

## Influence of Strong Electronegativity Groups -Cl as the Adsorption Center of PTA@MIL-101-NH<sub>2</sub>-Cl for the Selective Hydrolysis of Cellulose into Glucose

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**Abstract.** In this paper, the catalyst PTA@MIL-101-NH<sub>2</sub>-Cl with various 2, 5-dichloroterephthalic acid was synthesized. Based on this, the effect of the strong negative groups -Cl on the crystal structure, molecular structure and thermal stability of the catalyst was studied. It was found that the immobilization of -Cl did not affect the structure of the catalyst, and it can improve the thermal stability of the catalyst to a certain extent. The mechanism of -Cl as the cellulose adsorption center in the directional hydrolysis of cellulose were analyzed. The strong negative groups -Cl form hydrogen bonds with the hydroxyl of cellulose to selectively adsorb cellulose, weaken the molecular hydrogen bonds of cellulose molecules to reduce the difficulty of cellulose hydrolysis and improve its hydrolysis efficiency. The yield of glucose obtained by the hydrolysis of cellulose after grafting-Cl catalyst was 81% higher than that without -Cl.

### Introduction

Plant fiber is considered to have a broad development prospects of renewable biomass energy raw materials. Cellulose as the main component of plant fiber can be transformed into glucose and then be converted into produce fructose, 5-hydroxymethyl furfural, levulinic acid, as well as sorbitol, mannitol, ethylene glycol, including polyols and other important energy substances and basic platform compounds [1]. The hydrolysis of cellulose into glucose is the necessary reaction process in the process of cellulose conversion. Therefore, the transformation of cellulose into glucose is the key to cellulose utilization [2-4].

The solid phase cellulose catalyst is regarded as the development direction of the cellulose hydrolysis reaction system because of its easy separation, high reuse rate and low environmental pollution [5]. The solid phase cellulose catalyst currently studied can be divided into sulfonated solid acid, hydrogen type zeolite, metal oxide, supported metal, heterophony acid. Keggin-type heteropolyacids with superacid and "quasi-liquid" properties are novel solid acid catalysts developed for the hydrolysis of cellulose in recent years. The counter-cation H<sup>+</sup> of Keggin-type heteropoly completely dissociated in water, shows strong Brønsted acidity[6]. It is the key to promote the hydrolysis of cellulose glycosidic bonds. At the same time, after the dissociation of the counter-cation H<sup>+</sup>, the electronegativity of the outer oxygen atoms of the heteropoly anions increases, which can be adsorbed with hydrogen bonds of cellulose -OH to promote cellulose hydrolysis and reduce the occurrence of glucose degradation reactions caused by the contact of heteropoly acids with glucose [7]. Phosphotungstic Acid (H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>, PTA) is considered to be more suitable for cellulose-directed catalytic hydrolysis because of its highest acid strength and highest outer oxygen atom electronegativity [8-10]. But PTA completely dissolved in the cellulose hydrolysis system

completely dissolved, the separation and recovery operation is complex and the quality loss is high. Therefore, Supporting PTA to carriers is the development direction of solid catalyst. The carrier immobilized PTA to achieve PTA solidification, reduce the solubility of PTA in water[11].

Metal organic frameworks (MOFs) are formed by self-assembly through coordination bond between bidentate or multidentate organic ligand and central metal ion . Due to its high specific surface area, porosity, MOFs are considered to be perfect carrier for PTA immobilization[12,13]. In different types of MOFs, the pore size of MIL-101 (Material Institute Lavoisier, MIL) is 2.9 nm and 3.4 nm, and the pore structure can accommodate PTA with a pore size of 1.2 nm and 1.6 nm [14], which limits PTA. While avoiding the loss of PTA quality. Therefore, MIL-101 is considered a good carrier of PTA. PTA immobilization and MIL-101 synthesis at the same time is the central means to fix PTA. PTA is encapsulated in the MOFs pore structure during the coordination of metal ions with organic ligands to form a framework structure. (PTA @ MIL-101) [15-17]. PTA @ MIL-101 plays a good catalytic performance in desulfurization, denitrification and alcoholysis [18,19]. Wang synthesized PTA @ MIL-101-NH<sub>2</sub> that PTA is immobilized by the chemical bond of PTA and amino groups. It was used to catalyze the desulfurization of dibenzothiophene by hydrogen peroxide. The reaction rate of PTA was only 4% [20].

