



Self-sustained oscillations of temperature and conversion in a packed bed microreactor during 2-methylpropene (isobutene) hydrogenation



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ABSTRACT

Hydrogenation of 2-methylpropene over commercial platinum catalyst has been studied in a packed bed microreactor. Using common dimensionless criteria and experimental diagnostic the presence of heat and mass transfer limitations has been detected. Analysis of experimental results has pointed to the presence of heat and mass transfer control. Consequently, only a limited set of data under the kinetic control regime could be collected. Self-sustained spontaneous and reproducible oscillations of 2-methylpropene conversion have been observed experimentally under certain conditions. The temperature of the catalyst bed well reflected the oscillatory course of 2-methylpropene conversion. The observed oscillations exhibited exceptionally long periods ranging from 11 to 22 h depending on the prevailing space velocity. The appearance of oscillations of the conversion has been ascribed to the complex interaction between the exothermic reaction, heat transfer and a reversible decrease in the catalyst activity. Possible mechanisms of temporary catalyst activity decrease have been proposed.

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1. Introduction

Industrial production of ethylene and propylene employs the steam cracking process for which light alkanes (C₄–C₅) represent very good raw materials. Light alkanes (C₄–C₅) are produced on a large scale by fluid catalytic cracking (FCC) and steam cracking as by-products that are often recycled into the steam cracking process. Unsaturated hydrocarbons in C₄–C₅ fractions, however, reduce the yield of ethylene and propylene as well as effective production time of pyrolysis reactors due to coke formation. Total hydrogenation of the C₄ and C₅ fractions may therefore substantially increase their value as steam cracking feedstock.

Composition of C₄ fractions depends on FCC or steam cracking process conditions as well as on the character of feedstock. However, the C₄ fractions contain large amount of 1,3-butadiene (in case of steam cracking) and butenes (trans-2-butene, cis-2-butene, isobutene (2-methylpropene, 2MP), 1-butene) accompanied by butanes (isobutane (2-methylpropane, 2MPA), n-butane) [1]. 1,3-Butadiene is a key component for synthetic rubber production and it is often separated from C₄ fraction by extraction or extractive distillation. Therefore, the C₄ fraction of interest, to be recycled

into the stream cracking after the complete hydrogenation, contains mainly butene isomers, butanes and only a residual amount of butadienes. The knowledge of hydrogenation kinetics of these hydrocarbon fractions is, therefore, of industrial significance for the C₄ hydrogenation unit design and scale-up.

The determination of the kinetics of hydrogenation of olefinic mixtures is a complex task requiring adequate experimental data and analysis by appropriate set of kinetic expressions [2]. Petroleum cuts such as C₄ or C₅ fractions are usually complex mixtures containing numerous chemically different molecules. To reduce the complexity of the kinetic model Galtier [3] identified two different approaches of model lumping applicable in petroleum refining processes.

As the mass and heat transfer effects may distort the intrinsic kinetics these transfer limitations should be eliminated by choosing a proper experimental system and optimizing process as demonstrated for example by Ardiaca [4] studying liquid-phase hydrogenation of 1,3-butadiene and n-butenes on Pd catalysts. Eventual presence of mass and heat transfer limitations can be assessed by evaluating common dimensionless criteria and by empirical diagnostic tests [5] reviewed in engineering handbooks [6–8].

Microreactors may be efficient tools to study the reaction kinetics. This was demonstrated in the study of methanol reforming [9] in a catalyst coated wall for or in the ethylene oxide formation [10].

