



Short communication

Unsteady-state operation of supported platinum catalysts for high conversion of methane



Sheedeh Fouladvand, Magnus Skoglundh, Per-Anders Carlsson*

Department of Chemistry and Chemical Engineering, and Competence Centre for Catalysis, Chalmers University of Technology, SE-412 96 Göteborg, Sweden

HIGHLIGHTS

- Unsteady-state operation enhances catalytic processes.
- Promoting methane oxidation by transient operation.
- Utilisation of temporary states with high catalytic activity.

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ABSTRACT

Total oxidation of methane over model monolith catalysts with platinum supported on alumina, alumina–ceria and ceria has been studied under unsteady-state operation of the feed gas stoichiometry. The general activity for methane oxidation follows the order Pt/alumina < Pt/alumina–ceria < Pt/ceria. Thanks to high catalytic activity at the gas composition switches, increased cycling frequency between oxygen excess and oxygen free conditions increases the average methane conversion significantly from 11% to 58% for Pt/alumina and from 25% to 87% for Pt/alumina–ceria. The corresponding stationary methane conversion is 10% and 19%, respectively. The underlying reason for the enhanced catalytic activity is likely twofold namely that periods with detrimentally high coverage of either oxygen or carbon are shortened and that the transients induce a highly active (chemical) state of the catalyst, thus, facilitating high average conversion of methane.

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1. Introduction

Industrial catalytic processes are generally operated at (nearly) steady-state conditions for many reasons, e.g., steady consumption of reactants and formation of products, optimal process conditions for high space-time yields and stability of the chemical reactor [1] motivated also by safety concerns. Despite this, operation of industrial catalytic processes at unsteady-state conditions may be beneficial in terms of catalytic activity and/or selectivity. This has been an area for research under long time and concepts like reversed-flow [2,3] and pulsed supply of reactants [4] have been studied both experimentally and theoretically. Knowledge in unsteady-state operation is also important for safe start-up and shut-down of industrial chemical processes. Furthermore, there are processes that almost exclusively operate under unsteady-state conditions. Catalytic converters for automotive exhaust aftertreatment is probably the most important example here. In the so-called

three-way catalyst (TWC) carbon monoxide, hydrocarbons, nitrogen oxides and oxygen simultaneously react to harmless products. The process is highly unsteady not only due to that vehicles more or less exclusively are driven at varying speed and load but also because deliberate cycling of the engine air-to-fuel ratio creates exhausts that continuously alternate between net-oxidizing and net-reducing composition. The TWC is highly efficient at elevated temperatures but considerably less effective at low temperatures.

To improve the low-temperature activity of TWCs, especially for the abatement of cold-start emissions, transient operation can be applied [5]. For example it has been shown that by use of periodic operation of the gas composition, the light-off temperature for conversion of hydrocarbons can be lowered by 50–75 °C over a TWC [6,7]. In this case the benefit with periodic operation is mainly due to a lowering of the CO self-poisoning, which has previously been studied in detail [8–11]. Unsteady-state operation of the exhaust composition has been shown beneficial also for total oxidation of saturated hydrocarbons, e.g., methane [12–15] and propane [16]. In these cases temporary high activity is observed during the switch from net-reducing to net-oxidizing conditions

* Corresponding author.

E-mail address: per-anders.carlsson@chalmers.se (P.-A. Carlsson).

and vice versa. For methane oxidation over alumina supported platinum this temporary high activity has been shown to stem either from the formation of a partially oxidized platinum surface that is more effective for dissociation of methane or, more likely, from a period with more reactive chemisorbed oxygen prior to oxide formation [17,18]. We mention that unsteady-state operation of the exhaust temperature also can be used to enhance the methane conversion over alumina supported platinum [19].

In the present study we consider the total oxidation of methane over supported platinum catalysts, i.e., Pt/Al₂O₃, Pt/Al₂O₃-CeO₂ and Pt/CeO₂ monolith catalysts, specifically exploring the possibility of unsteady-state operation as to influence the (average) catalytic activity.

2. Materials and methods

Powder catalysts with 4 wt.% Pt supported on Al₂O₃, Al₂O₃-CeO₂ and CeO₂ were prepared by incipient wetness impregnation [20]. The samples are from here referred to as Pt/Al, Pt/AlCe and Pt/Ce, respectively. Transient activity tests were performed with monolith samples in a continuous gas-flow reactor, which has been described in detail elsewhere [21]. The monolith samples were prepared by coating 200 mg of the respective powder catalyst onto cordierite monolith substrates ($L = 15$ mm, $\phi = 12$ mm) as described in reference [20]. The inlet gas temperature 15 mm upstream the catalyst and the catalyst temperature were separately measured by type k thermocouples and a PID regulator was used to control the inlet gas temperature. The feed gas was controlled via a set of mass flow controllers (Bronkhorst LOW- ΔP -FLOW) and introduced to the reactor by air-actuated high-speed gas valves (Valco, VICI) that allow fast changes of the feed composition. The flow throughout the experiment was 500 ml/min, corresponding to 15,000 h⁻¹ GHSV and a residence time of 0.2 s. A mass spectrometer (Prisma, Pfeiffer) was used to measure the mass-to-charge ratio of the relevant components in the reactor outlet. The catalyst samples were pretreated with the feed gas consisting of 0.3 vol.%

