Kinetics of the catalytic coupling reaction of carbon monoxide to diethyl oxalate over Pd-Fe/α-Al$_2$O$_3$ catalyst

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Abstract

The reaction kinetics of the catalytic coupling reaction of carbon monoxide to diethyl oxalate was studied in the presence of ethyl nitrite over supported palladium catalyst in gaseous phase at atmospheric pressure. The experiments were performed in a continuous flow fixed-bed differential type reactor. It was discovered that the rate-determining step is the surface reaction between adsorbed species and that ethyl nitrite dissociates into ethoxy radical (EtO$^-$) and NO species and are adsorbed on two active sites. The kinetic model was proposed, with which some observations concerning with the reaction behaviors of the system can be readily accounted for. In the presence of hydrogen, the kinetics of the reaction system was also investigated. It was revealed that hydrogen, with adsorption and dissociation, reacts with adsorbed ethoxy radical to ethanol.
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1. Introduction

The use of carbon monoxide from coal or natural gas to produce dialkyl oxalate is an important research area in C$_1$ chemical technology. This new synthetic methodology is of great significance to overcome drawbacks of such traditional technologies as the production of dialkyl oxalate, oxalic acid, ethylene glycol and intermediates of pesticides, dyestuffs and pharmaceuticals.

Two chemical reactions taking place simultaneously are involved in the process: coupling reaction and regeneration reaction. The coupling reaction is the synthesis of diethyl oxalate from carbon monoxide and ethyl nitrite over the supported palladium catalyst.

$$2CO + 2EtONO \rightarrow (COOEt)_2 + 2NO \qquad (1)$$

In regeneration reaction, nitrogen monoxide produced in the coupling reaction reacts with alcohol and oxygen to form ethyl nitrite. The ethyl nitrite formed is then recycled as feed to the coupling reaction.

$$2NO + 2EtOH + \tfrac{1}{2}O_2 \rightarrow 2EtONO + H_2O \qquad (2)$$
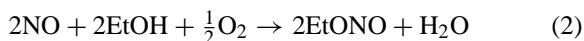
Ethyl nitrite, acting as reoxidizing agent for Pd(0), can promote efficiently carbon monoxide coupling reaction in the presence of palladium catalyst. In comparison with other technologies, this process has favorable economics, without environmental pollution. So, several groups around the world have devoted significant effort to the development of the process [1–7].

Ma et al. [8] studied the kinetic of the reaction over Pd/Al$_2$O$_3$ with 1 wt.% of palladium in a fixed-bed

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Nomenclature

E_i	activation energy or adsorption energy $(J\,mol^{-1})$
K_{67}	K_6/K_7
K_i	kinetic constants
K_{0i}	pre-exponential factors
m_{CO}	CO flow rate $(mol\,s^{-1})$
n	slope
n_i	reaction order of the component i
P_i	partial pressure of the component i at the reactor inlet (Pa)
r	correlation coefficient
$-r_{CO}$	reaction rate (disappearance of CO) $(mmol\,kg^{-1}\,s^{-1})$
$-r_{H_2}$	reaction rate (disappearance of H_2) $(mmol\,kg^{-1}\,s^{-1})$
R	universal gas constant $(J\,mol^{-1}\,K^{-1})$
T	reaction temperature (K)
W	weight of catalyst (g)
X_{CO}	CO conversion (%)
X_{H_2}	H_2 conversion (%)
Z	free active site of the catalyst

integral type reactor. However, their investigation was mainly based on mathematical derivation, short of research on intrinsic behaviors of the reaction. In the present contribution, by contrast, reaction rate in dependence on the partial pressures was comprehensively examined, based on which the reaction mechanism was proposed and the rate expression was derived. Furthermore, explanations were given for some perplexing problems in the literature.

