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Catalyst screening and kinetic studies using microchannel reactors

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Abstract

A multi-parallel microchannel reactor system is described, as related to catalyst screening and discovery for heat-intensive heterogeneous catalytic reactions. Example systems are detailed in which the rapid heat transfer of the screening device is utilized to maintain isothermal operation in multiple channels for catalyst screening as well as kinetic investigations. The advantages of the system and pertinent results are discussed, specifically for Fischer–Tropsch synthesis and methanol steam reforming applications.

Keywords: High throughput catalyst screening; Microchannel reactor; Kinetics studies; Combinatorial catalysis

1. Introduction

Just as the pharmaceutical industry has benefited from rapid parallel screening techniques, catalysis research stands to benefit much the same way from rapid parallel catalyst testing systems. Parallel screening of catalyst formulations, if conducted with proper control and data acquisition implementation, can significantly decrease the time and cost associated with new catalyst discovery. The desire in high throughput screening is to maintain precise control over the reactor and maintain an isothermal condition during operation, especially when investigating exergetic reactions. Any significant deviation from isothermal operation will call into questioning the results obtained in such a system, as screening different catalysts under disparate conditions yields questionable results at best. In various studies such as discovering new compositions, determining intrinsic kinetics, or studying new feedstocks, it is of the utmost importance that catalysts are evaluated at reactor conditions where concentration and temperature gradients are minimized, so that required information obtained on catalyst activity, selectivity, and life represents the nature. However, this is often difficult to achieve in many highly exothermic or endothermic chemical reactions.

Since the main concerns in catalyst screening involve heat and mass transfer, microchannel reactors have become a keen area of interest for parallel catalyst screening. The intrinsic advantages of microchannel reactors have been described extensively elsewhere [1–3]. Because microchannel reactors have characteristically small transport distances, the heat and mass transfer limitations that often plague catalytic processes can be largely avoided. Furthermore, if the catalyst being developed is ultimately to be deployed in a microchannel reactor system, the results of the screening will directly translate to the process, including detailed kinetic behavior elucidation.

Several groups have demonstrated success in applying multi-parallel heterogeneous catalyst screening techniques for various chemical processes [4]. Much of the investigation of high-throughput screening has focused on batch micro-reactors such as systems developed by Symyx [5,6]. Automation is key to enabling such systems, where dozens of batch micro-reactors are operated in parallel. Others have taken the approach of utilizing microchannel flow reactors for catalyst screening purposes. However, even with microchannel reactors, it may still be difficult to achieve isothermal operations in microchannel reactors that do not have an active cooling mechanism built in. Additionally, even if the same average catalyst bed temperatures can be maintained among parallel streams, any hot spots in the catalyst bed, or differences in temperature profile will obfuscate the results.

The focus of this paper is to provide a brief summary of our parallel microchannel flow reactors for screening heterogeneous

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catalysts, especially those that will be deployed in microchannel reactors, and potentially involving multi-phase reactions. Others have developed parallel systems specifically for flow through operation, such as Hoffmann et al. [7,8], Senkan et al. [9], Men et al. [10], Fung and Ho [11], Muller et al. [12], Rodemerck et al. [13], Zech et al. [14,15], Rebrov et al. [16], and Steinfeldt et al. [17], and most of these have microchannel architectures. The reactions investigated in these studies include low-temperature CO oxidation [7,13], CH_4 oxidation [8,12,14,15], cyclohexane dehydrogenation [9], methanol steam reforming [10], methanol-to-olefins [11], hydrodesulfurization [11], CH_4 oxidative coupling [13], ammonia oxidation in the explosive region [16], and oxidative dehydrogenation of propane [17].

Our system differs from the aforementioned studies in that it provides both active heating and active cooling, thus making it suitable for both endothermic and exothermic reaction studies. Furthermore, the ability to maintain isothermal conditions lends itself to intrinsic kinetic investigations in parallel reactors. In conventional laboratory testing units, the reactor is placed in a furnace or a fluidized sand bath. The latter case generally gives a more uniform temperature along the reactor wall than does a tube furnace, but it may be more difficult to operate. The tube reactor in a furnace usually exhibits low heat transfer rates between the furnace wall and the catalyst bed. Local hot or cold spots can be generated during the reaction, which in turn may lead to poor selectivity and rapid deactivation. We propose and demonstrate a third approach, as described below.

