Kinetics and Mechanism of Methanol Carbonylation over Rh-Y Zeolite

NOBUO TAKAHASHI, YUICHI ORIKASA, AND TATSUAKI YASHIMA[1]

Department of Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152, Japan

Methanol carbonylation over Rh–Y zeolite was studied kinetically at 428 to 473 K under atmospheric pressure. For low conversions of methanol, methyl acetate was the only carbonylation product observed. The reaction was first order in methyl iodide and zero order in both methanol and carbon monoxide. The apparent activation energy was 5.65×10^4 J/mol in the temperature range studied. Carbonylations in the ethanol–methyl iodide, methanol–ethyl iodide, and deuterated methanol–methyl iodide systems were studied to clarify the reaction mechanism. From these results, the reaction mechanism for this carbonylation is proposed as follows: (i) the oxidative addition of methyl iodide to an active Rh site, (ii) the insertion of carbon monoxide into the methyl–Rh bond, (iii) the formation of methyl acetate by methanolysis of the acetyl–Rh bond, (iv) the reductive dissociation of hydrogen iodide to reform the active site, and (v) the regeneration of methyl iodide by the reaction of hydrogen iodide with methanol. This reaction mechanism is quite similar to that proposed for the homogeneous rhodium complex catalyst.

INTRODUCTION

In our previous paper (*1*), we reported that Rh–Y zeolite prepared by an ion exchange procedure shows a high catalytic activity for the carbonylation of methanol in the presence of methyl iodide. In a continuous flow system, the Rh–Y catalyst maintains constant activity for more than 10 hr under atmospheric pressure. For the carbonylation, the specific activity of Rh–Y exceeds that of other heterogeneous catalysts, such as charcoal-supported rhodium chloride (*2*) and polymer-bound rhodium complex (*3*). It has been found that methyl acetate is an initial product of the carbonylation, but it is not observed without methyl iodide (*1*). The same phenomena have been observed in this carbonylation

[1] To whom correspondence should be addressed.

over Rh–X zeolite catalyst (*4–6*). These results resemble that for the homogeneous rhodium complex catalyst. So, it is expected that the behavior of the Rh–Y catalyst is similar to that of the homogeneous rhodium complex catalyst.

A reaction mechanism which includes an oxidative addition of methyl iodide to an active monovalent rhodium species has been proposed for the homogeneous rhodium complex catalysts (*7–9*). The methyl group, from which the acetyl group is formed during carbonylation, is believed to be supplied by the methyl iodide. This conclusion is based on kinetic results, i.e., the rate of carbonylation is proportional to the concentration of methyl iodide and independent of those of both carbon monoxide and methanol. However, any further evidence to support this mechanism has not
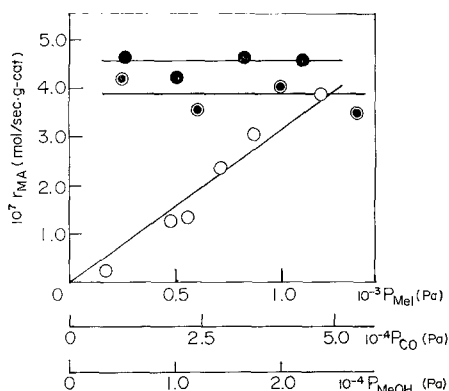
FIG. 1. Effect of partial pressure of raw materials on methyl acetate formation rate. O, methyl iodide (a); ●, carbon monoxide (b); ◉, methanol (c). Reaction conditions: catalyst, Rh–Y; temperature, 443 K; W/F, 5.8 × 10³ g·sec/mol; P_{MeI}, (b) 1.19 × 10³ Pa, (c) 1.03 × 10³ Pa; P_{CO}, (a) 3.07 × 10⁴ Pa, (c) 3.30 × 10⁴ Pa; P_{MeOH}, (a) 1.19 × 10⁴ Pa, (b) 1.19 × 10⁴ Pa.

been found. During this investigation, the carbonylation of methanol was kinetically studied to obtain some information about the catalytic behavior of Rh–Y. Furthermore, to clarify the role of methyl iodide, the carbonylation of deuterated methanol (CD₃OD) was carried out and the distribution of deuterated methyl groups in the product was determined. A mechanism for the carbonylation of methanol over Rh–Y zeolite is discussed based on these results.

