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Liquid phase catalytic oxidation of aliphatic alcohols mixtures

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Abstract

The catalytic oxidation of aliphatic alcohols to carboxilic acids in aqueous solution was carried out in a fixed-bed upflow reactor by a Pd–Al_2O_3 catalyst. The conversion rate was measured at different gas phase velocities, alcohol concentrations and oxygen partial pressures. Single alcohol solutions, binary and ternary mixtures were tested to investigate the role of mass transfer and the influence of the reaction media composition on the reactor performance. A sensible increase of the conversion rate of single reactants was observed when mixtures of different alcohols were oxidised. The positive mixture effect seems to be related to the enhancement of the gas–liquid mass transfer coefficient.

1. Introduction

The performance of multiphase catalytic reactors can be remarkably affected by hydrodynamic factors, interphase mass transfer resistances and contacting effectiveness between the fluids and the solid catalyst. The effective wetting of the catalytic particles and the radial distribution of the liquid phase are major phenomena in trickle-bed reactors [1,2] while the findings of experimental investigations have shown that hydrodynamics and liquid–solid contacting effectiveness play a minor role in concurrent upflow equipments [3,4]. In this case liquid phase plug-flow and full catalyst wetting are acceptable assumptions and the reactor performance depends predominantly on the reaction kinetics and the mass transfer of the key reactants. The literature reports a number of liquid–solid and gas–liquid mass transfer correlations derived from experimental tests with reactive and non-reactive systems. The coefficients determined by different correlations frequently show considerable inconsistencies [5]. This might be due to the interaction between transport phenomena and fast heterogeneous chemical reactions [6,7] as well as to the influence of the physical properties of the fluids on mass transfer (e.g. gas–liquid volumetric coefficients include an interfacial area term that is sensibly affected by the surface tension of the liquid phase). The aim of this work was to point out the role of mass

Table 1
Reaction media initial compositions (molar fractions of alcohols $x_a \cdot 10^4$)

Mixture	Ethanol	Propanol	Butanol
#1	–	6.5	–
#2	6.5	6.5	–
#3		6.5	6.5
#4		6.5	3.0
#5	1.8	3.5	1.8
#6	–	–	6.5
#7	6.5	–	6.5
#8	1.8	1.8	3.5

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transfer in a fixed-bed upflow reactor by experimental tests in presence of fast chemical reactions. Mass transfer coefficients experimentally determined were compared with literature correlations to evaluate the influence of the reaction media composition on transport phenomena. The oxidation of aliphatic alcohols to carboxilic acids was chosen as a test reaction. The reaction kinetics is well known from the literature in the case of ethanol oxidation [8] and the results of kinetic investigations show that a simple Langmuir–Hinshelwood rate equation can be used also in the case of propanol and butanol [9].

2. Experimental

The experimental apparatus is shown in Fig. 1. The reactions are carried out in a 0.05 m internal diameter packed bubble column. The reactor contains 0.148 kg of 3.2×3.6 mm cylindrical pellets of 0.5% Pd on a γ-alumina catalyst with egg-shell metal distribution (active layer thickness 0.218 mm). The catalytic bed of 0.25 m length is preceded by a calming section filled by inert structured packings where liquid and gas phase attain the equilibrium conditions. The experimental apparatus is operated in a batch manner by gas and liquid phases recycle. The fluids leaving the top of the packed column are cooled to the room temperature and received in a 0.015 m^3 mixed tank. The pressure in the recycle reservoir is controlled by pure oxygen injection.

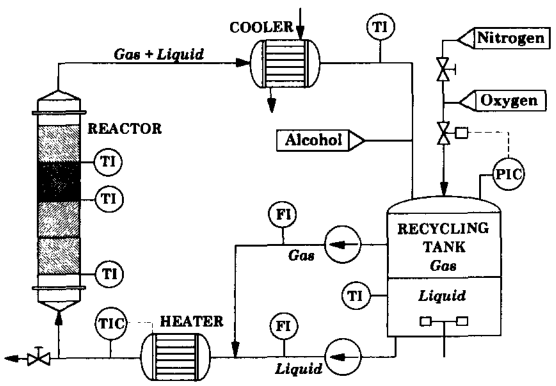


Fig. 1. Experimental apparatus.

