Rate constant for CO insertion in the hydroformylation of ethene on Rh/SiO_2 as determined by pulse surface reaction rate analysis

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Received 14 March 1991; accepted 25 June 1991

A new method of pulse surface reaction rate analysis (PSRA) was proposed for determining the rate constant of the step of CO insertion in ethene hydroformylation. On pulsing ethene onto Rh/SiO_2 via the continuous flow of a mixture of CO and H_2, propanal was found to be produced gradually. It is revealed here that rate analysis of the dynamic behavior of produced propanal allows the determination of the rate constant for CO insertion. The effect of metal carbonate and oxides, added to the catalyst, on CO insertion was discussed in terms of the rate constant determined.

Keywords: CO hydrogenation; CO insertion; hydroformylation; pulse reaction; rate constant; Rh/SiO_2

1. Introduction

The hydrogenation of CO is composed of several steps including the adsorption of CO and H_2, the dissociation of adsorbed CO to form surface carbon and oxygen species, the polymerization of surface carbon species to adsorbed hydrocarbons with various numbers of carbon atoms, and their hydrogenation [1–4]. In addition to these steps, CO insertion into the bond between the metal atom and the carbon of surface carbon species is a requisite step for producing C_2-oxygenates from syngas [5,6]. It would, therefore, be desirable for such a complicated reaction to measure the rate of the individual steps involved in CO hydrogenation, so that the activity and the selectivity are efficiently controlled. We proposed a pulse surface reaction rate analysis (PSRA) method for determining the rate constants for the dissociation of adsorbed CO and for the hydrogenation of surface carbon species to produce CH_4 (k_{CO} and k_{CH_x}, respectively) [7–10] and demonstrated the applicability of PSRA to catalyst design in CO hydrogenation [11–15]. These two rate constants allow us to discuss to some extent the selectivity of C_2-oxygenates in CO hydrogenation, because the selectivity should be affected by k_{CO} and k_{CHx} [15]. However, it is more relevant to measure the rate of the CO insertion step. The purpose of the present study is, therefore, to determine the rate constant of the CO insertion step and also to discuss the effect of additives on this step in terms of the rate constant for the Rh/SiO_2 catalyst.

2. Experimental

Silica-supported Rh catalyst (metal loading, 5 wt%) was prepared by impregnating SiO_2 (Davison 57) with an aqueous solution of $RhCl_3$ followed by drying at 393 K overnight and reduction at 673 K for 2 h. Catalysts with additives were prepared by impregnating the Rh/SiO_2 in an aqueous solution of additive metal salts. The dynamic behavior of propanal was measured by using a new PSRA apparatus. It was composed of a continuous flow microreactor combined via a six-way valve with a gas chromatograph (Yanaco HSG-1) which was equipped with a flame ionization detector and with PEG-1500 as a separation column. A small amount of ethene was pulsed from the inlet of the reactant pulse onto a catalyst through the continuous flow of a mixture of CO, H_2, and He (5, 5, and 40 cm^3 min^{-1}, respectively). Helium was used as the carrier gas. Propanal, which was negligible before the pulse, was produced from the reaction of the pulsed ethene with the mixture of CO and H_2. The six-way valve was adjusted so that the produced propanal was collected in a liquid nitrogen trap for a certain period just after the ethene pulse. After the production was over, the six-way valve was turned so that the propanal in the trap was transferred to the gas chromatograph for determining its amount. The collection and the subsequent analysis were repeated by varying the period for collecting propanal. The rate constant for CO insertion was determined from analyzing the dynamic behavior of the produced propanal. The rate constants, k_{CO} and k_{CH_x}, were determined in the manner described previously [7–10]. Steady-state CO hydrogenation was carried out at 553 K under pressure (2.0 MPa). The details are described elsewhere [14,15].