2. Multi-channel microreactors

The schematic of the combinatorial reactor assembly is shown in Fig. 1. One module typically incorporates five parallel slots that serve as independent reactors. The gap of microchannel slots can be adjusted from 0.25 to 1.52 mm to accommodate reactions with different heat duties. The catalyst powder is located in the lower portion of the channel so that the reactants can be preheated to a desired temperature before contacting the catalyst bed. Inert metallic or ceramic frits are used to hold the catalyst in place and provide good heat transfer. The microchannel catalytic slots are "sandwiched" by two separated oil heating/cooling channels, which are designed to provide rapid heat exchange and maintain uniform reactor temperature. The heat exchange fluids such as high temperature oil flow through the channel in a cross flow pattern relative to the process gas streams. A Julabo® brand circulating oil bath was used to circulate the oil and provide heat duty to the microchannel reactors. Reactions take place in the catalyst bed with uniform reactor wall temperature as measured by the thermocouples in the thermal wells. For example, for the methanol steam reforming and Fischer–Tropsch synthesis reactions studied, the reactor wall temperature is typically controlled within a very narrow limit among five screen channels (less than 1 °C within the range of 250–400 °C, and at pressures up to 1000 psig). Six thermocouples inserted in thermal wells are used to measure the temperature profile of the reactor body during the operation. Each reactor channel is fed by a mass flow controller, providing stable molar flow rates. The GHSV can be varied from 1000 to 80,000 h^{-1}. This enables investigation of catalysts over a wide range of process conditions. The reactor system also allows for different catalyst pretreatment procedures and various feed compositions. The controlled heating program of the Julabo provides convenient and precise control of catalyst temperature during the catalyst activation steps. Pneumatic switching valves located downstream regulate the flow paths and select gas streams for analysis. A back-pressure regulator is used to maintain the same system pressure for all channels. A rapid quench and collection system is located downstream of the back-pressure regulator. Non-condensable gaseous products are analyzed by an online micro gas chromatograph (GC) (Agilent QUADH G2891A). The GC is equipped with Molsieve 5 A (10 m), PPQ (8 m), OV-1 (2 μm, 10 m) and OV-1 (1.2 μm, 4 m) columns. The analysis of the effluent gas products typically takes less than 2 min. The liquid samples can be analyzed by either GC or LC. Overall carbon balance and hydrogen balance are routinely found to be greater than 97%. All process data, such as temperature, pressure, and flowrates, are recorded with a Lab View data acquisition system in a computer and displayed in real time. It is worthwhile to note that the number of five parallel reactors is not a fixed value. Stacking of multiple modules can be conveniently implemented to meet high throughput screening demands. With such a fast screening device, a large matrix of catalyst formulations can be screened in a relatively short period of time.

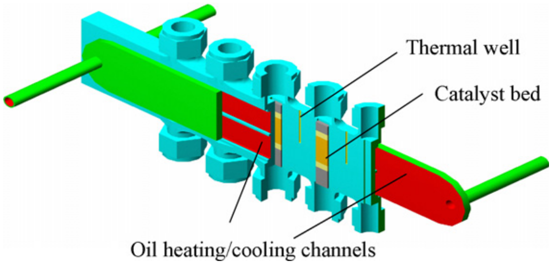

Fig. 1. Schematic of combinatorial testing reactor.

3. Screening of heterogeneous catalysts for exothermic and endothermic reactions

The multi-channel-screening reactor has been successfully applied in catalyst testing in our group. Typical examples include development of highly active and selective Fischer–Tropsch synthesis catalysts. These represent catalytic systems with strongly exothermic reactions. The microchannel reactor has also been implemented in catalyst testing and kinetic studies for endothermic reactions such as the steam reforming of methanol. The following sections show case studies of these applications.

3.1. Fischer–Tropsch synthesis catalyst development

Fischer–Tropsch synthesis is a catalytic CO hydrogenation process that results in the production of a mixture of paraffins, olefins, oxygenates, and water. It is highly desirable to synthesize hydrocarbons with high selectivity to C_5^+ and low selectivity to light products, particularly CH_4, in order to minimize recycle in the gas conversion process. It is well known that transport limitations inherent in this gas–liquid–solid phase reaction scheme play a significant role in the product selectivity. For instance, strong exothermic effect in the synthesis process enhances methanation [18], and diffusion limitations on reactants or products control the chain growth and affects secondary reactions [19]. Conventional lab reactor testing uses a microtubular fixed bed which still shows large exothermicity in a wide range of conditions, particularly at short residence times (<1 s) and high temperatures (above 210 °C). As an example, Fischer–Tropsch synthesis in a microtubular reactor with an i.d. of 4 mm on a Co-based catalyst was simulated at 210 °C and 20 atm with a GHSV of 18,000 h^{-1} (H_2/CO = 2). The details of the reactor simulation are described elsewhere [20]. Fig. 2 shows the bed temperature profile in such a microtubular reactor by finite element numerical modeling at an overall CO conversion of 62%. The temperature gradient shows local hot spots in the bed. The maximum temperature excursion can be as high as 29 °C even at moderate synthesis conditions such as a GHSV of 18,000 h^{-1} and wall temperature of 210 °C. In such cases, intrinsic catalyst activity is overestimated as the catalyst sees a high average temperature. When various catalyst compositions are investigated, performance differences could be masked by such temperature non-uniformity. In order to reduce such heat transfer resistances, bed dilution using inert materials with high thermal conductivity such as SiC is usually employed to mitigate temperature gradients. However, catalyst dilution may change the hydrodynamic behavior and cause a large pressure drop. In addition, the dilution introduces foreign materials and gives unnecessary trouble in separating them from the spent catalysts for post-reaction characterization. The microchannel reactor approach provides a unique solution to such problems, in which the catalyst can be kinetically characterized. For example, modeling results shown in Fig. 3 indicate that the hot spots can be largely eliminated under the identical conditions as that used in the 4 mm microtubular reactor. The maximum temperature gradient was found to be less than 1 °C in comparison to 29 °C in the case of using microtubular reactor at the same wall temperature.

