

A STUDY OF SILICA-SUPPORTED CROSS-LINKED POLY(MALEIC ACID- CO-STYRENE)-PLATINUM COMPLEX IN THE HYDROGENATION OF *p*-CRESOL

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ABSTRACT

A silica-supported cross-linked poly(maleic acid-co-styrene)-platinum complex (PMS-Pt) has been prepared and found to be active in the hydrogenation of *p*-cresol under mild conditions (303–323K, 1.01×10^5 Pa). In this hydrogenation system water serves as a solvent and *p*-cresol can be converted to 4-methylcyclohexanol quantitatively via 4-methylcyclohexanone as intermediate.

INTRODUCTION

The catalytic hydrogenation of alkylphenols is of interest not only because of the commercial use of this reaction^[1], but also in the respect of the research related to catalytic activity and reaction mechanism. The reactivity of alkylphenols is lower than that of phenol in the catalytic hydrogenation, which is attributed to an electronic effect on the aromatic ring related to the addition of alkyl substituents^[2].

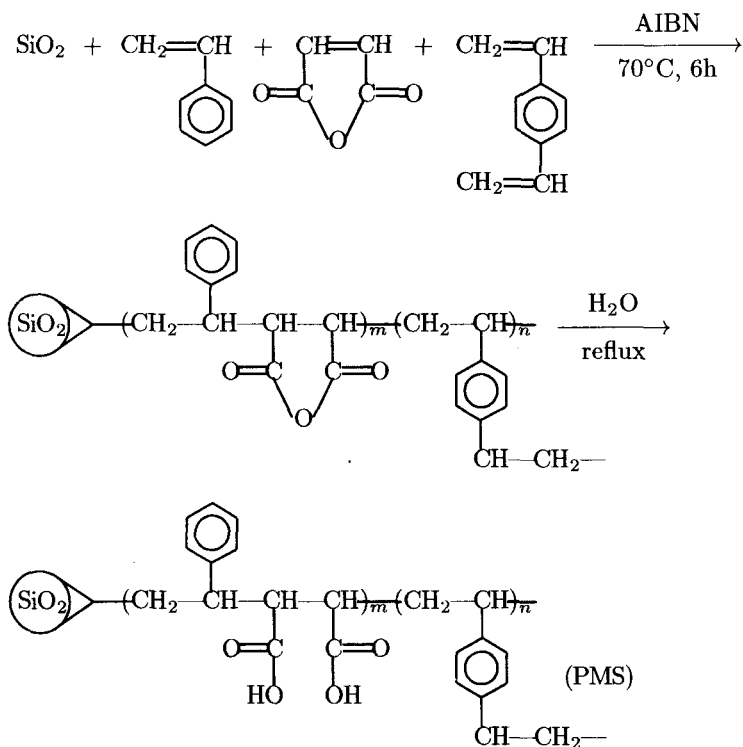
In the previous papers^[3,4], it has been shown that the hydrogenation of phenol can be catalyzed by starch-poly- γ -aminopropylsiloxane (ST-NH₂-Pt) and silica-supported polytitazane-platinum complex (Ti-N-Pt) at room temperature under atmospheric pressure to give cyclohexanol in 100% yield. Recently, a silica-supported cross-linked poly(maleic acid-co-styrene)-platinum complex (PMS-Pt) was prepared and found to be a very active catalyst for the hydrogenation of *p*-cresol under mild conditions (303–323K, 11.01×10^5 Pa). In this hydrogenation system water serves as a solvent and *p*-cresol can be converted to 4-methylcyclohexanol quantitatively via 4-methylcyclohexanone as an intermediate.

EXPERIMENTAL

1. Preparation of silica-supported cross-linked poly(maleic acid-co-styrene) (PMS)

10.4 g (0.1 mol) maleic anhydride, 9.8 g (0.1 mol) styrene, 5.0 mmol divinylbenzene and 180 ml benzene were placed in a flask with a mechanical stirrer, thermometer and reflux condenser. After resolution of maleic anhydride, 12.0 g silica gel and 2, 2'-azoisobutyronitrile (AIBN) (0.35 mmol) were added, and the copolymerization was carried out at 343K for 6 h. The copolymer was obtained as a white powder. This white powder product was hydrolyzed with water at refluxing temperature for 5 h. to obtain silica-supported cross-linked poly(maleic acid -co-styrene) (PMS) was obtained.

