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Solid effects on gas–liquid mass transfer in catalytic slurry system of isobutene hydration over fine ion exchange resin particles

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Abstract

To study solid effects on gas–liquid mass transfer in slurry system accompanied by chemical reaction, the experiments of isobutene hydration over fine cation exchanger resin were performed in three-phase slurry catalytic reactor. The mathematical model for the reactor with multi-parameter estimation procedures was developed to obtain the volumetric liquid-side mass transfer coefficient (k_La). The experimental study with different catalyst particle sizes and catalyst solid loadings has shown that gas–liquid mass transfer can be significantly enhanced by chemical reaction on the surface of fine catalyst particles in the liquid film at low solid concentrations. The k_La increases with decreasing catalyst particles mean size, and with increasing catalyst loading.

Keywords: Gas–liquid mass transfer; Enhancement; Isobutene hydration; Resin particles

1. Introduction

The effect of small particles on the gas-absorption rate in slurry system at low solid concentrations has been investigated by many authors [1–7]. It has become known that the addition of fine particles to gas–liquid system caused an enhancement of gas-absorption rate when the particle size is the same or less than the liquid film thickness, whereas larger particles showed almost no effect [5]. The enhancement factor E, to describe the enhancement effect, was defined as the ratio of volumetric gas–liquid mass transfer coefficients $k_La/(k_La)_0$, with index 0 indication of no solids present. Joly-Vuillemin et al. [6] reported that E was up to 1.6 in slurry catalytic hydrogenation of adiponitrile over raney nickel. Py et al. [5] found that E was 1–4 for sulphur dioxide absorption in slurries of sulphuric acid solutions and activated carbon. Lindner et al. [4] reported that E in the bubble column and stirred autoclave was 1–4 for hydrogen transfer in slurries of carbon-supported catalyst. And most of the experimental studies on the enhancement effect of catalyst particles with physical adsorption and chemical reaction concerned active carbon particles in aqueous media.

Gas–liquid mass transfer enhancement by particles suspended in the liquid phase has been investigated by several authors [7]. Various mechanisms have been proposed for describing this enhancement [8], i.e. shuttling or grazing, boundary layer mixing, coalescence inhibition, and boundary layer reaction. When fine particles catalyze a chemical reaction at the gas–liquid interface, significant conversion occurs within the diffusion layer and the concentration gradient of gaseous reactants increases, thereby increasing the mass transfer rate. Gas–liquid mass transfer enhancement due to chemical reaction is a function of the lyophobicity and activity of the catalyst particles, and of the turbulence intensity in the liquid film. And inside the porous particle mass transport and reaction are in parallel (on the catalyst carrier) or in series (on the active sites). Therefore, the mechanisms of mass transfer enhancement due to adsorption, reaction or catalytic effects on the surface of fine catalyst particles still need further study.

The aim of this work is to study the effect of fine resin catalyst particles on gas–liquid mass transfer in the reaction system of isobutene hydration, which can provide basic data for new slurry system and for further study on enhancement mechanism. In this paper, the experiments were performed in a stirred slurry reactor

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Nomenclature

a	surface area of gas bubbles per unit volume of the liquid (m^2/m^3)
a_s	particle surface area per unit volume liquid (m^2/m^3)
C	concentration (mol/m^3)
C^*	equilibrium concentration (mol/m^3)
d_p	particle diameter (m)
D	diffusion coefficient (m^2/s)
$\bar{e}$	power input per unit mass (W/kg)
E	enhancement factor
k	reaction rate constant ($m^6/(kmol\,kg\,s)$)
k_L	gas–liquid mass transfer coefficient (m/s)
k_S	liquid–solid mass transfer coefficient (m/s)
K_A	inhibition constant for tert-butyl alcohol ($m^3/kmol$)
K_C	chemical reaction equilibrium constant ($m^3/kmol$)
m_c	catalyst weight per unit volume solution (kg/m^3)
R	chemical reaction rate (kmol/kg s)
t	time (s)
T	temperature (K)
x	mole fraction of isobutene in liquid phase at equilibrium

Subscripts

A	tert-butyl alcohol
B	isobutene
L	liquid phase
S	solid phase
W	water

Greek letters

ε_s	holdup of dispersed solid phase
ε	porosity of particle
μ	viscosity ($N\,s/m^2$)
ρ	density (kg/m^3)
υ	kinetics viscosity (m^2/s)

with semi-batch process at first. Then the volumetric liquid-side mass transfer coefficient k_La was obtained by the mathematical model with multi-parameter estimation procedures. And the enhancement factors were obtained in the catalytic slurry with various catalyst particles sizes and catalyst loadings.