A single batch run involves the following steps:
(1) system loading with water and nitrogen + oxygen gas mixture;
(2) start-up of the experimental apparatus;
(3) liquid reactants (alcohols) injection;
(4) periodic sampling of the liquid from the recycle tank and from the reactor.

The liquid samples are analyzed by a gaschromatograph to evaluate the alcohol concentration so that the total amount of the reactants can be calculated. The reaction rate is determined by the slope of the alcohol amount versus time curve. The mass balance in the experimental system is checked by the measurement of the oxygen injected in the system by the pressure control system. The reactor is almost differential with respect to the liquid reactants since the relative conversion per single pass is always lower than 0.02.

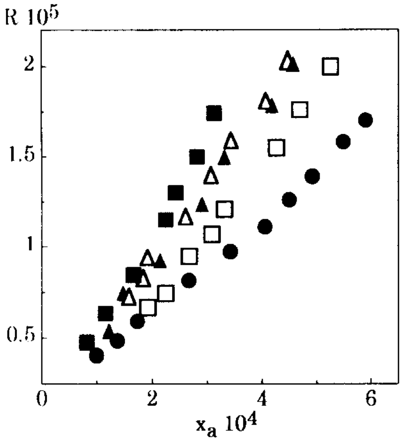
3. Results

The reaction rates of propanol and butanol vs. the alcohol concentration at $T = 353$ K, $v_L = 0.003$ m/s, $v_G = 0.05$ m/s and $p_o = 63$ kPa are presented in Figs. 2 and 3, respectively. The set of mixtures compositions at the start of batch experimental runs is shown in Table 1.

The pictures clearly show that the conversion of single alcohols increases gradually in the presence of other reactants in the aqueous media. Since the kinetic model of alcohol oxidation on Palladium catalysts is based on the reaction of adsorbed alcohols and molecular oxygen in the liquid phase [8,9], the absence of competition between the organic reactants for the adsorption sites might be explained in terms of mass transfer rate control.

To point out the role of mass transfer limitations the reaction rates experimentally observed are compared with rates calculated by a reactor model.

The heterogeneous model is based on the following assumptions:



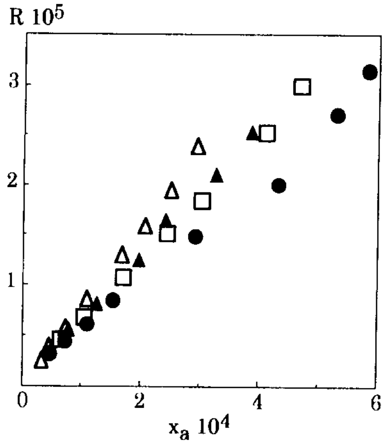


Fig. 2. Propanol reaction rate. Mixture: (●) #1; (□) #2; (△) #3; (▲) #4; (■) #5.

Fig. 3. Butanol reaction rate. Mixture: (●) #6; (□) #7; (▲) #3; (△) #8.

(a) the intrinsic reaction kinetics is oxygen first order [9];
(b) no alcohol concentration gradients take place in the reactor as the molar ratio between these reactants and oxygen in the liquid phase is very high and the conversion along the catalytic bed is negligible;
(c) at the inlet of the catalytic section of the reactor the liquid phase is uniformly saturated by oxygen;
(d) solid–liquid contacting effectiveness is unitary and axial dispersion in the packed-bed is negligible [3,4].

The local mass balance of the key reactant (oxygen) is:

$$v_L\cdot\frac{dx_o}{dz}=(ka)_{GL}\cdot x_o^* - \left[\frac{(1-\epsilon)\cdot\eta\cdot k_r\cdot(ka)_{LS}}{(ka)_{LS}+(1-\epsilon)\cdot\eta\cdot k_r}+(ka)_{GL}\right]\cdot x_o \quad (1)$$

with initial condition: $z=0, x_o=x_o^*$.