EXPERIMENTAL

Rhodium trichloride trihydrate was obtained from Nippon Engelhard Co. Methanol and methyl iodide, obtained from Wako Pure Chemical Ind. Ltd., were used without any further purification, and carbon monoxide was obtained from Takachiho Chemical Ind. Co. Deuterated methanol (CD₃OD) was obtained from Merck Japan Co.

Rhodium Y zeolite catalyst was prepared by a conventional cation exchange method at 353 K using NaY(SK-40) and a rhodium chloride aqueous solution adjusted

to pH 5.3 by the addition of sodium hydroxide. The rhodium content of the catalyst, which was determined by atomic absorption spectrometry, was 4.2 × 10⁻⁵ g-atom/g-cat (4.4% of degree of ion exchange as Rh³⁺). No cation exchanged except Na and Rh could be detected, but a small amount of proton would be present in our catalyst. From the measurement of X-ray diffraction it was estimated that a small portion of the Rh–Y framework was decomposed.

Methanol carbonylation was carried out in a fixed-bed type apparatus with a continuous flow system at atmospheric pressure. Details of the experimental procedure were described in the previous paper (1). The partial pressure of each reactant was changed while the total pressure was maintained at atmospheric pressure by the addition of helium.

The carbonylation of deuterated methanol was carried out in a glass reactor with a recirculating system (volume: 280 ml) connected to a vacuum line. Rh–Y (1.0 g) was placed in the reactor and evacuated at room temperature for 2 hr. After the catalyst bed was heated to reaction temperature by an electric heater, deuterated methanol, methyl iodide, and carbon monoxide were introduced into the reaction system to start the carbonylation. A small portion of the reaction mixture, except carbon monoxide, was collected in a trap cooled with liquid nitrogen.

The reaction mixture was analyzed by a gas chromatograph to determine the composition, and was also analyzed by a mass fragment chromatograph (Shimazu LKB 9000 gas chromatograph-mass spectrometer) to determine the distribution of deuterated methyl groups in methyl acetate and methyl iodide.

RESULTS AND DISCUSSION

Rh–Y is remarkably active for methanol carbonylation, and its specific activity is almost the same as that of the homo-

geneous rhodium complex catalyst. At less than 30% conversion of methanol, methyl acetate is the only carbonylation product, with dimethyl ether formed as byproduct. It has been found that on Rh–Y catalyst, no methanol carbonylation occurs in the absence of methyl iodide, and almost all of the methyl iodide (over 95%) is recoverable from the reaction mixture.

The effect of the methyl iodide partial pressure on the steady state formation rate of methyl acetate (r_{MA}) is shown in Fig. 1. The rate is proportional to the partial pressure of methyl iodide. The effects of the partial pressures of carbon monoxide and methanol on r_{MA} are shown in Fig. 1. The formation rate is approximately zero order with respect to the partial pressures of both carbon monoxide and methanol. The apparent activation energy for the carbonylation in the reaction temperature range from 428 to 473 K is 5.65 × 10⁴ J/mol from Fig. 2.

From these results, the rate expression and the apparent activation energy over Rh–Y are represented as Eq. (1). These are quite similar to those for the homogeneous rhodium complex catalyst [Eq. (2)] (9).

Rh–Y:

$$r_{MA} = kP_{MeI}^{1}P_{CO}^{0}P_{MeOH}^{0},$$
$$E = 5.65 \times 10^{4} \text{ J/mol} \qquad (1)$$

Homogeneous rhodium complex:

$$r = k'[MeI][CO]^{0}[MeOH]^{0},$$
$$E = 6.15 \times 10^{4} \text{ J/mol} \qquad (2)$$

From a comparison of Eqs. (1) and (2), the active rhodium sites on the Rh–Y appear to be quite similar to the active rhodium species in the homogeneous rhodium complex catalyst, and the reaction mechanisms of both systems are the same. However, we believe that this reaction does not
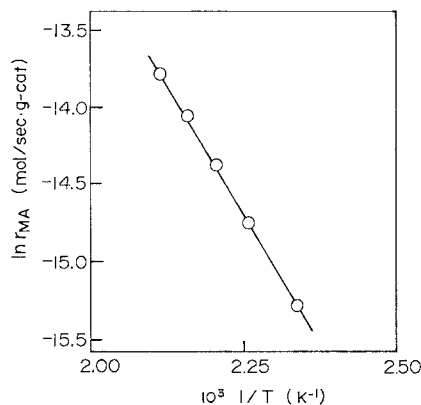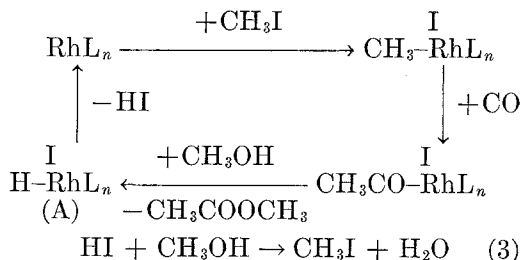