2. Experiment

Since the solubility of isobutene gas in water is low for the system of isobutene hydration to tert-butyl alcohol, the gas–liquid mass transfer is particularly important to determine the average conversion rates in the slurry reactor. And the reaction rate is very low in the primary stage of reaction when catalytic solid volume fraction is low. But the isobutene solubility in water can be increased by the product tertiary butyl alcohol [9]. The equilibrium concentration of isobutene gas in the liquid phase can be increased in the process of reaction. On the other hand, the high tertiary butyl alcohol concentrations can accelerate the reverse reaction of tertiary butyl alcohol dehydration [10]. So the experiments of gas–liquid mass transfer enhancement by fine catalyst particles were limited to the initial stage of reaction in which tertiary butyl alcohol concentrations were less than 2 kmol/m^3. The macroporous cation exchange resin NKC-9 (from Nankai university material research center) particles were used as a catalyst for isobutene hydration reaction. The diameter range of commercial product catalyst particles is from 0.18 to 0.3 mm and the average pore diameter is 56 nm. The catalyst particles with various sizes were prepared by colloid mill wet grinding with distilled water as wetting agent. The particles size depends on the distance of gear wheels of colloid mill and the distance can be adjusted. The mixture of water and particles after grinding were segregated into various fractions through a centrifugal classifier. The particles volume mean diameter D [4,3] in the prepared catalyst mixture was measured by a laser granulometer (Malvern 2000) and the particles sizes range of each acceptable sample were within D [4,3] $(1 \pm 30\%)$. Then the catalyst was ready to use.

The experiments were carried out in a stirred autoclave reactor with a total volume of 1 dm^3, equipped with an automatic temperature controller and a variable speed two-bladed impeller agitator, batch with respect to the liquid–solid suspension and continuous with respect to isobutene gas. The component concentrations in the liquid phase were measured with a HP4890D gas chromatograph. The chromatographic column is HP-Innowax (60 m × 0.032 mm). The reaction pressure was maintained constant at 0.74 MPa, which controlled by the saturated vapor pressure of isobutene gas. The temperature of reactor was held within $77 \pm 0.5\,°C$.

In a typical isobutene hydration experiment, known quantity liquid–solid suspension was charged into the reactor, stirred and heated to the desired temperature. After the air in the reactor was displaced by isobutene gas two or three times, the reactor was inflated with isobutene gas and pressurized to the desired level. The instant that the pressure was achieved was assumed to be the start of the reaction. The component concentrations of liquid samples were determined at definite time intervals.

3. Mass transfer modelling

For gaseous reactant being absorbed in the liquid phase mass transfer and reaction inside the porous catalyst particles, there have resistances in series that control the overall conversion rate according to film theory, that is the resistance to mass transfer in the gas phase, to mass transfer in the liquid phase at the gas–liquid interface, to mass transfer in the liquid phase at the liquid–solid interface, and to reaction at the external catalyst surface. To obtain the volumetric gas–liquid mass transfer coefficient (k_La) of isobutene gas in the slurry reactor, the following hypotheses were adopted to represent the dynamic behavior of the reactor:

(1) The liquid and suspended phases were perfect mixing; (2) the resistance of transfer within gas phase was negligible; (3) all the solid particles were completely immersed in the liquid and that there were no direct contact between gas bubbles and solid particles; (4) solid particles were assumed to be spherical and uniform; (5) the resistance of inner diffusion in the solid phase was negligible when the catalyst particle size was small; (6) the temperature was uniform in reactor everywhere.