2. Experimental

Ethyl nitrite was generated in a special vessel in which an amount of 50 ml ethanol was added and reacted with nitrogen monoxide and oxygen at ca. 308 K. The coupling reaction experiments were performed in a flow-type apparatus with a glass-made fixed-bed reactor in gaseous phase at atmospheric pressure. The reactor tube, with a 1.2 cm internal diameter and a 30 cm length, was electrically heated with a temperature control accuracy of ±0.5 K. The gas mixtures before and after each reaction were analyzed by gas

Table 1
The properties of the catalyst

Diameter (mm)	0.3
Density $(g\,cm^{-3})$	0.880
Specific surface $(m^2\,g^{-1})$	8.25
Pore volume $(cm^3\,g^{-1})$	0.57
Mean pore size (nm)	85.0

chromatography equipped with a capillary column and a thermal conductivity detector.

Pd-Fe/α-Al$_2$O$_3$ with 1 wt.% of palladium and 0.5 wt.% of iron was used as catalyst. The catalyst was prepared by impregnation in 20 wt.% aqueous solution of PdCl$_2$ and 5 wt.% FeCl$_3$·H$_2$O and then dried in air at ca. 393 K for 12 h. In each experiment, the mass of the catalyst amounted to 0.15 g, and its particle size was about 0.3 mm. The catalyst was admixed with 1.75 g quartz of the same particle size and then was pretreated in situ with a purge of pure hydrogen for 4 h at 623 K. The basic properties of the catalyst employed here were reported in Table 1.

3. Result

3.1. Preliminary experiments

It was found in a preliminary experiment at 393 K with a stoichiometric gas mixture that the laws of a differential reactor could be applied to this coupling reaction system with a conversion up to about 10 wt.%. The dependence of the reaction rate $-r_{CO}$ on the conversion X_{CO} is

$$-r_{CO} = \frac{m_{CO}X_{CO}}{100w} \tag{3}$$

In further experiments, it was confirmed that neither film diffusion nor pore diffusion exert a significant influence on the reaction rate, at least as long as the conversion remains below this level. Furthermore, measurements of the time-on-stream behavior during 100 h revealed that the conversion remains unchanged, indicating that no catalyst deactivation occurred.

3.2. Dependence of reaction rate $-r_{CO}$ on the partial pressures

To determine the reaction orders n_i, the partial pressures of each component was systematically varied at
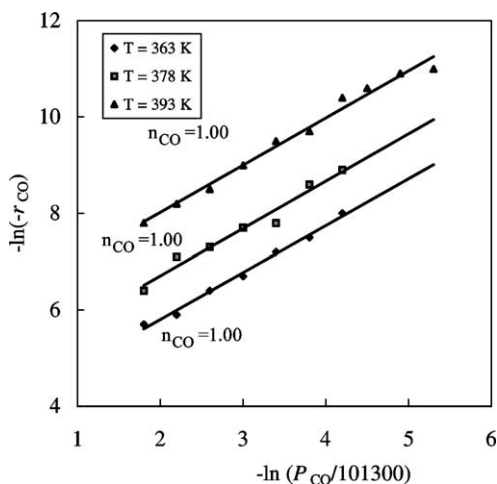
Fig. 1. Reaction rate $-r_{CO}$ as a function of the partial pressure P_{CO} ($P_{EtONO} = 3.9$ kPa, $P_{(COOEt)_2} = 0$, $P_{NO} = 0$).

reaction temperature T from 363 to 393 K, whereas the partial pressures of other components were kept constant (cf. Figs. 1–4). The reaction order with respect to carbon monoxide was found to be around 1, whereas the reaction rate depends comparatively weakly on the partial pressure of ethyl nitrite with reaction orders of between 0.6 and 0.8 depending on the reaction temperature. Nitrogen monoxide is inhibiting with reaction orders of about -0.75 also being a function of temperature. Diethyl oxalate also suppresses the reaction rate with a reaction order of about -0.1.
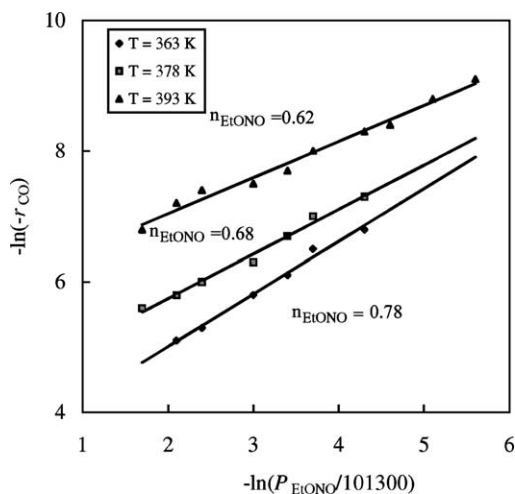