Our group has synthesized PTA @ MIL-101-NH<sub>2</sub>-Cl that strong negative groups -Cl were grafted into MIL-101[21]. It plays a very good role in the hydrolysis of cellulose. But the mechanism of the strong electronegative group -Cl improving the hydrolytic yield of cellulose has not been discussed.

This work discussed the effect of the grafting of strong electronegative groups -Cl on the crystal structure and Thermal Stability of the catalyst. the catalyst with different -Cl grafting amount was obtained by changing the amount of 2,5-dichloroterephthalic acid (TA-Cl) in the catalyst synthesis. The mechanism of directional hydrolysis of cellulose catalyzed by chlorine catalyst PTA @ MIL-101-NH<sub>2</sub>-Cl was analyzed from the viewpoint of the selective adsorption of cellulose.

## **Experimental**

### **Materials**

2-nitroterephthalic acid (TA-NH<sub>2</sub> , 98%), 2,5-dichloroterephthalic acid (TA-Cl, 98%) were purchased from Micxy Chemical Reagent Co.,Ltd.(Chengdu,China). Phosphotungstic acid (PTA, AR), FeCl<sub>3</sub>·6H<sub>2</sub>O (AR), N,N-dimethylformamide (DMF, AR), Avicel (AR) and other common chemicals and solvents used were all purchased from commercial sources and were analytical reagents. All the chemicals in this study were used without further purification.

### **Experimentation**

#### ***PTA@MIL-101-NH<sub>2</sub> -Cl Synthesis***

The catalyst PTA@MIL-101-NH<sub>2</sub>-Cl was synthesized by autoclaving FeCl<sub>3</sub>·6H<sub>2</sub>O, 2-nitroterephthalic acid (TA-NH<sub>2</sub>, 98%), 2,5-dichloroterephthalic acid (TA-Cl, 98%) and Phosphotungstic acid (PTA, AR) mixture in N,N-dimethylformamide (DMF, AR) through one-pot synthesis. 0.75 g (4.14mmol) of TA-NH<sub>2</sub>, 2.25 g (8.32mmol) of FeCl<sub>3</sub>·6H<sub>2</sub>O , 1.00g (0.3mmol) PTA and and TA-Cl(0g, 0.485g, 0.970g, 1.458g, 1.944g)were dissolved in 50 mL of DMF to obtain the catalysts with various -Cl content. The mixture solution was heated to 110 °C for 16 h without stirring in a Teflon-lined steel autoclave bomb with a total volume of 100mL. The product was separated by centrifugation, washed with DMF at ambient temperature and finally dried at 80°C for over 10h under vacuum. The catalysts were named as PTA@MIL-101-NH<sub>2</sub> -Cl(n), (“n” stands for the amount of TA-Cl added in the synthesis process, n=0, 2, 4, 6, 8.)

#### ***Cellobiose and Glucose Adsorption***

0.6g catalyst, 0.6g glucose or 0.54g cellobiose were added into 12 mL water in a microtube and vortexed. The mixture solution was divided into 6 equal portions in 6 microtubes. All samples were

kept at room temperature and vortexed every 5 min. One microtube was taken and centrifuged at the time of 25 min, 50 min, 75 min, 100 min, and 125 min respectively.

### *Avicel Hydrolysis*

0.04g avicel, 0.12g catalyst was added to 10 mL distilled water in 25-mL glass tubes and mixed well. Hydrolysis was conducted in oil bath at 180°C for 11h. After reaction, the mixture solution were isolated by centrifugation to obtain liquid products and solid residue respectively.

### **Characterization**

#### *X-ray Diffraction*

To analyze the crystal structure change of the catalyst and the avicel crystallinity, the catalyst and the hydrolysis residues were detected by X-ray diffractometer (XRD) D8 Advance X-ray Diffraction system and Bruker AXS with a copper target tube radiation (Cu K $\alpha$ 1) producing X-rays at a wavelength of 0.15418 nm. Samples were placed on a quartz plate and were scanned from 5° to 60° (2 $\theta$ ) at scan speed of 1.2 ° min<sup>-1</sup>, a scan step of 0.02 °, 1.0 ° DS-SS slits, 8.0-mm RS slit for monochromator.

