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Chun-Wei Chen[a]; Hong Yu[a]; Mei-Yu Huang[a]; Ying-Yan Jiang[a]
[a] Institute of Chemistry, Academia Sinica, Beijing, China

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MACROMOLECULAR REPORTS, A32(SUPPL. 7), 1039–1051 (1995)

CATALYTIC HYDROGENATION OF ISOMERIC CRESOLS OVER A SILICA-SUPPORTED CROSS-LINKED POLY[(MALEIC ACID)-CO-STYRENE]-PLATINUM COMPLEX

Chun-Wei CHEN*, Hong YU, Mei-Yu HUANG, & Ying-Yan JIANG
Institute of Chemistry, Academia Sinica, Beijing, 100080, China

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ABSTRACT

A silica-supported cross-linked poly[(maleic acid)-co-styrene]-platinum complex (PMS-Pt) has been prepared and characterized by means of FT-IR and XPS. It was found to be an active and stable catalyst in the hydrogenation of isomeric cresols in the temperature of 30-50°C and at atmospheric pressure. The effects of various reaction parameters, such as COOH/Pt mole ratio in the complex, catalyst quantity, reaction temperature, solvents and additives etc., on the hydrogenation of cresols have been studied. It is suggested that methylcyclohexanones are formed as intermediates, and these will undergo further hydrogenation to give methylcyclohexanols.

Keywords: hydrogenation, cresol, cross-linked poly[(maleic acid)-co-styrene], platinum complex

INTRODUCTION

Alkylated cyclohexanols are easily produced by catalytic hydrogenation of the parent phenols. Some of these cyclohexanols like menthol and 2- and 4-tert-

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butylcyclohexanol are important intermediates for the fragrance and perfume industry [1]. Thus, the hydrogenation studies of cresols will provide improvements in these processes.

In comparison with the reactivity of phenol, that of alkylphenols is decreased for the electronic effect on the aromatic rings related to the addition of alkyl substituents. Schumann et al.[2] reported the kinetic study of nickel-catalyzed gas-phase hydrogenation of o-cresol in the temperature range 150°C-240°C and at atmospheric pressure. In our previous papers,[3,4] the hydrogenation of phenol can be catalyzed by starch-poly-γ-aminopropylsiloxane (ST-NH_2-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 an active and stable catalyst in the hydrogenation of three isomeric cresols under mild conditions (30-50°C, 1 atm). Comparative studies on the hydrogenation of three isomeric cresols were conducted in this paper. Isomeric cresols can be converted quantitatively to methylcyclohexanols, via related methylcyclohexanones as intermediates. In order to optimize the reaction, the influence of various reaction parameters on hydrogenation of cresols over PMS-Pt has been studied.

EXPERIMENTAL

Materials and measurements

All reagents and solvents were AR grade. Chloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$) is supplied by Beijing Chemicals Co. Styrene and divinylbenzene were distilled under reduced pressure and 2, 2'-azo-isobutyronitrile (AIBN) was purified by recrystallization prior to use, while other reagents and solvents were used as purchased.

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The FT-IR spectra were recorded on a BRUKER IFS 113V FT-IR spectrophotometer at 2 cm^{-1} resolution in the range of 4000-200 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 (1486.6 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 Model 103) was used with a 2.0-m steel column of Silicone SE-30 on silica (80-100 mesh) for quantitative analysis. The products were identified in comparison with authentic samples.