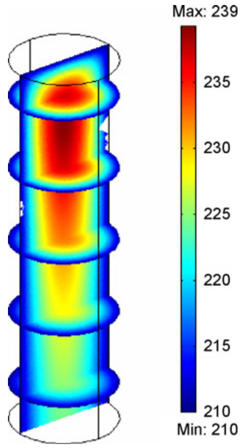

Fig. 2. Temperature profiles in a conventional tubular reactor for Fischer–Tropsch synthesis (*P* = 20 atm, reactor wall temperature at 210 °C H_2/CO = 2, GHSV = 18,000 h^{-1}). Overall conversion level for the conventional tubular reactor is 62%.

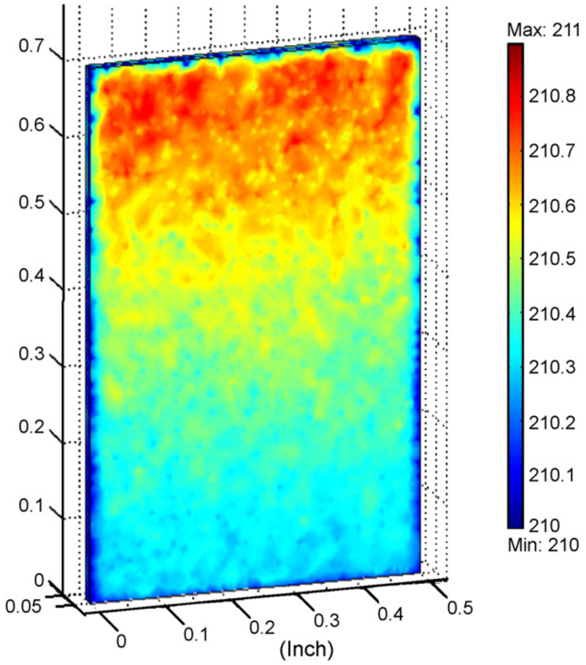

Fig. 3. Temperature profiles in a microchannel reactor for Fischer–Tropsch synthesis (*P* = 20 atm, reactor wall temperature at 210 °C H_2/CO = 2, GHSV = 18,000 h^{-1}). Overall conversion level is 50%.

Before acquiring and comparing activity data of different catalysts in the multi-channel reactors, the five channels of each reactor module were packed with the same catalyst and operated at the same space velocity to confirm the reproducibility among the five channels. Fig. 4 shows the performance of the Co-based catalysts in the five channels at identical conditions. It can be seen that the standard deviation of CO

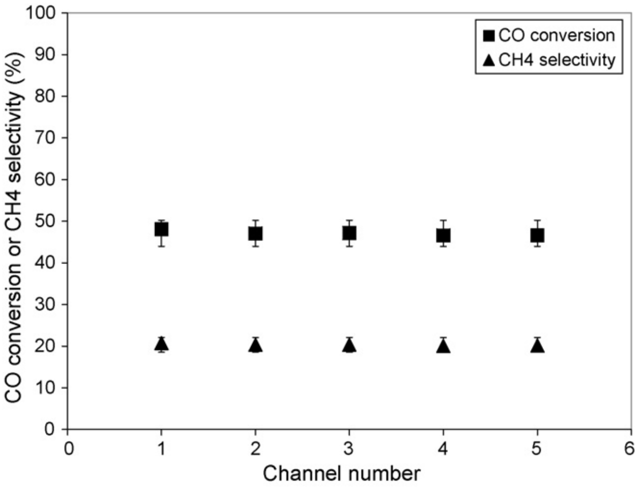

Fig. 4. Performance of the same catalyst (13814-126) in the five channels at identical Fischer–Tropsch synthesis conditions (*T* = 250 °C, *P* = 5 atm, GHSV = 24,000 h^{-1}, H_2/CO = 2).