The reaction rate decreases along the packed-bed according to the equation due to the gradient of the concentration of oxygen in the liquid phase:

$$R(z)=(1-\epsilon)\cdot\eta\cdot k_r\cdot C_t\cdot\left(\frac{(ka)_{LS}\cdot x_o(z)}{(ka)_{LS}+(1-\epsilon)\cdot\eta\cdot k_r}\right) \quad (2)$$

The average reaction rate in the reactor can be determined by integration of Eq. (1):

$$R=\frac{C_t\cdot\psi\cdot v_L}{[\psi+(ka)_{GL}]\cdot L}\cdot\left\{\psi\cdot x_o^*+\frac{(ka)_{GL}\cdot x_o^*\cdot L\cdot[\psi+(ka)_{GL}]}{v_L}-\exp\left(\ln(\psi\cdot x_o^*)-\frac{L\cdot[\psi+(ka)_{GL}]}{v_L}\right)\right\} \quad (3)$$

where:

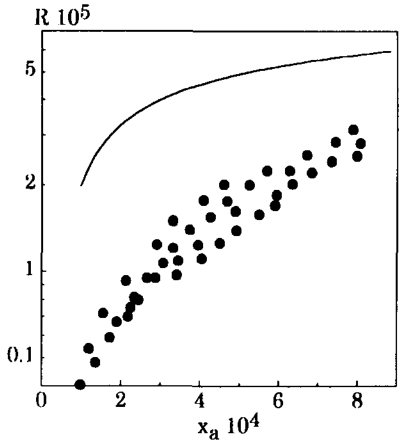
$$\psi=\frac{(ka)_{LS}\cdot(1-\epsilon)\cdot\eta\cdot k_r}{(ka)_{LS}+(1-\epsilon)\cdot\eta\cdot k_r}$$

Increasing the transport coefficients $(ka)_{LS}$ and $(ka)_{GL}$ the axial gradient of the concentration of oxygen in the liquid phase decrease and the average reaction rate tends to the maximum:

$$R=(1-\epsilon)\cdot\eta\cdot k_r\cdot C_t\cdot x_o^* \quad (4)$$

In Figs. 4 and 5 the experimental reaction rates of propanol and butanol at $v_L=0.003$ m/s, $v_G=0.05$ m/s, $T=353$ K and $p_o=63$ kPa are compared with the maximum rate defined by Eq. (4).

The results reported in the figures prove the presence of transport limitations seeing that the experimental data lie below the maximum rate line. The weight of mass transfer resistances, rep-



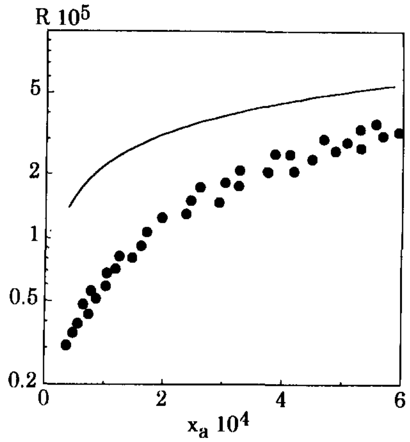


Fig. 4. Propanol reaction rate. (●) Experimental; (—) Eq. (4).

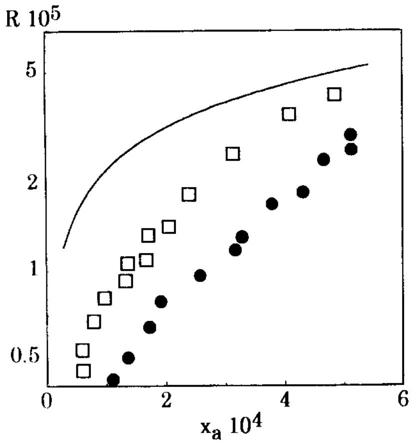
Fig. 5. Butanol reaction rate. (●) Experimental; (—) Eq. (4).

resented by the distance between the experimental points and the model line, slightly decreases by increasing the alcohol concentration. This is in agreement with the results of ethanol oxidation tests both in trickle-bed and upflow concurrent reactors [4,17]. In the light of this finding the promotion of the oxidation reactions observed during mixtures tests might be explained in terms of enhancement of mass transfer due to the higher total concentration of the alcohols.