General procedure for hydrogenation of cresols

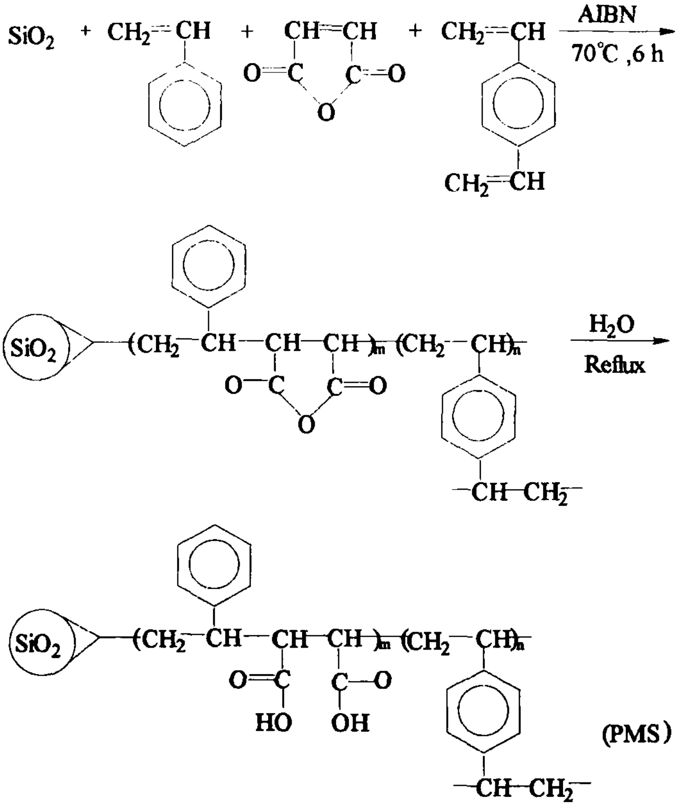
The hydrogenation reaction was carried out under atmospheric pressure of hydrogen in a reaction flask connected to an hydrogen burette. For example, p-cresol (1 mmol), PMS-Pt catalyst (Pt content, 0.05 mmol) and solvent (5 mL) were added into 50-mL round-bottom flask with a magnetic stirrer. The reaction was monitored according to the uptake of hydrogen. The reaction products were detected by GC using small aliquots of reaction liquid withdrawn with a syringe at regular intervals.

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 500-mL flask with a mechanical stirrer, thermometer and reflux condenser. After resolution of maleic anhydride, 12.0 g silica gel (specific surface area: 90 m^2/g) and 2, 2'-azo-isobutyronitrile (AIBN) (0.35 mmol) were added, and the copolymerization was carried out at 70°C for 6 h. The copolymer was deposited onto the surface of silica. After filtration, a white solid was obtained; it was hydrolyzed with water at refluxing temperature for 5 h. Silica-supported cross-linked poly[(maleic acid)-co-styrene] (PMS) was obtained and its carboxylic acid group (COOH) content was 2.56 mmol/g, which was determined by acid-base titration. Synthetic routes for PMS are shown in the following scheme.

Preparation of PMS-Pt complex

Several PMS-Pt complexes with different mole ratios of COOH/Pt were prepared from PMS and chloroplatinic acid in ethanol. A typical example is given for the preparation of a PMS-Pt catalyst with mole ratio of COOH/Pt = 10.



Scheme. Synthesis of silica-supported cross-linked poly[(maleic acid)-co-styrene]

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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 120 °C. The PMS-Pt complex was characterized by FT-IR and XPS.

RESULTS AND DISCUSSION

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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. Meanwhile, the broad -OH absorption weakened and band near 1550 cm^{-1} due to symmetrical vibrations of the COO^- grouping [5] 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. Similar IR result was obtained by Manzi and coworkers in charaterizing a polymer bound palladium acetate catalyst[6].

Table 1 summarizes 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. There is distinct difference in the $Pt_{4f7/2}$ binding energy between polymer-supported platinum catalyst and chloroplatinic acid. The value in PMS-Pt is 1.4 eV lower than that in chloroplatinic acid. 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.

TABLE 1

XPS data for PMS, PMS-Pt and chloroplatinic acid

XPS peak	Binding energy (eV)		
	PMS	PMS-Pt	$H_2PtCl_6 \cdot 6H_2O$
Si_{2P}	104.2	104.2	-
C_{1S}	284.6	284.6	-
O_{1S}	531.0	532.6	-
$Pt_{4f7/2}$	-	73.9	75.3
Cl_{2P}	-	199.5	199.4

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On the basis of XPS measurements, the binding energy of $Pt_{4f7/2}$ 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.

