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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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To cite this Article Huang, M. Y. , Ren, C. Y. and Jiang, Y. Y.(1987) 'Oxygenation of Isopropanol and Ethanol Catalyzed by a Silica-Supported Polysilazane-Platinum Complex', *Journal of Macromolecular Science, Part A*, 24: 3, 269 – 275

To link to this Article: DOI: 10.1080/00222338708074444

URL: <http://dx.doi.org/10.1080/00222338708074444>

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OXYGENATION OF ISOPROPANOL AND ETHANOL CATALYZED BY A SILICA-SUPPORTED POLYSILAZANE-PLATINUM COMPLEX

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ABSTRACT

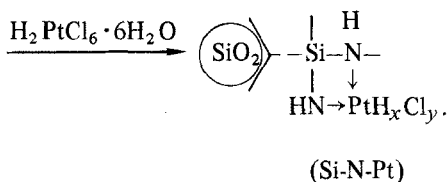
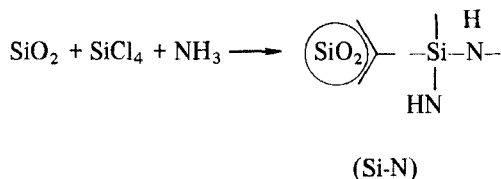
A new inorganic polymer-platinum complex, silica-supported polysilazane-platinum complex, has been prepared and found capable of catalyzing the oxygenation of both isopropanol to acetone and of ethanol to acetaldehyde in high yield (90%) at room temperature under atmospheric oxygen pressure. This inorganic polymer complex is very stable and can be reused several times without any appreciable change in catalytic activity.

INTRODUCTION

Acetone is manufactured by oxygenation of isopropanol in the presence of copper at high temperature (300°C). When a sulfonated polystyrene-cobalt complex is used as catalyst, isopropanol can be oxygenated at 50°C, but the yield of acetone is only 5-6% [1]. The manufacture of acetaldehyde by oxygenation of ethanol catalyzed by silver also requires a high temperature (500°C). When the phenanthroline-Cu complex is used as catalyst, a large amount of acetic acid is produced as a by-product and the reaction stops spontaneously unless the acetic acid is neutralized by alkali at the proper time [2]. $(\text{Cu}(4,4'\text{-Me}_2\text{-bpy})_2)\text{Cl}$ or $(\text{Cu}(\text{bpy})_2)\text{Cl}$ can also catalyze the oxygenation of

ethanol to acetaldehyde at 15°C. However, these complexes are very unstable and lose their catalytic activity after 10 h [3].

We recently prepared a new inorganic polymer-platinum complex, silica-supported polysilazane-platinum complex (abbreviated Si-N-Pt), by the following procedure:



We used it as the catalyst for the oxygenation of isopropanol to acetone and of ethanol to acetaldehyde at room temperature and under 1 atm of oxygen pressure. The experimental results showed that Si-N-Pt is an extremely active, selective, and stable catalyst for these reactions.

EXPERIMENTAL

Preparation of Silica-Supported Polysilazane (Si-N)

Petroleum ether (200 mL), 10 g of silicon tetrachloride, and 10 g fumed silica (surface area, 370 m²/g) were placed in a flask equipped with a stirrer, a gas inlet tube, and a gas outlet tube. The mixture was stirred and then ammonia was passed into the flask for about 6 h until the product became alkaline. This is an exothermic reaction, so the flask must be cooled by a water bath during the reaction. The product was filtered and dried, then heated at 400-500°C in a furnace to sublime the by-product ammonium chloride. The final product, silica-supported polysilazane (Si-N), is a fine white powder; its nitrogen content is 8.0 wt% (determined by elementary analysis).

TABLE 1. XPS Data for Si-N-Pt, Si-N, and H₂PtCl₆

XPS peak	Binding energy, eV		
	Si-N-Pt	Si-N	H ₂ PtCl ₆
Pt _{4f} 7/4	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

Preparation of Silica-Supported Polysilazane-Platinum Complex (Si-N-Pt)

Several samples of Si-N-Pt with different N/Pt gram-atomic ratio were prepared. For example, 0.026 g (0.05 mmol) of H₂PtCl₆ · 6H₂O, 0.21 g (0.2 mg atom N) of Si-N and 16 mL of ethanol were placed in a three-necked 50-mL flask equipped with a stirrer, a reflux condenser, and a gas inlet tube. The mixture was refluxed under nitrogen for 6 h. The white solid particles became black, and the pale yellow solution became colorless and transparent during the reaction. The product was filtered, then dried at 100°C. The final product, silica-supported polysilazane-platinum complex (Si-N-Pt), is a fine grey powder. The gram atomic ratio of N/Pt is 4 (calculated from the amounts of Si-N-Pt and H₂PtCl₆ · 6H₂O used). The complex was characterized by XPS.