FIG. 2. Effect of reaction temperature on methyl acetate formation rate. Reaction conditions: catalyst, Rh–Y; W/F, 5.8 × 10³ g·sec/mol; P_{MeI}, 1.03 × 10³ Pa; P_{CO}, 3.07 × 10⁴ Pa; P_{MeOH}, 1.19 × 10⁴ Pa.

proceed in the condensed liquid phase, because it could be expected that a capillary condensation of water and/or methanol in the zeolite pore does not occur at such higher reaction temperature than their boiling points, and sufficiently lower partial pressures than their vapor pressures.

The following reaction mechanism has been proposed for the homogeneous rhodium complex catalyst (7–9).

$$RhL_n \xrightarrow{\ +CH_3I\ } CH_3\text{–}RhL_n$$

$$\uparrow -HI \qquad\qquad \downarrow +CO$$

$$\overset{I}{\underset{(A)}{H\text{–}RhL_n}} \xleftarrow[-CH_3COOCH_3]{+CH_3OH} \overset{I}{CH_3CO\text{–}RhL_n}$$

$$HI + CH_3OH \rightarrow CH_3I + H_2O \qquad (3)$$

First, the oxidative addition of methyl iodide to the active rhodium species occurs. After that, there is the successive insertion of carbon monoxide to CH₃–Rh bond, the elimination of methyl acetate by methanolysis, the reductive dissociation of HI from the rhodium species (A), and the regeneration of methyl iodide by Eq. (3). The first step, the oxidative addition of methyl

TABLE 1

Carbonylations in the Ethanol–Methyliodide and Methanol–Ethyliodide Systems[a]

Reactants		W/F $(10^4$ g·sec/ mol)	Conversion of ROH (mol%)	Percentage of total R'I (mol%)		Formation rate $(10^{-7}$ mol/sec·g-cat)			
						CH_3CO-		C_2H_5CO-	
ROH	R'I			CH_3I	C_2H_5I	$r_{MA}{}^b$	$r_{EA}{}^c$	$r_{MP}{}^d$	$r_{PA}{}^e$
C_2H_5OH	CH_3I	0.5	6.0	94.8	5.2	Trace	3.5	N.D.[f]	N.D.
C_2H_5OH	CH_3I	3.2	45.2	68.5	31.5	Trace	9.9	N.D.	N.D.
CH_3OH	C_2H_5I	3.2	54.7	32.2	67.8	4.3	0.5	1.7	1.9

[a] Reaction conditions: catalyst, Rh–Y; reactant molar ratio, CO/ROH/R'I = 8/2/1; temperature, 443 K.

[b] Methylacetate.

[c] Ethylacetate.

[d] Methylpropionate.

[e] Propionic acid.

[f] N.D., not detected.

iodide, is believed to be the rate-determining step. The above mechanism is supported by the observation of a first order dependence of the carbonylation rate on the methyl iodide concentration. According to this reaction mechanism, the methyl group in the acetyl group must be derived from methyl iodide.

In order to confirm this mechanism, carbonylations of ethanol–methyl iodide and methanol–ethyl iodide systems were studied. If the rate of the alkyl group exchange reaction between alcohol and iodine compounds is slow, ethyl acetate or methyl propionate must be a major carbonylation product. The results are summarized in Table 1. In the case of the ethanol–methyl iodide system, the major carbonylation product is ethyl acetate, and neither methyl propionate nor propionic acid is formed. This result supports the proposed mechanism in which the alkyl group forming the acyl group is supplied by the iodine compound. However, in the case of the methanol–ethyl iodide system, not only propionic acid and methyl propionate, which were formed from the carbonylation of the ethyl group, were produced, but methyl acetate

was also produced. Moreover, the formation rate of methyl acetate was the fastest among the carbonylations. It is suggested that an exchange reaction between alkyl groups occurs, and the methyl group reacts more readily with carbon monoxide than the ethyl group. Therefore, the proposed mechanism could not be confirmed by these experiments only.

