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Direct Non-oxidative Methane Conversion in a Millisecond Catalytic Wall Reactor

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Abstract: Direct non-oxidative methane conversion (DNMC) has been recognized as a key technology for application of natural gas in the chemical and energy industries. High reaction temperature and low catalyst durability, due to endothermic reaction nature and coke deposition, are two main challenges. We show that a millisecond catalytic wall reactor enables stable methane conversion, C₂₊ selectivity, coke yield and long-term durability. These effects originate from initiation of DNMC on reactor wall, and maintenance of the reaction by gas phase chemistry in reactor compartment. The performance results obtained under various temperatures and gas flow rates form a basis for optimizing lighter C₂ or heavier aromatic products. A process simulation done by Aspen Plus explored the practical implications of the catalytic wall reactor. High carbon and thermal efficiencies and low cost in reactor materials are realized for the technoeconomic process viability of the DNMC technology.

Methane (CH₄), the main constituent of natural gas, is deemed to be an alternative source to replace crude oil for the production of chemicals and fuel^[1]. CH₄ conversion has been explored by indirect processes of CH₄ to synthesis gas followed by Fischer-Trøpsch synthesis of higher hydrocarbons^[2] or oxidative coupling reactions. Even with low efficiency, high capital cost and high carbon dioxide emissions, the synthesis gas route is the dominant industrial practice. Direct non-oxidative methane conversion (DNMC) is a promising route to convert natural gas into value-added petrochemicals such as ethylene and benzene, w hen combined are referred to as C₂₊ hydrocarbons, in one step. The reaction, how ever, is challenged by high-temperature endothermic nature, low C₂₊ yields and coke formation^[3].

Past research efforts have studied non-catalytic^[4] and catalytic DNMC^[5] for CH₄ conversion. The non-catalytic route focuses on CH₄ pyrolysis to achieve high acetylene yield, but temperature above 1973 K is required^[4a, 6]. In catalytic DNMC, the metal loaded zeolite catalysts are used at temperature below 950 K, but CH₄ conversion is low accompanied with fast catalyst deactivation^[7]. The recently reported iron/silica (Fe/SiO₂) catalyst is effective for DNMC, which has high CH₄ conversion and C₂₊ yields.^[5b] High reaction temperatures exceeding 1200 K and high heat supply for CH₄ activation on Fe/SiO₂ catalyst are required, and these challenge the fixed-bed reactor design and operation. Technoeconomic and environmental aspects require efficient chemical reactor systems that are low-cost, simple manufacturing and capable of supplying heat for the highly endothermic DNMC reaction.

We innovated the DNMC technology by designing a millisecond catalytic wall reactor (Fig. 1) that manipulates CH_4

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conversion, product selectivity and coke formation to realize its technoeconomic viability. The reactant flows in the reactor channel, and reaction initiates on the wall surface and happens both on reactor w all and in reactor channel. The diffusion time of reactant to the reactive wall is within millisecond (refer to S3.21 in Supporting Information). Such short-contact-time is viable for chemical synthesis from alkanes, such as oxidative dehydrogenation of hydrocarbons for olefins^[8] or hydrogen production^[9]. Placing catalyst directly onto the inner and outer w alls of reactor promotes heat transfer in thermal boundary layers so that heat released by exothermic reaction on one side of the reactor can be effectively coupled to heat supply for endothermic reaction on the opposite side^[10]. Therefore, the process can be run autothermally and almost adiabatically with a residence time of approximately a few milliseconds. It also guarantees a very high throughput using smaller amount of catalyst, energy and capital costs, compared to the traditional technology. How ever, such concept has never been attempted in DNMC reaction.



Fig. 1. Schematic of catalytic wall reactor for CH_4 conversion into C_{2*} hy drocarbons and H_2 in DNMC process.

Our study on the millisecond catalytic w all reactor originated from a critically low surface area of Fe/SiO2 catalyst to activate DNMC in the fixed-bed reactor (Fig. S2(a)). It should be noted that acetylene, ethylene, ethane, benzene, toluene, naphthalene and coke were the products formed in the DNMC reaction, as shown in our precious work[12]. The Brunauer-Emmett-Teller surface area of our synthesized Fe/SiO₂ catalyst is 0.38 m² g⁻¹. By fixing the catalyst bed length with guartz-balanced particles, the surface area of Fe/SiO₂ catalyst was varied from 0 to 0.15 m^2 , equivalent to 0 to 100 wt% mass percentage of Fe/SiO₂ in the catalyst bed. CH₄ conversion was < 1.0% in the blank reactor (Fig. S2(b)), increased to 5.7% in the reactor packed with quartz particles, and then increased to 10.3% by using 0.036 m^2 (or 25) wt%) Fe/SiO₂ in catalyst bed, and maintained at ~11.0% with further increase in Fe/SiO₂ catalyst quantity. The coke selectivity was the highest in the fixed-bed reactor packed with quartzbalance particles but decreased with increasing Fe/SiO₂ usage in the catalyst bed. Clearly, a critically small active surface area of Fe/SiO₂ catalyst is sufficient to enable the DNMC. The further increase in Fe/SiO₂ catalyst usage did not increase CH₄ conversion, suggesting that the DNMC is not an exclusive