3. Results and discussion

DETERMINATION OF THE RATE CONSTANT FOR CO INSERTION

Fig. 1 shows the amount of propanal produced at 453 K for a certain period after the ethene pulse. The amount of propanal increased gradually with time to reach a constant value. Ethane was also produced but its production was over

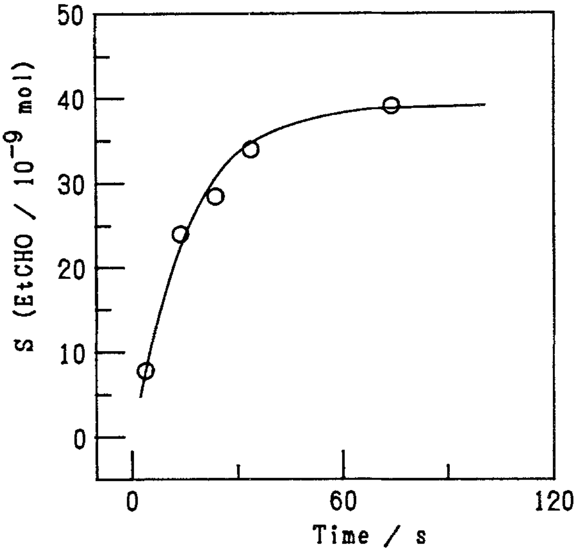

Fig. 1. The amount of propanal produced from ethene pulsed onto Rh/SiO_2 at 453 K through a continuously flowing $CO/H_2/He$ mixture. A solid line is obtained from the calculation according to eq. (4) with a least-squares fit.

within 15 s. Since gaseous ethene was immediately flown away from the catalyst bed together with the carrier gas, almost all propanal should be produced from adsorbed ethene (or ethyl) species. Therefore, the constant value observed corresponds to the amount of the adsorbed species converting to propanal.

In the reaction of ethene with a mixture of CO and H_2, propanal production involves CO insertion into metal-ethyl species [16,17]:

$$(C_2H_5)_{ad} + (CO)_{ad} \xrightarrow{(H)_{ad}} C_2H_5CHO \qquad \text{(i)}$$

where the subscript 'ad' denotes the adsorbed species. Ethane observed in the product must be produced from direct hydrogenation of $(C_2H_5)_{ad}$. It is interesting to note that the production behavior is completely different between propanal and ethane, although they are from the common intermediate. If the active site is also common, $(C_2H_5)_{ad}$ should be consumed exclusively by direct hydrogenation to ethane, because the production of propanal is slow under the present reaction conditions. Therefore, the observed results suggest that the active site responsible for propanal production is different from that for ethane production. In the reaction of ethene with a mixture of CO and H_2, alkali salts added to Rh/TiO_2 were reported to affect differently the production between propanal and ethane [18], which, in accordance with our suggestion, may provide the evidence for the difference in the active site between them.

According to eq. (i), the rate of the production of propanal, $r(t)$, is

$$r(t) = (\mathrm{d}N_P/\mathrm{d}t) = -(\mathrm{d}N_E/\mathrm{d}t) = k_I N_{CO} N_E \qquad (1)$$

where N_P, N_E, and N_{CO} are the respective numbers of produced propanal, adsorbed ethyl species to be converted to propanal, and adsorbed CO species, and k_I is the rate constant for CO insertion and probably affected by the concentration of $(H)_{ad}$. The hydrogenation of CO has been found to show zero or negative order dependence with respect to the CO partial pressure, which means that surface metal sites are covered almost completely with CO molecules [19,20]. Therefore, N_{CO} is considered to be constant under the continuous flow of a mixture of CO and H_2 and as a result, eq. (1) is

$$r(t) = -(\mathrm{d}N_E/\mathrm{d}t) = k_{AI}N_E \tag{2}$$

where k_{AI} is an apparent rate constant for CO insertion, which is a function of N_{CO}. Integration of eq. (2) leads to

$$N_E = N_E^0 \exp(-k_{AI}t) \tag{3}$$

where N_E^0 is N_E at $t = 0$. The amount of the propanal (S) produced in a period t is

$$S = N_E^0 - N_E = N_E^0\{1 - \exp(-k_{AI}t)\} \tag{4}$$

Eq. (4) indicates that the rate constant can be determined from a least-square fit of the relationship between the amount of the produced propanal and the reaction time. A combination of $N_E^0 = 39.0 \times 10^{-9}$ mol and $k_{AI} = 0.064$ s^{-1} gives the solid line shown in fig. 1. As shown, agreement between the experimentally obtained values and calculated ones is satisfactory.

