



Pd/CeO₂ catalysts as powder in a fixed-bed reactor and as coating in a stacked foil microreactor for the methanol synthesis



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ABSTRACT

Pd/CeO₂ as a catalyst for methanol synthesis has been studied in a microreactor consisting of 14 structured foils in a fixed-bed laboratory reactor. Methanol synthesis was carried out at 80 bar and 300 °C with a syngas composition of H₂/CO/CO₂/N₂ = 65/25/5/5. It was found that Pd/CeO₂ as a foil coating was more active than the Pd/CeO₂ powder catalyst on a Pd/CeO₂ mass basis, both initially and after stabilization. In order to understand the Pd/CeO₂ catalyst properties, both as a coating on the structured foils and as nanoparticles, techniques such as TEM, SEM, XRD and chemisorption were employed to characterize the catalysts before and after reaction experiments. The activity of the Pd/CeO₂ foil coating is substantially better than the Pd/CeO₂ powder despite significantly higher Pd dispersion of the Pd/CeO₂ powder. This is ascribed to the Pd nanoparticles of the powder catalyst being partly covered by the ceria upon preparation and reduction. This prevents the accessibility of Pd to the gaseous reactants. A higher number of active sites are initially present in both catalysts, leading to high initial activity for methane as well as methanol formation. This may be explained by good interfacial contact between Pd and CeO₂ created during preparation and reduction to form sites that are gradually lost under reaction conditions by a combination of sintering/agglomeration and enhanced coverage of the Pd by ceria layers.

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1. Introduction

Natural gas represents a global energy resource similar in size to that of crude oil. Approximately 50% of gas reserves could be considered as “stranded”, i.e. lacking pipelines or other infrastructure for transport directly to the market [1]. 50% of the stranded gas is located off-shore. Exploiting offshore gas presents challenges that could possibly be overcome by offshore conversion to methanol, synthetic gasoline/diesel (Fischer-Tropsch technology) or dimethyl ether (DME), processes that may be referred to as gas-to-liquids (GTL) technology. For offshore GTL, a barge-mountable production unit would require compact, efficient, robust, light weight, reliable and safe technologies, whereas existing technology is favored by economy of scale and does not meet the requirements for floating installations.

Microstructured reactors [2–4], in which the reaction occurs in parallel channels or structures of critical dimensions ranging from a few μm to a few mm, may represent an interesting potential for off-shore GTL technology. Compared to conventional reactors, the high surface-to-volume ratios resulting from the narrow reaction volumes significantly enhance the heat and mass transfer [5–8]. Highly exothermic reactions may be carried out at nearly isothermal conditions [9,10] or even with controlled temperature gradients over the reactor [11]. The suppression of hot spots not only results in safe operation, but helps prolonging the lifetime of the catalysts [12,13]. It may also reduce the extent of undesirable side reactions, leading to higher selectivity [14,15]. This may again allow for accommodation of catalysts with 1–2 orders of magnitude higher activity than existing technology in certain cases. Eventually, this could lead to increased product yields, improved energy efficiency, smaller process footprints and reduced capital costs [16].

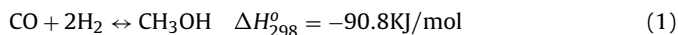
Methanol is one of the basic intermediates in the chemical industry and is also being used as a fuel additive and as a clean burning fuel. It is the starting point for formaldehyde, methyl *tert*-butyl

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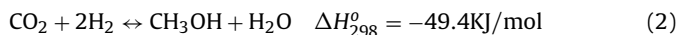
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ether and several solvents [17,18]. Methanol can also be converted to olefins (ethene, propene, etc.) by recently developed processes [19]. Industrial production of methanol is carried out directly from synthesis gas over a CuO/ZnO/Al₂O₃ catalyst. The main reactions for the formation of methanol from syngas are:

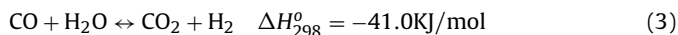
Methanol synthesis from CO:



Methanol synthesis from CO₂:



The two methanol forming reactions are coupled by the water gas shift reaction:



The advantages of the CuO/ZnO/Al₂O₃ catalyst are many, since it has relatively low cost and high selectivity to methanol, and the system is mature and well-developed. Possible disadvantages include the tendency towards sintering at temperatures greater than 270–300 °C [20] and a reaction mechanism that requires carbon dioxide to be present in the feed, resulting in water as a by-product in the reaction. Supported palladium has been suggested as an alternative catalyst because the reaction mechanism proceeds via carbon monoxide [21] and because it is possibly a more active metal than copper. However, reports on the activity and selectivity of Pd catalysts have not been too encouraging when compared to Cu-based catalysts [21–24]. Shen et al. [25,26] have reported that Pd in combination with ceria as support or promoter exhibited higher activity for methanol synthesis from carbon monoxide and hydrogen than the conventional Cu-based catalysts. The high catalytic activity was attributed to the presence of Pd species in the cationic form (close to +1), due to strong interaction between Pd and ceria [27]. Moreover, Pd based catalysts may be an alternative to Cu-based catalyst as they possess better tolerance towards sulphur poisoning [28], which is becoming increasingly important for coal or biomass derived synthesis gas feed.

