Fabrication of micro-reactors using tape-casting methods

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We have developed a simple, rapid, and inexpensive method for the fabrication of micro-channel reactors using tape-casting methods. Rectangular channels, with self-contained heaters, were fabricated with cross-sectional dimensions of 500 μm × 800 μm and 1000 μm × 800 μm. The conduits were loaded with Pd and Pd/alumina catalysts using a syringe. To demonstrate the capabilities of this methodology, n-butane oxidation rates were measured between 300 and 700 K. Because free-radical reactions are suppressed by the small channel size, it was possible to measure catalytic rates within the flammability limits. Based on the results, it appears that micro-reactors formed using tape-casting methods may be useful for initial catalyst screening.

KEY WORDS: micro-reactors; combinatorial catalysis; n-butane oxidation; Pd; tape-casting

1. Introduction

Combinatorial approaches have been responsible for significant advances in the pharmaceutical industry in the last decade [1], and it is hoped that these methodologies can provide similar contributions for heterogeneous catalysis [1–4]. Because combinatorial approaches require the screening of large numbers of catalysts, one needs a large number of relatively inexpensive micro-reactors. There are obvious advantages if these micro-reactors can be incorporated into a system that can be easily automated, allowing catalysts to be added and reactions monitored without complicated piping arrangements. Indeed, several reactor systems have been described for performing these kinds of tests [1,3,5–8], including one that is commercially available [9].

In this paper, we describe a method for making micro-channel reactors with tape-casting technology. Because tape casting is inexpensive and highly flexible, the method could allow a large number of reactors, with channel sizes ranging from less than 100 μm to 10 mm, to be formed on a single, disposable plate. In principle, the reactors can be made of any oxide material. We have used alumina-based tapes that were developed for the electronics industry because of the available knowledge base for co-firing of multi-layer laminates and the availability of various inks for the formation and co-firing of resistors and conductors [10,11]. Furthermore, alumina is inert for many reactions and can be used at relatively high temperatures. In previous work, one of us has shown that heating elements and temperature sensors can be easily incorporated into the fabrication procedure [12]. Progress has also been made to include miniature pumps and valves [13].

In the present study, we will demonstrate the measurement of oxidation rates for n-butane on Pd catalysts in 500 μm × 800 μm and 1000 μm × 800 μm rectangular channels over temperatures ranging from 300 to 700 K. Procedures for loading the catalyst and monitoring the reaction rates will also be described.

2. Experimental

The micro-reactor was fabricated with low temperature, co-fired ceramic tapes (LTCC, DuPont 951 AX). Ceramic tapes provide an easy, inexpensive, and rapid platform for the integration of passive electronics and fluidics. One can go from a design to a device in a matter of days. The tapes are commercially available in thicknesses starting from $\sim$111 μm. It is possible to cast thinner tapes. In their pre-fired state, the ceramic tapes consist of oxide particles, glass frit, and organic binder (that can be made from photoresist). The pre-fired tapes can be machined by laser, milling, chemical means, and photolithography [11]. Metallic paths can be either printed or processed photolithographically to form electrodes, resistors, conductors, and thermistors. Conduit sizes may range from $\sim$10 μm to a few millimeters. Upon firing, the organic binder burns out, the oxide particles sinter, and the tapes solidify. Many tapes ($>$80) can be stacked together, laminated, and co-fired to form monolithic structures with complex, three-dimensional mazes of fluidic conduits, electronic circuits, and electrodes. Glass windows and other materials can be readily attached to the tapes.