To check the reliability of the kinetic model and to confirm the statement about the influence of the reactant concentration on mass transfer a further set of experiments is carried out at different operating conditions. Figs. 6 and 7 show that the consequence of mass transfer decreases by increasing the gas phase velocity and reducing the oxygen partial pressure in the reactor. At p_o lower than 20 kPa the fitting of the experimental results with the maximum rate line is quite good showing a negligible influence of mass transfer resistance on the reactor performance. Under these operating conditions the reaction becomes slower and mass transfer is no more the rate controlling step. The positive effect of the increasing gas flow rate is probably due to the enhancement of the gas–liquid mass transfer coefficient.

Mass transfer coefficients can be determined by fitting the model average rate defined by Eq. (3) with the experimentally observed value. Overall coefficients calculated by the fitting procedure are compared in Figs. 8 and 9 with those obtained by literature correlations.

Liquid–solid mass transfer coefficients are determined using the Mochizuki equations [10,11] since other correlations [12,13] are not able to fit the results of kinetic tests [9]. The choice for gas–liquid mass transfer coefficient is more controversial. Three different equations have been tested: Specchia et al. [14], Reiss [15] and Saada [16] (represented in the figures by line a, b and c, respectively). The results show that literature correlations can be used just for a first estimate of the average value of the mass transfer coefficient, but mixture and reactant concentration effects are not correctly accounted for by any equation. The best results in terms of average values are obtained using the Reiss correlation for gas–liquid coefficient. The enhancement of mass transfer observed at high total concentration of alcohols might be due to the influence of these organic compounds on the physical properties of the liquid phase. Aliphatic alcohols are surface active species in aqueous solutions and the reduction of surface tension positively affects gas–liquid mass transfer by increasing the interfacial area and improving the gas phase radial distribution. Visual observations of bubbling conditions in the



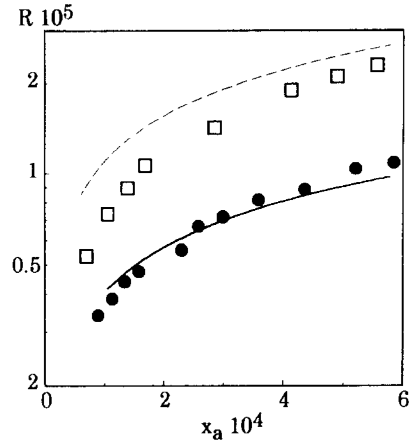
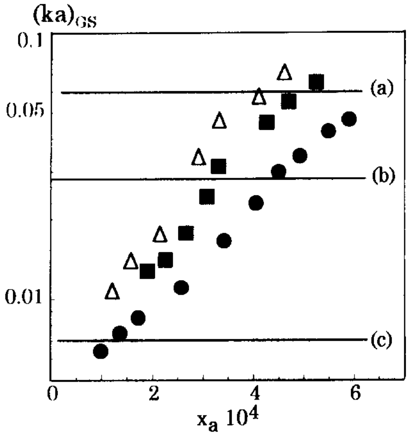


Fig. 6. Butanol reaction rate. Experiments at v_G (m/s): (●) 0.026; (□) 0.112; (—) calculated by Eq. (4).

Fig. 7. Butanol reaction rate. $p_o = 30$ kPa: (□) exp.; (—) Eq. (4), $p_o = 20$ kPa: ($\gg$) exp.; (---) Eq. (4).



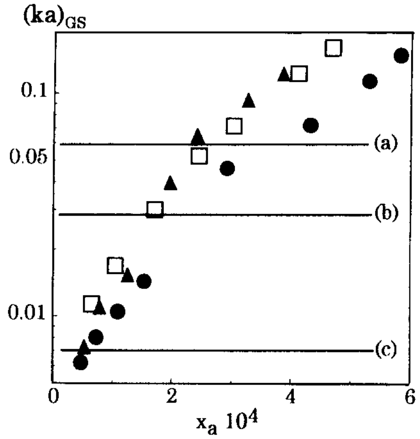


Fig. 8. $(ka)_{GS}$ vs. propanol molar fraction, $p_o = 63$ kPa and $v_G = 0.05$ m/s. Reaction media: (●) #1; (■) #2; (△) #3.