With the hypothesis mentioned above, the mass balance equations of the slurry reactor can be written as follows:

$$\begin{aligned}
&(1-\varepsilon_{\mathrm{S}})\frac{\mathrm{d}C_{\mathrm{BL}}}{\mathrm{d}t} = k_{\mathrm{BL}}a(C^{*}_{\mathrm{BL}}-C_{\mathrm{BL}}) - k_{\mathrm{BS}}a_{\mathrm{S}}(C_{\mathrm{BL}}-C_{\mathrm{BS}})\\
&(1-\varepsilon_{\mathrm{S}})\frac{\mathrm{d}C_{\mathrm{WL}}}{\mathrm{d}t} = k_{\mathrm{WL}}a(C^{*}_{\mathrm{WL}}-C_{\mathrm{WL}}) - k_{\mathrm{WS}}a_{\mathrm{S}}(C_{\mathrm{WL}}-C_{\mathrm{WS}})\\
&(1-\varepsilon_{\mathrm{S}})\frac{\mathrm{d}C_{\mathrm{AL}}}{\mathrm{d}t} = k_{\mathrm{AS}}a_{\mathrm{S}}(C_{\mathrm{AS}}-C_{\mathrm{AL}}) - k_{\mathrm{AL}}a(C_{\mathrm{AL}}-C^{*}_{\mathrm{AL}})\\
&(1-\varepsilon)\varepsilon_{\mathrm{S}}\frac{\mathrm{d}C_{\mathrm{BS}}}{\mathrm{d}t} = k_{\mathrm{BS}}a_{\mathrm{S}}(C_{\mathrm{BL}}-C_{\mathrm{BS}}) - (1-\varepsilon)\rho_{\mathrm{S}}R(C_{\mathrm{BS}},C_{\mathrm{WS}},C_{\mathrm{AS}})\\
&(1-\varepsilon)\varepsilon_{\mathrm{S}}\frac{\mathrm{d}C_{\mathrm{WS}}}{\mathrm{d}t} = k_{\mathrm{WS}}a_{\mathrm{S}}(C_{\mathrm{WL}}-C_{\mathrm{WS}}) - (1-\varepsilon)\rho_{\mathrm{S}}R(C_{\mathrm{BS}},C_{\mathrm{WS}},C_{\mathrm{AS}})\\
&(1-\varepsilon)\varepsilon_{\mathrm{S}}\frac{\mathrm{d}C_{\mathrm{AS}}}{\mathrm{d}t} = (1-\varepsilon)\rho_{\mathrm{S}}R(C_{\mathrm{BS}},C_{\mathrm{WS}},C_{\mathrm{AS}}) - k_{\mathrm{AS}}a_{\mathrm{S}}(C_{\mathrm{AS}}-C_{\mathrm{AL}})
\end{aligned} \tag{1}$$

with the initial condition:

$$\begin{aligned}
t=0\quad &C_{\mathrm{BL}} = C_{\mathrm{BS}} = 0\\
&C_{\mathrm{WL}} = C_{\mathrm{WS}} = C_{\mathrm{W0}}\\
&C_{\mathrm{AL}} = C_{\mathrm{AS}} = C_{\mathrm{A0}}
\end{aligned}$$

To solve the ordinary differential Eq. (1), some parameters need to be determined firstly. The solid-liquid mass transfer coefficient can be estimated from empirical correlation [11]. Based on the boundary layer theory, mass transfer to particles submerged in a fluid was generally described by

$$Sh = 2 + C Re^{n_1} Sc^{n_2} \tag{2}$$

In Eq. (2) the Sherwood number (*Sh*), Reynolds number (*Re*), and Schmidt number (*Sc*) were defined, respectively, as:

$$Sh = \frac{k_{\mathrm{S}}d_{\mathrm{p}}}{D_{\mathrm{AB}}},\qquad Sc = \frac{\mu_{\mathrm{L}}}{\rho_{\mathrm{L}}D_{\mathrm{AB}}},\qquad Re = \left(\frac{\bar{e}d_{\mathrm{p}}^{4}}{v_{\mathrm{L}}^{3}}\right)^{1/3}$$

For ion exchange resin catalyst particles in stirred tank reactor, the constants C, n_1, and n_2 in Eq. (2) are 0.4, 3/4, 1/3, respectively [12]. The surface area of the catalyst particles per unit volume solution a_{s} ($\mathrm{m}^2/\mathrm{m}^3$ liquid) can be estimated using

$$a_{\mathrm{s}} = \frac{6.0m_{\mathrm{c}}}{\rho_{\mathrm{s}}d_{\mathrm{p}}} \tag{3}$$

