Chemical Engineering Science 155 (2016) 201–209

Contents lists available at ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces

Kinetic investigations of the steam reforming of methanol over a $Pt/In_2O_3/Al_2O_3$ catalyst in microchannels

M. Wichert [a,*], R. Zapf [a], A. Ziogas [a], G. Kolb [a], E. Klemm [b]

[a] Fraunhofer ICT-IMM, Carl-Zeiss-Str.18-20, 55129 Mainz, Germany
[b] Universität Stuttgart, ITC, Pfaffenwaldring 55, 70569 Stuttgart, Germany

HIGHLIGHTS

- Application of a microreactor with external recycle for kinetic measurements.
- Advanced kinetic characterization of a previously patented highly active catalyst.
- Highly reproducible performance of the catalyst during kinetic measurements.
- Determination of starting values for parameter estimation by simulated annealing.
- Derivation of a mechanistic rate model by formulation of Langmuir sorption equilibria.

ARTICLE INFO

Article history:
Received 4 March 2016
Received in revised form
8 July 2016
Accepted 6 August 2016
Available online 8 August 2016

Keywords:
Kinetics
Methanol
Reforming
Platinum
Recycle reactor
Microreactor

ABSTRACT

A kinetic study of methanol steam reforming over bimetallic $Pt/In_2O_3/Al_2O_3$ catalyst was carried out. The kinetic measurements were performed in a microstructured monolithic reactor with an external recycle free of temperature and concentration gradients. By the help of residence time distribution measurements it could be verified that the reactor showed the behaviour of an ideal continuous stirred tank reactor (CSTR). The absence of external and internal concentration gradients could be proven by corresponding experiments and theoretical diagnostic criteria.

The kinetic measurements performed by variation of the reactant inlet partial pressures revealed that in the temperature range from 310 °C to 355 °C the molar rate of methanol consumption mainly depends on the methanol partial pressure, especially at higher temperatures, whereas there is only minor dependence on the water partial pressure. Carbon dioxide has no inhibiting effect, whereas hydrogen showed a weak inhibiting effect.

Two power laws and three Langmuir-Hinshelwood rate equations were created for the modelling of the kinetic data. Power laws could not be fitted to the measured values. Therefore the uses of Langmuir-Hinshelwood rate laws with temperature dependent sorption constants are inevitable for the modelling. The model discrimination revealed that the rate law derived from a mechanism, which assumes the dehydrogenation of an adsorbed methoxy-species as rate determining step, described the measured kinetic data second best. Optimum agreement between observed and predicted molar rates of methanol consumption was obtained when applying a Langmuir-Hinshelwood rate law assuming dissociative methanol and molecular water adsorption on the catalyst surface. Dissociative adsorption of water and methanol at the same active site may be excluded. This leads to a better evaluation of the models that assume molecular water adsorption at the same site where methanol ties or the ones with no participation of water in the rate determining step (RDS) under discrimination.

1. Introduction

Power generators which utilize PEM fuel cell technology and on-board hydrogen production through fuel processing are under development since the end of the last millennium (Edwards et al., 1998) (Patil et al., 2004). Liquid and gaseous hydrocarbons or alcohols are the fuels which are most widely used in development projects and practical applications.

The high gravimetric energy density of 22 MJ/kg, easy handling

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* Corresponding author.
E-mail address: martin.wichert@imm.fraunhofer.de (M. Wichert).

http://dx.doi.org/10.1016/j.ces.2016.08.009
0009-2509/

Nomenclature

$c_{i,0}$	concentration of component i in the feed, mol m^{-3}
D_{eff}	effective diffusion coefficient, m^2 s^{-1}
E_{act}	Activation energy, J mol^{-1}
$E(t)$	Spectrum of residence times, s^{-1}
$\Delta H_{298}{}^0$	molar reaction enthalpy at $T=298$ K and p_0 $=101{,}325$ Pa, J mol^{-1}
ΔH_i	molar heat of adsorption, J mol^{-1}
k_0	frequency factor
k	reaction rate constant or number of parameters, mol s^{-1} kg$_{Cat}{}^{-1}$
K_i	sorption constant of component i, Pa^{-1}
K_∞	pre-exponential factor, Pa^{-1}
$\dot{n}_i$	molar flow of component i, mol s^{-1}
N	number of data points
p_i	partial pressure of component i, Pa
PEM	polymer electrolyte membrane
R	universal gas constant, J K^{-1} mol^{-1} or molar rate of methanol consumption, mol s^{-1} kg$_{Cat}{}^{-1}$
r	reaction rate, mol kg^{-1} s^{-1}
$(r_{eff})_V$	effective reaction rate related to the volume of the reaction space, mol s^{-1} m^{-3}
SS	sum of squares of the residuals of a regression
T	absolute temperature, K
t	time period, s
α	reaction order of methanol
β	reaction order of water
δ_K	thickness of catalyst layer, m
φ	recycle ratio
θ_0	rate of unoccupied surface sites

and relatively high availability make methanol well suited for its application as fuel for portable, mobile or stationary fuel cell/fuel processor systems of smaller scale. The endothermic steam reforming of methanol produces a hydrogen containing reformate as shown in the following Eq. (1) and was subject of scientific investigations over the last forty years (Pour et al., 1975; Santacesaria and Carra, 1983; Cao et al., 2004).

$$CH_3OH+H_2O \rightleftarrows CO_2+3H_2 \quad \Delta H^0_{298}= +49.53\ \text{kJ/mol} \tag{1}$$

A relatively low reaction temperature is required to achieve high conversion of methanol compared to other hydrocarbons or alcohols. Under these conditions only minor amounts of carbon monoxide will be produced by reverse water-gas shift (rWGS) or methanol decomposition (DEC).