Fig. 2. Reaction rate $-r_{CO}$ as a function of the partial pressure P_{EtONO} ($P_{CO} = 4.1$ kPa, $P_{(COOEt)_2} = 0$, $P_{NO} = 0$).
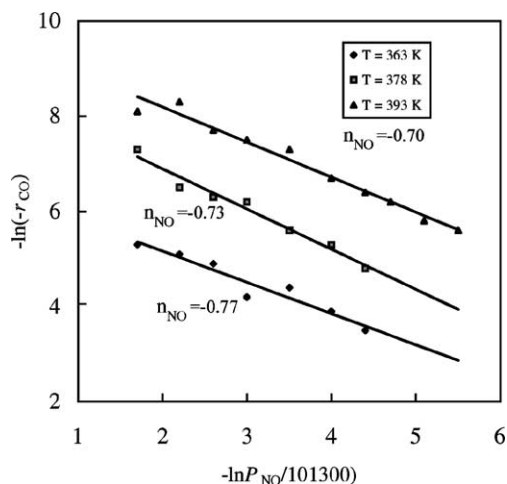

Fig. 3. Reaction rate $-r_{CO}$ as a function of the partial pressure P_{NO} ($P_{CO} = 4.3$ kPa, $P_{EtONO} = 4.1$ kPa, $P_{(COOEt)_2} = 0$).

3.3. Mechanistic considerations

Starting from different plausible mechanisms, Hougen–Watson type rate expressions were derived. The best fit of the experimental data was achieved on the basis of the following reaction mechanism (Z is a free active site and the adsorption of the inert gas, nitrogen, is negligible):
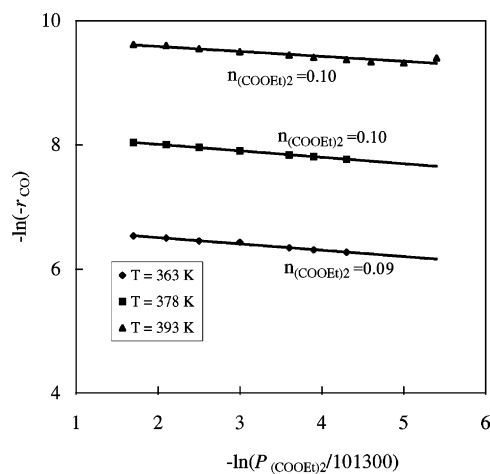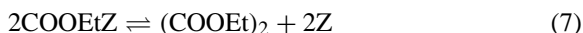
$$CO + Z \rightleftharpoons COZ \qquad (4)$$

Fig. 4. Reaction rate $-r_{CO}$ as a function of the partial pressure $P_{(COOEt)_2}$ ($P_{H_2} = 4.2$ kPa, $P_{EtONO} = 4.5$ kPa, $P_{NO} = 0$).