These differences in the hydrogenation of cresols are illustrated by the experimental results listed in Table 2. The initial rate of hydrogenation of cresols depends on the relative position of the methyl and hydroxy substituents. The rate decreases in the following order: m-cresol > p-cresol > o-cresol. This trend is attributed to the differences in the electron densities of the aromatic ring related to the relative position of the substituents. The methyl and the hydroxy groups are conjugated in the o- and p-cresols, whereas they are not in the m-cresol. The steric hindrance may be responsible for the consistently low rate for o-cresol. A similar reactivity trend was obtained by Samchenko et al [7] when they studied catalytic hydrogenation of alkylphenols over a nickel-chromium catalyst. At the same time, maximum ketone yield also has some relationship with the relative position of the substituents. According to the experimental data, the maximum ketone yield drops in the series m-cresol > o-cresol > p-cresol.

TABLE 2
Hydrogenation of three isomeric cresols over PMS-Pt.[a]

Substrate	Initial hydrogenation rate (mL/min)	Conversion (%)	Max. ketone yield (%)
m-cresol	1.26	100	49.6
p-cresol	1.09	97.2	36.0
o-cresol	0.89	88.5	40.6

[a] Catalyst, PMS-Pt, COOH/Pt = 10, Pt, 0.05 mmol; substrate, 1mmol; solvent, cyclohexane, 5 mL; 50°C; 6 h; 1 atm.

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The mole ratio of COOH/Pt is of great importance for the complex as is shown in Figure 1. It can be seen that the catalytic activity is greatly affected by mole ratio of COOH/Pt in the complex. At the mole ratio COOH/Pt=10, a maximum hydrogenation rate was observed. The coordinative unsaturation of central metal atom in the polymer metal complex may be destroyed at too high COOH/Pt ratios. On the other hand, the alteration of ligand/metal ratio results in an promotion or abatement of the isolation of active sites in catalyst [8]. Therefore, the alternation in COOH/Pt mole ratio will affect the catalytic activity of PMS-Pt catalyst. We have also studied the catalytic activity of chloroplatinic acid and the support PMS without complexation with platinum, respectively. The support is inactive in the hydrogenation of cresol under the same conditions as in Figure 1. The activity of chloroplatinic acid is very low in the hydrogenation. Moreover, the activity of the metallic precursor supported only on silica is also very low. These results indicate that high activity of PMS-Pt results from its platinum complex and the organic polymeric matrix deposited on the silica gel plays an important role in activating the complex.

Figure 2 shows the diagram for product distributions vs. the reaction time in p-cresol hydrogenation over PMS-Pt. The concentration of p-cresol shows a fast and continuous decrease in the course of hydrogenation, which indicates the high

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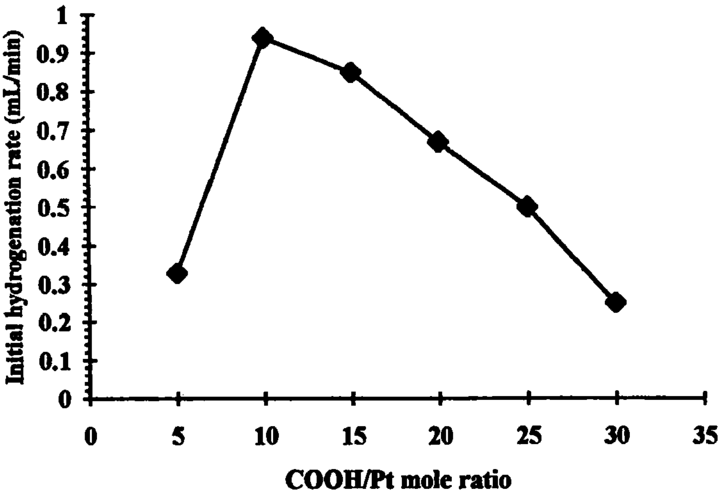


Fig. 1 Influence of COOH/Pt mole ratio in the complex on initial hydrogenation rate .Catalyst: PMS-Pt, Pt, 0.05 mmol; substrate, p-cresol, 1 mmol; solvent, cyclohexane, 5 mL; 30°C, 1 atm.

