

POLYMER-PLATINUM COMPLEX CATALYSTS FOR OXIDATION OF METHANOL TO FORMALDEHYDE*

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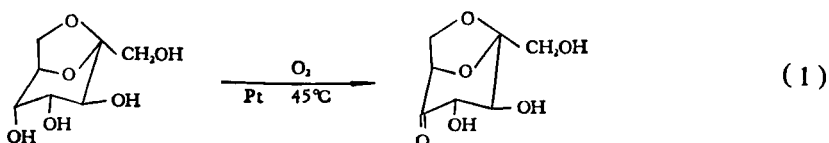
ABSTRACT

Two kinds of polymer-platinum complexes: silica-supported poly- γ -diphenylphosphinopropyl-siloxane-platinum complex and silica-supported polyphenylsilazane-platinum complex, have been found very active and selective in catalyzation of oxidation of methanol to formaldehyde at room temperature and under an atmospheric oxygen pressure. Their catalytic activities are greatly affected by P or N/Pt gram atomic ratio.

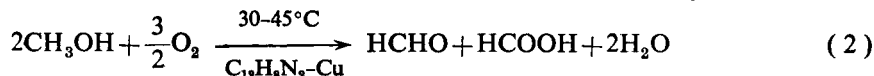
INTRODUCTION

Formaldehyde is an important raw material for chemical industry. The annual output of formaldehyde calculated as 37—40% water solution amounts to several millions tons in the world. It is manufactured by oxidation of methanol with $\text{MoO}_3\text{-Fe}_2\text{O}_3$, Cu-Zn or Ag at high temperature (300—750°C)^[1]. So it is better if the reaction can be carried out at mild conditions by an active catalyst.

Hydroxy groups in polyhydroxy-alcohol could be partially oxidized in the presence of platinum at low temperature (45°C)^[2, 3]. For example:



Methanol can be oxidized to formaldehyde catalyzed by phenanthroline-Cu complex at 30—45°C^[4]. But in this process a large amount of formic acid is produced at the same time, and the reaction will stop spontaneously if formic acid is not neutralized by alkali in time.



Therefore, this is not a good method for manufacture of formaldehyde. Moreover this complex has the common disadvantages of organometallic complexes used as homogeneous catalysts: it is unstable and difficult to recover from the reaction products. In order to overcome the disadvantages of organometallic complex catalysts, intensive researches on polymer-metal complexes used as heterogeneous catalysts have been carried out during

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2. Preparation of silica-supported polyphenylsilazane-platinum complex (Si-N-Pt)

Several samples of Si-N-Pt with different N/Pt gram atomic ratio were prepared. For example, 1 g (5.84 mg atom of N) of Si-N (N, 8.18 wt %), 15 ml of butanol and 0.303 g (0.584 mmol) of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ were placed in a flask equipped with a magnetic stirrer, a reflux condenser and a gas inlet tube. The mixture was refluxed under nitrogen for 6 hrs. The solid particles became dark grey, and the solution became colorless and transparent during the reaction. The product was filtered, washed with ethanol, and dried in vacuo to obtain 1.024 g of grey powder (Si-N-Pt). The gram atomic ratio of N/Pt was 10. The infrared spectrum showed that the product was a polymer-Pt complex (trans Pt-chloride stretching appeared at 339 cm^{-1} [8]). The complex was also characterized by XPS. Table 1 shows the XPS data for Si-N-Pt, Si-N and H_2PtCl_6 . It can be seen that the Si_{2p} and O_{1s} binding energies of Si-N-Pt are similar to that of Si-N, and the Cl_{2p} binding energy of Si-N-Pt is similar to that of H_2PtCl_6 . However, the difference of N_{1s} binding energies between Si-N-Pt and Si-N is 1.5 eV, and the difference of $\text{Pt}_{4f_{7/2}}$ binding energies between Si-N-Pt and H_2PtCl_6 is 3.1 eV. These results show that the coordination bonds are formed between two nitrogen atoms and a platinum atom in the complex.

Table 1 XPS data for Si-N-Pt, Si-N and H_2PtCl_6

XPS Peak	Binding energy (eV)		
	Si-N-Pt	Si-N	H_2PtCl_6
$\text{Pt}_{4f_{7/2}}$	72.4		75.5
N_{1s}	401.9	400.4	
Si_{2p}	104.3	104.4	
O_{1s}	533.4	533.6	
Cl_{2p}	199.2		199.4

3. Oxidation of methanol

Si-P-Pt or Si-N-Pt, methanol and water were placed in a flask connected to a gas pipette and an oxygen store measuring cylinder. The flask was put in a thermostat. The system was alternately evacuated and flushed with oxygen five times, and oxygen pressure was set at about 1 atm. The reaction mixture was stirred by magnetic stirrer, then the volume of oxygen absorbed was measured. The reaction products were analyzed by G. L. C.