The solubilities C^{*}_{A} in aqueous tertiary butyl alcohol were determined experimentally and correlated with experimental data in similar reaction temperature and pressure [13]. The correlation equation can be given by

$$C^{*}_{\mathrm{A}} = \exp(a + b/T);\qquad a = 7.738C_{\mathrm{A}} - 20.303;$$
$$b = -2454.32C_{\mathrm{A}} + 5717.43 \tag{4}$$

The stoichiometry of the isobutene hydration reaction can be represented by

$$\mathrm{C_4H_8\,(G) + H_2O\,(L) \rightleftharpoons C_4H_{10}O\,(L)} \tag{5}$$

The kinetics equation [14] for isobutene hydration catalyzed by cation exchange resin can be represented by a rate equation such as:

$$R = \frac{k(C_{\mathrm{B}}C_{\mathrm{W}} - C_{\mathrm{A}}/K_{\mathrm{C}})}{(1+K_{\mathrm{A}}C_{\mathrm{A}})^2} \tag{6}$$

In this paper, the kinetics equation parameters (k, K_{C}, K_{A}) need to be recalculated due to different reaction conditions, such as temperature, pressure, catalyst particle size, stirring speed.

The ordinary differential Eq. (1) with its initial condition can be solved by the four-order Runge-Kutta algorithm. While the volumetric mass transfer coefficient $k_{\mathrm{L}}a$ and the kinetics equation parameters (k, K_{C}, K_{A}) in Eq. (1) were unknown parameter, the model equations were solved together with the procedure for multi-parameter estimation. The calculation process is discussed as follows. The initial values of parameters $k_{\mathrm{L}}a$, k, K_{C}, K_{A} were given firstly, the component concentrations of liquid in reaction process were obtained by the numerical solution of Eq. (1). Then the parameters were adjusted by experimental data and calculated values of component concentrations according to the least square method. When the deviation of experimental data and calculated values was very little, the values of parameters were determined. The concentrations of water and tertiary butyl alcohol in gas phase were assumed invariability in the calculation process. Some parameters used in model were presented in Table 1.

Table 1
The parameters value used in the model

D_{AW}	$2.959 \times 10^{-9}\ \mathrm{m^2/s}$	D_{BW}	$3.246 \times 10^{-9}\ \mathrm{m^2/s}$
D_{WW}	$5.499 \times 10^{-9}\ \mathrm{m^2/s}$	$\bar{e}$	0.031 W/kg
μ_{AW}	0.874 mPa s	T	350 K
μ_{BW}	0.12 mPa s	ρ_{A}	$666\ \mathrm{kg/m^3}$
μ_{WW}	0.37 mPa s	ρ_{B}	$560\ \mathrm{kg/m^3}$
$w_{\mathrm{B}}, w_{\mathrm{W}}, w_{\mathrm{A}}$	0.1, 0.6, 0.3	ρ_{W}	$974\ \mathrm{kg/m^3}$
		ρ_{S}	$700\ \mathrm{kg/m^3}$

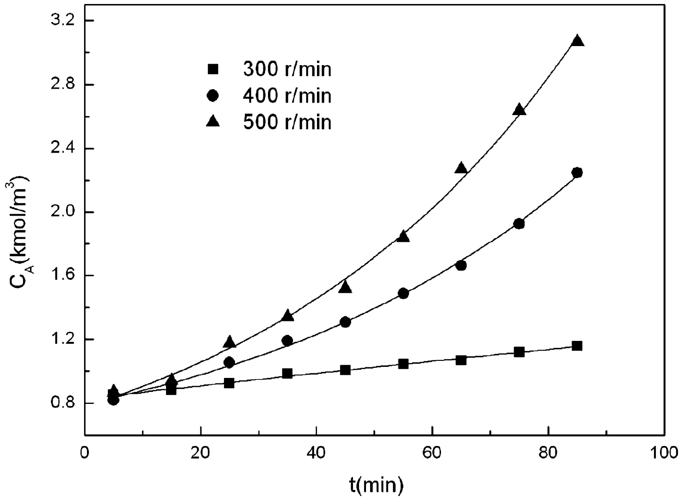


Fig. 1. The dependence of concentration of tert-butyl alcohol on the reaction time at different stirring speed. $T = 350$ K, $P = 0.74$ MPa, water volume = 450 cm^3, catalyst loading = 20 kg/m^3, particle diameter = 53.68 μm, and initial concentration of tert-butyl alcohol = 1.0 kmol/m^3.