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heterogeneous reaction, but a mixed heterogeneoushomogeneous netw ork, consistent with report by Bao et al.^[5b].

The requirement for small amount (i.e. surface area) of Fe/SiO₂ catalyst in DNMC suggests the potential to develop millisecond catalytic wall reactors comprised of a catalyst coating layer on the reactor wall that offers equivalent catalyst surface area to that in the fixed-bed reactor. The calculation shows that a reactor tube with inner diameter of 4.3 mm and length of 228.6 mm offers 0.036 m² of surface area, same as that of 25 wt% Fe/SiO₂ mixed with 75wt% guartz-balance particles in the catalyst bed in Fig. S2(a). We, therefore, explored for the first time the development of Fe/SiO₂ millisecond catalytic wall reactor for DNMC. The manufacturing process includes the curving of softened straight quartz tube into "U" shape, loading of Fe/SiO2 into U-shaped quartz tube channel, heating of both Fe/SiO2 catalyst and quartz tube to melting temperature, and finally discharging of unmelted catalyst residue. The low cost and abundance of catalyst materials enabled fabrication of the catalytic wall reactor using commercial processes such as extrusion, which produces active surfaces on both sides of the reactor. The simplicity of reactor manufacturing process indicates the great potential in industrial practice of DNMC technology.



Fig. 2. (a) CH₄ conversion and product selectivity in different catalyst/reactor settings: (i) blank quartz reactor, (ii) Fe/SiO₂ catalyst packed in quartz reactor, (iii) cataly tic wall reactor coated with Fe/SiO₂ catalyst and (iv) Fe/SiO₂ catalyst packed in catalytic wall reactor; (b) Long-term stability test of DNMC reaction in cataly tic wall reactor. (1273 K, 20 mL min⁻¹ gas flow rate, CH₄:N₂ = 9:1 (N₂ internal standard), 1 atm pressure, 0.075wt% Fe in Fe/SiO₂, 0.375 g catalyst.)

We tested the catalytic wall reactor performance and compared it to the DNMC in non-catalytic quartz reactor, a fixed-

bed guartz reactor packed with Fe/SiO₂ catalyst, and a catalytic w all reactor loaded with Fe/SiO₂, respectively. In sequence, these four reactor/catalyst settings presented 0.8%, 7.9%, 11.3% and 11.0% CH₄ conversions (Fig. 2a). The result confirms that the Fe/SiO₂ catalyst was successfully incorporated into the guartz tube wall. Coke formation follows a steady state rate in the catalytic wall reactor (refer to S3.3.3). This data suggests that a homogeneous gas phase reaction might play a dominant role after DNMC initiation by the heterogeneous catalyst surface. The long-term stability of the catalytic wall reactor for DNMC was tested by running the reaction at 1273 K for 50 h (Fig. 2b). CH₄ conversion was kept stable at ~11.3%, C₂ (30.3%), benzene (21.2%), toluene (6.6 %) and naphthalene (32.4%) selectivity remained constant, and the total selectivity to these products (C_{2+}) were kept at >91.0%. The slight spikes at reaction times of ~12 and ~32 hours were caused by the temperature fluctuation, as show n in Fig. S3. A reproducibility test showed that the data were reproducible in multiple tests with multiple catalytic wall reactors made following the same procedure (Fig. S4). The combination of high CH₄ conversion, high product selectivity and excellent stability in the catalytic wall reactor is undeniably remarkable.



Fig. 3. (a) CH₄ conversion; (b) C_{2+} selectivity; (c) C_{2+} yields; and (d) coke yield, respectively, as a function of reaction temperature and feed gas flow rate. (C_{2+} selectivity and yield and coke yield are calculated from the carbon-atom basis.)

