

# A NOVEL COPOLYMER – BOUND CIS– DICARBONYLRHODIUM COMPLEX FOR THE CARBONYLATION OF METHANOL TO ACETIC ACID AND ACETIC ANHYDRIDE

YUAN Guoqing (袁国卿) CHEN Yuying (陈予英) and CHEN Rongyao (陈荣耀)

(*Institute of Chemistry, Academia Sinica, Beijing*)

## ABSTRACT

A series of porous microspheres of linear and ethylene diacrylate (M') cross-linked copolymers of 2-vinylpyridine (V) and methyl acrylate (M) reacted with tetracarbonyldichlorodirrhodium to form a series of cis-dicarbonylrhodium chelate complex (MVRh and MVM'Rh). They are thermally stable yet very reactive in the carbonylation of methanol to acetic acid, and of methanol-acetic acid mixture to acetic acid and acetic anhydride with a selectivity of 100% under relatively mild and anhydrous conditions.

Both the carbonylation of methanol to acetic acid<sup>[1]</sup> and of methyl acetate to acetic anhydride<sup>[2]</sup> involve the unstable dicarbonyldiiodorhodate anionic complex<sup>[3]</sup> as the catalytically active species<sup>[4, 5, 6]</sup>. On the contrary, cis-dicarbonylrhodium cationic complex coordinated with a slightly crosslinked copolymer of 2-vinylpyridine and styrene showed a good thermal stability but a low activity in this regard<sup>[7]</sup>. This finding has now been modified to cis-dicarbonylrhodium cationic complex coordinated with a series of linear or ethylene diacrylate (M') crosslinked copolymers of 2-vinylpyridine (V) and methyl acrylate (M) in the attempt to introduce a little instability to the heterogenized complex to improve its catalytic activity.

## EXPERIMENTAL

### 1. Preparation of the copolymer ligands (MV) and (MVM').

The copolymer ligands were prepared in the usual way by dissolving the initiator in the mixture of monomers, crosslinking agent and kerosene diluent. This mixture was then added into an aqueous solution of 10% sodium sulfate stirring at 60 °C to make a dispersion. Subsequently a slurry of kieselguhr in water was added into this dispersion and finally the resulting mixture was kept at 70 °C for 24 hours to complete the copolymerization. Kieselguhr was then washed out with alkali and the microspheric copolymer ligand obtained was extracted with hot acetone and dried in vacuum to a constant weight.

### 2. Preparation of the cis-dicarbonylrhodium cationic complexes (MVRh) and (MVM'Rh).

The complex was prepared by adding a methanol solution of tetracarbonyldichlorodirrhodium into the microspheric copolymer ligand (MV)

Received May 14, 1988

This work was supported by a Grant from the National Natural Science Foundation of China.

or (MVM') suspension in methanol, and then an aqueous solution of sodium salt was used to remove the loosely bound chloride to yield the yellow particles of *cis*-dicarbonylrhodium cationic complex (MVRh) or (MVM'Rh). After successive washing with water, methanol and diethyl ether, the complex was stored and dried in the desiccator over potassium hydroxide pellets.

### 3. Carbonylation reaction

The carbonylation reaction was carried out batchwise in a magnetic stirring autoclave of 160 mL capacity with a stirring rate above 400 rpm. All chemicals used were analytical reagents. Carbon monoxide was purchased from the Beijing Research Institute of Chemical Industries, Ministry of Chemical Industries, without further refinement. The reaction products were analyzed by the 103-Gas Chromatograph manufactured by the Shanghai Analytical Instrument Company with fixed phase GDX-203 and GDX-502, column length 2 m, column temperature 160 °C, hydrogen as carrier gas, flow rate 70 mL/minute, and bridge current 200 mA.

## RESULTS AND DISCUSSION

### 1. Characterization of complex MVM'Rh

#### (a) Scanning electron microscope (SEM) and electron microprobe (EMP) studies



Fig. 1 Scanning electron photomicrograph of (MVM'Rh)

The scanning electron photomicrograph (Fig. 1) shows the large porosity and high specific surface of the yellow microspheric complex (MVM'Rh), which were estimated at the range of 250 — 500 Å and 70 — 90 m<sup>2</sup>g<sup>-1</sup>, respectively. These properties provide well for the utilization of the heterogenized complex in a slurry or suspension reactor.