Fig. 9. $(ka)_{GS}$ vs. butanol molar fraction, $p_o = 63$ kPa and $v_G = 0.05$ m/s. Reaction media: (●) #6; (□) #7; (▲) #3.

packed-bed confirm this hypothesis. The average bubble size decreases significantly when the reactants are injected in the liquid phase. The most active reactant in this field is butyl alcohol which also gives the major mixture effects (see Fig. 2).

4. Nomenclature

C_t	total concentration of the liquid phase (kmol/m^3)
k_r	pseudo-first order kinetic constant (s^{-1})
$(ka)_{GL}$	gas–liquid mass transfer coefficient (s^{-1})
$(ka)_{LS}$	liquid–solid mass transfer coefficient (s^{-1})
$(ka)_{GS}$	$= [1/(ka)_{GL} + 1/(ka)_{LS}]^{-1}$ overall mass transfer coefficient (s^{-1})
L	packing length (m)
p_o	oxygen partial pressure (kPa)
R	reaction rate (kmol/s m^3)
v_G	gas phase superficial velocity (m/s)
v_L	liquid phase superficial velocity (m/s)
x_o	oxygen molar fraction in the bulk of the liquid, dimensionless

x_o^*	oxygen molar fraction at the gas–liquid interface, dimensionless
x_o^s	oxygen molar fraction at the external catalyst surface, dimensionless
x_a	alcohol molar fraction in the liquid, dimensionless
z	reactor axial coordinate (m)
ϵ	packed-bed porosity, dimensionless
η	catalyst effectiveness factor, dimensionless

References

[1] M. Herskowitz and J.M. Smith, AIChE J., 24 (1978) 439.
[2] A.J. Colombo, G. Baldi and S. Sicardi, Chem. Eng. Sci., 31 (1976) 1101.
[3] I. Mazzarino, S. Sicardi and G. Baldi, Chem. Eng. J., 36 (1987) 151.
[4] I. Mazzarino, M. Occhetti, G. Baldi and S. Sicardi., Chem. Eng. Commun., 75 (1989) 225.
[5] P.A. Ramachandran and R.V. Chaudari, Three-Phase Catalytic Reactors, Gordon and Breach, New York, 1983.
[6] F. Turek and R. Lange, Chem. Eng. Sci., 36 (1981) 569.
[7] G. Baldi, A. Gianetto, S. Sicardi, V. Specchia and I. Mazzarino, Can. J. Chem. Eng., 63 (1985) 62.
[8] S. Hsu and J.A. Ruether, Ind. Eng. Chem. Proc. Des. Dev., 17 (1978) 524.
[9] F. Chiampo, I. Mazzarino, R. Conti, S. Sicardi and A. Gianetto, Atti Accad. Sci. Torino, 123 (1989) 63.
[10] S. Mochizuki and T. Matsui, Chem. Eng. Sci., 29 (1974) 1328.
[11] S. Mochizuki, AIChE J., 24 (1978) 1138.
[12] V. Specchia, G. Baldi and A. Gianetto, Ind. Eng. Chem. Proc. Des. Dev., 17 (1978) 362.
[13] E. Wilson and C. Geankoplis, Ind. Eng. Chem. Fundam., 5 (1966) 9.
[14] V. Specchia, S. Sicardi and A. Gianetto, AIChE J., 20 (1974) 646.
[15] L.P. Reiss, Ind. Eng. Chem. Proc. Des. Dev., 6 (1967) 486.
[16] N.Y. Saada, Chim. Ind. Genie Chim., 105 (1972) 1415.
[17] V. Tukac, I. Mazzarino and G. Baldi, Chem. Eng. Sci., 41 (1986) 17.