Table 2
Values of K_{0i}, E_i

i	K_{0i}	K_{0i} unit	E_i (J mol^{-1})
1	9.84×10^{-8}	Pa^{-1}	5.87×10^4
2	3.24×10^{-2}	–	1.28×10^3
3	4.13×10^3	Pa^{-1}	-1.17×10^4
4	2.72×10^{-6}	Pa$^{-1/2}$	4.65×10^4
5	2.21×10^2	Pa^{-1} mol kg^{-1} s^{-1}	-1.36×10^4

$$EtONO + 2Z \rightleftharpoons EtOZ + NOZ \tag{5}$$

$$COZ + EtOZ \rightarrow COOEtZ \tag{6}$$

$$2COOEtZ \rightleftharpoons (COOEt)_2 + 2Z \tag{7}$$

$$NOZ \rightleftharpoons NO + Z \tag{8}$$

In Eq. (5), ethyl nitrite is first dissociate into adsorbed ethoxy radical (EtO$^-$) and NO, whereupon ethoxy radical reacts in Eq. (6) with absorbed carbon monoxide to absorbed alkoxycarboxide (COOEt), which further associates to diethyl oxalate, as shown in Eq. (7). In Eq. (8), the gas of NO forms from adsorbed nitrogen monoxide. For the derivation of the rate expression the assumptions were made that steps (4), (5), (7) and (8) are in equilibrium and that step (6) is the sole rate-determining reaction. The resulting Hougen–Watson type rate expression is depicted as follows:

$$-r_{CO} = \frac{K_5 P_{CO} P_{EtONO} P_{NO}^{-1}}{(1 + K_1 P_{CO} + K_2 P_{EtONO} P_{NO}^{-1} + K_3 P_{NO} + K_4 P_{(COOEt)_2}^{1/2})^2} \tag{9}$$

The constant K_i ($i = 1, 2, 3, 4, 6$) were determined by means of nonlinear regression. They are functions of the reaction temperature:

$$K_i = K_{0i} \exp\left(\frac{E_i}{RT}\right) \tag{10}$$

The values of K_{0i}, E_i are reported in Table 2.

The reaction rate calculated with Eq. (9) is plotted versus the observed reaction rate in Fig. 5. With a slope n of 1.04 and a correlation coefficient r of 0.97, the goodness of fit is excellent.

The estimated value of enthalpy change for the chemisorption of CO on palladium catalyst (58.7 kJ mol^{-1}) compares well with the reported value by Conrad et al. [9] confirming in a sense the validity of the proposed kinetic model.
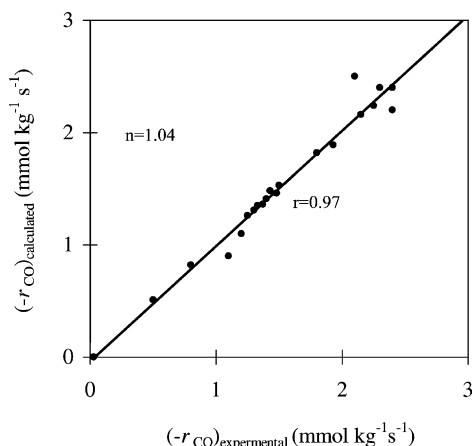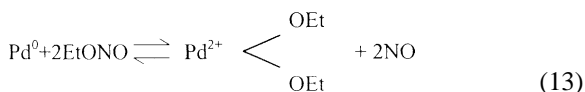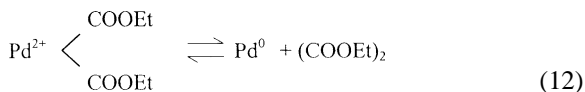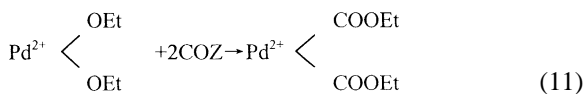

Fig. 5. Calculated vs. experimentally observed reaction rate at $T = 398$ K in the presence of hydrogen.

4. Discussion

4.1. Inhibition of nitrogen monoxide

Uchiumi et al. [2] discovered that nitrogen monoxide suppresses the reaction rate. Thermodynamically, reaction (1) is an irreversible reaction with Gibbs free energy $\Delta G_{298}^\circ = -192.26$ kJ mol^{-1}. The inhibiting effect of nitrogen monoxide seems unconceivable.