EMP studies (Fig. 2) show that rhodium distributes homogeneously over the outermost surface and inner cavity of the microspheric copolymer ligand. This

homogeneity means that rhodium is present in a mononuclear state of a complex as shown in (Fig. 2, b), not in a polynuclear state as a cluster of rhodium atoms.

#### (b) X-Ray photoelectron spectroscopy (XPS) studies

As the copolymer ligand contains the donor N from pyridine and donor O from alkoxy carbonyl group on the one hand, and homopolymer of methyl acrylate can not form a stable *cis*-dicarbonylrhodium complex with tetracarbonyldichlorodirhodium on the other hand, the yellow complex (MVM'Rh) must consist of a coordination bond between N and Rh, and probably another one between O and Rh due to the hybrid nature of the copolymer ligand and the steric adjacency between pyridine ring and alkoxy carbonyl group in the copolymer backbone. XPS studies clarify this situation.



Fig.2 EMP photograph of (MVM 'Rh)

(a) Surface of (MVM 'Rh)

(b) Homogeneous distribution of rhodium over the portion shown in Fig. 2, a .

**Table 1** Binding energy (BE) and full width at half maximum (FWHM) of different (MVM ' )'s and the corresponding (MVM 'Rh)'s .

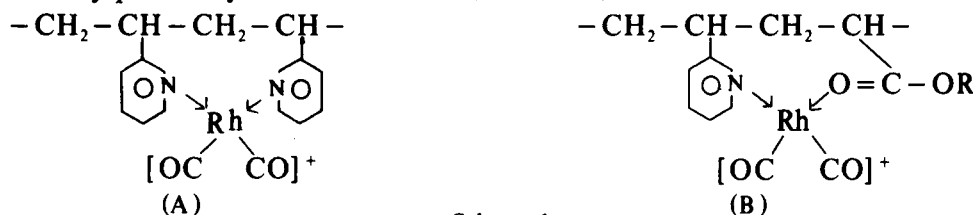
| Sample No.                           | V content in MVM '(%) | N <sub>1s</sub> |           | O <sub>1s</sub> |           | C <sub>1s</sub> |           | Rh <sub>3d<sub>5/2</sub></sub> |           | Cl      |
|--------------------------------------|-----------------------|-----------------|-----------|-----------------|-----------|-----------------|-----------|--------------------------------|-----------|---------|
|                                      |                       | BE (eV)         | FWHM (eV) | BE (eV)         | FWHM (eV) | BE (eV)         | FWHM (eV) | BE (eV)                        | FWHM (eV) | BE (eV) |
| MVM '1                               | 53.10                 | 398.2           | 1.9       | 532.3           | 3.0       | 285.0           | 2.1       |                                |           |         |
| MVM '2                               | 70.70                 | 398.2           | 1.9       | 532.2           | 3.0       | 285.0           | 2.3       |                                |           |         |
| MVM '3                               | 78.98                 | 398.1           | 2.0       | 532.2           | 3.0       | 285.0           | 2.2       |                                |           |         |
| MVM '4                               | 88.84                 | 398.3           | 2.0       | 532.3           | 3.0       | 285.0           | 2.3       |                                |           |         |
| MVM 'Rh-1                            |                       | 399.3           | 3.3       | 532.5           | 3.5       | 285.0           | 2.8       | 308.9                          | 2.7       |         |
| MVM 'Rh-2                            |                       | 399.2           | 3.2       | 532.8           | 3.6       | 285.0           | 2.7       | 308.9                          | 2.8       |         |
| MVM 'Rh-3                            |                       | 399.3           | 3.2       | 532.7           | 3.6       | 285.0           | 2.8       | 308.8                          | 2.7       |         |
| MVM 'Rh-4                            |                       | 399.4           | 3.3       | 532.9           | 3.7       | 285.0           | 2.7       | 308.8                          | 2.8       |         |
| Rh (CO) <sub>2</sub> Cl <sub>2</sub> |                       |                 |           | 532.4           |           |                 |           | 310.0                          |           | 199.5   |