Synthetic routes for PMS are shown in Scheme 1.



Scheme 1 Synthesis of silica-supported cross-linked poly(maleic acid -co-styrene)

2. Preparation of PMS-Pt complex

A typical example is given for the preparation of a PMS-Pt catalysts with mole ratio of $\text{COOH}/\text{Pt} = 10$. Under nitrogen atmosphere, 0.47 g of PMS (carboxylic group content, 2.56 mmol/g), 0.12 mmol of chloroplatinic acid and 10 ml of ethanol were added to a reaction flask with a magnetic stirrer and a reflux condenser. The

reaction mixture was stirred and heated to reflux for 12 h. After filtration, the powder-like grey polymer metal complex was washed with ethanol and dried at 393K.

3. Hydrogenation of *p*-cresol

The hydrogenation reaction was carried out under atmospheric pressure in a reaction flask connected to a hydrogen burette. The hydrogenation reaction system was alternatively evacuated and flushed with hydrogen for several times. Then, the volume of hydrogen absorbed was measured. In order to investigate the pH effects on the course of the hydrogenation, hydrochloric acid or sodium hydroxide were added to the solvent to obtain the acidic or alkaline solution, respectively.

4. Measurements

FTIR spectra were recorded on a BRUKER IFS 113V FTIR spectrophotometer at 2 cm^{-1} resolution in the range of $4000\text{--}200\text{ cm}^{-1}$ on KBr pellets. The X-ray photoelectron spectroscopy (XPS) data were recorded on the PHI 5300 ESCA system (Perkin-Elmer) using an aluminium cathode (1486.65 eV) as the X-ray source, and the system energy calibration is based on the binding energy of adventitious carbon (284.6 eV). A hydrogen flame gas chromatograph (Shanghai 103) was used with a 2.0-m steel column of Silicone SE-30 on silica (80—100 mesh) for quantitative analysis. The products was identified in comparison with authentic samples.

RESULTS AND DISCUSSION

The polymer-supported platinum complex and the PMS support have been analyzed by FT-IR. Coordination of the carboxylic acid group to platinum is characterized by an increase in the CO stretching frequency. For the platinum complexes formed here, such a shift is clearly seen. The FT-IR spectrum of PMS had broad absorption at 1712 cm^{-1} (carboxylic acid groups). In the FT-IR spectrum of PMS-Pt, the absorption peak of carboxylic acid groups shifted from 1712 cm^{-1} to 1721 cm^{-1} because of coordination with platinum (COOH--Pt). Sherrington et al.^[5] characterized the polymer-supported Pd(II) Wacker-type catalysts by IR spectroscopy. They found that the $\text{C}\equiv\text{N}$ vibration band shifts to higher frequency for the coordination of $\text{RC}\equiv\text{N}$ to Palladium(II).

Meanwhile, the broad --OH absorption weakened and band near 1550 cm^{-1} due to symmetrical vibrations of the COO^- grouping^[6] did not appear in the FT-IR spectrum of PMS-Pt. These IR results are indicative of carboxylic acid group being involved in the coordination reaction. Although the true environment of the metal species is not clearly known, because of the random nature of the copolymers it can

be expected that a number of different species will be present, viz. some with single carboxylic group ligand and some with two ligands to each platinum center. Similar IR result was obtained by Manzi and coworkers in characterizing a polymer bound palladium acetate catalyst^[7].

Table 1 shows the X-ray photoelectron spectroscopy (XPS) data for PMS, PMS-Pt and chloroplatinic acid. It can be seen that the binding energies of C_{1s} and Si_{2p} in PMS-Pt are similar to those in PMS. However, the difference in binding energy of O_{1s} between PMS and PMS-Pt is about 1.6 eV. The difference in binding energy of Pt_{4f_{7/2}} between PMS-Pt and chloroplatinic acid is about 1.4 eV. These results show that coordinate bonds are formed between platinum atoms and oxygen atoms in the complex, in good accordance with the results of FT-IR analyses.

