

STUDY OF CARBONYLATION OF METHANOL TO ACETIC ACID AND ACETIC ANHYDRIDE OVER A BIDENTATE POLYMER BOUND CIS-DICARBONYLRHODIUM COMPLEX AS CATALYST*

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ABSTRACT

Copolymer of 2-vinylpyridine and vinylacetate coordinated with dicarbonylrhodium used as a catalyst for carbonylation of methanol to acetic acid and anhydride has been studied. The structural characteristics of the copolymer ligand and complex, and the influences of the reaction conditions on the carbonylation catalyzed by this polymer complex have been investigated. In comparison with small molecule catalyst of Rh complex, the bidentate copolymer coordinated complex has better thermal stability. The reaction mechanism of the carbonylation reaction is also illustrated.

INTRODUCTION

As a new catalyst system for preparing acetic acid and its related compounds, polymer-coordinated Rh complex, synthesized from bidentate copolymer ligand and tetracarbonyldichloride-dirhodium compound was studied. It has been proved to be of high activity, excellent selectivity and thermal stability, and to be high efficiency for recovery of the Rh component after reaction^[1-3]. Recently, a series of such kind of polymer-coordinated Rh complex have been studied by the authors, mainly made from nitrogen-containing, oxygen-containing linear copolymer and their rhodium complex^[4,5].

In this paper, on the basis of our previous research, we use the copolymer of 2-vinylpyridine and vinyl acetate (PPA) as a new polymer ligand to prepare the

coordinated Rh catalyst (PPARh). The structure of the catalyst has been characterized by using FT-IR, XPS, and its catalytic reaction of carbonylation of methanol to acetic acid and acetic anhydride has been monitored by GC. In accordance with the experimental results, the kinetics and mechanism of these catalytic reactions are also discussed.

EXPERIMENTAL

1. Preparation of copolymer ligand (PPA)

The copolymer ligand was prepared in the routine way, AIBN(0.5wt%) as an initiator was dissolved in a mixture of monomers composed of 0.076mol 2-vinyl pyridine, 0.304mol vinyl acetate and 30ml benzene, and then heated at temperature 65°C for 8h under vigorous stirring. A certain amount of ether was added into the reaction mixture, the copolymer resin was precipitated out, and then was redissolved in CH₂Cl₂ and reprecipitated by ether for several times, finally the product was dried in a vacuum desiccator to constant weight.

2. Preparation of complex (PPARh)

The copolymer ligand (PPA) was dissolved in CH₂Cl₂, and a certain proportion of Rh₂(CO)₄Cl₂ in methanol solution was slowly added into the former solution in an ice bath drop by drop under stirring for 10min. After the completion of above reaction, an equal mole of NaBPh₄ is added to react with the product. Then the reaction product was precipitated by corresponding amount of ether and washed by cold methanol for several times, finally dried in a vacuum desiccator to constant weight.

3. Structure determination of the ligand and the complex catalyst

All the XPS and IR spectral data were obtained on Kratos AEI Es-320 energy spectrometer and IR-10 spectrophotometer, respectively.

4. Evaluation of catalytic activities

The carbonylation reaction was carried out in a 160ml autoclave with magnetic stirring of about 400 rpm. The products were analyzed by the GC-8810 gas chromatograph.

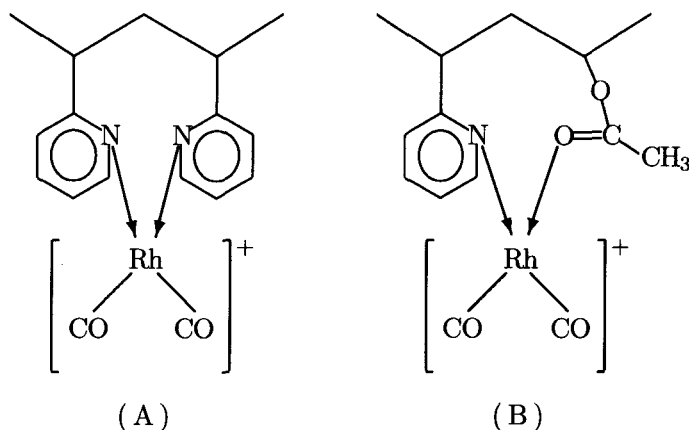
RESULTS AND DISCUSSIONS

1. Structural characteristics of copolymer ligands and complex

As shown in Table 1, the N_{1s} binding energy is moved from 398.8eV to 399.3eV, O_{1s} binding energy from 532.5eV to 533.1eV and Rh_{3d5/2} from 311.2 to 310.2eV when the copolymer ligand coordinate with Rh₂(CO)₄Cl₂. It is indicated that the

charge transfer in both N, O and Rh atoms has taken place during the formation of polymer-coordinated complex. Obviously, $Rh_{3d\ 5/2}$ binding energy in the complex is lower than that of $Rh_2(CO)_4Cl_2$. Rh atom plays the role as an electron acceptor, thus it forms $N \rightarrow Rh$ and $O \rightarrow Rh$ coordinated bond with N and O atoms as two donors^[6].

