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Comparison of performance of microreactor and semi-batch reactor for catalytic hydrogenation of *o*-nitroanisole

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Abstract

Hydrogenation reactions are ubiquitous in the fine chemicals and pharmaceutical industries. Conventionally, the kinetic studies of hydrogenation reactions are conducted in slurry or batch reactors. The kinetics of fast hydrogenation reactions is often difficult to study in a batch reactor because of the poor mass transfer characteristics of this system. The use of a microchannel reactor for such reactions provides improved mass transfer rates which may ensure that the reaction operates close to intrinsic kinetics. In the present study, a laboratory semi-batch reactor (25 mL) and a packed-bed microreactor (775 μm ID) were evaluated to determine the reactor system that would be best suited for conducting the kinetic study of hydrogenation reactions. For this purpose, hydrogenation of *o*-nitroanisole to *o*-anisidine in methanol was selected as a model three-phase reaction. The reaction rates in the two reactor systems were found to be similar under the conditions used for kinetic experiments. Therefore, both batch and microreactors are suitable for studying the kinetics of this reaction. Subsequently, the two reactors were modeled and the modeling results were used to determine the mass transfer coefficients in the two systems under typical operating conditions. The mass transfer coefficients in the microreactor were found to be two orders of magnitude higher than in the semi-batch reactor. This order of magnitude difference in the mass transfer coefficients enables the microreactor to obtain intrinsic kinetics data for fast hydrogenation reactions with half lives in the order of magnitude between 10^0 and 10^2 s.

Keywords: Catalytic hydrogenation; Fixed-bed microreactor; Semi-batch reactor; Reactor modeling; Kinetics; Mass transfer analysis

1. Introduction

Catalytic hydrogenation has evolved as a key process for the manufacture of fine chemicals and pharmaceuticals constituting about 10–20% of all the reactions in the pharmaceutical industry [1]. For example, catalytic hydrogenation of nitro compounds is important in the synthesis of drugs such as Viagra, Zyvox, Agenerase [2] and antimalarial drugs [3]. Similarly, hydrogenation of 2,4-dinitro toluene to toluene diamine is an important step in the production of polyurethane [3] and in the manufacture of TDI (toluene di-isocyanate), a fine chemical [4]. The diverse applications of catalytic hydrogenation lead to significant advances in the way these reactions are conducted in the pharmaceutical and fine chemical industries.

Various types of reactor designs such as trickle bed [5], fixed bed [6] and slurry [4,7] reactors have been used in commercial operation. The types of reactor systems used for multi-phase hydrogenation reactions depend upon the type of reaction and the phase behavior of the catalyst and the reactants. All three-phase processes involve steps of gas–liquid, liquid–solid and intra-particle mass transfer and chemical reaction. The relative importance of these individual steps depends upon the type of contact between these phases provided by the reactor system. Therefore, the choice of the reactor is important for optimum performance.

In the pharmaceutical industry, most of the multi-phase hydrogenation reactions are conducted in large slurry batch or semi-batch reactors, where the catalyst is suspended in the liquid, which is continuously agitated with a stirrer. The interest in slurry batch reactors derives from their industrial importance in the manufacture of important intermediates for dyes, agrochemicals and pharmaceuticals, often produced on a large industrial scale [3]. Also, the laboratory semi-batch reactor or

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Nomenclature

a	mass of the catalyst per unit volume of the microreactor (g/L)
a_1	mass of the catalyst per unit volume of the semi-batch reactor (g/L)
$C_{\text{anisidine}}$	concentration of anisidine (mol/L)
C_{A}	concentration of limiting reactant (mol/L)
C_{hydrogen}	concentration of hydrogen (mol/L)
$C_{\text{H,b}}$	concentration of the hydrogen in the bulk liquid (mol/L)
$C_{\text{H,c}}$	concentration of the hydrogen at the catalyst surface (mol/L)
$C_{\text{H,sat}}$	saturation concentration of hydrogen at the gas–liquid interface obtained from the hydrogen solubility data (mol/L)
C_{H_2}	concentration of hydrogen (mol/L)
$C_{\text{intermediate}}$	concentration of intermediate (mol/L)
C_{nitro}	concentration of nitroanisole (mol/L)
C_{N}	concentration of nitroanisole (mol/L)
$k_{\text{gl}}a_{\text{gl}}$	liquid side mass transfer coefficient (s^{-1})
$k_{\text{ls}}a_{\text{ls}}$	liquid/solid mass transfer coefficient (s^{-1})
k_r	intrinsic rate constant (s^{-1})
k_{I}	intrinsic kinetic rate constant for reaction I (L^2/g h mol)
k_{II}	intrinsic kinetic rate constant for reaction II (mol/g h)
K_{N}	equilibrium constant for nitroanisole in reaction I (L/mol)
$K_{\text{H}_2\text{I}}$	equilibrium constant for hydrogen in reaction I (L/mol)
$K_{\text{H}_2\text{II}}$	equilibrium constant for hydrogen in reaction II (L/mol)
K_{la}	overall mass transfer coefficient (s^{-1})
K_{I}	equilibrium constant for intermediate in reaction I (L/mol)
r	reaction rate (mol/L s)
r_1	reaction rate for reaction I (mol/g h)
r_2	reaction rate for reaction II (mol/g h)
t	reaction time (min)
v_{l}	liquid superficial velocity (cm/s)
z	distance from the entrance of the reactor (cm)