RESULTS AND DISCUSSION

Fig. 1 shows the relationship between the rate of oxidation of methanol and P/Pt gram atomic ratio in Si-P-Pt at room temperature and under atmospheric pressure. It can be seen that the catalytic activity is greatly affected by the P/Pt gram atomic ratios in the complex. An optimum rate appears at a P/Pt ratio of about 4.

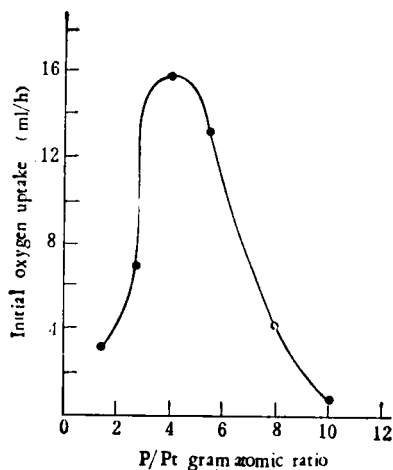


Fig. 1 The relationship between the rate of oxidation of methanol and P/Pt gram atomic ratio in Si-P-Pt Complex: 0.02 mg atom Pt; methanol, 0.06 mol; water, 5 ml; 25°C, 1 atm O_2 .

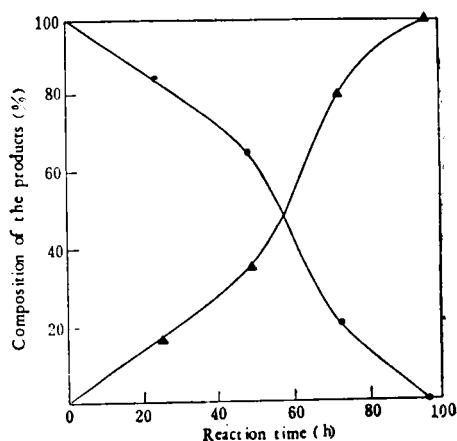


Fig. 2 The relationship between the reaction time and the product composition Si-P-Pt: 0.04 mg atom Pt; P/Pt, 4; methanol, 0.005 mol; water, 8 ml; 30°C, 1 atm O_2 .
● methanol; ▲ formaldehyde.

The relationship between the reaction time and the product composition is shown in Fig. 2. Although the reaction was carried out not so rapidly, yet methanol was converted to formaldehyde in 100% yield, and no formic acid was produced. This result shows that Si-P-Pt is not only a highly active catalyst but also a highly selective catalyst.

As shown in Fig. 3, the oxidation rate was greatly affected by change in temperature. The most proper temperature is in the range of 20–50°C. Raising the temperature further decreases the rate of oxidation conversely. Possibly, this is due to the evaporation of methanol at higher temperature causes methanol and oxygen can not contact with Si-P-Pt sufficiently.

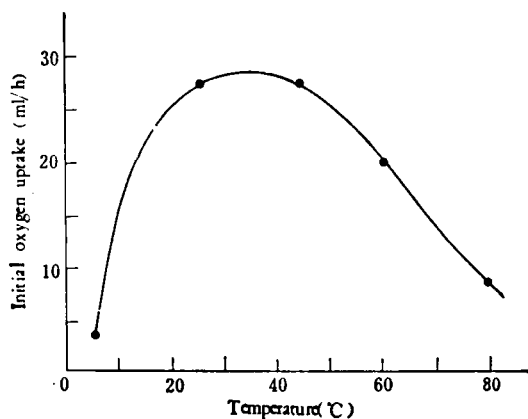


Fig. 3 Influence of temperature on the rate of oxidation of methanol.
Si-P-Pt: 0.02 mg atom Pt; P/Pt, 4;
methanol, 0.06 mol; water, 5 ml; 1 atm O_2 .

The experimental results show that the oxidation rate was also affected remarkably by the addition of acid or alkali. When acid was added, the reaction was hindered, but with alkali the reaction could be promoted. Fig. 4 shows the influence of the amounts of sodium hydroxide on the rate of oxidation of methanol. It can be seen that the addition of alkali could increase the rate of oxidation several times. However, formic acid was also formed in addition to formaldehyde. Therefore, the addition of alkali is not a good method for promoting the reaction.