Since the composition of copolymer prepared by free radical polymerization is mainly affected by the actual values of the radical reactivity ratios, namely r_a and r_b . According to the rule, the two monomers, 2-vinyl pyridine and vinyl acetate, were copolymerized in optimal proportion, and the formed copolymer was reacted with $Rh_2(CO)_4Cl_2$ to give the end complex. Since the radical reactivity ratio r_{VP} is much larger than r_{VA} so the copolymer may be composed of PVP and PVA homogeneous segments and PPA heterogeneous segment. However, the PVA homogeneous segment can not form a stable complex with $Rh_2(CO)_4Cl_2$ ^[6], and as shown in Scheme 1, there are only two types of coordinated structure in the complex.



Scheme 1 Structure of the complexes (A)PVPRh and (B)PPARh

Table 1 Binding energies of copolymer ligand (PPA) and complex (PPARh)

Compound	Binding energy		
	$N_{1s\ 3/2}$	$O_{1s\ 3/2}$	$R_{3d\ 5/2}$
PPA ligand	398.8	532.5	
PPARh complex	399.3	533.1	310.2
$Rh_2(CO)_4Cl_2$			311.2

IR-spectrum of the complex (PPARh) further reveals that both N and O atoms have coordinated with rhodium. From Fig. 1, only two absorption bands at 2030 and 2100cm^{-1} in structure (A) can be observed, but two additional absorption bands

at 2000 and 2080 cm^{-1} appear in structure(B), and the intensities of which increase with the increasing of Rh content. This is in accord with the previous report^[1].

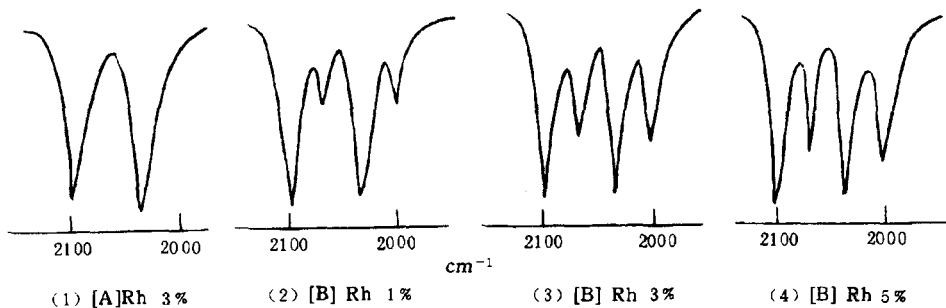


Fig. 1 IR-spectra of C=O absorption band in structure [A] and [B]

2. Catalytic activity of the complex PPARh

(a) Effect of the concentration of rhodium complex

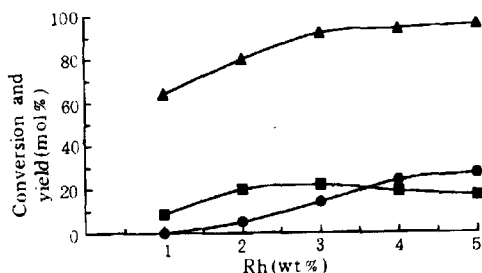


Fig. 2 Relation between the content of rhodium and reaction conversion

Condition: CH_3OH 0.1mol, CH_3I 0.02mol, P_{co} 45 kg/cm^2 (ini.), t 5h, T 150°C

▲ methanol(conv.); ■ methyl acetate(yield); ● acetic acid(yield)

Differing from the previous studies^[7], the concentration of rhodium has been changed not by simple variation of the quantity of rhodium complex used, but by synthesizing a series of complex as with different rhodium contents (Table 2). It was found from Fig.2 that the more the quantity of rhodium in the complex, the higher is its catalyst activity, presumably, the more the carbonyl rhodium ions, the more is the active center for rate determining of oxidized additive reaction. Therefore the cocatalyst CH_3I becomes more effective, and the reaction is further accelerated.

It is shown in Fig.3 that the rate of forming acetic acid or methyl acetate is increased as temperature is going up. Its catalytic activity has not changed until the temperature reached 180°C. Brodzki employed small molecular pyridine derivative as a one-dentated ligand to prepare the Rh complex catalyst and used it to methanol

carbonylation reaction^[8]. When the reaction temperature rose to 160°C, its catalytic activity was apparently decreased because of the decomposition of complex. In comparison with small molecule catalyst of Rh complex, the bidentated copolymer coordinated complex catalyst is much better in its thermal stability.