#### *FT-IR*

Fourier Transform Infrared Spectra (FT-IR) was recorded with KBr disk containing the powder sample with the FT-IR spectrometer (Nicolet Magna 550) in the range of 4000-500 cm<sup>-1</sup>. The catalysts were detected by FT-IR to analyze the change of characteristic groups of the catalyst after grafting -Cl.

#### *TGA*

Thermal Gravimetric Analysis. The thermal stability of the samples was characterized with a thermal gravimetric analyzer (NETZSCH STA449F3A-1084-M). The samples were heated from 30 to 600 °C at a heating rate of 10 °C·min<sup>-1</sup> in nitrogen atmosphere.

#### *HPAEC-PAD*

High performance anion exchange chromatography-pulsed amperometric detection (HPAEC-PAD) was used to determine distribution of liquid products in avicel hydrolysis, cellobiose and glucose in adsorption experiment. Before analysis, the liquid samples were filtered using a syringe filter (0.22 $\mu$ m, PVDF). Glucose, cellobiose in the liquid products were analyzed by HPAEC-PAD equipped with a Dionex ICS-3000 ion chromatography (IC) system. Test conditions were as follows: an analytical column of CarboPacTMPA20 (3 $\times$ 150 mm), guard column (3 $\times$ 30 mm), column temperature 30°C, NaOH as mobile-phase, flow velocity 0.3 mL/min, a gradient elution method, namely eluting 1.5mM NaOH for 3min, 15mM NaOH between 3 and 20 min and 32mM NaOH between 20 and 50 min.

## **Results and Discussion**

### **The Crystal Structure Change of PTA@MIL-101-NH<sub>2</sub>-Cl After Grafted -Cl**

The XRD pattern of the sample is shown in Fig. 1. Even though There is a slight difference in the intensity of the diffraction peak, the diffraction peak appears in the vicinity of 2 $\theta$ =8°~9° that the peak position coincides with the peak position of MIL-101 (Fig. 1), indicating that the different TA -Cl / PTA samples have the MIL-101 type crystal structure, and the change of the graft amount of -Cl does not have obvious influence on the crystal structure of the synthesized sample. It can be seen from the Figure that each sample exhibits a diffraction peak due to the increase of the charge density of the crystal structure after loading PTA at 2 $\theta$  = 7.6°, indicating that PTA is successfully immobilized on the sample[22].

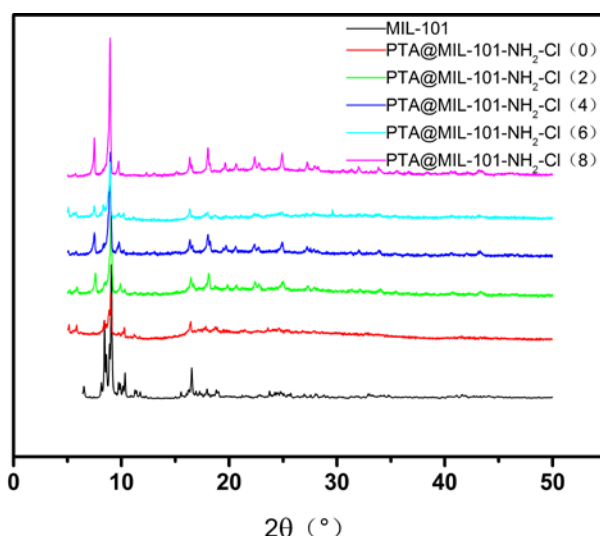


Fig. 1 XRD patterns of samples with various TA-Cl :( TA-Cl =0 mmol, 2 mmol, 4 mmol, 6 mmol, 8 mmol)and the simulated XRD patterns of MIL-101.