In fact, Eqs. (4)–(8) can be redepicted in an explicit form as:

$$Pd^{2+} \begin{array}{c} OEt \\ < \\ OEt \end{array} + 2COZ \rightarrow Pd^{2+} \begin{array}{c} COOEt \\ < \\ COOEt \end{array} \tag{11}$$

$$Pd^{2+} \begin{array}{c} COOEt \\ < \\ COOEt \end{array} \rightleftharpoons Pd^0 + (COOEt)_2 \tag{12}$$

$$Pd^0 + 2EtONO \underset{\longleftarrow}{\overset{\longrightarrow}{\rightleftharpoons}} Pd^{2+} \begin{array}{c} OEt \\ < \\ OEt \end{array} + 2NO \tag{13}$$

The inhibiting effect of nitrogen monoxide on the reaction rate can be readily accounted for due to the fact that reaction (13) is in equilibrium and that nitrogen monoxide suppresses the formation of ethoxy

radical (EtO^-). Diethyl oxalate also has somewhat inhibiting effect as shown in Eq. (12).

4.2. Reaction performance in the presence of hydrogen

In industrial practice, carbon monoxide is mainly obtained from syngas and in such process hydrogen is an inherent concomitant. It is necessary to investigate the effect of hydrogen on the coupling reaction performance. Li et al. [10] have studied deliberately the effect of hydrogen on the reaction behaviors. They discovered that (1) a single other reaction occurs in the presence of hydrogen, i.e.

$$H_2 + 2EtONO \rightarrow 2EtOH + 2NO \quad (14)$$
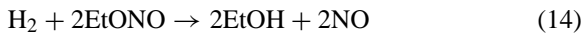
(2) hydrogen suppresses the reaction rate $-r_{CO}$; (3) the conversion of carbon monoxide is recovered immediately after removing hydrogen from the system; and (4) with the increase of reaction temperature, the effect of hydrogen on the reaction rate decreases.

As for the reactions concerning with hydrogen in the system, the following reaction mechanism can be readily envisaged. The surface reaction is also assumed to be the rate-determining step.

$$H_2 + 2Z \rightleftharpoons 2HZ \quad (15)$$

$$EtOZ + HZ \rightarrow EtOH + 2Z \quad (16)$$

In combination with Eqs. (4)–(8), the resulting Hougen–Watson type rate expressions are:

Fig. 6. Conversion of CO or H_2 as a function of H_2 concentration ($T = 393$ K). See Li et al. [10].

is plotted versus ($\sqrt{1 - X_{H_2}} - 1$) corresponding to the experimental conversion data of Fig. 6. A nearly unitary correlation coefficient (0.9982) confirms the validity of the proposed mechanism and kinetic model.

The main differences between the reaction mechanism presented here and the one proposed by Ma et al. [8] are the rate-determining steps and the adsorption of ethyl nitrite. Whereas in the mechanism envisaged here, the surface reaction is the sole rate-determining step and ethyl nitrite cleaves into ethoxy radical and NO species and adsorbed on two active sites, it has been suggested in the work of Ma et al. [8] that the adsorption of carbon monoxide is the rate-determining

$$-r_{CO} = \frac{K_6 P_{CO} P_{EtONO} P_{NO}^{-1}}{(1 + K_1 P_{CO} + K_2 P_{EtONO} P_{NO}^{-1} + K_3 P_{NO} + K_4 P_{(COOEt)_2}^{1/2} + K_5 P_{H_2}^{1/2})^2} \quad (17)$$

$$-r_{H_2} = \frac{K_7 P_{H_2}^{1/2} P_{EtONO} P_{NO}^{-1}}{(1 + K_1 P_{CO} + K_2 P_{EtONO} P_{NO}^{-1} + K_3 P_{NO} + K_4 P_{(COOEt)_2}^{1/2} + K_5 P_{H_2}^{1/2})^2} \quad (18)$$

Dividing Eq. (17) by Eq. (18) gives the ratio

$$\frac{r_{CO}}{r_{H_2}} = \frac{dP_{CO}}{dP_{H_2}} = K_{67} \frac{P_{CO}}{P_{H_2}^{1/2}} \quad (19)$$