To demonstrate the usefulness of the tape technology for the fabrication of micro-reactors, a relatively simple design was implemented here. Figures 1 and 2 depict, respectively, an explosive view and a cross-section of the micro-reactor. The reactor consisted of four parts that were ma-

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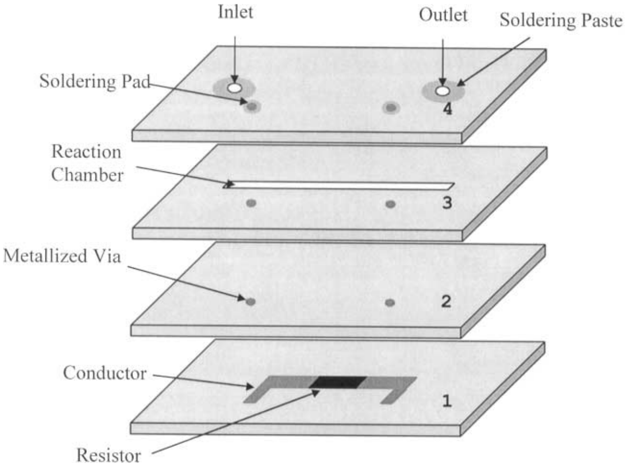

Figure 1. An explosive view of the micro-reactor.

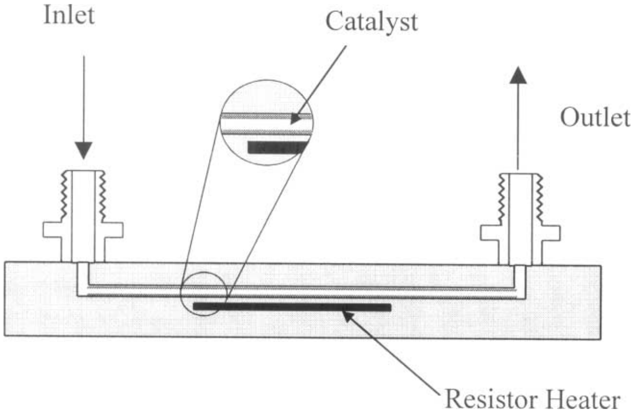

Figure 2. A cross-section of the micro-reactor.

chined together (each part consisted of a few laminated layers). A joule heater (resistor, DuPont 1421) and conductors (DuPont 6145) were printed on layer 1 (the number of each layer is indicated in figure 1). Layer 2 separated the resistor from the reaction conduit and provided vertical metal-filled vias for electrical connections. The vias consisted of silver paste (DuPont 6141) filled wells. Layer 3 contained the reaction conduit, which had a rectangular cross-section. Two different conduit sizes were fabricated with post-fired dimensions of 500 μm × 800 μm and 1000 μm × 800 μm. The lengths of the conduits and the heated sections were, respectively, 47 and 17 mm. Layer 4 contained inlet and exit ports and soldering pads (Ag–Pd paste, DuPont 6134). After machining, the layers were aligned, stacked, and co-fired to form a monolithic device. A cross-section of the completed device is depicted in figure 2. Our prototype was equipped with a single reaction conduit; however, it would be an easy matter to fabricate devices with multiple conduits for massive parallel and serial processing. Moreover, the device can be equipped with integrated thermistors [12] for *in situ* temperature measurement and with sensors for flow rate measurement [11].

The Pd or Pd/alumina catalysts were added to the micro-channels using a syringe. In the first set of experiments, a 4.0 wt%, aqueous solution of $(NH_3)_4Pd(NO_3)_2$ (Alfa Aesar) was used to deposit a known amount of Pd on the channel walls. In the second set of experiments, a 1 wt% Pd/alumina catalyst [14] was loaded into the micro-reactors by first making an aqueous slurry (50 mg catalyst in 1.0 ml distilled water), then adding the slurry using a syringe. After the addition of the catalysts, the micro-reactors were dried at 383 K overnight, and subsequently calcined in air at 873 K for about 8 h.

Finally, $1/8''$ fittings were soldered to the soldering pads to accommodate connections with external tubing. The entrance and exit ports (figures 1 and 2) were located sufficiently far from the heated section so that the temperature at their locations was well below the solder's melting temperature. A stainless-steel tube was connected to the exit fitting to collect the reaction products. If more than one micro-conduits were to be incorporated into the ceramic plate and one wished to automate the system, one could use compression seals. The premixed reactants were supplied with a flexible tube.

