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Influence of hydrocarbons and thiophene on catalytic fixed bed methanation

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ABSTRACT

The economics of decentralized methanation units require a reduced complexity of the gas cleanup of gasification-derived syngas resulting in higher concentrations of organic sulfur compounds, e.g. thiophene. The influence of thiophene as single compound as well as in combination with higher hydrocarbons on catalytic fixed bed methanation has been experimentally examined in a series of bench-scale tests with a commercial Ni catalyst. The change of activity of the catalytic fixed bed was studied by methanation under well-defined reference settings. For intermediate catalyst treatment the impurities thiophene, as major sulfur species unremoved by acid gas scrubbing, as well as ethene and naphthalene as major hydrocarbon species in syngas, have been chosen. In all experiments thiophene addition showed a slow but steadily-ongoing deactivation of the catalytic fixed bed with catalyst consumption varying from 0.6 to 1.7 $g_{catalyst}/mmol_{C4H4S}$. Addition of 1.0 vol.% ethene to the feedgas resulted in significant increase of the pressure drop over the fixed bed, whereas simultaneous addition of thiophene and ethene, as well as single or combined addition of naphthalene, did not cause any increase of the pressure drop. The results were compared to the sulfur passivated steam reforming but in case of methanation no similar mechanism is likely to exist.

1. Introduction

Synthetic Natural Gas (SNG) as alternative for natural gas has been of interest in a periodical manner within the last decades. The oil crises of 1970s led to intensive research on utilisation of domestic coal resources as substitute for oil and culminated finally in the erection of the first commercial large-scale coal-to-SNG plant in North Dakota with Lurgi methanation technology [1]. The next period with intensified research activities was related to methanation of biomass derived syngas accompanying the grant-aided raise of renewable energies in Europe. Several groups focused on small-scale biomass-to-SNG processes [2–4], whereby the BioSNG project led to a first 1 MW pilot SNG-plant with fluidized bed methanation at the Güssing gasifier [5]. The GoBiGas project of Göteborg Energi demonstrated the technical feasibility of biomass-to-SNG in industrial scale [6]. Nowadays, the SNG production by CO_2-methanation as part of power-to-gas concepts raised large interest [7–11].

Both, the decentralized biomass and power-to-gas concepts require lower specific investment costs and therefore reduced complexity to become competitive with established large-scale technologies. In opposite to power-to-gas concepts, biomass derived syngas suffers in general a high tar and sulfur content which is lowered in one or several process steps. The tradeoff between the level of gas cleaning and complexity of the overall biomass-to-SNG process chain is considered as the bottleneck of SNG production. As a consequence of a simplified gas cleanup the methanation catalyst will suffer an increased content of impurities.

Methanation technology has been available for several decades and originated from the CO removal at ammonia plants utilizing Fe based catalysts, which are prone to CO poising [12]. A thorough overview of different methanation technologies and their progress was given recently by Kopyscinski [1] and Rönsch [12]. As a conclusion, it can be summarized that series of adiabatic fixed bed reactors still form the state-of-the art technology, namely Haldor Topsoes TREMP and HICOM process of British Gas Corporation. Contrary, related to the aforementioned CO_2 methanation or onsite hydrogen production, several groups are working on structured reactors for processes with high heat of reaction in general

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Nomenclature

Latin letters

X	conversion, %
T	temperature, °C
L	reactor length, mm
m	mass, g
$\dot{n}$	molar flow, mol s^{-1}
p	pressure, kPa
t	injection time, ms
z	axial reactor coordinate, mm
x	fraction of species i, –

Subscripts

i	species i, –
max	maximum
L	length single axial temperature profile
m,n	temperature profiles m,n

Abbreviations

DFT	density functional theory
GHSV	gas hourly space velocity, h^{-1}
RDS	rate determining step
SNG	Substitute Natural Gas
$C_{10}H_8$	naphthalene
C_2H_4	ethene
C_2H_2	acetylene
C_4H_4S	thiophene
C_2H_6S	ethanethiol

Greek letters

ρ	density, kg m^{-3}

[13–15] or specially dedicated to methanation which are suited very well for small scale and decentralized power-to-gas applications [16–19]. It can be assumed that the focus on new SNG projects is likely to remain, at least in Europe, on small-scale biomass-to-SNG plants, as discussed in [20].