Table 1 shows the XPS data for Si-N-Pt, Si-N, and H₂PtCl₆. 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 H₂PtCl₆. However, the difference of N_{1s} binding energies between Si-N-Pt and Si-N is 1.5 eV, and the difference of Pt_{4f} 7/2 binding energies between Si-N-Pt and H₂PtCl₆ is 3.1 eV. These results show that coordination bonds are formed between the nitrogen atoms and a platinum atom in the complex.

Oxygenation of Isopropanol and Ethanol

Si-N-Pt (Pt, 0.05 mg atom), water (5 mL), and isopropanol or ethanol (0.005 mol) were placed in a glass reactor with a gas inlet tube, a gas outlet

tube, and a jacket. The reactor was fixed on a shaker and connected to a gas burette and an oxygen storage bottle. Constant-temperature water was passed through the jacket from a water bath. The system was alternately evacuated and flushed with oxygen five times, and oxygen pressure was set at about 1 atm. The reaction mixture was shaken, then the volume of oxygen absorbed was measured. The reaction products were analyzed by gas chromatography.

RESULTS AND DISCUSSION

Figure 1 shows the relationship between the rate of oxygenation of isopropanol and the N/Pt gram atomic ratio in Si-N-Pt at room temperature and under atmospheric pressure. It can be seen that the catalytic activity is greatly affected by the N/Pt gram atomic ratio in the complex. An optimum rate appears at an N/Pt ratio of about 4.

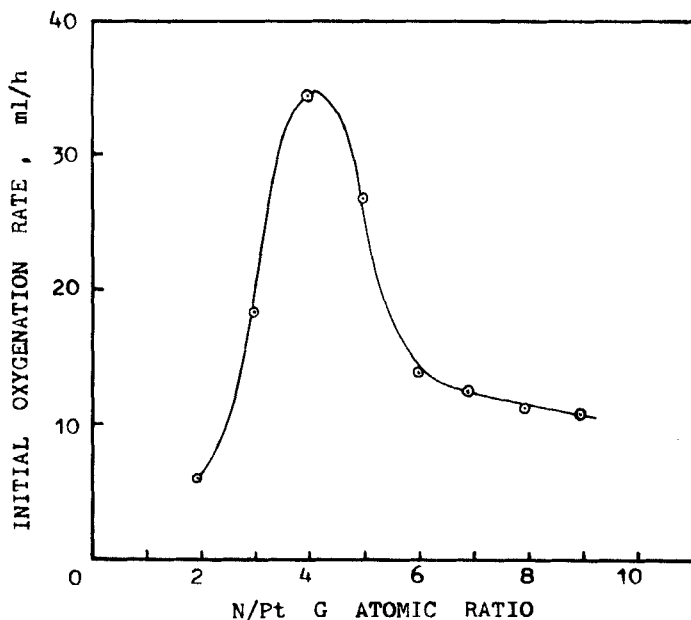


FIG. 1. Relationship between the rate of hydrogenation of isopropanol and the N/Pt gram atomic ratio in Si-N-Pt. Si-N-Pt: Pt, 0.05 mg atom; N/Pt, 7; isopropanol, 0.005 mol; water, 5 mL; 25°C; 1 atm O₂.

