



Operando determination of the liquid-solid mass transfer coefficient during 1-octene hydrogenation



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HIGHLIGHTS

- Mapping of chemical composition within catalyst pellets down a fixed-bed reactor.
- Data reveal switch in selectivity along the reactor.
- Product accumulation inside catalyst pellets arising from mass transfer limitations.
- Direct calculation of liquid-solid mass transfer during 1-octene hydrogenation.

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ABSTRACT

Spatially-resolved and unresolved magnetic resonance measurements are used in combination with a partial least squares regression (PLSR) method to measure chemical composition within catalyst pellets during the 1-octene hydrogenation reaction occurring in a fixed bed of 0.3 wt% Pd/Al₂O₃ catalyst pellets. The PLSR method is used to discriminate between chemical species within and external to the void space of the catalyst pellets. The spatially-resolved data show that the hydrogenation and isomerisation reactions are dominant in the upper and lower region of the reactor, respectively. The local intra-pellet compositions also show product accumulation inside catalyst pellets consistent with reaction occurring under conditions of mass transfer limitation. An average measure of the intra-pellet composition within the whole bed was then used to estimate the liquid-solid mass transfer coefficient during the course of the reaction. The values of k_{LS} obtained from the NMR measurements were in the range $0.15 \times 10^{-5} \text{ m s}^{-1} < k_{LS} < 0.25 \times 10^{-5} \text{ m s}^{-1}$, for reactor operating conditions characterised by gas and liquid Reynolds numbers $0.2 < Re_L < 0.6$ and $0.1 < Re_G < 0.3$; these values are shown to be consistent with those predicted by existing literature correlations. Closest agreement was found with values predicted from dissolution experiments performed under similar hydrodynamic conditions in trickle flow. In addition to introducing a method for the direct measurement of k_{LS} , the data presented also confirm that estimates of k_{LS} are more accurate when performed in an environment in which the hydrodynamics and fluid-solid contacting conditions are representative of the system of interest.

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1. Introduction

In heterogeneous catalysis, understanding of the coupling of mass transport and reaction at the local pellet scale is central to our ability to design catalysts and operate catalytic processes effectively (Dudukovic et al., 1999; Dudukovic, 2010). The liquid-solid mass transfer is characterised by the liquid-solid mass transfer coefficient k_{LS} . Measurement of k_{LS} is not straightforward, with

measurements being made outside the reactor (*ex situ*) on systems demonstrating liquid-solid mass transfer limitation, or on the working reactor (*in situ*) in which case k_{LS} is usually a parameter in the modelling of the reaction data. *Ex situ* methods have the advantage that they are easy to implement and can provide a direct measurement of k_{LS} . However, the obvious disadvantage is that the measurement is not taking place in the real reactor environment and in many cases will be taking place in systems in which the chemical species and hydrodynamic regimes differ from those found in the particular reaction of interest. Examples of *ex situ* methods include the dissolution method (Goto and Smith, 1975; Ruether et al., 1980; Sylvester and Pitayagulsarn, 1975), the electrochemical method (Burghardt et al., 1995; Chou et al., 1979;

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Nomenclature

a	specific surface area of the bed [m^{-1}]	N	number of testing samples
a_w	external wetted surface area [m^2]	p	number of y variables or components in a mixture
b	number of principal components	$Re_{L,G}$	$u_{L,G}\rho_{L,G}d_p/\mu_{L,G}$, liquid and gas Reynolds number [-]
\mathbf{b}	matrix of regression parameters	Re'_L	Re/h_t , modified Reynolds number [-]
C_0	inter-pellet 1-octene concentration [mol m^{-3}]	$RMSEP$	root mean square error of prediction
C_S	1-octene concentration on the external surface of catalyst pellets [mol m^{-3}]	Sc	$\mu_L/(\rho_L D)$, liquid Schmidt number [-]
$C_{in,out}$	1-octene concentration at the inlet and outlet of the reactor [mol m^{-3}]	Sh	$k_{LS}d_p/D$, Sherwood number [-]
C_{intra}	intra-pellet 1-octene concentration [mol m^{-3}]	$u_{L,G}$	superficial velocities of liquid and gas [m s^{-1}]
ΔC	concentration difference between inter- and intra-pellet liquid [mol m^{-3}]	V_c	volume of the catalyst bed [m^3]
D	diffusivity of 1-octene [$\text{m}^2 \text{s}^{-1}$]	X	conversion [-]
d_p	equivalent diameter of pellets [m]	\mathbf{X}	matrix of spectra
F_L	liquid molar flow rate of 1-octene [mol s^{-1}]	\mathbf{X}_{new}	matrix of new spectral data
G	volumetric gas flow rate [ml min^{-1}]	\mathbf{Y}	matrix of mixture compositions
h_t	total liquid holdup [-]	y_i, \hat{y}_i	the actual and model prediction values of composition, respectively
k_{LS}	liquid-solid mass transfer coefficient [m s^{-1}]	ε_b	bed porosity [-]
L	volumetric liquid flow rate [ml min^{-1}]	ϕ	wetting efficiency [-]
l_b	length of the bed [cm]	$\rho_{L,G}$	densities of liquid and gas [kg m^{-3}]
m	number of x variables or spectral pixel number	δ	external film thickness [m]
n	number of samples	$\mu_{L,G}$	viscosities of liquid and gas [$\text{kg m}^{-1} \text{s}^{-1}$]