Fig. 5 shows the oxidation results of methanol by Si-N-Pt at room temperature and an atmospheric oxygen pressure. The catalytic activity is also markedly affected by the N/Pt gram atomic ratio in the complex. An optimum rate appears when the ratio is about 20.

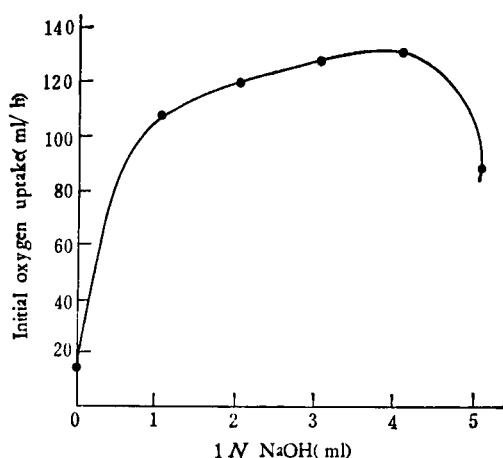


Fig. 4 Influence of the amounts of sodium hydroxide on the rate of oxidation of methanol
Si-P-Pt: 0.02 mg atom Pt; P/Pt, 4;
methanol, 0.06 mol; water, 5 ml;
30°C, 1 atm O₂.

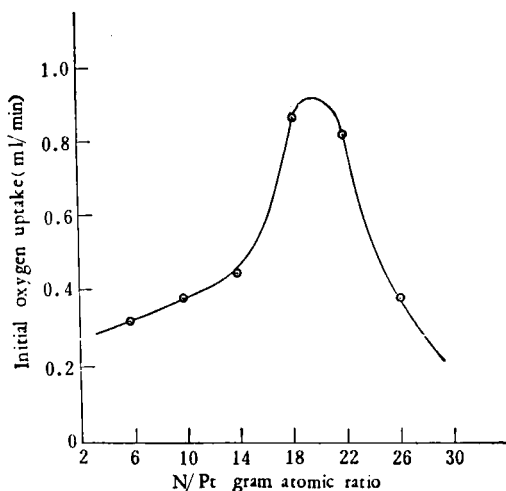


Fig. 5 Oxidation rate of methanol catalyzed by Si-N-Pt
Complex: 0.05 mg atom Pt; methanol, 0.2 ml; water, 5 ml; 30°, 1 atm O₂.

Si-N-Pt is also a highly active catalyst for oxidation of methanol and has high selectivity too. Formaldehyde was also obtained in 100% yield, and formic acid was not produced.

Table 2 shows the stability of Si-N-Pt in the reusing processes. It is a stable catalyst, and can be reused several times without any appreciable change in catalytic activity. It remains unchanged after standing in the air for over a year.

It is well known that the Si-N bond of low molecular organosilazane such as hexamethylsilazane is easily hydrolyzed^[9]. However, the polymer support of Si-N-Pt: highly cross-linked polyphenylsilazane, is very stable even in the boiling water. This property may be correlated with the stability of Si-N-Pt.

There are many polymer-metal complexes being used as catalyst for various reactions. The polymer supports (ligands) used include organic polymers such as polyacrylonitrile^[10], polyvinylpyrrolidone^[11], and polyamide^[12]; and organosilicon polymers such as poly- γ -aminopropylsiloxane^[13], poly- γ -cyanopropylsiloxane^[14], poly- γ -diphenylphosphinopropylsiloxane^[6, 7] and poly- γ -mercaptopropylsiloxane^[15]. Their donor atom such as nitrogen,

Table 2 The stability of Si-N-Pt in reusing processes

Number of reusing times	Initial oxygen uptake (ml/min)	Time for completing oxidation** (hr)
0*	0.30	21
1	0.30	21
2	0.29	21
3	0.33	21

Complex: N/Pt g atomic ratio, 10; Pt, 0.05 mg atom; methanol, 0.2 ml; water, 5 ml; 30°C, 1 atm.

* with fresh catalyst; ** conversion, 100%.

sulphur or phosphorus is connected to a carbon atom in organic group. While in the case of Si-N-Pt, the donor atom, nitrogen, is connected with Si atom. This example suggests that a new series of inorganic polymer-metal complexes may be prepared and applied as effective catalysts in the near future.

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