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Kinetics research on fast exothermic reaction between cyclohexanecarboxylic acid and oleum in microreactor

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ABSTRACT

Microreactors are effective tools for the intensification of fast exothermic chemical reactions. In this work, we focus on the kinetics study of a microreacting process to provide a deeper understanding of the transport and reaction performance within microreactors. An experimental setup incorporating an online kinetic measurement method was developed based on the temperature–conversion relationship in the cyclohexanecarboxylic acid–oleum reaction – a crucial reaction for the preparation of ε-caprolactam. The reactant conversion was successfully recorded in a reaction time of less than 1.0 s, and it was determined that the reaction rate was mainly controlled by the mixing of reactants. The mass transfer coefficient in the microreactor reached 10^{-4} m/s, and the observed selectivity of the main-product was higher than 97%. Based on the experimental results, a single-droplet model was developed to establish a better understanding of the temperature and concentration distributions in the reacting system as well as analyze the effect of drop size on main-product selectivity.

1. Introduction

Fast exothermic reactions play essential roles in the chemical engineering industry for their wide applications. Although these types of reactions have appeared hundreds of years until now, people still find they are hard to operate. Many fast exothermal reactions take place in batch reactors with low reaction efficiencies, low yield and low safety. In recent years, however, the introduction of micro-structured chemical system has brought about many new advantages for those reactions, including higher product yield, higher space rate, lower energy consumption and safer operation [1–3]. Fast mixing can be obtained in microreactors with residence times on the millisecond level [4] while high volumetric heat transfer coefficients 10 times larger than those observed in common heat exchangers can be obtained in microcontactors [5]. Because of their excellent mixing and transport performance, many different types of chemical reactions have been intensified using microreactors, such as fast precipitation reaction for nanoparticles [6], strong exothermic polymerization for polymer materials [7], and dangerous organic synthesis with reactive reactants [8].

Microreactors are effective tools for improving fast exothermic reaction processes, especially for solving low selectivity problems. The efficient mixing of reactants, fast heat removal and controllable reaction time allow the overall reaction process to be controlled more effectively, resulting in a higher selectivity of the main-products. The Friedel–Crafts aminoalkylation reaction is a classic example of a reaction system to which a microreactor can be applied. Nagaki et al. reported 92% main-product yields by using micromixing technology [9]. In a different study, Park and Kim carried out an oxidative Heck reaction in a dual-channel microreactor [10]. Their results showed significant improvements in yield, selectivity, and reaction time in microreactors over traditional batch reactors. Jovanovic et al. reported a selective alkylation reaction of phenylacetonitrile in a 250-μm internal diameter microchannel reactor [11]. They found both the conversion and selectivity in their microreactor increased significantly compared with a stirred reactor. In our previous work, we also studied the enhancement of selectivity in fast exothermic consecutive reactions using the reaction between cyclohexanecarboxylic acid and oleum, a crucial process for the preparation of ε-caprolactam. Microreactors generating microdroplets in a liquid–liquid multiphase reaction process were used to enhance reactant mixing and main-product selectivity which reached levels (>97%) much higher than those in common batch reactors [12,13].

Except for the advantage research of microreactors, deeply understanding the transport and reaction characteristics of microreacting process is very important for further development of microreaction technology. In this work we investigate the appar-

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Nomenclature

AH^+	protonated cyclohexanecarboxylic acid
AS	mixed anhydride
by-P	by-products
CCA	cyclohexanecarboxylic acid
C_i	concentration, i refers to CCA, H_2SO_4, HSO_{4^-}, SO_3, AS, AH^+, by-P (mol/m^3)
Cp_{alkyl}	heat capacity of alkyl-hydrocarbons, alkyl refers to C_6H_{14}, C_7H_{16}, C_8H_{18} [kJ/(kg °C)]
Cp_{CCA}	heat capacity of CCA [kJ/(kg °C)]
Cp_{oleum}	heat capacity of oleum [kJ/(kg °C)]
D	diffusion coefficient (m^2/s)
D_{in}	diffusion coefficient in the droplet (m^2/s)
D_{out}	diffusion coefficient out of the droplet (m^2/s)
d	inner diameter of the reaction pipe (m)
d_{av}	average droplet diameter (m)
d_{32}	Sauter-mean droplet diameter (m)
Ha	Hatta number ($\mathrm{Ha}=\sqrt{\kappa_m C^0_{SO_3} D_{in}/k_C}$)
k	thermal conductivity [W/(m °C)]
k_C	mass transfer coefficient of CCA (m/s)
k_Ca	volumetric mass transfer coefficient of CCA (1/s)
k_{in}	thermal conductivity in the droplet [W/(m °C)]
k_{out}	thermal conductivity out of the droplet [W/(m °C)]
$\overline{K}_b$	equilibrium constant of proton exchange reaction
$\overline{K}_m$	equilibrium constant of mixed anhydride formation reaction
M_{CCA}	molecular weight of CCA (g/mol)
$M_{H_2SO_4}$	molecular weight of H_2SO_4 (g/mol)
M_{SO_3}	molecular weight of SO_3 (g/mol)
n_{CCA}	molar transport rate of CCA (mol/s)
Q_{oil}	volume feeding rate of oil phase (m^3/s)
Q_{oleum}	volume feeding rate of oleum (m^3/s)
q	heat source in model equation (W/m^3)
q_r	released heat flux of the reacting system (W)
R	reaction source in model equation [mol/(m^{3}s)]
s	cross-sectional area of the mixing channel (m)
T	temperature (°C, K)
T_C^{in}	inlet temperature of continuous phase (°C)
T_D^{in}	inlet temperature of dispersed phase (°C)
u_T	average velocity in microreactor [$u_T=4(Q_{oil}+Q_{oleum})/\pi d^2$, m/s]
u_C	average velocity of continuous phase in micromixer ($u_C=Q_{oil}/s$, m/s)
V	inner volume of the microreactor (m^3)
x_{CCA}	mass concentration of CCA in the feeding oil (wt%)
x'_{CCA}	mass concentration of CCA in the hydrolyzed oil phase (wt%)
x_{SO_3}	mass concentration of SO_3 in the feeding oleum (wt%)
ΔC_m	concentration driving force (mol/m^3)
$\Delta_r H_M$	reaction enthalpy of mixed anhydride formation reaction (kJ/mol SO_3)
$\Delta_r H_P$	reaction enthalpy of proton exchange reaction (kJ/mol H_2SO_4)
Φ_{oleum}	conversion of oleum
κ_m	kinetic constant of the main reactions [m^3/(s mol)]
κ_s	kinetic constant the of side reactions (1/s)
γ	interfacial tension (N/m)
μ_C	viscosity of continuous phase (Pa s)
ρ_{oil}	density of oil phase (kg/m^3)
ρ_{oleum}	density of oleum (kg/m^3)
φ	phase ratio of dispersed phase
τ	reaction time (s)

