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Selective methanation of carbon oxides in a microchannel reactor—Primary screening and impact of gas additives

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Abstract

Selective removal of CO by methanation of carbon oxides has been performed over wash-coated supported metal catalysts in a microchannel reactor with simulated reformate feeding. The primary screening over a series of Ru and Ni-based catalysts shows that methanation activity is markedly dependent on the type of metal, the metal loadings and the promoter. $Ni/CaO/Al_2O_3$ catalyst exhibits the highest methanation activity with CO conversion higher than 93% and a relatively low conversion of CO_2 into methane among investigated catalysts at 300 °C under the operating condition. The appropriate temperature for selective methanation was identified to be 250 °C below which CO methanation preferentially and exclusively occurs. The effect of reaction temperature and gas additives such as steam and gaseous oxygen on the methanation performance is presented in terms of catalytic activity, selectivity, and methane yield. The regulation of carbon oxides methanation on $Ni/CaO/Al_2O_3$ catalyst by gaseous oxygen was realized by a switchover of the reaction pathway from combustion reaction in the presence of gas phase oxygen to the methanation upon the complete consumption of oxygen and the dynamic behaviour of catalyst surface induced by the interplay of the catalyst surface and the gas phase reactants.

Keywords: Microchannel reactor; Methanation; Heterogeneous catalysis; CO removal; Hydrogen purification

1. Introduction

Future energy generation for stationary, distributed and mobile applications will be based to a significant extent upon fuel cell technology [1]. The most promising fuel-cell technology for transport applications appears to be the Polymer Electrolyte Membrane Fuel Cell (PEMFC) fueled by hydrogen. Hydrogen powered fuel cells are expected to become important energy carriers for sustained energy consumption with reduced impact on the environment [2]. However, hydrogen fuel cells present obvious problems with generation, storage, and distribution. Pressurized vessels or metal hydrides in a vehicle occupy space, increase weight, and decrease fuel efficiency. As a result, attention has been focused on the conversion of more readily available fuels to hydrogen, either on board of a vehicle [3] or at a service station. The conversion of hydrocarbons and alcohols may be achieved by catalytic reforming or by partial oxidation [4]. In the short to medium term, fuel processing will play a significant role in hydrogen production for fuel cell applications, because the already existing distribution network to supply the consumer with fossil fuels will support the introduction of fuel cell technology onto the market place. One of the major problems for the introduction of low temperature PEMFC as the power source for electrically operated vehicles is the delivery of ‘‘nearly-CO-free’’ feed gas, which becomes problematic whenever H_2 is generated from fuels such as methanol or gasoline, as the fuel cell anodes can be poisoned even by trace impurities of CO. As a consequence, it is essential to reduce CO content to the level below 50 ppm for state-of-art PtRu anode electrocatalysts, and, preferably, below 10 ppm for Pt anode electrocatalysts [5].

Theoretically, there are several methods to reduce carbon monoxide to the levels acceptable for a fuel cell [6]. It is feasible to separate hydrogen by diffusion through a CO filtering membrane [7] but the membrane is expensive and it usually requires a compressor owing to high pressure. The most studied system for the removal of final traces of CO has been the selective oxidation of CO in a H_2-rich atmosphere (PROX)

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over the last years since it has the ability to remove CO down to 10 ppm [8–10]. The catalytic hydrogenation of carbon monoxide and carbon dioxide also produces a large variety of products ranging from methane and methanol to higher molecular weight hydrocarbons and alcohols [11,12]. The methanation of CO and CO_2 as well as the related Fischer–Tropsch reaction have been extensively studied and reviewed. CO_x methanation may have another practical application as a means of CO removal from process gases for gas separation purposes and is also being discussed as an alternative to PROX in fuel processors for mobile fuel cell applications. Recently, selective methanation of carbon monoxide has emerged as a promising route to remove CO in the reformate stream down to 20 ppm for the use of polymer electrolyte fuel cells [13,14].

Microchannel reactors have been employed to minimize the complicated chemical plants mainly due to their advantages for chemical reactions such as several orders of magnitude higher surface to volume ratio compared to traditional chemical reactors and enhanced heat transfer and mass transfer in the reduced dimensions of microchannels [15]. The process intensification benefits of micro process engineering for gas phase reactions [16–19] are consequently within focus of the world-wide research related to fuel processing for small and medium sized application.