Table 2 Concentrations of rhodium active site

Rh content (wt%)	1	2	3	4	5
Quantity of catalyst used (g)	0.10	0.1	0.1	0.1	0.11
Concentration of Rh (m mol/l)	2.43	4.81	7.25	9.63	12.14

(b) Effect of temperature on the reaction

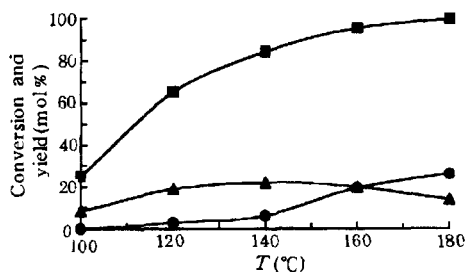


Fig. 3 Relation between concentration and temperature

Condition: CH₃OH 0.2mol, CH₃I 0.04mol, Cat. 0.12g, P_{co} 45kg/cm²(ini.), t 3h

▲ methanol(conv.); ■ methyl acetate(yield); ● acetic acid(yield)

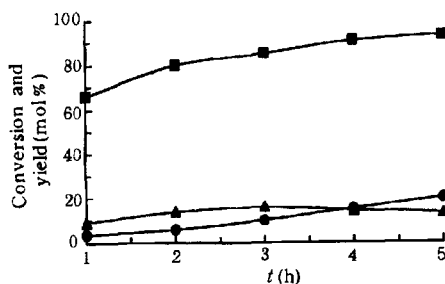


Fig. 4 Carbonylation of methanol to acetic acid by catalyst PPARh

Condition: CH₃OH 0.7mol, CH₃I 0.12mol, Cat. 0.4g P_{co} 45kg/cm²(ini.), T 150°C

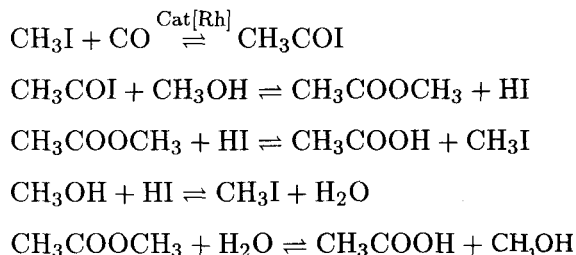
▲ methanol(conv.); ■ methyl acetate(yield); ● acetic acid(yield)

(c) Dependence of concentration on reaction time

(1) The conversion of methanol to methyl acetate and acetic acid

As seen from Fig.4, this carbonylation reaction is a multiple-step successive reaction, first the methanol is converted to acetic acetate, and then to the end product, acetic acid. The conversion rate of methanol is relatively fast, but the formation

rate of acetic acid is slower, and the building-up of methyl acetate is manifested. Obviously, the second step is the rate determining-step in this reaction. Based on the above result, the reaction may be written as follows:



(2) The conversion of methyl acetate to acetic anhydride

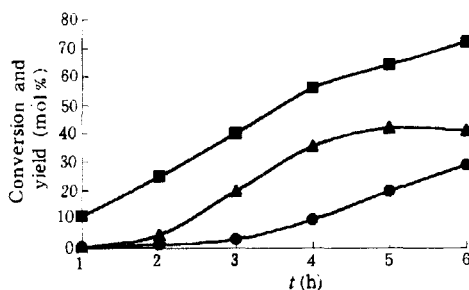
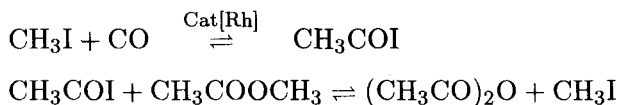


Fig. 5 Conversion of methyl acetate to acetic anhydride by PPARh catalyst

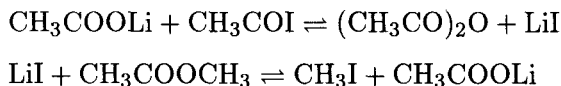
Condition: $\text{CH}_3\text{COOCH}_3$ 0.4mol, CH_3I 0.12mol, CH_3COOLi 0.03mol, Cat. 0.42g, P_{co} 45kg/cm²(ini.), T 150°C

■ methyl acetate (conv.); ▲ acetic acid (yield); ● acetic anhydride (yield)

When only CH_3I is used as the cocatalyst, the reaction is very slow, and the reactions may be expressed as follows:

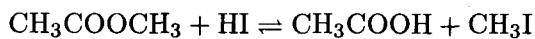
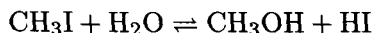


It is shown in Fig.5, if LiOAc exists^[9], the rate of reaction becomes quicker. It may be assumed as



However, from Fig.5, it shows that acetic acid is formed first, and this can be explained that the compound CH_3COOLi contains two crystal water, so the

following reactions probably occurred:



Keywords:

Bidentate polymer; *cis*-Dicarbonylrhodium complex; Carbonylation of methanol;
Reaction mechanism

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