



Kinetic study of CO preferential oxidation over Pt–Rh/ γ -Al₂O₃ catalyst in a micro-structured recycle reactor

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ARTICLE INFO

Article history:

Available online 6 August 2008

Keywords:

Kinetic study
Preferential oxidation
CO
Microstructured
Recycle reactor

ABSTRACT

A micro-structured recycle reactor was developed for studying the kinetics of heterogeneously catalysed gas phase reactions. The preferential CO oxidation reaction over Pt–Rh/ γ -Al₂O₃ catalyst in reformat surrogate containing up to 60 vol.% H₂ was investigated over a wide range of CO concentrations (0.5–2.0 vol.%) between one and four times O₂ excess ($\lambda = 1$ –4). Initial concentration of H₂O and CO₂ were 2.5 vol.% and up to 20 vol.%, respectively, and their influence on the reaction rate was investigated as well. Measurements in a microreactor showed that the optimum temperature for the preferential oxidation process (PROX) was \sim 180 °C. Methanation and reverse water-gas shift reaction in this range were insignificant. The quantitative determination of CO oxidation rates as a function of CO, O₂, H₂ and CO₂ concentration between 150 °C and 190 °C led to reaction orders of -0.58 for CO and $+0.88$ for O₂, at an apparent activation energy of 92.9 kJ/mol. The addition of either H₂ or CO₂, decrease the CO oxidation rate.

The study of H₂ oxidation rate as a function of H₂, O₂ and CO revealed reaction orders of -0.26 , 0.09 and -0.06 , respectively.

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1. Introduction

Microreaction technology is a relatively new concept which offers the possibility of miniaturization of conventional reactors while providing the same throughput. One of the first micro-structured devices was reported in literature in 1989. With the tools of micro-fabrication, several novel reactor configurations can be fabricated allowing different design concepts not feasible with conventional packed-bed technology. Such microchannel reactors or microreactors typically carry small channels with dimensions in the sub-millimeter range, which reduces diffusive transport limitations. This also results in a relatively large surface area-to-volume ratio and increased driving forces for heat and mass transport. This translates into short response times. The pressure drop in microchannels is substantially lower compared to packed-bed reactors. The unique flow and heat-/mass transfer properties have led to process improvements [1–10]. These benefits, however, need to be significant to counter-balance the higher production cost of microreactors compared to fixed-bed reactors.

Besides the application of microreactors as production devices, they bear advantages as laboratory tools for catalyst screening and for the determination of kinetics. The choice of a suitable reactor for carrying out experiments under conditions such that meaningful kinetic rate expressions can be obtained is of great importance. This is particularly true for catalytic reactions in which transport effects such as pore diffusion come into the picture, which make the scale-up of conventional fixed bed reactors from the laboratory to the pilot or even to the industrial scale a challenging task. This situation changes when micro-structured reactors are applied. Exactly the same optimum operating conditions as identified in the laboratory scale may be applied when scaling up the reactor. This is usually done by numbering up the channels in a much bigger reactor, which is consequently not “micro” anymore as far as outer dimensions are concerned. The channel dimensions and consequently the fluid-dynamic conditions within the channels remain the same.

For kinetic measurements, the integral reactor (plug flow reactor, PFR) is problematic, because it exhibits a concentration gradient and the solution of its material balance demands integration. On the other hand, the conversion of a differential reactor (continuous stirred tank reactor) represents directly the reaction rate and permits the derivation of simple algebraic reactor

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Nomenclature

AIC	Akaike's Information Criterion
$C(t)$	output concentration of gas (moles/l)
$C_1(t)$	inlet concentration of gas (moles/l)
Cat	catalyst
$[i]$	concentration of gas species i (vol.%)
E_A	activation energy (kJ/mole)
E	residence time distribution (s^{-1})
F_{in}	inlet flow rate (l/min)
F_R	recycle flow rate (l/min)
ΔH	reaction enthalpy (kJ/mole)
k_0	pre-exponential factor ($ml^{1-(\alpha+\beta+\gamma+\delta)} g_{cat}^{-1} s^{-1}$)
k_i	constants of species i (ml^{-1})
h_i	constants of species i (ml^{-1})
r	reaction rate ($ml g_{cat}^{-1} s^{-1}$)
R	universal gas constant ($kJ mole^{-1} K^{-1}$)
t_m	mean residence time (s)
T	temperature (K)
V	vessel volume (ml)
WHSV	weight hourly space velocity ($lh^{-1} g_{cat}^{-1}$)

Greek symbols

α	CO exponential factor in CO reaction rate
β	O ₂ exponential factor in CO reaction rate
γ	H ₂ exponential factor in CO reaction rate
δ	CO ₂ exponential factor in CO reaction rate
θ_i	surface coverage of species i
κ	CO exponential factor in H ₂ reaction rate
λ	O/CO ratio
ν	O ₂ exponential factor in H ₂ reaction rate
π	H ₂ exponential factor in H ₂ reaction rate
τ	residence time (s)

model equations. To approach the behaviour of an ideal continuously stirred tank reactor (CSTR), a recycle reactor must be constructed.

