

Kinetics of Vapor-Phase Carbonylation of Ethanol on Ni-Zn/C Catalyst*

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Abstract A novel heterogeneous Ni-Zn/C catalyst was used for vapor-phase carbonylation of ethanol under atmospheric pressure. Experiments were designed with the elimination of mass-transfer resistances. The data of primary reactions in the carbonylation were collected with a differential tubular reactor. Power law rate models were employed to express the conversion of ethanol and the yields of ethyl propionate and diethyl ether. The results obtained with the models were in agreement with the experimental data.

Keywords ethanol, carbonylation, kinetics, catalysis, nickel catalyst

1 INTRODUCTION

Ethanol is a common product from sustainable resources. Its application is very interesting and promising. Recently the carbonylation of ethanol to propionic acid or ethyl propionate is an attractive and economic process in the chemical industry^[1,2]. There are advantages of the heterogeneous carbonylation in comparison with the liquid homogeneous catalyst system, so the use of a heterogeneous catalyst seems very interesting. Many research efforts have been indulged in search of an appropriate catalyst to carry out vapor phase carbonylation under atmospheric pressure^[2-5]. A novel Ni-Zn/C catalyst has been reported to have a high activity and selectivity for the vapor phase carbonylation of ethanol to ethyl propionate^[3]. Ethyl iodide was found to be essential in the cases, and the rate-determining step of the reaction was discovered to be the cleavage of the C—I bond of ethyl iodide^[2,3].

Kinetic analysis of a vapor-phase carbonylation of ethanol with the novel catalyst is presented in this paper. A differential reactor was employed, in which resistances of the pore and external film were eliminated in the reaction experiments. A complete kinetic analysis involving all reactions is complicated. The analysis can be markedly simplified in a differential tubular reactor. The reactor generates data without interference from products, thus both secondary and reversible reactions can be neglected. Another advantage of a differential reactor involves the diminution of temperature and concentration gradients in the reactor, simplifying the kinetic analysis significantly. Power law models were used to represent the primary reaction data. Parameters of the models were determined from the data by means of linear regression.

2 EXPERIMENTAL

2.1 Preparation of catalyst

The catalysts were prepared by incipient impregnation. A commercially available granular activated carbon (olive shell based, in 24–48 mesh particle size, provided by Shanghai Activated Carbon Factory) was used for support. Ni-Zn/C catalyst was prepared by first impregnating nickel nitrate aqueous solution for 4 h, followed by drying the slurry, and then impregnating zinc nitrate aqueous solution. The slurry was then dried in vacuum at 393 K for 12 h. The active Ni-Zn/C catalyst was generated from the dried material by reduction conducted *in situ* prior to each reaction run. Nickel and zinc loadings on the catalyst were 5% and 3.5% (by mass) respectively.

2.2 Carbonylation

The reaction was carried out under atmospheric pressure in a tubular Pyrex reactor (8 mm ID). The catalyst bed contained a mixture of catalyst (70–80 mesh, 150 mg) and powdered quartz (1500 mg). The latter was employed to diminish both the gas channeling and the temperature gradient in the bed. Each carbonylation experiment was initiated with catalyst reduction performed *in situ* at 673 K with flowing H₂ for 3 h. Kinetic data were not collected until the catalyst was activated. In a typical run, the data were collected after the catalyst was on stream for 4 h.

The partial pressures of ethanol, carbon monoxide, and ethyl iodide in the carbonylation were varied by regulation of reactant flow rates. Ethanol and ethyl iodide were fed by a syringe pump whereas carbon monoxide and nitrogen were fed from gas cylinders. The flow rates of the gases were set by means of mass-flow controllers. The partial pressure of each

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reactant was varied in turn while partial pressures of the other two were maintained constant. The independent partial pressure variation was accomplished through usage of nitrogen in the feed, which compensated for variation of a reactant. The conversion of ethanol was limited to less than 10% so as to obtain a differential mode of operation, which furnished the advantage of minimizing interference caused by carbonylation products. The complicated data analysis due to concentration and temperature gradients was also markedly simplified.