While Eq. (19) re-expresses in terms of X_{CO} and X_{H_2}, the following can be derived

$$\ln(1 - X_{CO}) = 2K_{67}(\sqrt{1 - X_{H_2}} - 1) \quad (20)$$

Fig. 6 shows the conversions of CO and H_2 as a function of hydrogen concentration at a given temperature, reported by Li et al. [10]. In Fig. 7, $\ln(1 - X_{CO})$
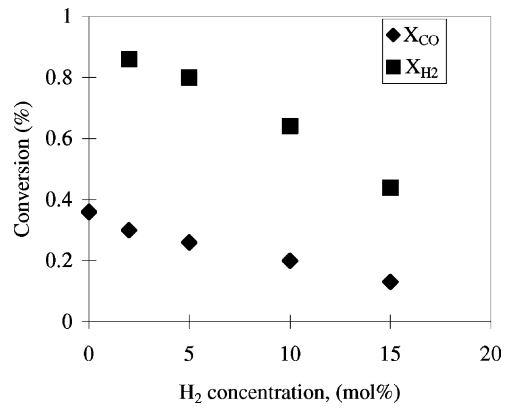
step and ethyl nitrite adsorbed on a single active sites without dissociation. Uchiumi et al. [2] observed that the partial pressure of ethanol does not affect the reaction rate, which cannot be accounted for with the rate expression from Ma et al. [8] but readily interpreted by Eqs. (17) and (18). In fact, it is known that an EtO–NO bond of alkyl nitrite is easily cleaved homolytically. The bond dissociation energy of ethyl nitrite into ethoxy radical and NO is estimated to be about 176 kJ mol^{-1}, which is considerably low
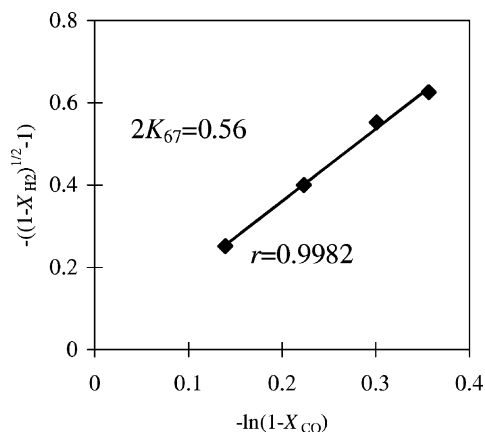
Fig. 7. $-\ln(1 - X_{CO})$ vs. $-((1 - X_{H_2})^{1/2} - 1)$ related to the points of Fig. 6.

(e.g. C–H, 414 kJ mol^{-1}; C–C, 347.2 kJ mol^{-1}; C–O, 359.8 kJ mol^{-1}; H–O, 464.2 kJ mol^{-1}). So, the assumption that ethyl nitrite dissociates into adsorbed ethoxy radical and NO is more reasonable. In this way, the occurrences in the work of Ma et al. [8] and Li et al. [10] are readily accounted for.

5. Conclusion

The kinetics of the catalytic coupling reaction of carbon monoxide to diethyl oxalate in the presence of ethyl nitrite over supported palladium is presented in this work. It was discovered that the surface reaction is the sole rate-determining step and that ethyl nitrite, due to rather low dissociation energy of EtO–NO bond, cleaves into adsorbed EtO$^-$ and NO species. Also, equilibrium exists between nitrogen monoxide

and adsorbed ethoxy radical species; therefore, nitrogen monoxide has an inhibiting effect on the reaction rate.

Moreover, hydrogen, with adsorption and dissociation, reacts with adsorbed ethoxy radical to ethanol. The rate-determining step is also the surface reaction between adsorbed species. Ethanol has no influence on the reaction rate.

In summary, the results presented here can give a satisfactory answer to the occurrences concerning with the reaction behaviors in our more than 10 years of research and the others.

Acknowledgements

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