In Table 1 the BE of N<sub>1s</sub>, O<sub>1s</sub>, C<sub>1s</sub> and Rh<sub>3d<sub>5/2</sub></sub> of four (MVM ' )'s and the corresponding dicarbonylrhodium complexes are listed . In all (MVM ' )'s the BE of N<sub>1s</sub> is 398.2 eV , and increases to 399.2 eV in the rhodium complexes . Correspondingly , the BE of O<sub>1s</sub> increases from 532.2 eV to 532.7 eV , which is higher than that in tetracarbonyldichloro - dirhodium of 532.4 eV . Besides , the BE of Rh<sub>3d<sub>5/2</sub></sub> drops from 310.0 eV of the reference compound , tetracarbonyldichlorodirhodium , to 308.9 eV in (MVM 'Rh)'s . Combining with the widening of FWHM , all of these demonstrate that rhodium coordinates with not only N but also O to form N → Rh and O → Rh coordination bonds .

### (c) Infrared spectroscopy studies

The infrared spectroscopic studies of the (MVRh)'s further reveal the coordination of both N and O with rhodium . When the rhodium content in (MVRh) is low (1%) , there are two absorption bands of terminal carbonyls at 2030 and 2100

$\text{cm}^{-1}$ , identical with that of the *cis*-dicarbonylrhodium complex coordinated with the slightly crosslinked copolymer of 2-vinylpyridine and styrene<sup>[7]</sup>. However, as the rhodium content in (MVRh) increases, two more absorption bands at 2080 and 2010  $\text{cm}^{-1}$  appear with increasing transmittance. These additional bands can only be attributed to the appearance of other species with *cis*-dicarbonylrhodium moiety. Here the only possibility is the structure B (Scheme 1).



Scheme 1

## 2. Properties of (MVRh) and (MVM'Rh)

### (a) Swelling

For the liquid phase catalysis of heterogenized complex catalyst, swelling of the catalyst in the reaction medium plays an important role to improve the mass transfer process and thus the catalytic activity<sup>[8]</sup>. The (MVM') ligand and (MVM'Rh) complex show an appreciable swelling at room temperature in various organic compounds.

**Table 2** Swelling - volume ratio of (MVM') and (MVM'Rh) in organic solvents

| Sample | MeOH | HOAc | (Ac) <sub>2</sub> O | AcOMe | MeI |
|--------|------|------|---------------------|-------|-----|
| MVM'   | 3.9  | 8.1  | 7.9                 | 2.9   | 2.8 |
| MVM'Rh | 2.3  | 3.5  | 3.1                 | 1.7   | 1.4 |

In the carbonylation of methanol the absorption rate of carbon monoxide was often accelerated when an appreciable amount of acetic acid was produced or acetic acid was used as solvent. This may be attributed to the swelling effect of the catalyst in acetic acid. The influence of acetic acid on the carbonylation of methanol will be discussed in the kinetic studies of the reaction<sup>[9,10]</sup>.

### (b) Carbonylation of methanol over (MVM'Rh)

During the carbonylation of methanol over (MVM'Rh) the changes of reactant and products in the liquid phase are shown in Fig. 3. Methyl acetate was always the intermediate found at the early stage and gradually converted to acetic acid. Methyl iodide did not change in quantity as long as methanol or methyl acetate was present in the system, and was recovered essentially quantitatively in a scale-up experiment. Acetic anhydride appeared in a prolonged experiment. No other compound was found as by-product. The selectivity is thus 100%. Dimethyl ether would appear as intermediate if the reaction was carried out under ill-stirring condition.

### (c) Carbonylation of methanol - acetic acid over (MVRh)

Under strictly anhydrous conditions methanol in glacial acetic acid was carbonylated to acetic acid and acetic anhydride. The conversions of reactants and yields of products in the liquid phase during the course of reaction are shown in Fig. 4.