The dependence of CH₄ conversion, C₂₊ selectivity and yields, and coke yield on temperatures and gas flow rates were measured (**Fig. 3**). CH₄ conversion increased proportionally with temperature and inversely with gas flow rate (**Fig. 3a**). The C₂₊ selectivity (**Fig. 3b**) has opposite dependence, while C₂₊ yield show s an increasing and then decreasing trend (**Fig. 3c**). Coke formation (**Fig. 3d**) follow s the same trend as CH₄ conversion. A maximum (25.4%) C₂₊ yield w as achieved at 1323 K and 20 mL min⁻¹ gas flow rate, which corresponds to 33.9% CH₄ conversion and 25.2% coke selectivity. Both C₂ and aromatics are desirable chemicals needed by the petrochemical industry. Although coke is not a popular product, its formation did not deteriorate the DNMC reaction. Tuning the gas flow rate and/or reaction

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temperature can tune the lighter C_2 or heavier aromatic selectivity, for the targeted processes and reactor operation. On the basis of our reactor configuration and coke formation rate, the time required to fill up the reactor by coking is estimated to vary from 98 hours to infinite amount of time (**Table S2**), which is potentially compatible with the industrial practice.



Fig. 4. Energy input for DNMC and output by coke combustion at corresponding CH_4 conversion and coke yield. The dashed line represents the energy input and output balanced from both reactions. The shaded circle indicates the feasible operation window of DNMC autothermally in the reactor.

We carried out the energy balance analysis (**Fig. 4**), based on standard heat of reaction from DNMC and coke combustion, respectively, to explore the techno feasibility of autothermal catalytic w all reactor. When CH₄ conversion is < 20%, the coke yield is < 3%. The heat supply for enabling DNMC reaction is higher than heat release from combustion of coke formed in DNMC. Oppositely, w hen CH₄ conversion is > 40% and the coke yield is > 15%, the heat release from coke combustion is higher than heat supply for DNMC. The energy balance betw een two reactions can be achieved w hen DNMC is run at ~33.9% CH₄ conversion with 25.4% C₂₊ yield. A recent agreement framework analysis for DNMC by Maravelias et al.^[11] suggests that the economically feasible DNMC is achievable at >25% CH₄ conversion, <20% coke formation and low catalyst cost. The DNMC in our catalytic w all reactor sufficiently meet these targets.

The process simulation using Aspen Plus tools was performed to evaluate the practical implications of the catalytic w all reactor. **Fig. S8(a)** presents the flow sheet for DNMC. A heat exchanger was incorporated to utilize heat released from coke combustion to raise the feed stream to reaction temperature, mimicking the autothermal process. The reactor configuration and operation are demonstrated conceptually in **Fig. S8(b)**. The Aspen Plus Utilities Object Manager and Economic Solver provided estimates for externally-supplied heating and cooling duties and costs (**Tables S3 and S4**). These calculations demonstrate a six-fold reduction in supplied energy costs from the autothermal process relative to a conventional system. The DNMC reaction produces multiple industrially-valuable chemicals and fuels – hydrogen, ethylene, benzene and naphthalene – w hose production rates are converted into retrievable prices (Tables S5 and S6). These results, in combination with the bw costs of CH₄ feedstock and reactor material, as well as simple reactor manufacturing process, demonstrate that DNMC in a catalytic wall reactor is an economically feasible and transformative technology for shifting the petrochemical sector to natural gas feedstock in industry.

In summary, a catalytic wall reactor made of a quartz tube and Fe/SiO₂ catalyst was created for the first time for DNMC. The performance of the catalytic wall reactor was studied under a range of temperatures in combination in combination with different feed gas flow rates. The obtained performance results formbasis for optimizing reaction conditions tow ards lighter C2 or heavier aromatic products from CH₄ feedstock. The integration of catalyst onto reactor wall eliminates catalyst packing and discharging steps that occur in the fixed-bed reactor. Coke was formed in the catalytic wall reactor, and its yield varied with the operating conditions, but did not deteriorate the DNMC. The coke formation could enable an autothermal operation of DNMC. The process simulation demonstrates a six-fold reduction in supplied energy costs from the autothermal process with integrated endothermic DNMC and exothermic coke combustion on opposite sides of reactor, relative to a conventional system. The high carbon and thermal efficiencies, low cost in reactor materials and simple reactor manufacturing process are concurrently realized, indicating the great technoeconomic process viability of the DNMC technology.

Experimental Section

The catalytic wall reactor was fabricated by heating a quartz tube packed with the Fe/SiO₂ catalyst to ~ 1973 K to fuse catalyst onto reactor wall. After discharging the non-fused catalyst, the reactor with a flow channel and catalyst on reactor wall was prepared. The catalyst was synthesized following our previous report^[12]. The materials and methods, DNMC reaction tests, DNMC reaction result analysis, energy balance analysis and process simulation of the catalytic wall reactor were described in details in the Supporting Information.

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Keywords: non-oxidative methane conversion • catalytic wall reactor • iron/silica catalyst • natural gas • process simulation

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