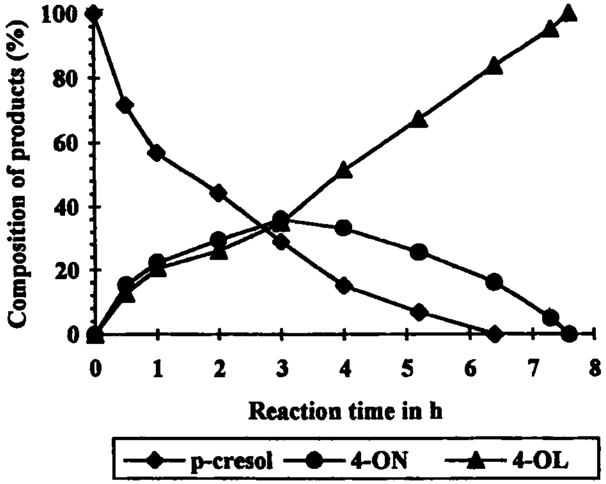
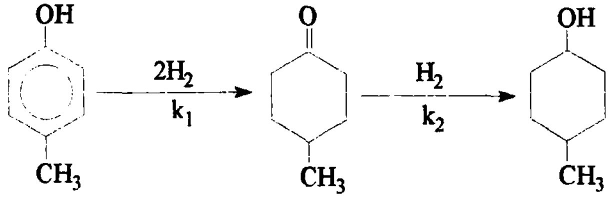


Fig. 2 Product distributions vs reaction time for hydrogenation of p-cresol over PMS-Pt: COOH/Pt=10; 50°C; Other conditions: same as in Figure 1. 4-ON = 4-methylcyclohexanone; 4-OL = 4-methylcyclohexanol.

activity of PMS-Pt catalyst. The substrate can be converted to 4-methylcyclohexanol quantitatively in 7.8 h. The concentration of 4-methylcyclohexanone rises to a maximum at about 3 h; afterwards it shows a continuous decrease. This behavior is consistent with a reaction mechanism going along a consecutive pathway, 4-methylcylohexanone being the intermediate which reacts with an additional mole of hydrogen to give a 4-methylcyclohexanol:



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Also the influence of the catalyst quantity on hydrogenation of p-cresol was investigated. The experimental results are shown in Table 3. The initial hydrogenation rate shows a fast increase as a result of increasing catalyst quantity. The substrate can be converted quantitatively in each case although the time for completing the reaction will increase with decreasing catalyst quantity. At a small catalyst quantity (large reactant/catalyst ratio), more 4-methylcyclohexanone may be desorbed from the catalyst surface and higher ketone yield is observed. At a high quantity, however, most of 4-methylcyclohexanone molecules may undergo further hydrogenation to give the end product without desorbing into the reaction mixture where they would compete with the unreacted p-cresol for adsorption. The maximum ketone yield is relative low in this case.

The influence of reaction temperature on the hydrogenation of p-cresol over PMS-Pt was listed in Table 4. At low temperature of 20-40°C, the initial hydrogenation rate increases with increasing temperature. At 50°C the rate reaches a maximum of about 1.09 mL/min and the conversion of p-cresol is

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TABLE 3

Hydrogenation of p-cresol at different substrate/catalyst ratios[a]

Pt in mmol	Ratio of substrate/catalyst	Initial hydrogenation rate (mL/min)	Conversion (%)	Max. ketone yield (%)
0.02	50.0	0.41	36.0	43.1
0.03	33.3	0.48	43.0	42.8
0.04	25.0	0.91	80.7	39.1
0.05	20.0	1.09	97.2	36.0
0.06	16.7	1.12	100	34.7

[a] COOH/Pt=10; 50°C; 6h; Other conditions: same as in Figure 1.