The flow rates of n-butane and O_2 were controlled with mass flow controllers (MKS, RS-485) and the products were monitored with an on-line GC (model SRI8610C, Hayesep Q column) equipped with a TCD detector. The temperature was monitored with a T type thermocouple and Omega (series 920) digital reader (resolution of 1 K). The thermocouple junction was inserted into a well machined on the surface of the tape next to the heated section. Although one can easily print thermistors on the ceramic layers, we have not done so in order to avoid the necessity of calibrating these thermistors. The pressure at the exit of the reactor was 760 Torr. The flow rates were always below 10 cm^3/min resulting in very small Reynolds numbers ($\mathrm{Re} < 1$) and insignificant pressure drops. The estimated pressure drop in the smaller conduit was less than 0.3 Torr. Therefore, we assumed that the pressure throughout the micro-conduit was nearly uniform. In all the reported rate measurements, the conversion of the limiting reagent was kept below 10%, so that differential conditions could be assumed. Before collecting the reaction data, the micro-reactors were run in the reaction feed at 573 K for about 4 h until the Pd catalyst was fully activated and the reaction rates reached a steady state. To ensure that the results were reproducible, each data point was measured at least three times.

3. Results and discussion

The conversion of n-butane as a function of temperature in the reactor with 1000 μm × 800 μm wide conduit is depicted in figure 3. The inlet concentrations were 675 Torr O_2 and 85 Torr C_4H_{10}. Data are shown for both the reactor without Pd and with 0.34 mg of Pd added by decomposition of $(NH_3)_4Pd(NO_3)_2$. Notice that no reaction occurred in the absence of Pd, even though the operating conditions were well within the flammability limits. In an earlier version of this reactor, a sparking element was added in an attempt to ignite the homogeneous, free-radical reaction; however, any homogeneous reactions were quickly extinguished in the small-volume reactor. Upon the addition of Pd, a significant fraction of the n-butane reacted at temperatures above 575 K. The rates remained constant with time and the only detectable products were CO_2 and water.

In order to determine the effect of reactor size and catalyst type, differential reaction rates were measured for n-butane consumption in 85 Torr n-butane and 675 Torr O_2 mixture. Figure 4 depicts the n-butane consumption rate in the (a) 1000 μm × 800 μm and (b) 500 μm × 800 μm wide conduits. In both cases, Pd was added by decomposition of $(NH_3)_4Pd(NO_3)_2$. Additionally, the figure shows the conversion rate for n-butane on the Pd/alumina catalyst in the (c) 1000 μm × 800 μm wide conduit. All of the rates have been normalized to the mass of Pd in the reactor. The rates for the Pd film in the 1000 μm × 800 μm (a) and 500 μm × 800 μm (b) reactors are similar, with the same activation energy of 90 ± 5 kJ/mol. Rates in the 500 μm × 800 μm reactor are slightly higher, probably due to the increased surface-to-volume ratio. The rates for the Pd/alumina catalyst in the 1000 μm × 800 μm reactor are approximately five times higher, probably due to the better dispersion of the Pd/alumina catalyst [15,16]; but the activation energy is almost identical, showing that diffusion limitations cannot be important.

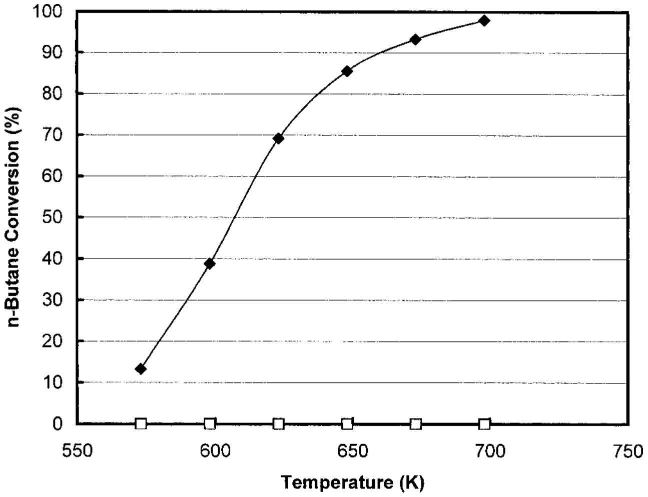

Figure 3. The light-off curves for n-butane oxidation in the micro-reactor (1000 μm × 800 μm) with (♦) or without Pd (□). Data were collected with a feed consisting of 1 ml/min n-butane and 8 ml/min O_2 and a total pressure of 760 Torr.

