

SYNTHESIS AND CHARACTERIZATION OF A SILICA-SUPPORTED CARBOXYMETHYLCELLULOSE PLATINUM COMPLEX AND ITS CATALYTIC BEHAVIORS FOR HYDROGENATION OF AROMATICS

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ABSTRACT

A silica-supported carboxymethylcellulose platinum complex (abbreviated as SiO₂-CMC-Pt) has been prepared and characterized by XPS. Its catalytic properties for hydrogenation of aromatic compounds were studied. The results showed that this catalyst could catalyze the hydrogenation of phenol, anisol, p-cresol, benzene and toluene to cyclohexanol, cyclohexyl methyl ether, p-methyl cyclohexanol, cyclohexane and methylcyclohexane, respectively in 100% yield at 30°C and 1 atm. In the hydrogenation of phenol, COO/Pt ratio in SiO₂-CMC-Pt has much influence on the initial hydrogenation rate and the selectivity for the intermediate product, cyclohexanone. The highest initial rate and the highest yield of cyclohexanone both occur at COO/Pt ratio of 6. The complex is stable during the reaction and can be used repeatedly.

INTRODUCTION

Polymer-supported transition metal complex catalysts have attracted much attention over the past two decades. There are many excellent reviews^[1,2] and monographs^[3,4] concerning the advances and achievements in this field. In these works, synthetic polymers were mostly employed as ligands for metals. However, little information has been reported on the application of natural polymers, such as chitosan, cellulose and starch. It is well known that natural polymers have the advantages of cheapness, easily available and non-toxic over synthesized polymers. Their structures are quite similar to that of enzyme catalysts which show high activities and selectivities in organisms. These special properties may render natural

polymers as a new kind of polymer ligands for transition metals. For example, silica-supported chitosan palladium complex could catalyze the hydrogenation of chloro-nitrobenzenes to chloro-anilines in 100% yield at 30°C and 1 atm pressure^[5].

Hydrogenation of aromatic compounds over homogeneous catalysts often proceeds under high temperature and high pressure and the catalysts are difficult to be recovered. These reactions have been accomplished at milder conditions when catalyzed by some synthetic polymer-supported catalysts, such as platinum complexes of silica-supported poly- γ -diphenylphosphinopropyl siloxane (Si-P-Pt)^[6], polyalumazane (Al-N-Pt)^[7] and starch-poly- γ -aminopropylsiloxane (ST-NH-Pt)^[8]. However, the use of natural polymer catalysts in catalyzing these reactions was rarely reported.

In this paper, a silica-supported carboxymethylcellulose platinum complex (SiO₂-CMC-Pt) has been prepared and used as catalyst for hydrogenation of aromatic compounds. The results showed that such catalyst is active, selective and stable for hydrogenation of aromatic compounds at much mild conditions.

EXPERIMENTAL

Preparation of silica-supported carboxymethylcellulose (abbr. as SiO₂-CMC)

15g carboxymethylcellulose sodium (supplied by Shanghai Chemical Reagent Co. with 6.5—8.5% content of Na and pH value 6.5—8.0) was placed in a flask containing 600ml water. After it was dissolved by stirring at 80°C, 30g precipitated silica was added to the solution, followed by 1000ml acetone. Carboxymethylcellulose sodium can be deposited on the surface of silica. The solid product was filtered out from the solution, dried and redissolved in 210ml of water. Acetic acid (containing small amount of HCl) was added to adjust the pH of solution to 2. After standing for 1 hour, SiO₂-CMC ligand was washed thoroughly with acetone until pH= 6, dried and powdered. The carbon content of the product was 11.2wt%, determined by elemental analysis.

Preparation of silica-supported carboxymethylcellulose-platinum complex (abbr. as SiO₂-CMC-Pt)

At a certain COO/Pt molar ratio, SiO₂-CMC ligand, H₂PtCl₆·6H₂O and ethanol were placed in a 25ml flask. The solution was refluxed for about 6h until the solution became transparent and colorless and the solid particle turned dark. After evaporation of the solvent, the complex SiO₂-CMC-Pt was dried and ready for use.

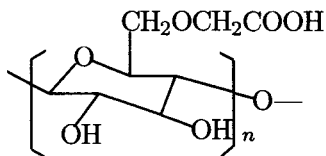
Hydrogenation reaction

The hydrogenation reaction was carried out under atmospheric pressure in a reactor connected with a hydrogen measuring tube and a hydrogen reservoir. The

hydrogenation reaction system was alternatively evacuated and purged with hydrogen for several times. Then, the volume of hydrogen absorbed was measured. After the completion of reaction, the catalyst was separated from the solution, the product was analyzed by using a gas chromatography.