The effluent gas from the reactor was sampled by a sampling valve and was immediately analyzed in a gas chromatograph. The conversion of ethanol and the selectivities of products are defined as Ref. [3].

3 RESULTS AND DISCUSSION

3.1 Stability of catalyst

Figure 1 shows that the conversion of ethanol on Ni-Zn/C steadily increases with reaction time on stream. The activation process lasts for about 3 h. The activity of the catalyst reaches a maximum at the end of the activation. No obvious deactivation is observed for the catalyst for at least 20 h after the activation is completed. Data for kinetic examinations are collected with the catalyst on stream during 4–18 h, the data are, therefore, considered as steady-state data.

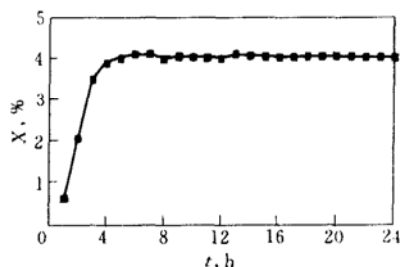


Figure 1 Stability of catalyst
(Reaction condition: $T=473$ K; $p=100$ kPa;
contact time= 1.15 g·h·mol $^{-1}$;
 $n_{CO}/n_{EtOH}/n_{EtI}/n_{N_2} = 2/1/0.1/2$)

3.2 Resistance of external film and pore

The significance of external film resistance was examined. The results are illustrated in Fig. 2. The data were obtained by passing reactants through the catalyst bed at varied rates of feed. The reaction temperature and the contact time were maintained constant. If the external film resistance is insignificant, the conversion is expected to be independent of the flow rate. Otherwise, external film resistance is present. External film resistance, as indicated in Fig. 2, can be neglected at a rate of flow exceeding 0.2 mol·h $^{-1}$.

The relative significance of external film resistance and surface reaction to the overall rate of reaction can

also be managed by the reaction temperature. With the reaction temperature diminishing, the rate of surface reaction decreases more quickly than the rate of transport through the film. As a consequence, decreased reaction temperature leads to a declined influence of external film and shifts the overall reaction to one with surface reaction control. The insignificance of external film resistance is illustrated in Fig. 2 at a flow rate of 0.2 mol·h $^{-1}$ and at a reaction temperature of 533 K. The experiments for kinetic data were therefore performed with a minimum flow rate of 0.2 mol·h $^{-1}$ and a maximum reaction temperature 533 K. The enforcement of the conditions ensured the data out of the influence of external film resistance.

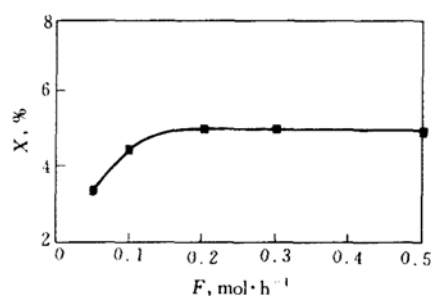


Figure 2 Effect of total molar flow rate on ethanol conversion

(Reaction condition: $T=533$ K; $p=100$ kPa;
contact time= 1.15 g·h·mol $^{-1}$;
 $n_{CO}/n_{EtOH}/n_{EtI}/n_{N_2} = 2/1/0.1/2$)

Pore resistance produces both concentration and temperature gradients within a catalyst particle, and distorts the rate data to yield erroneous kinetic conclusions. The utilization of small particles can diminish the variations of concentration and temperature between the center and surface of the particle. The experiment shows that pore resistance can be neglected in a particle less 40 mesh.

3.3 Effect of partial pressures

The rates of ethanol conversion and product formation under the different partial pressures of reactants were shown in Tables 1–3.