EFFECT OF ADDITIVES ON CO INSERTION

For Rh/SiO$_2$ with various kinds of additives, k_{AI} was determined and the results are summarized in table 1 together with k_{CO} and k_{CH_x}. Oxides of Ti, V, Cr, and Mn increased k_{AI}, while those of Ni, Cu, and Zn decreased it. Table 1 also summarizes the selectivities of C$_2$-oxygenates, CH$_4$, and higher hydrocarbons in continuous flow CO hydrogenation. It may be natural to expect that the oxides of Ti, V, Cr, and Mn added to Rh/SiO$_2$ increase the C$_2$-oxygenates selectivity and those of Ni, Cu, and Zn decrease it. Table 1 shows that the addition of the latter oxides led to the decrease in the selectivity, as expected. However, the addition of the former oxides did not lead to selectivity increase. In the previous study [15], we discussed the selectivity in CO hydrogenation on the basis of the rate constant for surface reaction. The discussion showed that the selectivity of C$_2$-oxygenates was affected not only by k_I but also by both k_{CO} and k_{CH_x}: small k_{CO} and k_{CH_x} are the favorable condition for the production of C$_2$-oxygenates, because large k_{CO} is preferable to the production of hydrocarbons and large k_{CH_x} is to that of CH$_4$. According to table 1, the oxides of Ti, V, Cr, and Mn also increase k_{CO} and k_{CH_x}. This condition is not favorable for C$_2$-oxygenates production, which may explain that the addition of oxides of Ti,

Table 1
Rate constant determined by PSRA and selectivity in steady-state CO hydrogenation on Rh/SiO_2

Additives	Rate constant × 100/s^{-1}			Selectivity [d]/%		
	k_{AI} [a]	k_{CO} [b]	k_{CH_x} [c]	C_2-oxygenates	CH_4	Hydrocarbons
none	6.40	1.95	0.507	55.8	27.3	14.2
K	5.88	0.274	0.0842	55.7	27.9	16.4
Ca	5.89	0.968	0.372	44.5	36.1	19.3
Ti	8.98	8.44	2.98	42.4	37.8	19.8
V	6.30	7.94	5.12	47.9	30.9	21.2
Cr	8.06	4.72	1.97	45.2	39.5	15.3
Mn	7.45	2.31	0.870	40.5	29.7	29.8
Fe	7.02	1.17	0.456	43.4	37.4	19.2
Co	5.96	0.536	0.217	26.7	27.6	45.6
Ni	3.83	0.664	0.281	26.3	50.1	23.6
Cu	4.01	0.359	0.131	21.4	68.3	10.4
Zn	2.89	0.118	0.0495	28.3	45.8	26.0

[a] Rate constant for CO insertion.
[b] Rate constant for C–O bond dissociation.
[c] Rate constant for the hydrogenation of surface carbon species.
[d] Methanol is excluded from the selectivity.

V, Cr, and Mn did not lead directly to the increase in the selectivity of C_2-oxygenates. The rates measured for individual steps suggest that it is difficult to increase the selectivity of a desired product in CO hydrogenation by adding only one component. Indeed, it was reported that a high performance Rh catalyst was developed by adding several kinds of metal oxides [21]. Each component may play its own role in the way that one component suppresses the dissociation of adsorbed CO and the other enhances CO insertion, resulting in the increase in the selectivity of C_2-oxygenates.

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