RESULTS AND DISCUSSION

The natural polymer, carboxymethylcellulose (CMC) has the following structure:



When SiO₂-CMC ligands reacted with H₂PtCl₆ · 6H₂O, the carboxyl and hydroxyl groups of CMC may form coordination bonds with Pt atoms. SiO₂-CMC-Pt complex was characterized by X-ray photoelectron spectroscopy (XPS). The XPS data was shown in Table 1, it was found that the binding energy of O_{1s} in SiO₂-CMC-Pt is higher than that in SiO₂-CMC, and the binding energy of Pt_{3d5/2} in complex is less than that in H₂PtCl₆. The change of Cl_{2p} binding energy may be attributed to the presence of different coordinate states of Cl atoms in the complexing. However, the binding energies of other elements have little change before and after complex. These results indicate that coordination bonds may be formed between oxygen and platinum atoms in the complex.

Table 1 XPS data for SiO₂-CMC, SiO₂-CMC-Pt and H₂PtCl₆

Sample	Binding energies (eV)				
	O _{1s}	Pt _{3d5/2}	Cl _{2p}	C _{1s}	Si _{2p}
SiO ₂ -CMC	532.1	—	—	284.6	103.1
SiO ₂ -CMC-Pt	532.5	71.5	198.0	284.7	103.1
H ₂ PtCl ₆	—	73.8	199.1	—	—

Table 2 shows the atomic concentration of different elements in SiO₂-CMC and SiO₂-CMC-Pt determined by XPS. It was found that certain amount of sodium still existed in SiO₂-CMC when it was treated with HCl. The amount of Na in SiO₂-CMC was higher than that in SiO₂-CMC-Pt. It means that an exchange reaction between Na and Pt has taken place during the complexing reaction. So the complex was formed through the coordination between carboxyl groups and platinum atoms.

Table 2 The atomic concentration of different elements in SiO₂-CMC and SiO₂-CMC-Pt

Sample	Atomic concentration (%)				
	C	Si	O	Na	Pt
SiO ₂ -CMC	31.89	18.23	48.69	1.19	—
SiO ₂ -CMC-Pt	33.02	18.07	48.46	0.14	0.32

Table 3 Catalytic hydrogenation of some aromatic compounds with SiO₂-CMC-Pt

Run	Substrate	Reaction time (min)	Conversion (%)	Product	Yield (%)
1	phenol	264	100	cyclohexanol	100
2	anisol	560	100	cyclohexyl methyl ether	100
3	benzene	124	100	cyclohexane	100
4	toluene	237	100	methyl cyclohexane	100
5	p-cresol	312	100	p-methyl cyclohexanol	100
6	hydroquinone	642	100	cyclohexanol	100
7	p-chlorophenol	420	100	cyclohexanol	100

SiO₂-CMC-Pt 0.02 mmol Pt; COO/Pt ratio= 6; substrate 1 mmol; cyclohexane 10 ml;
30°C, 1 atm

SiO₂-CMC-Pt was used as a catalyst for the hydrogenation of some aromatic compounds at 30°C and 1 atm mild conditions. The results were shown in Table 3. It was found that SiO₂-CMC-Pt could catalyze the hydrogenation of phenol, anisol, p-cresol, benzene and toluene to cyclohexanol, cyclohexyl methyl ether, p-methylcyclohexanol, cyclohexane and methylcyclohexane in 100% yield without the formation of by-products. However, in the hydrogenation of hydroquinone and p-chlorophenol, both the products were cyclohexanol, apparently, hydrogenolysis took place in these two cases. It is worthy to mention that in catalyzing the hydrogenation of anisol, the yield of cyclohexyl methyl ether could be 100%. However, small amount of anisol would hydrogenolyse to cyclohexanol in the presence of Si-P-Pt^[8] or Al-N-Pt^[9]. From the above results, it was found that SiO₂-CMC-Pt is an active and selective catalyst for hydrogenation of aromatic compounds.

Hydrogenation of phenol catalyzed by SiO₂-CMC-Pt was studied in more detail. As seen in Fig. 1, the hydrogenation activity of SiO₂-CMC-Pt was much affected by the COO/Pt ratio, and the highest initial hydrogenation rate presented at COO/Pt

ratio of 6. Increasing or decreasing the COO/Pt ratios would deactivate the catalyst greatly.