In the present study, we have screened supported noble and base metal catalysts to decrease the CO concentration of the simulated methanol steam reforming reformate through the selective CO_x methanation at 150–350 °C and ambient pressure within an isothermal microchannel reactor. In addition, the effect of additional reactants such as steam and oxygen over $Ni/CaO/Al_2O_3$ catalyst was investigated and a distinct catalytic behaviour of Ni-based catalyst is presented, illustrating how gas phase molecules can dominate the reactivity and selectivity of surface reactions and regulate the switchover of the reaction paths for carbon oxide methanation reaction.

2. Experimental

2.1. Catalyst preparation

The microchannel sheets were coated with the respective catalysts to facilitate the appropriate chemical reactions. Two preparation methods may be applied to coat the catalysts (self-made or commercial) onto the microchannel surface.

The self-made catalyst coatings presented in this paper were exclusively based upon alumina carriers. Catalysts were prepared first by wash-coating alumina onto the microchannels. Therefore, the microchannels were filled manually with alumina carrier suspension and excess suspension was removed. The alumina suspension (20 wt.%) in deionized water contained also 5 wt.% polyvinyl alcohol (from Fluka) as a binder and 1 wt.% acetic acid. After drying at room temperature and calcination at a temperature of 600 °C in air, the alumina carrier coating was then impregnated with the desired amount of precursor (metal salt solutions). After drying, the coatings were calcined in air for 6 h at 450 °C. For checking purposes, the amount of the catalyst loaded onto the microchannel was then determined by measuring the weight gain after calcination. To coat the commercial catalyst, a direct wash-coating protocol (as already described above) with the commercial catalyst suspension was applied followed by an appropriate temperature treatment.

Details of this wash-coating procedure were described in our previous studies [20,21]. The deposited washcoats showed very good adhesion not only for fresh samples but also after application-oriented tests [22].

All the metal loadings of the catalysts in this context are based on weight percentage, i.e. wt.%. To make high performance micro-reactors, the inlet and outlet geometry of the micro-structured reactors was optimized by Computational Fluid Dynamics and numerical simulation to ensure the uniform flow distribution in the reactor.

2.2. Experimental set-up

The experimental apparatus consists of the feeding system, the microchannel reactor and the analysis section with an on-line gas chromatograph, which has been described in details elsewhere [23]. Gas mixtures required for the methanation reaction were regulated by the respective mass flow controllers (BRONKHORST HI-TEC). Water regulated by a liquid flow meter was vaporized by a laboratory scale evaporator (BRONKHOST CEM) and fed into the micro-reactor. CO and CO_2 methanation was carried out in a flow-type apparatus with a microchannel reactor at atmospheric pressure and a temperature range from 150 to 350 °C. The microreactor was powered by a heating cartridge regulated by a PID temperature controller with a K-type thermocouple inserted into the wall of the reactor. The

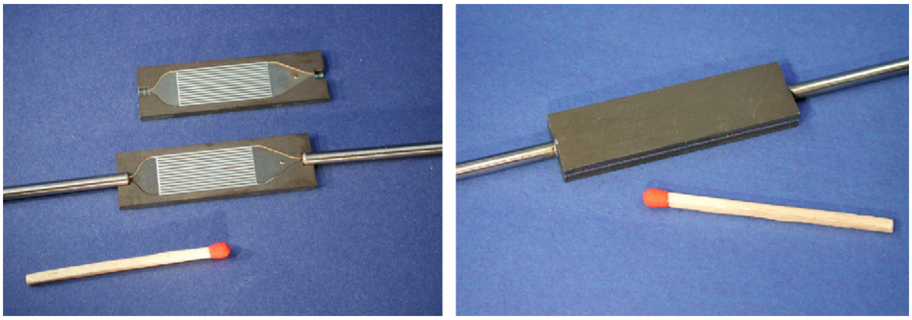

Fig. 1. Sandwiched microchannel reactor for methanation test. *Left*: coated platelets with capillary. *Right*: laser-welded reactor.