3H_8	C_4H_{10}	iso-C_4H_{10}
Conversion (%)				
Alkane	34	16	10	3
Oxygen	100	99	90	70
Carbon selectivity (%)				
Olefins	62	58	36	<1
Oxygenates	7	9	40	<0.2
Alkanes	13	10	<1	Trace
CO + CO_2	18	23	24	99
Temperature (°C)				
Surface	900	850	800	800
Gas	580	504	400	395

We observed that the alkane conversion and the oxygenate selectivity change significantly as the gauze restructures under operating conditions over a period of several hours. Many hours of operation were required to achieve the steady conversions and selectivities shown in Table 1. It is also essential that the catalysts be operated above 800°C and nearly adiabatically because carbon forms on the surface at lower temperatures, and the reaction extinguishes above the 7/1 C/O ratio used for the data in Table 1.

Scanning electron micrographs revealed that the surface of the gauze roughens dramatically with continued exposure to partial oxidation conditions (Fig. 2). Roughening of the wire surface destabilizes the boundary layer and leads to separation. This promotes mixing in the boundary layer, improves mass transport between the gas and the surface, and enhances

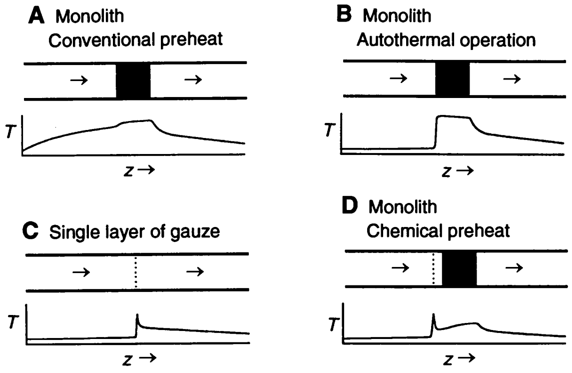

Fig. 1. Sketches of temperature (*T*) versus position *z* for the monolith and gauze reactors. (**A**) Chemical reactor that uses low-activity catalysts such as metal oxides, which require conventional preheat to achieve significant reaction across the catalyst. However, preheat allows homogeneous reaction to occur before reactants contact the catalyst. (**B**) Reactor that uses a high-activity catalyst such as metal-coated monolith, that rapidly heats the reactants to reaction temperature but cools slowly by heat transfer through the reactor wall. (**C**) Reactor with a single layer of metal gauze that rapidly heats the reactants to the reaction temperature and then rapidly quenches the products with cold reactants that bypass the catalyst. (**D**) Reactor that combines a single layer of gauze to rapidly preheat the reactants chemically to the reaction temperature followed by a reactive oxide monolith. The lower activity of the oxide surfaces compared with the metal surfaces requires higher reactant temperatures that could result in significant homogeneous thermal reactions, but the use of chemical preheating minimizes these reactions.

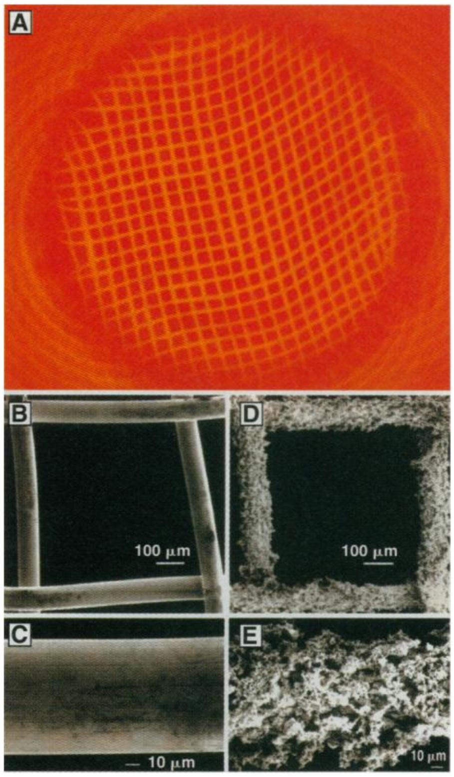

Fig. 2. Single gauze reactor. (**A**) Photograph of an ignited 1.8-cm-diameter Pt–10% Rh gauze reactor catalyzing the partial oxidation of butane. Although the reactants are supplied at 25°C, reaction on the surface of the gauze heats it to >800°C. Arcs around the gauze are reflections from the quartz tube. (**B** and **C**) Scanning electron micrographs of the gauze before reaction show a smooth surface. (**D**) Scanning electron micrograph of the Pt gauze used to catalyze the partial oxidation of butane shows significant roughening and facet formation after exposure of the gauze to partial oxidation conditions for ~50 hours. (**E**) Higher magnification of this surface shows extensive faceting, which promotes mass transfer mixing.

mixing between hot and cold gases. Under reaction conditions, the gauze surface temperature exceeds 800°C as measured by optical pyrometry. Closer inspection of the roughened surface revealed metal facets (Fig. 2E) and the energy dispersive x-ray analysis indicated that the structures are metallic.

The high transparency (81%) of the gauze combined with short contact times leads to a significant amount of reactants passing between the catalytic wires. The high O_2 conversion achieved with a single layer of gauze strongly suggests that significant homogeneous reaction takes place in the wake region behind the gauze wires. However, reaction products in the wake are rapidly quenched by the cold feed gas that bypasses the catalyst, as sketched in Fig. 3. The decrease in alkane reactivity with increasing chain length is counterintuitive because alkane reactivity generally increases with chain length (6). This result suggests a dominant heterogeneous role in the initiation of reactions.