On the basis of XPS measurements, the binding energy of Pt_{4f_{7/2}} in PMS-Pt is higher than that of Pt(0) (71.0 eV) but lower than that of Pt(IV) (75.3 eV).[†] This indicates the platinum is not in a single valence state, but split into three states (Pt(0), Pt(II) and Pt(IV)). The formation of low valent platinum species (Pt(0), Pt(II)) may be due to the reduction property of the solvent ethanol used in the preparation of the polymer-metal complex.

Table 1 XPS data for PMS, PMS-Pt and chloroplatinic acid

XPS peak	Binding energy (eV)		
	PMS	PMS-Pt	H ₂ PtCl ₆ · 6H ₂ O
C _{1s}	284.6	284.6	—
Si _{2p}	104.2	104.2	—
O _{1s}	531.0	532.6	—
Pt _{4f_{7/2}}	—	73.9	75.3

Fig. 1 shows the influence of COOH/Pt mole ratio in the complex on the initial hydrogenation rate. It can be seen that the mole ratio of COOH/Pt is of great importance for the complex in the hydrogenation of p-cresol. At the mole ratio COOH/Pt = 10/1, the complex, PMS-Pt, shows an optimum catalytic activity and the initial hydrogenation rate is about 0.62 ml/min. The variation of the ligand/metal ratio may alter the coordination unsaturation of the central metals. On the other hand, the variation may promote or abate the isolation of active sites in the polymer-metal complex, thus affecting the activity of the polymer-metal complex^[8].

The influence of reaction temperature on the catalytic activity of PMS-Pt in the hydrogenation of p-cresol was shown in Table 2. At the low temperatures of 293–313K, the initial hydrogenation rate and the p-cresol conversion increased very fast with increasing temperature. At 323K the rate reached its maximum of about

0.62 ml/min and the intermediate, 4-methylcyclohexanone, was also converted to the end product. At temperatures higher than 323K the initial hydrogenation rate decreased slightly. This may be due to the evaporation of solvent which can cause a little decrease of partial hydrogen pressure in the reaction flask. In addition, hydrogen availability is of great importance in catalytic hydrogenation^[9]. Influence of solvent on hydrogenation rate may be directly proportional to the solubility of hydrogen in the solvent. Especially, the consumption of hydrogen easily can exceed the rate at which hydrogen is supplied to the catalyst when noble metals are selected as hydrogenation catalysts^[10]. It should be noted that hydrogen solubility in water is relatively high and varies slightly in the temperature range of 303—333K^[11]. Therefore, water is a suitable solvent in the hydrogenation of p-cresol over PMS-Pt.

Table 2 Influence of reaction temperature on the catalytic activity of PMS-Pt in the hydrogenation of p-cresol^{a)}

Temperature (K)	Initial hydrogen uptake (ml/min)	Conversion (%)	Products yield (%) ^{b)}	
			4-ONE	4-OL
293	0.25	75	15.8	59.2
303	0.40	92	9.2	82.8
313	0.53	100	4.0	96.0
323	0.62	100	0	100
333	0.49	100	6.0	94.0

^{a)} Catalyst, PMS-Pt, COOH/Ph= 10, Pt, 0.05 mmol; substrate, p-cresol, 1 mmol; solvent, water, 5 ml; reaction time, 6h; 1.01×10^5 Pa.

^{b)} 4-ONE=4-methylcyclohexanone; 4-OL=4-methylcyclohexanol.