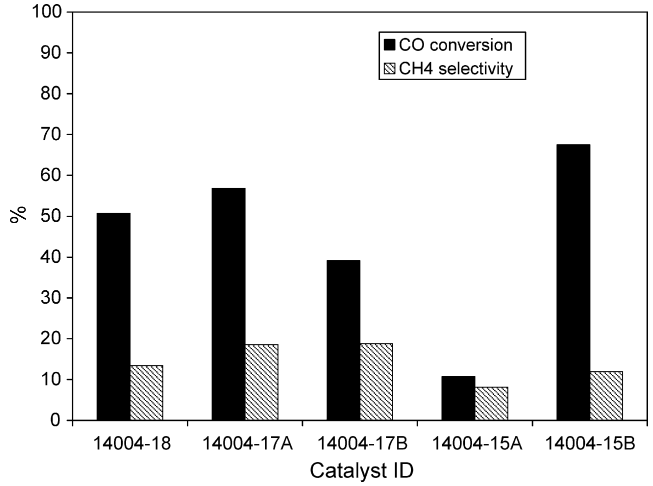

Fig. 5. Catalyst performance evaluation in the microchannel reactors at identical Fischer–Tropsch synthesis conditions (T = 240 °C, P = 15 atm, GHSV = 12,200 h^{-1}, H_2/CO = 2).

conversion was less than 5%, and the relative difference of methane selectivity was less than 3%. The difference among the six-thermocouple readings (measured in the thermal wells as indicated in Fig. 1) was less than 0.5 °C. When the new compositions were tested, a benchmark catalyst was always used in the same module to provide a baseline. Fig. 5 shows the CO conversion and methane selectivity for the four new catalysts (CoRe on an alumina support with various Co loadings and Co/Re ratios), compared to the benchmark catalyst 14004-18. It clearly shows the activity and selectivity improvement if any. For example, the catalyst 14004-17A gives higher CO conversion and was considered to be more active than the benchmark catalyst, but the selectivity to heavy hydrocarbons was low as indicated by high methane selectivity. The catalyst 14004-15A was selective to heavy hydrocarbons as evidenced by low methane selectivity but the activity was low. In this particular batch of testing, catalyst 14004-15B was discovered to be a better catalyst than the benchmark catalyst for FT synthesis in terms of high CO conversion and low methane selectivity. In such a way, over 200 catalyst compositions were screened using four parallel 5-channel modules (20 channels) over a relatively short period of time. In our Fischer–Tropsch catalyst development effort, this catalyst screening tool has played a significant role in identifying the highly active and selective catalysts, which yields 60% one-pass CO conversion at a GHSV of 60,000 h^{-1} while maintaining low methane selectivity (<10%) and high chain growth probability (>0.9) [21]. Such a GHSV in the microchannel reactor is about 15 times faster than that in a conventional fixed bed technology developed by leading industrial organizations [22].

3.2. Kinetic studies of steam reforming of methanol

As demonstrated in above exothermic catalytic system for Fischer–Tropsch synthesis, the microchannel reactor presents a highly isothermal environment for catalyst evaluation, and it is ideal for use in studying reaction kinetics. This idea was also applied to endothermic reactions such as steam reforming of methanol for hydrogen production for fuel cell applications. A single channel with active heat exchange as descrived above was used to decouple transport phenomena from chemical reactions for intrinsic kinetics study. The catalytic portion of the reactor is a microchannel slot with the gap width of 0.508 mm.

A liquid methanol and water mixture is pumped into a microchannel vaporizer with precise flowrate settings. The methanol and water vapor are then blended with N_2 carrier gas, passing through a 25-ml surge tank, where the reactants are preheated to the process temperature and which holds some head pressure for steady operation. Steam reforming reactions take place in the catalyst bed with uniform reactor temperature. The reactor provides an isothermal environment for rate measurement of the endothermic methanol steam reforming reactions over a Pd/ZnO catalyst in a wide temperature range (160–310 °C). The apparent activation energy and rate equation have been determined experimentally as described in our previous publication [23]. This result provided kinetic data for the design of a micro fuel processor for small fuel cell applications, as described elsewhere [24–26].

4. Conclusion

A microchannel reactor based combinatorial system with active heat removal was used for fast catalyst screening and reaction kinetics studies. It has advantages in reducing heat and mass transfer limitation. Combinatorial activity testing in the multi-channel microreactors has significantly accelerated the exploratory efforts in the identification of highly active and selective catalyst for Fisher–Tropsch synthesis as an example. This unique tool also allows us to develop catalysts with direct applications to microchannel reactors at early stage of research and development and minimizes potential ‘‘scale up’’ or ‘‘catalyst transformation’’ issues when catalyst of choice is later deployed in multi-channel and modular microchannel reactors.

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