In the case of the deuterated methanol (CD_3OD)–methyl iodide system, it is expected that the difference of reactivity between methyl and deuterated methyl groups is small, very much in contrast with that between methyl and ethyl groups. So, it should be possible to distinguish whether methyl iodide carbonylation or methanol direct carbonylation occurs over Rh–Y catalyst, when the distribution of deuterated methyl groups is measured in the methyl acetate produced from the $CD_3OD–CH_3I$ system. But, this requires that the rate of the methyl group exchange reaction between CD_3OD and CH_3I is not too fast as compared with the carbonylation. When methyl iodide is carbonylated, CH_3COOCD_3 must be produced, and when methanol is directly carbonylated,

CD_3COOCD_3 must be produced. The results of carbonylation in the $CD_3OD–CH_3I$ system are shown in Fig. 3. The fraction of CH_3I in the total methyl iodide decreased with increasing methanol conversion. This result shows that the alkyl group exchange reaction does not reach the equilibrium state during this run. Therefore, an analysis of the deuterated methyl group distribution in the methyl acetate produced could provide some useful information with regard to the reaction path. Mass numbers 43 and 46 correspond to $CH_3CO–$ and $CD_3CO–$, and mass numbers 74, 77, and 80 correspond to CH_3COOCH_3, CD_3COOCH_3 or CH_3COOCD_3, and CD_3COOCD_3, respectively. If methanol were directly carbonylated, the fraction of $CH_3CO–$, $CH_3CO–/(CH_3CO– + CD_3CO–)$ would increase with methanol conversion, because the fraction of CH_3OH in the total methanol should increase with reaction time by the exchange reaction of methyl groups between methyl iodide and methanol. However, the fraction of $CH_3CO–$ in the acetyl groups decreased with methanol conversion.
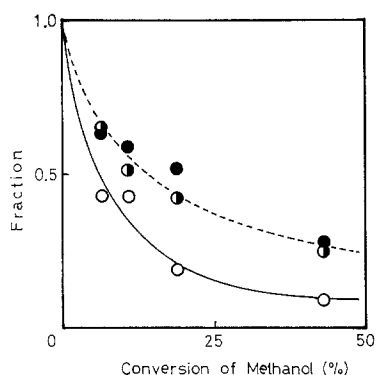

FIG. 3. Changes in the fractions: $CH_3I/(CH_3I + CD_3I)$, $CH_3CO–/(CH_3CO– + CD_3CO–)$, and $MN(77)/(MN(74) + MN(77) + MN(80))$, with methanol conversion. $\bigcirc$, $CH_3I/(CH_3I+CD_3I)$; $\bullet$, $CH_3CO–/(CH_3CO– + CD_3CO–)$; $\ominus$, $MN(77)/(MN(74) + MN(77) + MN(80))$. Reaction conditions: catalyst, Rh–Y; temperature, 443 K; initial pressure of CD_3OD, 1.1×10^4 Pa; CO, 2.6×10^4 Pa; CH_3I, 1.1×10^3 Pa.

The dotted line in Fig. 3 shows the calculated value of $CH_3CO–/(CH_3CO– + CD_3CO–)$ which is based on the fraction of CH_3I and following assumptions, i.e., there is no isotopic effect, the acetyl group is made only from methyl iodide, and there is no exchange of methyl groups between the acetyl group and other compounds. As shown in the Fig. 3, the experimental values agree very well with the calculated values. Moreover, the change in the fraction of $CH_3CO–$ with methanol conversion consistently agrees with that in the fraction of mass number 77 (MN77), (MN77)/[(MN74) + (MN77) + (MN80)]. This result shows that almost all of the mass number 77 product is CH_3COOCD_3. It is clear that neither inter- nor intramolecular exchange reaction of methyl groups of methyl acetate occurs.

It is concluded that on Rh–Y catalyst, methanol is not directly carbonylated, but methyl iodide is carbonylated. Namely, methyl acetate formation over Rh–Y proceeds through the following paths which are the same as those proposed for the homogeneous rhodium complex catalyst: (i) the oxidative addition of methyl iodide to the active rhodium site, (ii) the insertion of carbon monoxide into the methyl–Rh bond, (iii) the formation of methyl acetate by methanolysis of the acetyl–Rh bond, (iv) the reductive dissociation of HI from the rhodium species (A) to reform the active rhodium site, and (v) the regeneration of methyl iodide by the reaction of HI with CH_3OH.

ACKNOWLEDGMENT

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