Arising from the interest in developing offshore GTL technologies, the topic of methanol synthesis in microstructured reactors became part of our research activities. We have previously studied Pd/CeO₂ catalyst as a coating in a stacked foil microreactor for methanol synthesis [29]. The coating was then compared with a CuO/ZnO/Al₂O₃ coating as well as a Pd/CeO₂ catalyst powder in a fixed-bed reactor. The Pd/CeO₂ coated foils showed higher methanol productivity than that of Cu system on a mole of active metal basis (Pd/Cu), although at higher temperature and with significantly higher methane by-product formation. In this study, we proceed to obtain more detailed understanding of the Pd/CeO₂ catalysts, both as a coating on the structured foils and as nanoparticles. TEM, SEM, XRD and chemisorption were therefore employed to characterize the catalysts before and after reaction experiments

2. Experimental

The stacked foil microreactor (SFMR) consisting of fourteen structured foils (Fig. 1) was made by Karlsruhe Institute of Technology (KIT) [29]. The structured and coated foils were stacked inside a steel (Alloy 800) housing, using graphite seals (Novaform SK, Frentzelit) to allow for high pressure. Two metal blocks, one below and one above the stack, were used to adapt the height of the stack to the housing and thereby ensuring leak tightness and minimal reactant bypass issues. The SFMR was electrically heated by 16 cartridges to maintain a uniform temperature profile, which was recorded by insertion of thermocouples into holes in the SFMR outer shell. The geometric dimensions of the SFMR structured foils were as follows: Channel width and height: 200 μm. Foil length

and width: 150 mm and 25 mm, respectively. Channel volume of stacked foils 4 200 mm³ and coated surface of stacked foils 63 000 mm².

The fixed-bed reactor (FBR) was made of a 1/2" 316 stainless steel tube with an internal diameter of 10 mm. 1 g of catalyst particles (50–120 μm) was kept in place by a stainless steel cylinder capped with a steel gauze inserted into the reactor bottom. The catalyst bed length was about 20 mm. The FBR was clamped inside an aluminum block and heated by a Kanthal furnace that was regulated against a thermocouple placed between the reactor and the aluminum block. The catalyst bed temperature was recorded by a movable thermocouple inside a thermowell centered inside the reactor. For comparison between foil and FBR experiments, the furnace temperature was adjusted so that the maximum bed temperature (T_{peak}) along the FBR axis corresponded to the practically isothermal mid-section SFMR temperature [29].

The Pd/CeO₂ foil coating was prepared by dripping a CeO₂ sol-gel, synthesized according to Ozer et al. [30] from cerium ammonium nitrate, uniformly over the microchannels. This was followed by drying at 70 °C overnight and calcination at 500 °C for 5 h in air. The CeO₂ layer was then dripped several times with a PdCl₂ solution (Sigma Aldrich, 5 wt% in 10 wt% HCl solution) until 10 wt% Pd/CeO₂ was obtained, and then dried and calcined as before. The catalyst mass obtained in SFMR is 181.3 mg. For fixed-bed experiments, a powder of 10 wt% Pd/CeO₂ was prepared by deposition-precipitation using CeO₂ nanopowder (Sigma Aldrich, d<25 nm) and PdCl₂ solution (Sigma Aldrich 5 wt% in 10 wt% HCl) as precursors. CeO₂ nanopowder was dispersed in the solution of PdCl₂. When adding a solution of Na₂CO₃, the palladium hydroxide would deposit-precipitate on the surface of the CeO₂ particles. The obtained powder was dried and then calcined in air at 500 °C. For the fixed-bed experiments, undiluted 50–120 μm particles of the catalyst powders were used.

The specific surface area (S_{BET}) of all the supports and catalysts was determined by N₂ adsorption at –196 °C using a Micromeritics Tristar 3000 instrument. The samples were filled into the sample tube and outgassed overnight under vacuum at 200 °C before measurements. The specific surface area was calculated by the BET (Brunauer-Emmet-Teller) equation. The total pore volume and pore size distribution were found applying the Barrett-Joyner-Halenda (BJH) method [31].

X-ray diffraction analysis of the CeO₂ support and the Pd/CeO₂ powders was performed on a Bruker AXS D8 Focus with D8 Goniometer, CuKα radiation (λ = 1.54 Å) and a Lynxeye detector. The XRD patterns were acquired in the 2θ-range of 20–90° with a step size of 0.03° and a step time of 0.6s. The diffractograms were compared with standards in a database (EVA) for phase identification [32].

Volumetric chemisorption of CO was performed at 313 K on a Micromeritics ASAP 2010C unit. The catalyst was loaded into a U-shaped quartz reactor and placed inside an electric furnace. The sample was initially evacuated at 313 K for one hour, and reduced in flowing hydrogen at 573 K for 16 h. The temperature was increased slowly by 1 K/min. After reduction, the sample was evacuated for 1 h at 573 K, for 30 min at 373 K and subsequently cooled to 313 K for adsorption measurement. The Pd dispersion (D, %) was calculated assuming that one Pd site was covered by one CO molecule.

High resolution-Inductively coupled plasma-Mass Spectrometry (HR-ICP-MS) was used to determine the actual catalyst composition of the Pd/CeO₂ powder. The analysis was performed by Molab AS. The sample was completely dissolved in a solution of 0.1 M HNO₃ and 0.1 vol% HF before analysis.

Scanning electron microscopy (SEM) was performed using a Zeiss Ultra instrument operated at beam voltage of 20 kV. SEM energy-dispersive X-ray spectroscopy (EDS) analysis and mapping was performed using a Bruker Quantex system.

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