



Conversion of hydrocarbon fuels to syngas in a short contact time catalytic reactor

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ABSTRACT

Some results of the theoretical and experimental research on the oxidative production of syngas from hydrocarbon fuels in catalytic reactors which operate at high temperatures and short contact times are presented. Pilot scale tests of the partial oxidation of methane, isooctane and gasoline have been carried out in nearly adiabatic conditions on structured catalysts developed at the Boriskov Institute of Catalysis and characterized by a low (≤ 0.5 wt./wt.%) content of noble metals. High yield of syngas and stable performance of the catalysts were revealed in the experiments. The details of interaction between chemical and physical processes inside adiabatic monolith reactor have been elucidated by mathematical modeling of the partial oxidation reaction on the base of catalyst detailed chemistry. The problems that emerged from the short contact time reactor operating on a pilot scale are also discussed.

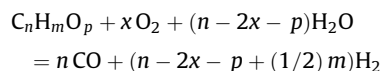
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1. Introduction

Hydrogen combustion and oxidation are pollution free and supply sufficient energy for transportation and other applications. This makes hydrogen a major candidate to meet the world energy demand. However, this simplest element and most plentiful gas in the universe does not exist alone in the nature. It always combines with other elements such as oxygen and carbon. Natural gas contains hydrogen (about 95% of natural gas is methane), as do biomass and hydrocarbons. Nowadays, almost all the hydrogen manufactured on a large scale is obtained by steam reforming of hydrocarbons. For the near term, this method of production will continue to dominate, although several other methods have been developed [1–5].

To avoid a hydrogen supply infrastructure and eliminate gaseous H_2 storage issues, production of hydrogen by the small-scale processing of conventional fuels near the end-user is considered to be a good solution. Catalysis offers a variety of options for the conversion of hydrocarbon fuel into hydrogen-rich gas. One of the most effective methods of generating hydrogen from hydrocarbon fuels is fuel reforming to produce synthesis gas or syngas ($H_2 + CO$). Generally, the primary fuel is converted into synthesis gas with air and (or) steam on a catalyst at high temperatures using one of three major techniques: steam

reforming, partial oxidation, and autothermal reforming [6]. Synthesis gas production by steam reforming is not feasible for the small-scale processing, because steam reformers are large and expensive plants that can hardly be scaled down. A considerable disadvantage of the steam reforming process is that it is an endothermic reaction. When discussing the three principal pathways, Ahmed and Krumpelt [7] demonstrate that the partial oxidation (direct partial oxidation where the feed reacts directly with air or enriched air with carefully balanced oxygen-to-fuel ratios) and autothermal reforming (indirect partial oxidation, as a combination of partial oxidation and steam reforming in stand-alone catalytic system) processes are more attractive for the small-scale practical applications. Contrary to widely held beliefs, these processes are also capable of higher reforming efficiencies than steam reforming. The gross oxidative reaction of syngas formation from a general fuel (hydrocarbon or oxygenate) can be described by the following expression:



The process is carried out in the presence of a catalyst which controls the product composition. Since the first publications [8–10], there has been a significant interest in the new catalytic processes that operate at high temperatures and under short contact times over structured catalysts. It has been shown that catalytic partial oxidation of methane provides close to 100% methane conversion and >90% synthesis gas yields in millisecond contact times. Compared to contact times of seconds in a steam

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reformer, the reactors can be three orders of magnitude smaller processing the same amount of synthesis gas. The authors could exclude the contribution of thermal either nonoxidative or oxidative pyrolysis on the basis of the high conversion achieved. Low coking was attributed to the fact that carbon-producing reactions (olefin cracking, Boudouard reaction, etc.) did not approach an equilibrium and that the presence of CO₂ and H₂O favored reforming of the carbon formed [10,11].

Structured catalysts are ceramic and metallic configurations which constitute both the catalyst support and the reactor. According to classification of Cybulski and Moulijn [12], there are three basic types:

- monoliths, in the form of continuous unitary structures (e.g. honeycombs, foams or interconnected fibers) containing small passages with the walls loaded with catalytically active agents;
- membrane catalysts—structures with permeable walls between passages, thus allowing selective transport of reactants or products; and
- arranged catalysts, which are either arrays of particles or sheets superimposed, to allow crossflow.