The partial-pressure dependences of the oxidation rates were examined at 573 K in the 1000 μm × 800 μm reactor using Pd formed by decomposition of $(NH_3)_4Pd(NO_3)_2$, with the data shown in figure 5. In these measurements, the flow rates for He, O_2 and n-butane were used to control the partial pressures. The O_2 dependence, shown in figure 5(a) for a fixed n-butane pressure of 60 Torr, is zeroth-order, indicating that Pd surface oxidation cannot be rate limiting under these conditions [17,18]. The n-butane dependence, shown in figure 5(b) for a fixed O_2 pressure of 700 Torr, suggests that there are two kinetic regimes. For n-butane pressures below 60 Torr, the reaction order is approximately 0.7, suggesting that the reaction is limited by the dissociative adsorption of n-butane on the surface [17–19]. For higher pressures, the rate becomes zeroth-order, suggesting that the reaction becomes limited by the rate of oxidation of carbonaceous species.

For purposes of the present study, the reader should notice that the rates we have observed agree well with the available data in the literature [20]. The temperature at which there is significant conversion in figure 3 is in excellent agreement with the light-off temperatures usually reported for alkane-oxidation reactions [21–24]. While the

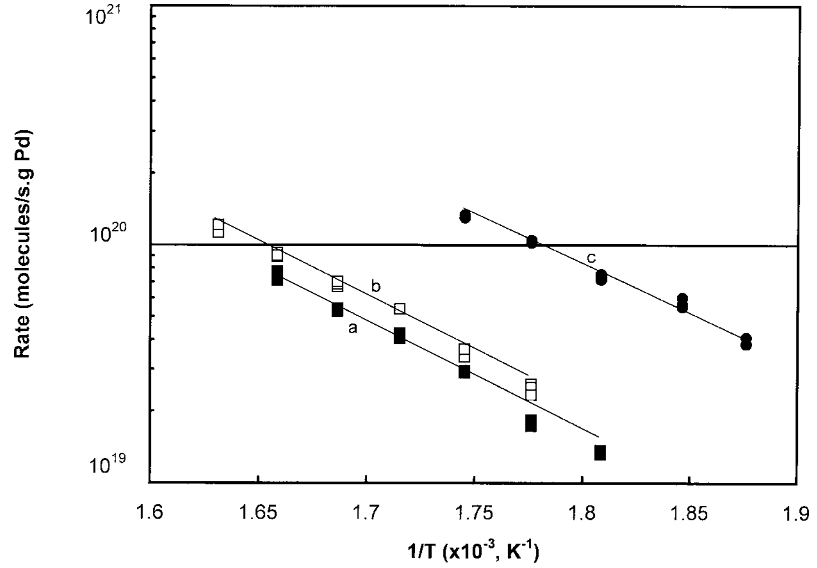

Figure 4. Arrhenius plots of n-butane oxidation in (a) 500 μm × 800 μm or (b) 1000 μm × 800 μm micro-reactors containing Pd and in (c) 1000 μm × 800 μm micro-reactor containing Pd/alumina. Data were collected with a feed consisting of 1 ml/min n-butane and 8 ml/min O_2 and a total pressure of 760 Torr.

activation energies calculated from the data in figure 4 are somewhat higher than are normally reported for oxidation of simple alkanes other than methane, a wide range of values, from ~50 to 90 kJ/mol, have been reported for this reaction [25,26], possibly due to variations in the kinetic regime where the measurements are performed. Finally, the mechanistic conclusions that we have reached based on the reaction orders are reasonable. More important than the rate data itself is the fact that rates were easily measured in the micro-channel reactors using small amounts of catalyst. Obviously, the tendency for *n*-butane to react homogeneously makes this a difficult reaction to control. However, the high surface-to-volume ratios in the micro-reactors inhibit free-radical reaction pathways, making it much easier to measure the heterogeneous reaction rates.