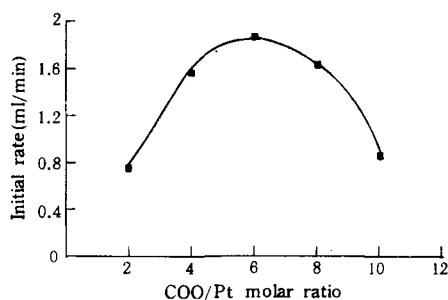


Fig. 1 Influence of COO/Pt ratio on the hydrogenation rate of phenol catalyzed by SiO₂-CMC-Pt.

SiO₂-CMC-Pt 0.02 mmol Pt; phenol 1 mmol; cyclohexane 10 ml; 30°C; 1 atm

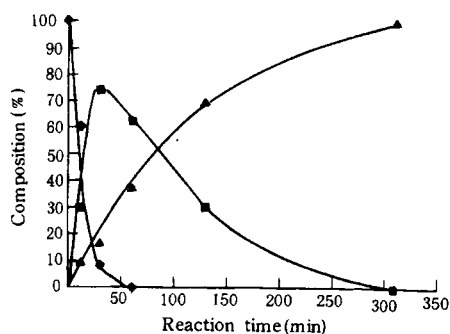
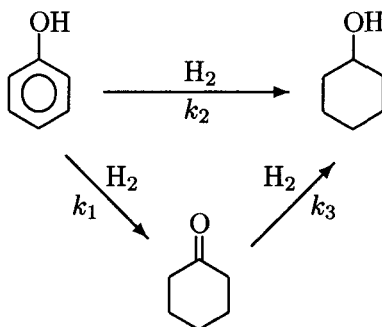


Fig. 2 Influence of reaction time on the composition in hydrogenation of phenol catalyzed by SiO₂-CMC-Pt.

SiO₂-CMC-Pt 0.02 mmol Pt;
COO/Pt ratio 6; phenol 1 mmol;
cyclohexane 10 ml; 30°C; 1 atm
● phenol; ■ cyclohexanone;
▲ cyclohexanol

The relationship between reaction time and the composition in the hydrogenation of phenol catalyzed by SiO₂-CMC-Pt at COO/Pt ratio of 6 is shown in Fig. 2.

It was easy to find that phenol could be hydrogenated both directly and indirectly, with cyclohexanone as intermediate product, to cyclohexanol. So the processing for hydrogenation of phenol could be written as follows:



Additionally, the hydrogenation rate for phenol to cyclohexanone (k_1) was found to be higher than that to cyclohexanol (k_2) in the initial 30 min, and the ratio of k_1/k_2 calculated from the slopes of the two curves in Fig. 2 is 3.5. A maximum yield of 74.1% was obtained at 30 min and thereafter, cyclohexanone would be slowly

converted to cyclohexanol with a final yield amounted to 100% at 308 min. However, if some less active catalysts were used, i.e., at COO/Pt ratio of 4 and 10, the ratio of k_1/k_2 would decrease to 3.0 and 2.2, and the highest yields of the intermediate product, cyclohexanone were 64.7% and 41.4%, respectively. So the higher the activity of the catalyst is, the more cyclohexanone would be produced during the hydrogenation of phenol. These results are of interesting from the industrial point of view because it may facilitate the synthesis of cyclohexanone directly through the hydrogenation of phenol at mild condition by using a carefully modified catalyst.

The complex also exhibits good stability in catalyzing hydrogenation reaction. As evidenced from Table 4, the catalytic activity and selectivity of SiO₂-CMC-Pt in hydrogenation of phenol showed little changed even after repeated use for four times.

Table 4 Recycling of SiO₂-CMC-Pt in hydrogenation of phenol

Recycle	Reaction time (min)	Conversion (%)	Product	Yield (%)
1	300	100	cyclohexanol	100
2	315	100	cyclohexanol	100
3	332	100	cyclohexanol	100
4	350	100	cyclohexanol	100

SiO₂-CMC-Pt 0.02 mmol; COO/Pt ratio 6; phenol 1 mmol for each experiment; cyclohexane 10ml; 30°C; 1 atm

Keywords:

Silica-supported carboxymethyl cellulose platinum complex; Hydrogenation; Aromatic compounds

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