Recent literature on partial oxidation reactions shows that there is a growing need to extend our conventional catalyst and reaction engineering knowledge base to this new reactor category, to have better understanding of flow contacting, multispecies transports and detailed reaction kinetics and their interactions in monolith reactors, to have improved understanding of reactor structure impact and materials (washcoat) influence on the catalyst performance [12–16]. The oxidation processes in the monolith reactor exhibit features not observed in conventional packed bed reactors. Indeed, due to the very high efficiency of the catalyst in such configurations, the structured catalysts operate at 800–1200 °C with the gas flow velocities of ca. 1 m/s with open channel catalyst structures for effective contact times of a few milliseconds. The process is autothermal and nearly adiabatic one. Preheating the feed enhances syngas selectivity, but no reactor preheat was often necessary other than that required to vaporize the fuel [17,18]. While the basic feasibility of the high-temperature catalytic oxidation reactions has been sufficiently demonstrated, many obstacles still remain to be solved on the way to an industrial application. In spite of the numerical research in this area, the performance targets for the fuel processing in the small scale still require the development of a catalyst which exhibits a high activity along with thermal and mechanical stability for the process. It also requires detailed thermodynamic and kinetic information about the reaction. Although the hydrocarbon reforming reactions proceed quickly and equilibrate rapidly, both radial and axial temperature gradients may arise in monolith reactors. The spatial distribution of temperature in the reactor results from the interplay of kinetics, hydrodynamics, heat transfer and process parameters [14,19,20].

This paper briefly reviews general results of the combined experimental and modeling investigation efforts currently being performed at the Boreskov Institute of Catalysis on the development of both the structured catalysts and technology for syngas production from hydrocarbon fuels in the axial and radial type reactors. The following scientific and technical approaches have been applied in the research and development program:

- synthesis of nanocrystalline active components comprising ceria–zirconia fluorite-like complex oxides promoted with small amount of noble metals was carried out to ensure conversion of hydrocarbons into syngas via a highly efficient route of pyrolysis-direct oxidation that depends on (a) ability of dispersed noble metals to dissociate hydrocarbons generating reactive C_xH_y and

H₂, and (b) mobility and reactivity of surface oxygen (hydroxyl groups) which are rapidly transferred to the metal particle-support oxides interface where they consume the surface C_xH_y-particles producing syngas;

- monolithic catalysts were developed by supporting the synthesized nanocrystalline active components onto the corundum and metallic substrates;
- thermodynamic equilibrium restrictions on the operational parameters have been outlined on the base of thermodynamic simulations;
- pilot scale experiments in structured reactors operated under nearly adiabatic conditions have been carried out;
- transient behavior of the monolith reactor during start-up (ignition) of the methane partial oxidation to synthesis gas over Pt/Ce–Zr–La catalyst has been studied in detail both experimentally and by simulation via mathematical modeling, thus providing the necessary bases for theoretical optimization of the catalyst-bed configuration and process parameters.

2. Experimental

2.1. Catalysts preparation and characterization

High-performance active components of the catalysts for selective oxidation of hydrocarbons (gaseous and liquid) into syngas at short contact times comprising nanocrystalline ceria–zirconia solid solutions doped by La, Pr, etc., and promoted with a small amount of noble metals (not higher than 0.5%) have been developed at the Boreskov Institute of Catalysis. The data of various physicochemical, kinetic and mechanistic investigations of the Pt/ceria (ceria–zirconia)-based materials in methane partial oxidation are reported elsewhere [21–36]. Ceria-based mixed oxides (Ce_xM_{1–x}O_y) are versatile solid oxygen exchangers. These materials have been investigated since the early 1990. Incorporation of zirconium into the ceria lattice creates a high concentration of defects improving, thus, the oxygen mobility and oxygen storage capacity [37]. At high (400–800 °C) temperatures, the redox cycle Ce³⁺ ⇌ Ce⁴⁺ + e⁻ facilitates oxygen storage and release from the bulk fluorite lattice. When combined with noble or non-noble metal particles, this makes them ideal candidates for catalytic oxidation applications such as partial oxidation of hydrocarbons into syngas [25].

The high-dispersed homogeneous solid ceria–zirconia solutions were synthesized by using the polymeric polyester precursors decomposition techniques [24,33,38]. Nanoparticles of active metals or their perovskite-like precursors of LaPt(Ni)O₃ and LaPt(Ru)O₃ type were supported via wet impregnation with the mixed solutions of chloride-free salts [24,26,33]. Reactivity and diffusion mobility of the bulk/surface oxygen were studied by using the methods known elsewhere [39–41] and based on oxygen isotope exchange, temperature-programmed reduction by carbon monoxide, methane and hydrogen in microcatalytic facilities.

The different types of fuel processing catalysts were fabricated:

Microspherical LaNiPt (9 wt.)/Ce–ZrOx (ca. 12 wt.)/γ-Al₂O₃ catalyst was prepared by wet impregnation of 1 mm diameter γ-Al₂O₃ spheres (BET surface area 150 m²/g) with the appropriate solutions.

Composite ceramometal monoliths (46 mm diameter, 23 mm length, ca. 300 cpsi channel density, ca. 0.3 porosity). The raw materials were Cr–Al alloy powder and CeO₂ powder (40 wt.%, prepared by decomposition of nitrate). To form a set of transport channels, easily burned organic fibers were inserted into the cermet matrix before the hydrothermal treatment stage (HTT) [26–28,33,41]. A row of parallel passageways (ca. 0.5 mm diameters) along the substrate monolith are inter-

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