TABLE 4

Influence of reaction temperature on the catalytic activity of PMS-Pt in the hydrogenation of p-cresol[a]

Temperature (°C)	Initial hydrogenation rate (mL/min)	Conversion[b] (%)	Products yield (%)[c]	
			4-ON	4-OL
20	0.53	46.3	9.3	14.7
40	1.03	92.1	13.1	10.9
50	1.09	97.2	14.3	9.7
60	1.07	95.4	15.0	9.0
70	0.95	87.5	17.7	6.3

[a] Catalyst, PMS-Pt, COOH/Pt = 10, Pt, 0.05 mmol; substrate, p-cresol, 1 mmol; solvent, cyclohexane, 5 mL; 1 atm.

[b] Reaction time, 6 h.

[c] The yields were obtained at p-cresol conversion of 24%.
4-ON= 4-methylcyclohexanone; 4-OL= 4-methylcyclohexanol.

97.2% in 6 h. At temperatures higher than 60°C distinct decreases in rate and conversion of p-cresol were observed. The evaporation of solvent will result in a decrease of partial pressure of hydrogen in the reaction flask, which may be responsible for the low hydrogenation rate. The yield of 4-methylcyclohexanone at the same p-cresol conversion of 24% increases with increasing temperature, namely the hydrogenation of p-cresol is much more sensitive to temperature than that of ketone intermediate.

The solvent is an importance factor that can be varied in order to control the activity and selectivity of polymer-supported hydrogenation catalysts. The solvent effects on the activity of PMS-Pt in the hydrogenation of p-cresol were shown in Table 5. The initial hydrogenation rate is very low in chloroform or THF. When the reaction is run in a cyclohexane solvent, the rate is the highest and the p-cresol conversion reaches 86% in 6 h. However, the catalytic activity in a alcohol solvent is relative low. On the one hand, changes of solvent will promote or abate the active site isolation for their different ability to swell the support, silica-supported cross-linked poly[(maleic acid)-co-styrene]. The polarity of the solvent, on the other hand, will lead to a polarity gradient through which the substrate must diffuse on going from the bulk solvent to the catalytic site. The polarity gradient can be altered by suitable adjusting the polarity of the solvent so as to decrease diffusional restrictions [9]. Therefore nonpolar cyclohexane is the optimum solvent for the hydrogenation of p-cresol over PMS-Pt. In addition, the acidic additive, HAc, is not favorable for the hydrogenation reaction. The catalyst is very stable in neutral solution and can be recycled more than three times without noticeable decrease of its activity in the hydrogenation of cresols.

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CONCLUSIONS

The present study has proved that silica-supported cross-linked poly[(maleic acid)-co-styrene]-platinum complex is an active and stable catalyst for the hydrogenation of isomeric cresols under mild conditions (30-50°C, 1 atm). Coordinate bonds has been formed between oxygen and platinum atoms in the complex according to FT-IR and XPS measurements. Cresols can be converted

TABLE 5

Influence of solvents on the hydrogenation of p-cresol over PMS-Pt[a)]

Solvent	Dielectric constant	Initial hydrogenation rate (mL/min)	Absorption of H_2 (mL)	Conversion of p-cresol (%)
Methanol	32.7	0.61	30.5	25
Ethanol	24.6	0.78	34.6	33.3
Isopropanol	19.9	0.46	17.3	21.9
THF	7.6	0.06	/	trace
Chloroform	4.8	0.23	4.3	4.6
Cyclohexane	2.0	0.94	60.2	86
Cyclohexane[b)]	2.0	0.52	19.1	24.2

[a)] COOH/Pt = 10; 6 h ; Other conditions: same as in Figure 1.

[b)] Additive: HAc, 0.5 mmol.

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quantitatively to methylcyclohexanols, via related methylcyclohexanones as intermediates. Reaction parameters, such as COOH/Pt mole ratio in the complex, temperature, catalyst concentration and solvent etc., have great effects on the catalytic hydrogenation of cresols over PMS-Pt.

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