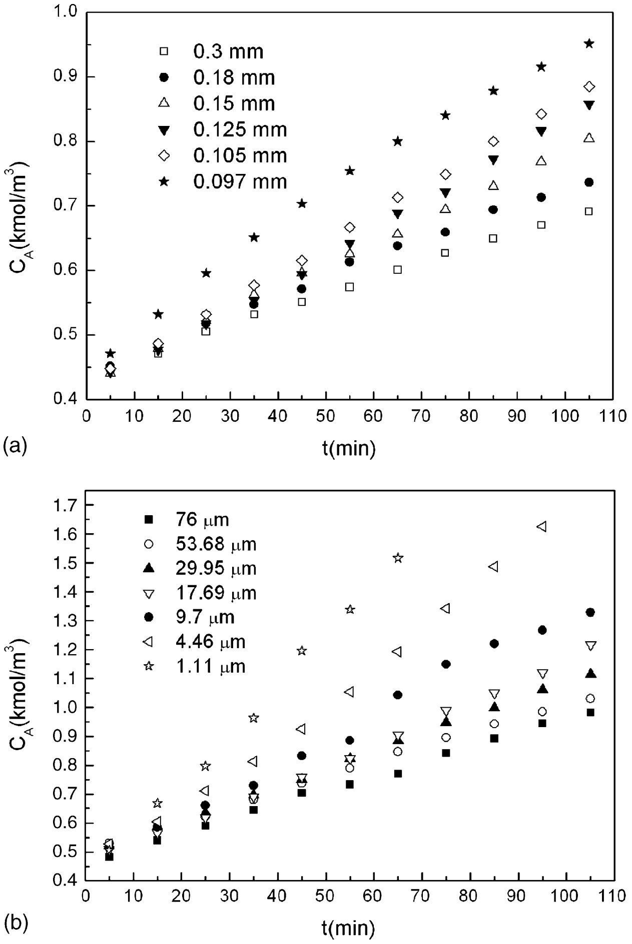


Fig. 2. The dependence of concentration of tert-butyl alcohol on the reaction time at different catalyst size. $T = 350$ K, $P = 0.74$ MPa, water volume = 450 cm^3, catalyst loading = 20 kg/m^3, stirring speed = 400 rpm, and initial concentration of tert-butyl alcohol = 0.5 kmol/m^3.

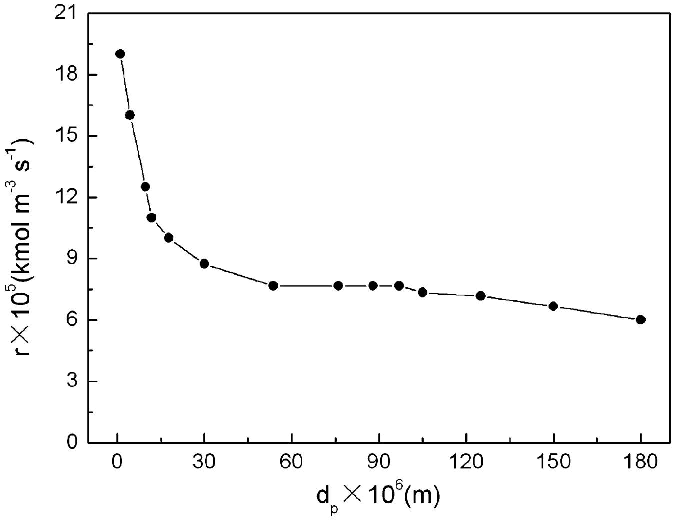


Fig. 3. The influence of particle size on the rate of reaction.

4. Results and discussion

In order to study the enhancement effect of fine catalyst particles on the gas–liquid mass transfer, the reaction should be held in mass transport-controlled conditions. As an important aspect influencing the gas–liquid mass transfer, the influence of stirring speed on the reaction rate is reported in Fig. 1. The data in Fig. 1 show that the reaction rate increases with increasing stirring speed. This convinces that the reaction is controlled by the mass transfer rate when stirring speeds are between 300 and 500 rpm. Therefore, stirring speed was set as 400 rpm in the experiments of catalyst particles sizes varied and catalyst loadings as well.