Rao and Drinkenburg, 1985), the ion exchange method (Yoshikawa et al., 1981) and the dynamic adsorption method (Tan and Smith, 1982). In the *in situ* approach, a correlation between k_{LS} and reactor operating properties such as liquid and gas flow velocities are usually assumed and the parameters of the correlation are then determined by regressing the reaction data onto the reactor model. Examples of the *in situ* approach include measurement of k_{LS} in the hydrogenation of α -methylstyrene (Morita and Smith, 1978), of styrene, 1-octene and toluene (Liu et al., 2005) and of linear and iso-octenes (Houwelingen and Nicol, 2011). Whilst k_{LS} is obtained under reaction conditions, this method relies on assumed reaction kinetics and the use of a correlation to define k_{LS} . Thus, the approach does not provide a direct measurement. In summary, a method that can provide a direct and non-invasive measurement of k_{LS} that is determined during operation of the catalyst in its working environment (i.e. under *operando* conditions) has not been reported. It is the purpose of this work to demonstrate a direct measurement of k_{LS} using magnetic resonance measurements of chemical composition within catalyst pellets (i.e. intra-pellet) made during 1-octene hydrogenation occurring in a fixed bed of 0.3 wt% Pd/Al₂O₃ catalyst pellets.

Tomographic and imaging methods, including capacitance and X-ray tomographies and magnetic resonance imaging (MRI) are increasingly applied to provide non-invasive and local measurements of multiphase reaction systems (Ranade et al., 2011). Of these, MRI is the only technique that can provide chemically-resolved information directly without need of any tracer or isotopic labels. MRI is now well-established as a technique for imaging hydrodynamics in fixed-bed reactors. These methods have been used to probe structure-flow correlations (Sederman et al., 1997) and local transitions in single-phase flow within packed beds (Johns et al., 2000); velocity imaging of both gas- and liquid-phase flow in a trickle bed (Sankey et al., 2009); and characterisation of the trickle-to-pulse hydrodynamic transition during trickle flow (Anadon et al., 2006), but the ability to track chemical conversion is less well-developed. Early applications of MRI to tracking reactions in heterogeneous catalytic reactors focussed on imaging of the ¹H nucleus (often referred to as proton MRI)

and include esterification reactions (Kuppers et al., 2002; Yuen et al., 2002, 2003) and the hydrogenation of α -methylstyrene (Koptuyg et al., 2004). Recently, a study of the gas phase ethylene hydrogenation reaction using ¹H NMR imaging has been reported by Ulpts et al. (2015). Whilst it is possible to spatially resolve the progress of reaction along the length of the reactor, accurate measurement of intra-pellet chemical composition has not been reported. This arises from two major measurement challenges in using ¹H MRI in this application. First, while MRI measurements of the ¹H nucleus are much favoured because of the high isotopic abundance of the ¹H nucleus and its high NMR sensitivity, it is associated with a narrow frequency range, termed the chemical-shift range, which means that it is difficult to unambiguously discriminate between different chemical species in a typical catalytic conversion. Second, the same chemical species will be present both inside and outside the catalyst pellets and one would therefore expect the magnetic resonance (MR) resonances to be indistinguishable for a given chemical species in the intra- and inter-pellet space. However, the interactions of a molecule within the confined pore space of the catalyst influence its nuclear spin-lattice (T_1) and spin-spin (T_2) relaxation times; the latter also acting to broaden the linewidth of the resonance. Thus, although it is challenging to distinguish the same species in the intra- and inter pellet space unambiguously it is, in principle, possible to do this and hence quantify intra-pellet composition during reaction. The first of these challenges was addressed by Akpa et al. (2005) who reported the application of ¹³C MRI to spatially-resolve conversion and selectivity during the competing etherification and hydration reactions of 2-methyl-2-butene in a fixed-bed reactor. The ¹³C nucleus has a chemical shift range of 200 ppm, compared to that of 10 ppm for ¹H observation. This approach was then used by Sederman et al. (2005) to obtain local compositions along the length of the reactor in a study of the hydrogenation of 1-octene in a trickle-bed reactor. In that work the use of ¹³C observation enabled discrimination of 1-octene, octane and 2-octene isomers (the two isomers were not resolved). Thus it was possible to track the extent of hydrogenation and isomerisation within the system which would not have been possible using ¹H observation.

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