O₂ and 0.1 vol.% CH₄ balanced with Ar at 400 °C for 10 min. The transient experiment was then initiated by removing oxygen from the feed for a period of 300 s while simultaneously compensating with addition of Ar to maintain constant total flow, after which oxygen was added to the feed again for another 300 s. This cycle was repeated before the same procedure was carried out with 150, 75, 50, 25, 15 and 10 s pulsing intervals.

3. Results and discussion

The results from the transient flow reactor experiments are presented in Figs. 1 and 2. Fig. 1 shows the methane conversion over the three catalysts versus time. In the experiments the pulsing frequency is gradually increased, i.e., the duration of the oxygen pulse is gradually shortened as indicated with blue figures on top of Fig. 1. It is clear for the Pt/alumina catalyst that the average methane conversion increases upon increasing pulsing frequency. For the alumina-ceria and ceria supported catalysts, the average methane conversion increases when the pulse length is successively shortened from 300 to 150, 75, 50, 25 and 15 s but for further shortening of the pulse length the average methane conversion remains unchanged. For each change of pulsing frequency (indicated by dashed lines) one cycle needs to be carried through before repeatable responses are established. Fig. 2 zooms in on the responses in methane conversion, oxygen breakthrough, reaction products and carbon balance in the case of 300, 150, 75 and 50 s pulse length. For the Pt/Al catalyst the conversion of methane increases rapidly from about 8% to 35% when oxygen is removed from the feed at $t = 0$ s, followed by a decline towards 6% conversion for the remaining of the rich phase. Upon introduction of oxygen, the methane conversion increases rapidly and reaches 55%. However, continuing the experiment under lean conditions, the methane conversion drops after about 30 s and approaches 8% during the remaining of the lean phase. After the drop in methane conversion the outlet oxygen concentration increases first rapidly and then more slowly towards 2700 ppm by the end of the lean phase.

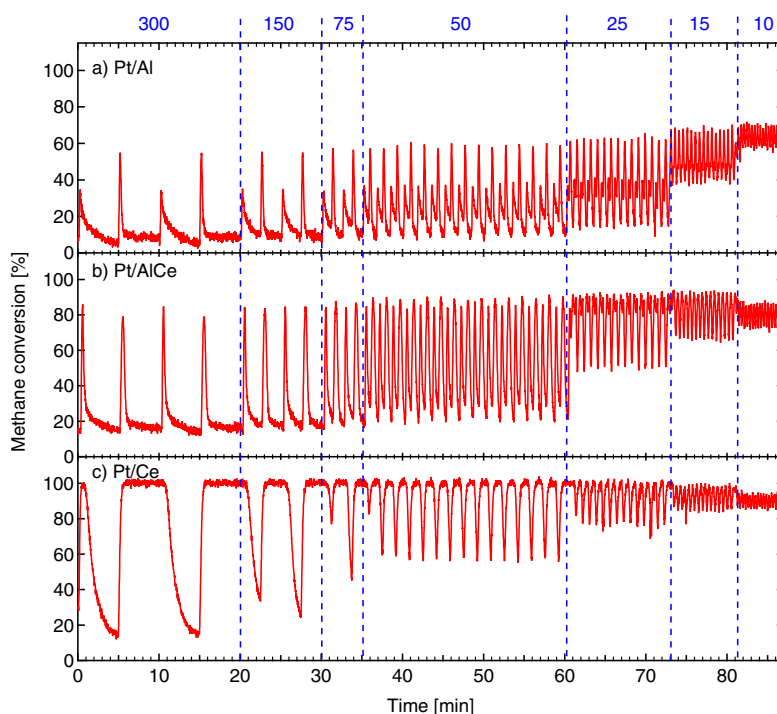


Fig. 1. Oxidation of 0.1% CH₄ over (a) 4-wt.% Pt/Al₂O₃, (b) 4-wt.% Pt/Al₂O₃-CeO₂ and (c) 4-wt.% Pt/CeO₂ catalysts while periodically varying the oxygen concentration between 0 ($S = 0$) and 3000 ppm ($S = 1.5$) at 400 °C, with pulse lengths 300, 150, 75, 50, 25, and 10 s.

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