From Fig. 3 and Fig. 4 it is revealed that under relatively mild conditions both crosslinked (MVM'Rh) and linear (MVRh) are very active to convert 80 - 90%

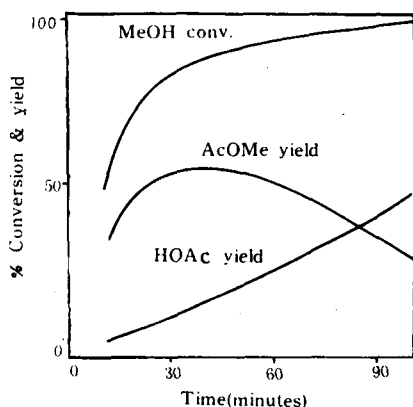


Fig.3 The carbonylation of methanol over (MVM Rh)\*

\* Reaction condition :  $\text{CH}_3\text{OH}$  0.5 mol ,  
 $\text{CH}_3\text{I}$  0.06 mol , Rh  $10^{-4}$  g · atom ,  
 $P_{\infty}$ (initial) 30 Kg ·  $\text{cm}^{-2}$  ,  
 temp .  $130 \pm 5$  °C .

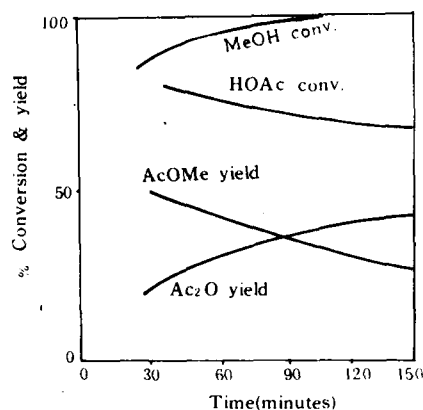


Fig.4 The carbonylation of methanol-acetic acid over (MVRh)\*

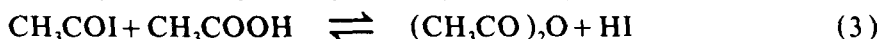
\* Reaction condition :  $\text{CH}_3\text{OH}$  0.4 mol ,  
 $\text{CH}_3\text{COOH}$  0.42 mol ,  $\text{CH}_3\text{I}$  0.066 mol ,  
 Rh  $10^{-4}$  g · atom ·  $P_{\infty}$ (initial) 30 Kg ·  $\text{cm}^{-2}$  ,  
 temp .  $130 \pm 5$  °C .

of the methanol to products within the first 30 minutes of reaction . The turnover rate of methanol converted is thus estimated at  $10^4$  mols/g · atom Rh/h . Raising the relative concentration of methyl iodide and the reaction temperature can further speed up the reaction . Methyl acetate and methyl iodide mixture could also be carbonylated to acetic anhydride by these catalysts at a much lower rate .

From Fig. 4 a series of reactions and equilibria can be deduced . The formation of acetyl iodide<sup>(1)</sup> starts these reactions .



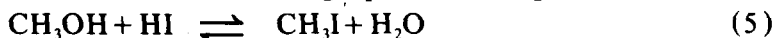
At the early stage of the reaction the concentrations of both methanol and acetic acid are relatively high , two competitive equilibria ensue .



At the same time esterification between methanol and acetic acid also occurs .



As the reaction proceeds on to a stage the concentrations of hydrogen iodide and water accumulate to such a level that the following equilibria take place .



As the reaction continues onward the concentration of methanol further diminishes , the reactions concerning methanol become of minor importance . On the other hand , the reaction between methyl acetate and hydrogen iodide formed instantaneously prevails . This is manifested in the lowering of the concentration of methyl acetate and the rising concentration of acetic anhydride . Methyl iodide liberated continues the reaction (1) and hence the reaction (3) . The following equilibria also occur .





Thermal stability and specificity of (MVM' Rh).

The crosslinked copolymer ligand (MVM') decomposed above 360 °C .

This thermal stability brought about the stabilization of (MVM' Rh) whose terminal carbonyl groups began to disappear completely at 240 °C in air . The activity of (MVM' Rh) increased with the rising of reaction temperature , and had been tested at 180 °C without deterioration . However , rhodium complexes coordinated with monodentate pyridine derivatives of low molecular weight lose their activity above 160 °C <sup>[11]</sup>.

Contrary to dicarbonyldiiodorhodate anionic complex which catalyzes the water gas shift reaction<sup>[12]</sup>, no carbon dioxide was ever found with (MVM' Rh) in the course of this investigation although water is assumed to form in the reaction .