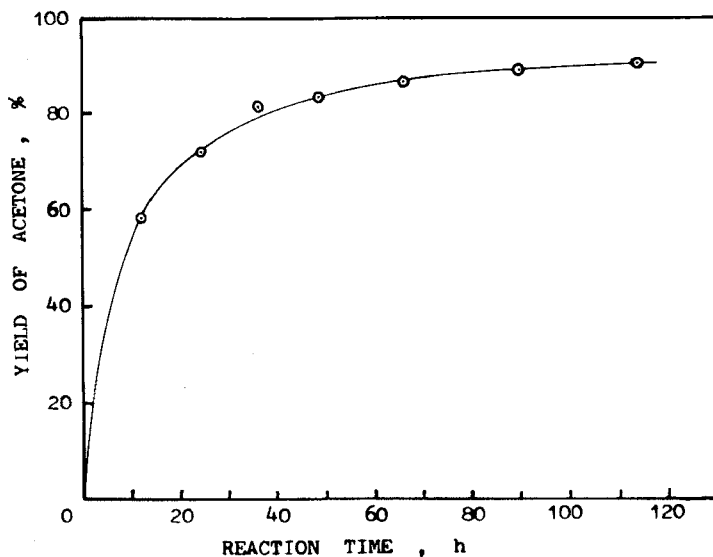


FIG. 2. Relationship between the reaction time and the yield of acetone in the oxygenation of isopropanol. Si-N-Pt: Pt, 0.05 mg atom; N/Pt, 7; isopropanol, 0.005 mol; water, 5 mL; 25°C; 1 atm O₂.

The relationship between the reaction time and the yield of acetone in the oxygenation of isopropanol is shown in Fig. 2. Although the reaction was not carried out very rapidly, isopropanol was converted to acetone in about 90% yield, and no by-product was obtained other than water.

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

It is well known that the Si-N bond of low molecular weight organosilazanes such as hexamethylsilazane is easily hydrolyzed [4]. However, the polymer ligand of Si-N-Pt is a highly crosslinked polysilazane, and it is very stable even in the boiling water. There are many polymer-metal complexes that have been used as catalysts for various reactions [5], but the polymer ligands are organic, so they are susceptible to oxidation during the oxygenation process. On the other hand, the inorganic polymer ligand, Si-N, is very stable under this condition, which may be related to the stability of the Si-N-Pt group in the oxygenation process.

TABLE 2. Stability of Si-N-Pt in the Oxygenation of Propanol^a

Number of times used previously	Yield of acetone, %
0	90
1	92
2	96
3	90
4	92

^aSi-N-Pt: Pt, 0.05 mg atom; N/Pt, 4; isopropanol, 0.005 mol; water, 5 mL; 25°C, 1 atm O₂.

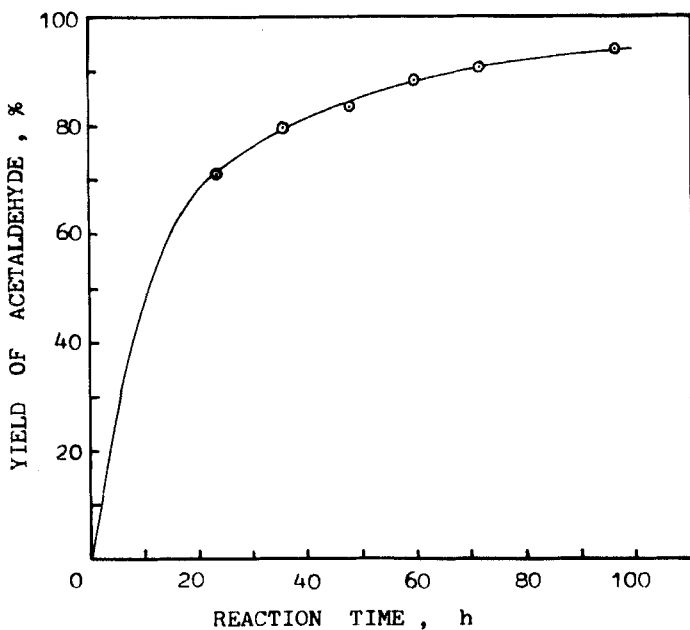


FIG. 3. Relationship between the reaction time and the yield of acetaldehyde in the oxygenation of ethanol. Si-N-Pt: Pt, 0.05 mg atom; N/Pt, 7; ethanol, 0.005 mol; water, 5 mL; 25°C; 1 atm O₂.

Figure 3 shows that, in the oxygenation of ethanol at room temperature and atmospheric oxygen pressure, the yield also amount to about 90%, while no acetic acid was obtained. This example also shows that Si-N-Pt is not only a active but also a selective catalyst for the oxygenation of alcohols, and it is very stable in the oxygenation of ethanol.

In general, the polymer ligand in the polymer-metal complex catalyst is organic, and its donor atom, such as nitrogen [6], sulfur [7], or phosphorus [8], is connected to a carbon atom in the organic group, while in the case of Si-N-Pt, the donor atom is connected to a Si atom. This example suggests that a new series of inorganic polymer-metal complexes may be prepared and used as effective catalysts for various kinds of reactions in the near future.

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