All presented reactor concepts have in common that they use Ni-based catalysts on varying supports due to low costs in comparison to precious metals. The use of Ni-based catalyst and its susceptibility to sulfur poisoning was addressed by several thorough reviews on catalyst deactivation [21–23]. Most of the numerous publications about sulfur poisoning deal with the major sulfur species H_2S as poison [24,25]. Thiophene exists in gasification derived synthesis gas at concentrations several magnitudes lower than H_2S [26,27] but is considered to pass without removal wet absorption processes at elevated temperatures, e.g. K_2CO_3 solvent [28], and common adsorption fixed beds, e.g. ZnO [28,29]. Furthermore, the adaption of hydro-desulfurization (HDS) from petrochemistry to convert organic sulfur compounds in synthesis gas with sulfidised transition metal catalysts does not yield full conversion, probably due to the lower partial pressures of hydrogen [30,31]. Rhyner et al. investigated also the conversion of thiophene over a noble metal catalyst at 620–750 °C [32], but the required high temperatures upstream methanation are unfavorable.

Therefore, thiophene remains, despite its low concentration in syngas, relevant for small-scale units (e.g. biomass) since gas cleaning for ultra clean syngas, e.g. Rectisol® process, is beyond the allowable plant complexity. This article aims for a contribution to the experimental investigation on how thiophene influences in combination with higher hydrocarbons catalytic fixed-bed methanation with a commercial Ni catalyst.

2. Materials and methods

2.1. Fundamentals on methanation

Synthesis gas derived from gasification of solid feedstocks contains mainly H_2, CO_2, CO, CH_4 and H_2O, which are converted in SNG production by the main reactions CO methanation (Eq. (1)), water-gas-shift reaction (WGS) (Eq. (2)) and Sabatier reaction (Eq. (3)) (Table 1). According to the high reaction heat and volume reduction of methanation reactions high pressures and low temperatures increase the selectivity towards methane.

Under certain conditions, the formation of solid carbon becomes significant even in thermodynamic equilibrium, which is considered by Boudoard reaction (Eq. (4)). In general, the carbonaceous deposits exist in various configurations but for equilibrium calculations only the graphitic configuration is considered [33].

Table 1
Relevant reactions in methanation.

	Reaction	ΔH_R^0 [kJ/mol]
(1)	$3\ H_2 + CO \rightleftharpoons CH_4 + H_2O$	−206
(2)	$H_2O + CO \rightleftharpoons CO_2 + H_2$	−41
(3)	$4\ H_2 + CO_2 \rightleftharpoons CH_4 + 2\ H_2O$	−165
(4)	$2\ CO \rightleftharpoons C + CO_2$	−173

It is commonly accepted that Langmuir-Hinshelwood reaction mechanism shows responsible for CO methanation with dissociative adsorption of CO and H_2 [34–36] but some authors suggest an Eley-Rideal mechanism – though the applied conditions in terms of p_{CO} differ strongly [37,38]. Yet, the detailed mechanism and rate determining step (RDS) is not clarified. Some publications favor the hydrogenation of C∗ or CH∗ at the surface as RDS, whereas others assume the formation of an intermediate COH∗ complex as rate determining step [39], which is supported by recent DFT calculations [40]. Sehested et al. discussed also the dissociation of CO on only 5% of Ni surface as RDS [38].

Several authors addressed the reaction kinetics with commercial Ni catalysts. One of the most common kinetics published by Xu & Froment are not well suited for low temperatures [41,42]. In opposite to this, Kopyscinski does not consider the methane steam reforming reaction since isothermal conditions at lower temperatures of 280–360 °C, typical for fluidized bed methanation, were assumed [40,41]. Both drawbacks were overcome by an adjustment of the kinetic expression by Rönsch et al. in [12], which includes also a thorough overview of published reaction mechanisms and kinetics related to methanation.

In addition to the main reactions in Table 1 side reactions can occur resulting in lower selectivity towards methane. In particular, an insufficient ratio of C-atoms to H-atoms on the catalyst surface could lead to the polymerization of adsorbed surface carbon atoms C_α towards a carbonaceous layer, which could cause the blockage of active sites or even the blockage of the reactor [23]. Depending on the vapor content the formation of whisker carbon could become significant in the temperature range typical for methanation, i.e. 300–600 °C [43]. This was thought in earlier days to be a