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Symbols and abbreviations

ΔH_r	reaction enthalpy (J/mol)
2MP	2-methylpropene (isobutene) (-)
2MPA	2-methylpropane (isobutane) (-)
a	dimensionless parameter for calculation $T_{out,real}$ (-)
A	pre-exponential factor ($\text{m}^3/\text{mol/s}$)
b	dimensionless parameter for calculation $T_{out,real}$ (-)
C_{2MP}	concentration of 2-methylpropene (mol/m^3)
C_{2MP}^0	initial concentration of 2-methylpropene (mol/m^3)
C_{2MPA}	concentration of 2-methylpropane (mol/m^3)
C_{H_2}	concentration of hydrogen (mol/m^3)
$C_{H_2}^0$	initial concentration of hydrogen (mol/m^3)
$C_{p,f}$	specific heat capacity of fluid (J/kg/K)
D_{2MP}	diffusivity of 2-methylpropene in hydrogen (m^2/s)
D_{eff}	effective diffusivity in a porous catalyst (m^2/s)
D_p	particle diameter (m)
D_r	inner diameter of the reactor cartridge (m)
E_a	activation energy (J/mol)
F	molar flow (mol/s)
F_{2MP}^0	initial molar flow of 2-methylpropene (mol/s)
h	convective heat transfer coefficient ($\text{J}/\text{m}^2/\text{s}/\text{K}$)
k	rate constant for second-order reaction ($\text{m}^3/\text{mol/s}$)
k_f	mass transfer coefficient (m/s)
L_b	bed length (m)
M_{2MP}	molecular weight of 2-methylpropene (g/mol)
M_{H_2}	molecular weight of hydrogen (g/mol)
n	reaction order (-)
Nu	Nusselt number $Nu = \lambda_f h / D_p$ (-)
p	pressure (bar)
Pr	Prandtl number $Pr = \mu_f C_{p,f} / \lambda_f$ (-)
R	universal gas constant (J/mol/K)
r_{2MP}	reaction rate of 2-methylpropene per unit catalyst mass ($\text{mol}/\text{s}/\text{g}$)
Re	Reynolds particle number $Re = \rho_f u D_p / \mu_f$ (-)
r_p	particle radius (m)
r_{pore}	catalyst pore radius (nm)
$r_{v,obs}$	observed reaction rate per unit particle volume $r_{v,obs} = r_{2MP} W / V_p$ ($\text{mol}/\text{s}/\text{m}^3$)
S_{BET}	specific surface area (m^2/g)
Sc	Schmidt number $Sc = \mu_f / \rho_f D_f$ (-)
Sh	Sherwood number $Sh = D_{2MP} k_f / D_p$ (-)
S_{meso}	specific surface area of mesopores (m^2/g)
t	time on stream (h)
T_b	bulk gas temperature (K)
T_{in}	inlet temperature (K)
TON	turn over number (g(2MP)/g(cat.))
T_{out}	outlet bed temperature (K)
$T_{out,real}$	outlet bed temperature corrected by Eq. (3) (K)
T_s	catalyst surface temperature (K)
u	superficial velocity (m/s)
V_b	bed volume (m^3)
V_{micro}	specific micropore volume (mm^3/g)
V_p	catalyst particle volume (m^3)
W	catalyst mass (g)
WHSV	weight hourly space velocity (g(2MP)/g(cat.)/h)
X_{2MP}	conversion of 2-methylpropene (-)

Greek letters

γ	dimensionless activation energy (-)
β	dimensionless maximum temperature rise (-)
ε	bed porosity (-)
χ	Maers number for interphase heat transport (-)

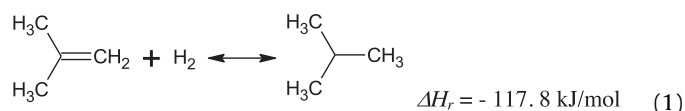
ω	Damköhler number for interphase mass transport (-)
τ	tortuosity of γ -alumina (-)
$\Sigma_{v,2MP}$	atomic diffusion volumes of 2MP (-)
Σ_{v,H_2}	atomic diffusion volumes of H_2 (-)
ρ_f	fluid density (kg/m^3)
μ_f	fluid dynamic viscosity (Pa s)
λ_f	heat conductivity of fluid ($\text{J}/\text{m}/\text{s}/\text{K}$)
λ_p	catalyst particle heat conductivity ($\text{J}/\text{m}/\text{s}/\text{K}$)
ε_p	catalyst particle porosity (-)

Intensive heat and mass transfer capabilities of microreactors as well as well-defined flow pattern help eliminate heat and mass transfer limitations, allowing the look in intrinsic kinetics. However, the reaction kinetics control regime in microreactors is not always a priori warranted.

This study aims at developing an experimental procedure for intrinsic kinetic data collection and evaluation of the model reaction using a packed bed microreactor. The developed methodology should enable us to study the kinetics of a complex C_4 mixture. For our study we substituted the C_4 mixture by a model reaction of gas phase hydrogenation of 2-methylpropene. This choice simplifies the experimental procedure and assessment of the mass and heat transfer limitations effects. The experiments were conducted under the industrially relevant conditions (80–120 °C, 20 bar) with a commercial Pt/ Al_2O_3 catalyst. The experimental procedure and the operating conditions (flowrates, catalyst mass, catalyst particle size, etc.) were optimized in order to determine the operating window for regime controlled by the reaction kinetics.

1.1. Reaction mechanism of 2-methylpropene hydrogenation

The hydrogenation of 2-methylpropene (2MP) to 2-methylpropane (2MPA) is a reversible equilibrium reaction (1).



This reaction was investigated on Pt/Sn based catalyst at temperatures about 400–500 °C and atmospheric pressure, coupled with 2MPA dehydrogenation [11–13] and modeled with a four-step Horiuti–Polanyi mechanism. However, the 2MP hydrogenation is thermodynamically favored at lower temperatures. 2MP hydrogenation over a Pt/ Al_2O_3 catalyst in a flow type of reactor was investigated at temperatures from 20 to 50 °C and pressure up to 4 atm and modeled by a Hougen–Watson kinetics [14]. The latter reaction model included terms describing competitive and non-competitive adsorption on a catalyst surface because both terms were necessary to correlate the experimental data.

The study of 2MP hydrogenation over Pt(111) single crystal at 20 °C and near ambient pressure by IR spectroscopy [15] has revealed that the hydrogenation proceeds by two competitive pathways; the physisorbed intermediate π -bonded 2MP undergoes the addition of hydrogen to form either isobutyl or *tert*-butyl group adsorbed on metal. Both groups undergo the terminal hydrogen addition, however the steric hindrance in the case of the *tert*-butyl group may prevent hydrogen from inserting into this species, which most probably causes a severe restriction of this pathway. In comparison with other straight-chain butenes the isobutene

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