4.1. *Effect of particle size*

The experimental results of the influence of particle size on the reaction rate are reported in Figs. 2 and 3. The data in Fig. 2 show the linear relationships between the concentration of tert-butyl alcohol and time. It can be seen from Fig. 3 that the reaction rate is inverse proportional to the particle size for catalyst particle diameters d_p greater than 97 μm or less than 53.68 μm and that for particle diameters between 53.68 and 97 μm the rate of reaction is constant. This phenomenon can be considered that for $d_p > 97$ μm, mass transfer resistance consists of the external diffusion resistance and the internal diffusion resistance and the internal diffusion resistance is the limiting resistance, for $d_p < 97$ μm, the internal diffusion resistance can be considered negligible, for $d_p < 53.68$ μm, chemical reaction on the catalyst particles surface and particles themselves in the liquid film can decrease the external diffusion resistance and enhance the rate of gas–liquid mass transfer. Therefore, 53.68 μm was used to

Table 2
The volumetric gas–liquid mass transfer in different catalytic particle diameter

Particle diameter (μm)	53.68	29.95	17.69	9.7	4.46	1.11
$k_La \times 10^2$ (s^{-1})	0.860	0.920	1.016	1.106	1.957	3.582

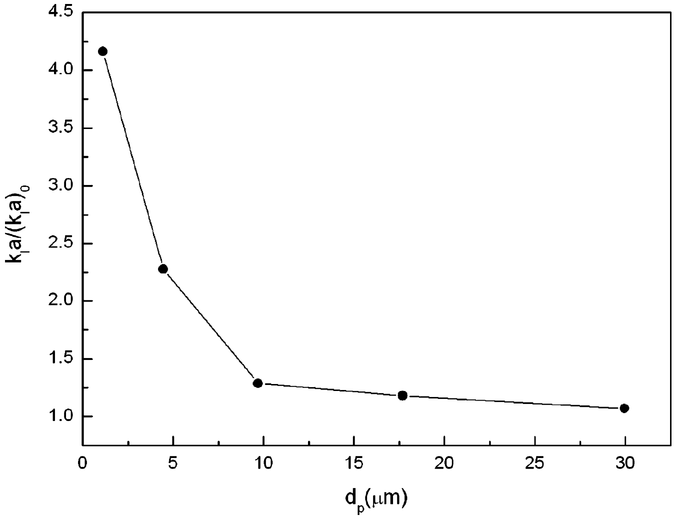
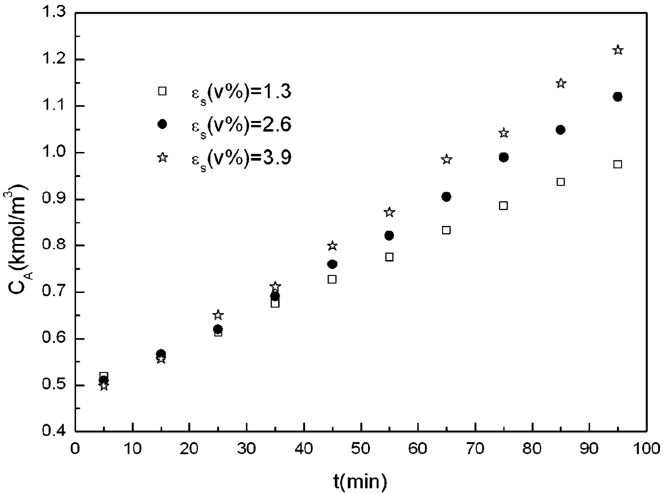
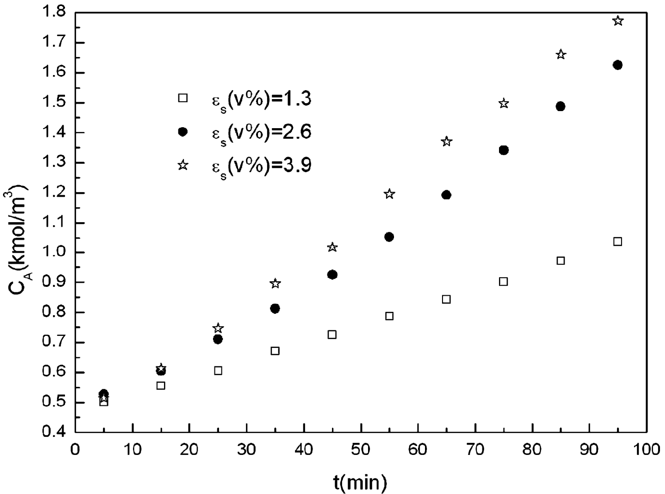