slurry reactor is often used as a tool to provide intrinsic kinetic data, which is used for the design of the large-scale catalytic reactors, and for better understanding of catalytic reaction mechanisms. Several examples of catalytic hydrogenation kinetic studies in batch reactors have been published previously from catalysis and reaction engineering viewpoint [7–9]. However, the kinetic studies for fast hydrogenation reactions are difficult to conduct in a batch reactor even at the highest stirrer speed. This is because for fast hydrogenation reactions the mass transfer effects become predominant over intrinsic kinetics. As a result the true intrinsic kinetic rates of fast hydrogenations reactions are masked by mass transfer limitations in batch reactors leading to reaction times longer than needed for the reaction to be controlled by intrinsic kinetics. For slow hydrogenation reactions, the batch reactor can be used to obtain intrinsic kinetic data. However, the volume of the batch reactor is another variable to determine if the reactor can be used to study intrinsic kinetics. As the volume of the batch reactor increases, there will be problems associated with non-uniform mixing. Inefficient mixing in large batch reactors may shift the process from kinetic region to a mass transfer controlled region [10]. This shift will have significant effect on the conversion, and the selectivity of the desired products.

In recent years, there has been a growing interest in utilizing microreactors for catalytic hydrogenation because of their numerous advantages over conventional reactors. Microchannel reactors with their small transverse dimensions possess extremely high surface to volume ratios and consequently exhibit enhanced heat and mass transfer rates. The small volume of the microreactor enables fast transport of the fluid layers thus reducing the reaction time and providing greater selectivity and higher product yield. The diffusion of gases into the liquid reactant often poses problems of mass transfer in conventional reactors. This can be overcome in microreactors by increasing the interfacial contact area between the two mixing fluids, or by reducing the characteristic length scale thereby forcing a reactant in one phase to mix, diffuse and react with the reactant in the second phase at the catalyst surface, thus improving the rate of mass transfer tremendously.

Several researchers have investigated gas–liquid–solid hydrogenation in microreactors by incorporating the catalyst into microreactors in different forms [11–13]. For example, Kreutzer et al. [11] used monolith reactors for hydrogenation of a nitro aromatic compound and observed several advantages of conducting this fast reaction in the monolith reactor, such as good mass transfer characteristics and low pressure drop. Similarly, Losey et al. [12] used microfabricated packed-bed reactors for the hydrogenation of cyclohexene. They observed that the mass transfer coefficients in the microreactor range from 5 to 15 s^{-1} which are nearly two orders of magnitude larger than the values obtained from laboratory trickle-bed reactors. Gavriilidis et al. [13] also conducted experimental studies on nitrobenzene hydrogenation in a microstructured falling film reactor and observed that the overall mass transfer rate in the microreactor is enhanced significantly with an enormous increase in surface area per unit reaction volume. The excellent mass transfer characteristics of the microreactor enable it to be used as a tool to obtain intrinsic kinetics information for fast hydrogenation reactions. There is limited literature available on the study of intrinsic kinetics of fast hydrogenation reactions in the microreactor in spite of its excellent mass transfer characteristics. Instead, all the kinetic studies were conducted in conventional batch or other reactors which exhibit poor mass transfer and mixing characteristics. These observations have led to the present study where the microreactor and semi-batch reactor were evaluated to study the extent to which these reactors can be used as efficient reactor systems for obtaining intrinsic kinetics data. For this