If a plug flow microreactor is operated in a way that most of the effluent stream is recycled, a small amount of feed is continuously added, and a small net-product stream continuously removed, a reactor system is obtained which has several advantages. By external or internal recycling of the gaseous phase, with recycle ratios (ratio of recycle flow and feed flow) greater than 25, perfect mixing can be achieved [11,12]. A further benefit lies in the fact that due to perfect mixing, that can be achieved at high recycle ratios, the material balances discharge like in the ideal, perfectly stirred CSTR. Perhaps the greatest advantage of this reactor type is its ability to control the catalysts temperature very accurately.

Theoretically, both the recycle reactors and CSTRs suit the above-described purposes equally well [2,12,13]. In practice the reactors used are never ideal; they can often be far from it. There are several reasons for this: the flow may have a preferential path in the tank, there may be dead zones in the tank, etc. [14]. The same applies to recycle reactors with internal circulation. External circulation may be achieved by mechanical recycle pumps as it is depicted in Fig. 1. Compared to internal circulation this setup has the advantage, that the recycle ratio is well-defined and easily determined.

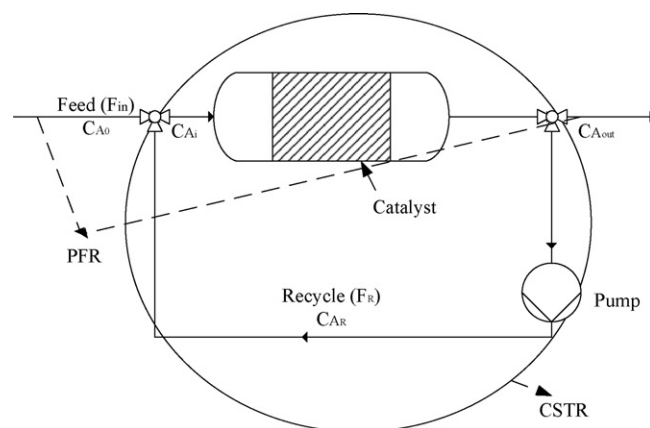


Fig. 1. Process diagram of a recycle reactor.

To make full use of the advantages and to avoid the difficulties associated with recycle reactors, one has to understand their performance characteristics and how this is related to the performance of commercial reactors. A basic requirement in the analysis of catalytic reactors is a rate expression for the reaction concerned. In the present paper we apply a recycle reactor for the study of the kinetics of the preferential oxidation of CO in the presence of O₂, H₂ and CO₂, i.e. for a gas composition equivalent to the reformat of a hydrocarbon reformer which was purified already by water-gas shift as first clean-up stage. A highly undesired side reaction in this case is the oxidation of hydrogen, which is also investigated.

The kinetic analysis was performed in three steps. Previously proposed reaction mechanisms were examined first, in order to derive the kinetic expressions. The second step comprises the setup of a suitable mathematical model and consists of two parts: firstly the selection of a reaction rate model and secondly the application of a suitable reactor model. Usually either power function models or hyperbolic models are used, the latter accounting for competitive adsorption of reactants.

The last step of the kinetic analysis consists in estimation of the model parameters. A comparison of results obtained from the parameter estimation method can be accomplished on the basis of the experimental test and of the quality of fits, which is affected by model errors, numerical errors and experimental errors.

2. Reactor and reaction system

2.1. Reactor characterization–residence time distribution

In order to predict the behavior of a reactor, the mass flow through the reactor should be determined. An ideally mixed reactor is by definition one that has identical concentrations at every point. A plug flow shows no mixing in the direction of the flow. Practical systems are often modeled by combining ideally mixed and plug flow reactors.

The residence time distribution (RTD, also exit age distribution), $E(t)$, indicates the time the fluid elements of a stream remain in the reactor and has the units of $time^{-1}$. It is convenient to represent the RTD as normalized distribution as shown in Fig. 2.

For comparison purposes, the mean residence time (t_m) was calculated by integrating the RTD:

$$t_m = \int_0^{\infty} t E(t) dt \quad (1)$$

The recycle loop has a defined volume V (cm^3) through which the fluid flow F_R (cm^3/s) is passed. The tracer introduced into the fluid

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