3.4 Rate model

The carbonylation of ethanol consists of several parallel and consecutive reactions. Ethyl propionate is the desired carbonylation product. Diethyl ether, a byproduct, is formed from a side reaction requiring only ethanol as the reactant. Both ethyl propionate and diethyl ether forms directly from the reactants and are considered as primary products, and the reactions forming primary products are the primary reactions. Propionic acid, which forms from the hydrolysis of ethyl propionate, is considered to be a secondary product^[4]. Propionic acid is not detected probably due to the small conversion of methanol in this work.

The kinetics of formation of propionic acid is hence not discussed.

Methane, which can be formed in various reaction

Table 1 The rates of ethanol conversion and products formation under different partial pressures (473 K)

Partial pressures, kPa			Reaction rates, mmol·g ⁻¹ ·h ⁻¹			
<i>P_C</i>	<i>P_E</i>	<i>P_I</i>	<i>r_E</i>	<i>r_M</i>	<i>r_D</i>	<i>r_P</i>
78	20	2.0	8.66	0.88	1.89	2.00
40	20	2.0	6.90	0.82	1.89	1.15
20	20	2.0	5.82	0.77	1.87	0.66
10	20	2.0	5.23	0.71	1.87	0.39
40	20	1.0	3.55	0.41	0.95	0.62
40	20	2.0	6.90	0.82	1.89	1.15
40	20	3.0	10.21	1.23	2.83	1.66
40	20	4.0	13.93	1.63	3.69	2.46
40	40	2.0	8.49	0.94	2.67	1.11
40	30	2.0	7.91	0.89	2.31	1.20
40	20	2.0	6.90	0.82	1.89	1.15
40	10	2.0	5.53	0.71	1.34	1.07

Table 2 The rates of ethanol conversion and products formation under different partial pressures (503 K)

Partial pressures, kPa			Reaction rates, mmol·g ⁻¹ ·h ⁻¹			
<i>P_C</i>	<i>P_E</i>	<i>P_I</i>	<i>r_E</i>	<i>r_M</i>	<i>r_D</i>	<i>r_P</i>
60	30	3.0	23.78	5.48	5.20	3.95
40	30	3.0	21.14	5.26	5.18	2.81
30	30	3.0	20.43	5.25	5.19	2.40
20	30	3.0	18.50	4.91	5.20	1.70
40	30	3.0	21.14	5.26	5.18	2.81
40	30	2.0	14.50	3.50	3.48	2.01
40	30	1.6	11.22	2.76	2.71	1.52
40	30	1.2	8.75	2.19	2.10	1.18
40	30	3.0	21.14	5.26	5.18	2.81
40	20	3.0	18.40	4.80	4.00	2.80
40	16	3.0	17.59	4.61	3.70	2.79
40	12	3.0	16.50	4.40	3.30	2.75

Table 3 The rates of ethanol conversion and products formation under different partial pressures (533 K)

Partial pressures, kPa			Reaction rates, mmol·g ⁻¹ ·h ⁻¹			
<i>P_C</i>	<i>P_E</i>	<i>P_I</i>	<i>r_E</i>	<i>r_M</i>	<i>r_D</i>	<i>r_P</i>
60	30	3.0	43.81	21.27	4.60	6.67
40	30	3.0	39.10	20.35	4.55	4.81
30	30	3.0	34.68	18.81	4.61	3.33
20	30	3.0	33.69	18.92	4.59	2.81
40	30	3.0	39.10	20.35	4.55	4.81
40	30	2.5	31.86	16.50	3.73	4.00
40	30	2.0	27.32	13.85	3.10	3.31
40	30	1.6	20.27	10.51	2.30	2.58
40	30	1.2	16.25	8.30	1.87	2.10
40	30	3.0	39.10	20.35	4.55	4.81
40	20	3.0	36.70	20.00	3.50	4.80
40	15	3.0	33.64	17.98	3.33	4.50
40	12	3.0	31.91	17.17	2.98	4.39

routes, is considered to be both a primary and a secondary product. The complicated situation is significantly simplified by means of a differential reactor, which enables us to collect kinetic data with a small conversion of ethanol. Therefore, reversible reactions and reactions involving products can be neglected, and only primary reactions need to be considered in these conditions.