The concentration vs. reaction time plots for hydrogenation of p-cresol were given in Fig. 2. In the hydrogenation of p-cresol, most of the substrate is converted to 4-methylcyclohexanol and very little intermediate product is found in the product mixture. Increasing the reaction time causes the 4-methylcyclohexanone (4-ONE) yield to rise slowly reaching a maximum at 2.3 h; afterwards a continuous decrease is observed. 4-Methylcyclohexanol yield shows a continuous and fast rise during the first 3 h, thereafter it levels off. This behavior is consistent with a reaction mechanism going along a consecutive pathway, 4-methylcyclohexanone being the intermediate which will be rapidly converted to 4-methylcyclohexanol (4-OL) during the reaction. These results suggest that the p-cresol is relatively strongly adsorbed onto the catalyst surface where hydrogenation takes place to give 4-methylcyclohexanone as a intermediate. The intermediate has no enough time to desorb before it is converted to the end product.

The effects of pH on the course of the p-cresol hydrogenation over PMS-Pt were

listed in Table 3. The ratio of initial rates of hydrogenation of p-cresol in neutral, acid (pH=4) and basic (pH=10) solutions was 10 : 68 : 26. These factors suggest that catalytic activity of PMS-Pt is diminished in acidic or alkaline condition. At the same time, the product distribution is also affected by the pH of the media. A higher fraction of the ketone is produced from p-cresol in the acidic media. The polymer supported platinum complex is more favorable than platinum oxide in the hydrogenation of aromatic compounds. Platinum oxide must be prerduced and promoted by acidic additives, or else the catalytic activity will be very low^[12].

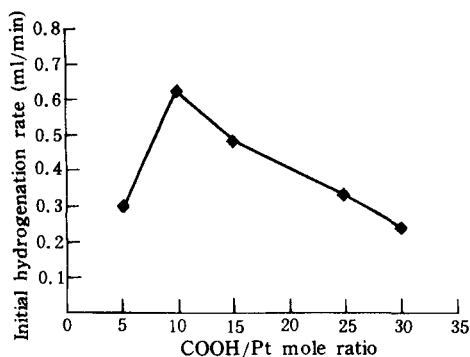


Fig.1 Influence of COOH/Pt mole ratio in PMS-Pt on the initial hydrogenation rate. Conditions: catalyst, PMS-Pt, Pt, 0.05 mmol; substrate, p-cresol, 1.0 mmol; solvent, water, 5 ml; 323K, 1.01×10^5 Pa

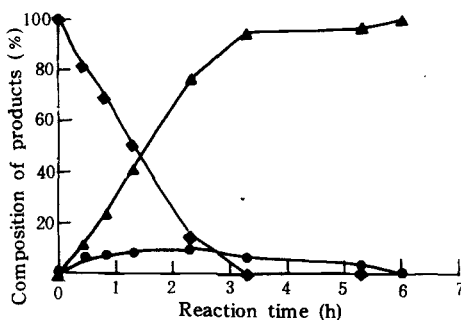


Fig.2 Product distribution vs. reaction time for hydrogenation of p-cresol over PMS-Pt: COOH/Pt= 10; Other conditions: the same as in Fig.1.

—●— p-cresol; —▲— 4-ONE; —◆— 4-OL

Table 3 Influence of pH value on the p-cresol hydrogenation over PMS-Pt ^{a)}

pH	Initial hydrogen uptake (ml/min)	Reaction time (h)	Conversion (%)	Products yield (%)	
				4-ONE	4-OL
1	0.37	5	100	7	93
4	0.42	3.5	100	6.3	93.7
7	0.62	3.3	100	5.4	94.6
10	0.16	6	68.2	6.6	61.6
13	0.1	16	16	0.5	15.5

^{a)} COOH/Pt=10; 323K, other conditions: the same as in Table 2

CONCLUSIONS

It has been found that silica-supported cross-linked poly(maleic acid-co-styrene)-

platinum complex is an active catalyst for *p*-cresol hydrogenation under mild conditions (323K, 1.01×10^5 Pa). The neutral solution is an optimum media for the complex. The ratio of initial rates hydrogenation of *p*-cresol in neutral, acid (pH=4) and basic (pH=10) solutions was 100 : 68 : 26. Water is a suitable solvent in the catalytic hydrogenation of *p*-cresol.

Keywords:

Hydrogenation; *p*-Cresol; Poly(maleic acid -co-styrene); Si-supported Pt complex

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