Especially mobile applications require low weight and volume of the overall system (Kolb, 2008). The energy demand of portable power generation and grid independent electrically driven tools alone amounts to 714 GWh in Europe (2009) (Kolb et al., 2009). One of the most prominent practical applications of fuel cell technology are small scale stationary systems, which have been commercialized by Ballard (Canada) as ElectraGen™ for telecom backup power supply in Africa and India (Fosberg, 2010). These systems utilize methanol as fuel, which is converted through fuel processing to hydrogen rich gas.

Based upon work of Iwasa et al. a group of novel bimetallic catalysts was developed and patented at Fraunhofer ICT-IMM for the steam reforming and oxidative steam reforming of methanol (Iwasa et al., 1998; Men et al., 2010; Men and Zapf, 2009).

The highest activity, long term stability and selectivity towards carbon dioxide was observed for an alloy of 15 wt% platinum and 30 wt% indium deposited on γ-alumina carrier (Kolb et al., 2011). Basic kinetic investigations were performed in the present study of methanol steam reforming to ultimately optimize the performance of this highly active catalyst. A monolithic microstructured reactor with an external recycle free of temperature and concentration gradients was used, which was applied with a similar design initially by Nikolaidis et al. (2009).

Previous investigations revealed that the optimum temperature range for the operation of the bimetallic $Pt/In_2O_3/Al_2O_3$ catalyst reaches from 325 °C to 375 °C at a steam-to-carbon ratio (S/C-ratio) of 1.5 (Kolb et al., 2011). In the whole range of the kinetic measurements, i.e. for reaction temperatures between 310 °C and 355 °C and S/C-ratios between 1.0 and 3.0, the methanol equilibrium conversion always exceeds 99.5% as calculated by ASPEN Plus rGibbs algorithm. Therefore the reverse reaction can be neglected when developing the kinetic models.

In this work, one rate model was derived from mechanistic considerations based upon a systematic study of the nature, stability and dynamics of surface species present under methanol steam reforming conditions over Pd/Ga_2O_3 and Pd_2Ga/Ga_2O_3 catalyst published by Haghofer et al. (2012). Their main mechanistic results are illustrated in Fig. 1 in the form of a catalytic cycle.

The cycle starts with a catalyst surface enriched with reactive oxygen surface sites (labelled O(lat) in Fig. 1) in the position 9 o'clock, which are formed by high temperature reduction at 400 °C in the presence of hydrogen. As a side-product of the reduction a bimetallic Pd_2Ga alloy is generated on the Ga_2O_3 surface which can be detected by XRD in-situ (Penner et al., 2009). The elementary steps (see Eqs (2)–(4)) of the alloy formation were further elucidated for the Pd/Ga_2O_3 catalyst by Haghofer et al. (2012) and Yamada et al. 1993):

$$4Pd+2H_2 \rightleftarrows 4Pd{-}H \tag{2}$$

$$4Pd{-}H+Ga_2O_3 \rightleftarrows 4Pd+Ga_2O+2H_2O \tag{3}$$

$$4Pd+Ga_2O \rightleftarrows 2Pd_2Ga+O\cdot \tag{4}$$

Treating the catalyst as described above leads to atomic

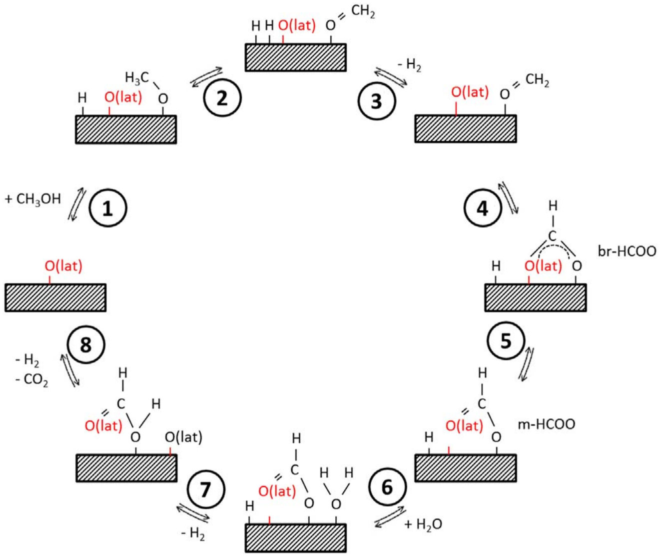

Fig. 1. Catalytic cycle of methanol steam reforming over Pd_2Ga/Ga_2O_3 catalyst based on investigations of Haghofer *et a*l. (set up by the author of the current paper) (Haghofer et al., 2012).