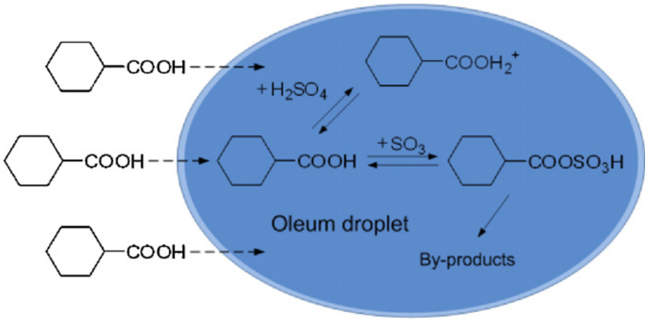


Fig. 1. Sketch view of the working system.

ent kinetics of cyclohexanecarboxylic acid–oleum reaction in a microreactor, a topic which, up to now, has not been frequently discussed in the literature before. An online kinetic measurement method was developed to measure the reactant conversions at different reaction times. The mixing performance in the microreactor was investigated experimentally, and a single droplet model was established to show the nature of the temperature and concentration distributions in the micro-scale reacting system.

2. Experiment and simulation

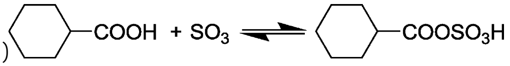
2.1. Working system

The reaction process between cyclohexanecarboxylic acid (CCA) and oleum, also referred to as the Premixing Reaction in the SINA process for the preparation of caprolactam [14], was selected as a representative fast exothermic reaction system. Fig. 1 shows this multiphase reaction system with a CCA dissolved alkyl-hydrocarbon solution, as the organic feed solution, and oleum as the sulfuric phase solution (Fig. A1). Throughout the process, the phase ratio between the oil and sulfuric acid phase was larger than 6, with the oil phase acting as the continuous phase. CCA first diffused from the continuous phase to the dispersed phase, followed by reactions between CCA and oleum in the droplet.

Two main reactions take place in this working system [13]. One is the proton exchange reaction between CCA and sulfuric acid:

(I)


The other is the mixed anhydride formation reaction between CCA and sulfur trioxide:

(II)


The mixed anhydride is the main-product, since it can react with nitrosylsulfuric acid to form caprolactam in the following process [15]. These two main reactions are ultra-fast reactions [16,17]. They take place almost instantaneously when the reactants meet and stop quickly when the feed stream is terminated [18]. The reactions are always shown as reversible in the literatures [19,20]. We measured the chemical equilibrium of the proton exchange reaction and determined the equilibrium constant, $\overline{K}_b$, shown in Eq. (1). According to previous studies, the equilibrium constant of the mixed anhydride formation reaction ($\overline{K}_m$) is 10^4 times greater than the proton exchange reaction [12,19]. Thus, both reactions can be seemed as irreversible processes for simplification with stoichiometric excess of CCA in all operations.

$$\overline{K}_b=\frac{C_{AH^+}C_{HSO_4^-}}{C_{CCA}C_{H_2SO_4}}=0.06\cdot\exp\left(\frac{13,900}{RT}\right)=19.4–8.4 \quad (20–70\,^\circ\mathrm{C}) \tag{1}$$

where AH^+ refers to the protonated cyclohexanecarboxylic acid. Both reactions are highly exothermal. Maggiorotti measured their