Fig. 4. The enhancement factor as function of different catalyst particles size.



(a) d_p=9.7 μm



(b) d_p=4.46 μm

Fig. 5. The dependence of concentration of tert-butyl alcohol on the reaction time at different catalyst volume fraction. $T = 350$ K, $P = 0.74$ MPa, water volume = 450 cm^3, stirring speed = 400 rpm, and initial concentration of tert-butyl alcohol = 0.5 kmol/m^3.

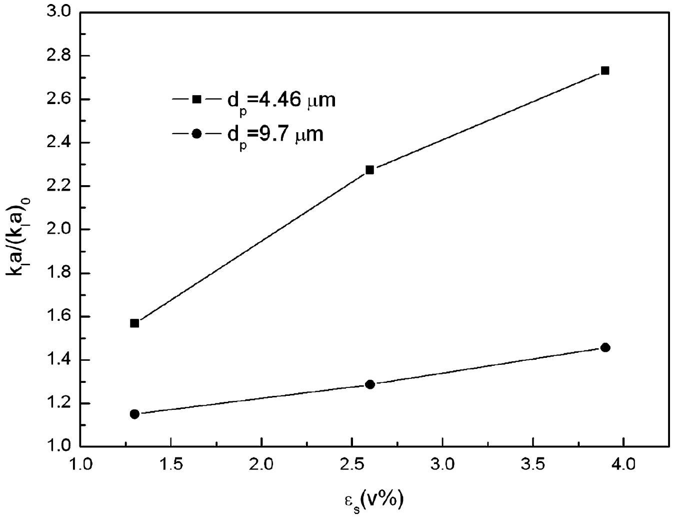


Fig. 6. The enhancement factor as function of solid volume fraction at different particles size.

references diameter for non-enhanced large catalyst particles, and the enhancement factor E was defined as $k_La/(k_La)_0$, $(k_La)_0$ refer to the volumetric mass transfer coefficient of isobutene with large particles under the same experimental conditions.

By model solving, the constants in kinetics Eq. (1) were obtained: $k = 8.4777 \times 10^{-6}$ m^6/(kmol kg s), $K_C = 9.4885$ m^3/kmol, $K_A = 1.4525$ m^3/kmol. The volumetric gas–liquid mass transfer coefficients with different particle sizes are presented in Table 2. Fig. 4 shows the enhancement of fine particles when the solid volume fraction was 0.026 m^3/m^3 slurry. It can be seen from Fig. 4 that the gas–liquid mass transfer rate increases considerably with decreasing catalyst particle size. This has been reported previously for the oxidation of glucose using Pt/C particles as catalyst [2] and for the oxidation of Na_2S using activated carbon particles as catalyst [1].

4.2. Influence of catalyst loading on the reaction rate

The influence of catalyst volume fraction on the reaction rate is reported in Fig. 5. The enhancement factors as a function of solid volume fraction are presented in Fig. 6. Figs. 5 and 6 show that the catalyst loading has a positive effect on the rate of gas–liquid mass transfer at low solid content and that the enhancement effect of small size particles is more notable than that of large size particles.

5. Conclusion

The solid effect on gas–liquid mass transfer in the initial stage of isobutene hydration was studied by dynamic simulation method with appropriate solution procedures in slurry reactor. The study has shown that fine cation exchange resin particles can enhance the isobutene gas mass transfer rate due to chemical reaction on the surface of catalyst particles in the liquid film at low solid content. At the same catalyst volume fraction in the slurry the volumetric mass transfer coefficient increases with decreasing catalyst particles mean size. At the same catalyst particles size the volumetric mass transfer coefficient increases with increasing catalyst loading.

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