Finally, it is easy to imagine a single plate with many micro-channels. The addition and testing of catalysts through automated procedures is clearly possible with this method.

4. Summary

We have demonstrated that catalytic rate measurements can be performed in micro-channel reactors fabricated through simple tape-casting methods. It was shown that catalysts can be introduced to the channels and reaction rates monitored using procedures that are easily adaptable to high-throughput methods. These highly flexible, inexpensive methods for making micro-channel reactors could prove to be very useful for catalyst screening.

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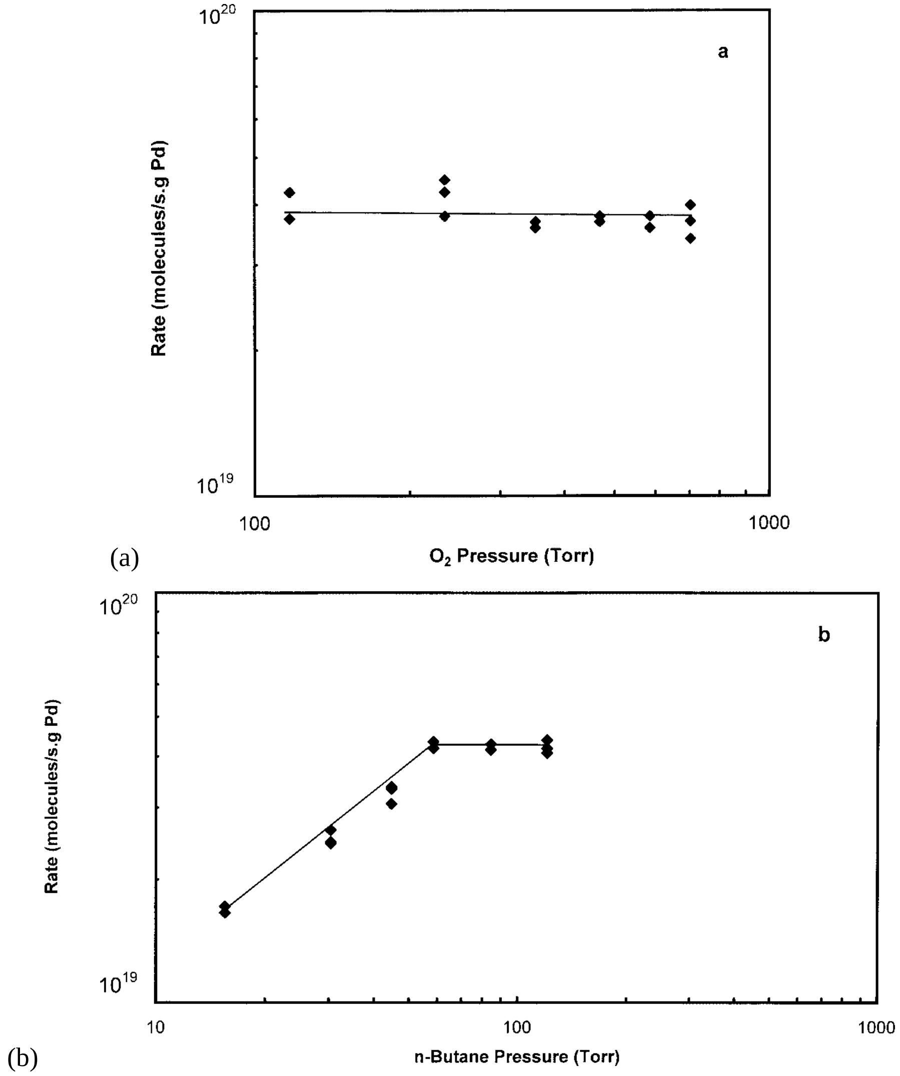

Figure 5. Partial-pressure dependence for *n*-butane oxidation at 573 K: (a) differential rates as a function of O_2 partial pressure with an *n*-butane partial pressure of 60 Torr; (b) differential rates as a function of *n*-butane partial pressure with an O_2 partial pressure of 700 Torr. Data were collected in the 1000 μm × 800 μm micro-reactor containing Pd with a total pressure of 760 Torr.

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