The rates of the conversion of ethanol and the formations of ethyl propionate, methane and diethyl ether were represented by power law models in the following form

$$r = k p_E^a p_C^b p_I^c$$

Furthermore, the rate constant is expressed in terms of the reaction temperature according to Arrhenius relation

$$k = k_0 \exp(-E/RT)$$

The resulting equation can be transformed into

$$\ln r = \ln k_0 - E/RT + a \ln p_E + b \ln p_C + c \ln p_I$$

The parameters, k_0 , E , a , b and c were determined by means of linear regression; which are listed in Table 4.

Table 4 Estimated parameters of the rate model

Rates	Parameters				
	k_0	E , kJ·mol ⁻¹	a	b	c
R_E	4.19×10^4	44.3	0.3	0.3	1.0
R_M	4.26×10^9	94.6	0.2	0.1	1.0
R_D	3.7	11.3	0.5	0.0	1.0
R_P	2.21×10^2	35.9	0.06	0.8	1.0

Model: $r = k_0 \exp(-E/RT) p_E^a p_C^b p_I^c$

As shown in Table 4, the reaction order of ethanol conversion and all products formation with respect to ethyl iodide was 1.0, indicating that the novel catalyst depended heavily on the iodide to promote the carbonylation. The same results were observed with Rh/Y and Ni/C catalysts for methanol carbonylation^[5,6]. The reaction order of ethyl propionate formation with respect to ethanol has the smallest value among the reactions, hence a decrease in partial pressure of ethanol leads to an increase of the selectivity for ethyl propionate. The selectivity to ethyl propionate increases further with the increase of partial pressure of CO and the decrease of the reaction temperature. The adequacy of the models was examined by comparing the calculated rates according to the model and experimental rates of ethyl propionate formation under different partial pressures (Table 5). The relative error of calculated results to experimental ones for ethyl propionate formation rate is within 4.7%.

Table 5 Comparison of the calculated rates and experimental rates of ethyl propionate formation under different partial pressures (503K)

p_C	p_E	p_I	r_P	r_P^*	$(r_P^* - r_P)/r_P^*$
60	30	3.0	3.95	3.99	+1.0%
40	30	3.0	2.81	2.89	+2.8%
30	30	3.0	2.40	2.30	-4.3%
20	30	3.0	1.70	1.66	-2.4%
40	30	2.0	2.01	1.92	-4.7%
40	30	1.6	1.52	1.53	+0.6%
40	30	1.2	1.18	1.16	-1.7%
40	20	3.0	2.80	2.82	+0.7%
40	16	3.0	2.79	2.78	-0.4%
40	12	3.0	2.75	2.73	-0.7%

r_P^* —calculation rates according to the rate model of ethyl propionate formation, $\text{mmol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$

Power law models were developed for primary reactions of carbonylation of ethanol on a novel Ni-Zn/C catalyst. Sufficient accuracy was obtained with the models to determine the formation rates of ethyl propionate and diethyl ether. The reaction orders of ethyl propionate formation with respect to ethanol and CO were respectively found to be 0.06 and 0.8 on Ni-Zn/C, and the reaction activation energy was $35.9\text{ kJ}\cdot\text{mol}^{-1}$.

NOMENCLATURE

E	activation energy, $\text{kJ}\cdot\text{mol}^{-1}$
F	total molar flow rate, $\text{mol}\cdot\text{h}^{-1}$
k	rate constant
k_0	frequency factor
n	amount of substance, mol
p_i	partial pressure of reactant i , kPa
R	gas constant, $8.314\text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
r_i	reaction rate of reactant or product i , $\text{mmol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$

T	reaction temperature, K
t	reaction time, h
X	conversion of ethanol (by mole), %

Superscripts

a	reaction order with respect to ethanol
b	reaction order with respect to carbon monoxide
c	reaction order with respect to ethyl iodide

Subscripts

C	carbon monoxide
D	diethyl ether
E	ethanol
I	ethyl iodide
M	methane
P	ethyl propionate

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