This specific and beneficial effect of the polymer in this case may involve a number of complicate factors and deserve a further study . The rigid backbone and the hybrid nature of copolymer to form a relatively unstable eight - membered chelate between a stabilizing borderline base pyridine<sup>[13]</sup> and a hard base alkoxycarbonyl group , and the stereochemistry about the active site may play an important role in this aspect .

#### Keywords :

Cis-dicarbonylrhodium cationic complexes ; Copolymer ligands ; Carbonylation of methanol to acetic acid and acetic anhydride

#### REFERENCES

- [1] (a) Paulik , F . E . and Roth , J . F . , *J . Chem . Soc . , Chem . Commun .* , 1968 , 1578 .  
 (b) Roth , J . F . ; Craddock , J . H . ; Hershman , A . and Paulik , F . E . , *Chem . Tech .* , 1971 , 600 .  
 (c) Forster , D . , *Adv . Organometal . Chem .* , 1979 , 17 , 255 and references therein .  
 (d) Eby , R . T . and Singleton , T . C . , in Leach , B . E . (Ed .) , "Applied Industrial Catalysis" , Academic , New York , (1983) , Vol . 1 , p . 275 and references therein .
- [2] (a) Hewlett , C . , *Ger . Offen .* 2,441,502 (1975) , *CA* 1975 , 83 , 96448/q .  
 (b) Rizkalla , R . and Winnick , C . N . , *Ger . Offen .* 2,610,035 (1976) , *CA* 1976 , 85 , 176870/e .  
 (c) Rizkalla , R . , *Ger . Offen .* 2,610,036 (1976) , *CA* 1976 , 85 , 159463/e .  
 (d) Kuckertz , H . , *Ger . Offen .* 2,450,965 (1976) , *CA* 1976 , 85 , 62675/n .  
 (e) Erpenbach , H . , Gehrman , K . , Kuebbeler , K . and Schmitz , K . , *Ger . Offen .* 2,836,084 (1980) , *CA* 1980 , 93 , 45992/m .
- [3] Vallarino , L . M . , *Inorg . Chem .* , 1965 , 4 , 161 .
- [4] Forster , D . , *Inorg . Chem .* , 1969 , 8 , 2556 .
- [5] Schrod , M . and Luft , G . , *J . Mol . Catal .* , 1983 , 22 , 169 .
- [6] Hickey , C . E . , and Maitlis , P . M . , *J . Chem . Soc . Chem . Commun .* , 1984 , 1609 .
- [7] Yuan Guoqing and Chen Rongyao in Shapiro , B . L . (Ed .) , "Organometallic Compounds Synthesis , Structure , and Theory" , Texas A & M University Press , College Station , (1983) , p . 244 .
- [8] (a) Chen Bushi , Feng Zhiming and Chen Rongyao , *Cuihua Xuebao (J . Catal . Dailan)* , 1980 , 1 , 213 .  
 (b) Kabanov , V . A . ; Martynova , M . A . ; Pluzhnov , S . K . ; Smetunyk , V . I . and Chediya , R . V . , *Kinet . Katal .* 1979 , 20 , 1012 , *CA* 1979 , 91 , 192729/t .
- [9] Chen Yuying , Yuan Guoqing and Chen Rongyao , The following paper .
- [10] (a) Hjortkjaer , J . and Jensen , O . R . , *Ind . Eng . Chem . , Prod . Res . Dev .* , 1976 , 15 , 46 .  
 (b) Schrod , M . , and Luft , G . , *Ind . Eng . Chem . , Prod . Res . Dev .* , 1981 , 20 , 649 .  
 (c) Dekleva , T . W . , and Forster , D . , *J . Am . Chem . Soc .* , 1985 , 107 , 3565 .
- [11] Brodzki , D . ; Leclere , C . ; Denise , B . and Pannetier , G . , *Bull . Soc . Chim . France* , 1976 , 61 .
- [12] Cheng , C . H . ; Hendricksen , D . E . and Eisenberg , R . , *J . Am . Chem . Soc .* , 1977 , 99 , 2791 .
- [13] Kuhushkin , Yu . N . ; Khostik , G . M . and Kondratenkov , G . P . , *Koord . Khim .* , 1979 , 5 , 1225 , *CA* 1979 , 91 , 184496/z .