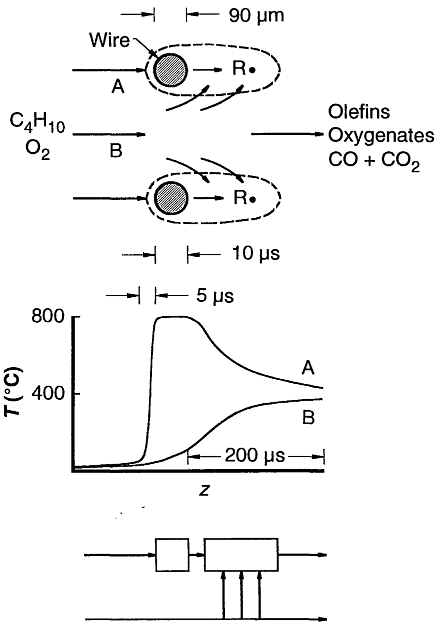

Fig. 3. Sketch of temperature profiles for a single layer of gauze for gas flowing around single gauze wires and between gauze wires. Gas flowing close to the wire is rapidly heated (~5 μs) to the wire surface temperature (~800°C), remains at this temperature for the contact time with the wire (~10 μs), and is rapidly quenched to 400°C by mixing with 25°C gas flowing between the wires (~200 μs). Reaction can continue by homogeneous chain propagation and branching behind the wire until quenching results in temperatures low enough to stabilize the chain carriers. The exit gas temperature should depend strongly on the gauze transparency and the heat transfer characteristics around the gauze. The process can be modeled as a two-stage adiabatic plug flow reactor with partial bypassing of the first stage as sketched at the bottom of the figure. Products from the first stage continue to react with the bypassed feed gas, which is introduced along the length of the second stage.

We suggest that butylene and aldehydes survive in the presence of catalyst surfaces at >800°C because the products are rapidly quenched by the cold feed gas that bypasses the wire surface. The mixing of the hot reacted gases (contacting the wires) and the cold unreacted gases (passing between the wires) occurs within a few wire diameters downstream of the gauze, which is at >800°C, and cools the products from 800° to ~400°C within 200 μs (Fig. 3) and allows selective production and survival of oxygenate. Increasing the number of gauze layers from one to five increased the olefin selectivity from 36 to 63% but decreased the oxygenate selectivity from 40 to 14%. The exit gas temperature from five gauze layers increased from 400°C (for a single gauze layer) to 830°C, which evidently produced smaller olefins and alkanes by cracking reactions and oxygenate decomposition.

The data suggest that oxygenates are produced by a heterogeneously assisted homogeneous reaction mechanism (*7*, *8*). Reactions originate on the hot catalytic surface, and the intermediates produced either undergo further reaction on the surface or desorb and participate in homogeneous chain reactions. A possible reaction pathway for butane is shown in Fig. 4. The first step must take place on the surface because the feed gas enters at temperatures too low for significant homogeneous radical initiation to occur. However, within the wake region the gas is at temperatures high enough to allow propagation of exothermic homogeneous reactions but too low for decarbonylation and dehydration (*8*).

One potentially important application of this technology is the use of a single gauze layer to provide chemical preheat for catalytic partial oxidation on oxide catalysts such as V_2O_5 (Fig. 1D). These catalysts have the potential to produce partial oxidation products, especially organic molecules containing oxygen, with high selectivity; however, their ignition temperatures are much higher than for noble metals, and considerable preheat is necessary to attain high conversion and sustain adiabatic operation. Conventional heat exchangers cannot accomplish this in times less than ~0.1 s (Fig. 1A), and for alkane-O_2 mixtures, considerable homogeneous reaction will occur before the reactants reach the oxide catalyst surface. By using a single layer of Pt gauze just before the oxide catalyst, the gases could be preheated in ~10 μs from room temperature to the desired reaction temperature. Rapid quenching between the gauze and the oxide monolith would then keep the conversions sufficiently low that both alkane and oxygen remain for reaction on the oxide.

We also note that this gauze reactor has been operated successfully at 70 m/s, which is one-fourth the velocity of sound. This occurs without "blow out" because the high thermal conductivity of the gauze transfers heat upstream to maintain reaction. These velocities suggest that sonic flow could be attained and that the supersonic quenching after the catalyst "nozzle" might further stabilize useful chemical species.

These laboratory reactors produce ~20 kg per day of aldehydes and butylene from butane, and a 0.3-m-diameter reactor should produce ~1000 metric tons per day of these chemicals at 70 m/s under these conditions. The results should be very sensitive to the geometry of the catalyst, such as wire diameter, transparency, and microstructure. The chemical composition of the catalyst should also play a dominant role in controlling selectivity and conversion. Higher pressures and velocities and staged catalysts with product removal and reactant addition between catalyst layers suggest that even higher yields and greater selectivities may be possible.

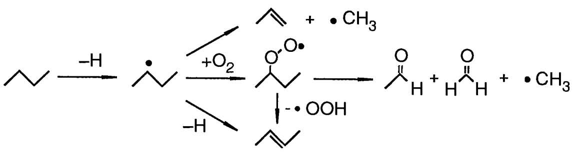

Fig. 4. Suggested reaction pathways for the partial oxidation of butane. Butane can be converted to olefins by dehydrogenation or cracking reactions or converted to oxygenates by an alkyl peroxy radical. The olefin-producing reactions occur both heterogeneously and homogeneously, but oxygenates are probably produced homogeneously within the boundary layer and the wake region behind the wire.

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12 September 1995; accepted 8 December 1995