### The Change of PTA@MIL-101-NH<sub>2</sub>-Cl After Grafted -Cl

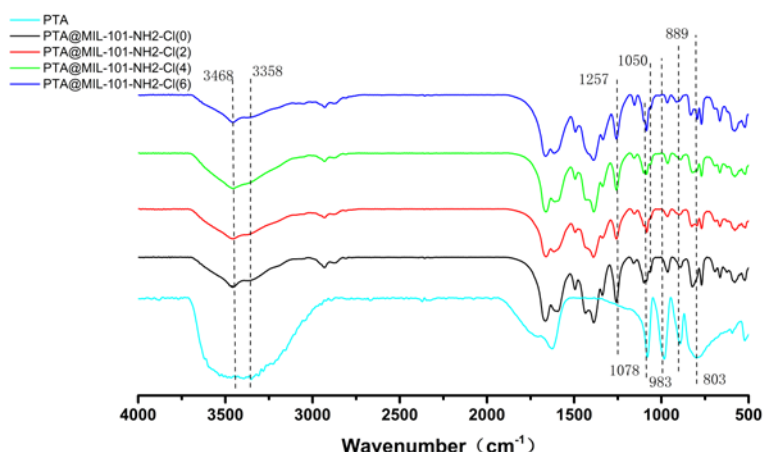


Fig. 2 FT-IR spectrum of samples with various TA-Cl :( TA-Cl =0 mmol, 2 mmol, 4 mmol, 6 mmol,)and the simulated FT-IR patterns of PTA.

The PTA immobilization change of PTA@MIL-101-NH<sub>2</sub> -Cl after grafted -Cl was analyzed by FT-IR. As shown in Fig.2, the spectra of PTA exhibited bands at 1078 cm<sup>-1</sup>, 983 cm<sup>-1</sup>, 889 cm<sup>-1</sup>, 803 cm<sup>-1</sup> respectively ascribed to stretching vibrations of P-O, W-Od (Od as terminal oxygen atom), W-Ob-W (Ob as oxygen atom bridging between corner sharing octahedras) and W-Oc-W (Oc as oxygen atom bridging between edge sharing octahedras)[23]. The bands at 3468 cm<sup>-1</sup> and 3358 cm<sup>-1</sup> corresponded to -NH<sub>3</sub><sup>+</sup> stretching vibration. The bands at 1257 cm<sup>-1</sup> and 1050 cm<sup>-1</sup> belonged to C-N and C-Cl stretching vibration[24]. It can be seen from Fig.2 that the adsorption peak of the catalyst containing PTA @ MIL-101-NH<sub>2</sub> -Cl at 1050 cm<sup>-1</sup> indicates that -Cl is present in the catalyst which proved -Cl is successfully grafted. Chlorine-containing catalysts and chlorine-free catalysts all have an absorption peak of -NH<sub>3</sub><sup>+</sup> at 3458 cm<sup>-1</sup> and 3366 cm<sup>-1</sup>(Fig.2). There is an absorption peak at 1257 cm<sup>-1</sup> belonging to C-N appears, indicating that all catalysts have achieved the grafting of -NH<sub>2</sub> . The presence of -NH<sub>3</sub><sup>+</sup> absorption peak indicates that -NH<sub>2</sub> is protonated by the electrostatic interaction with PTA. The bands at 1078 cm<sup>-1</sup>, 889 cm<sup>-1</sup> ascribed to P-O and W-Ob-W stretching vibrations were similar to those in the spectra of PTA. However, the bands belonging to W-Oc-W split into a maximum at 826 cm<sup>-1</sup> with a shoulder at 792 cm<sup>-1</sup>, the bands at 983 cm<sup>-1</sup> ascribed to W-Od shifted to smaller wavenumber and became insensitive.. This is because the H<sup>+</sup> of PTA connected with its anion Oc and Od, but the electrostatic interaction of PTA and -NH<sub>2</sub> led to the electron density of Oc

and Od decreased [25] which contributed to the changes of absorption peak of the peak position and intensity. All catalysts have the same changes of W-Oc-W and W-Od absorption peak, which indicated that the grafting of -Cl does not affect the electrostatic interaction between PTA and -NH<sub>2</sub>.

### Thermal Stability of PTA@MIL-101-NH<sub>2</sub>-Cl after grafted -Cl

**Thermal Stability of PTA@MIL-101-NH<sub>2</sub>-Cl.** TGA (a) and DTG (b) curves of the catalysts with different -Cl content are shown in Fig.3. The thermal degradation of PTA@MIL-101-NH<sub>2</sub>-Cl involves dehydration and the decomposition of Metal-organic frameworks. All the samples show an initial weight loss in the range of 30–100 °C associated with the evaporation of water, and the weight loss rate in the range of 10%–30%. The second weight loss stage occurs at 100 ~ 310 °C, the weight loss rate is about 18%, this is mainly caused by the removal of amino, hydroxyl and chlorine groups in the framework [5]. When the temperature is in the range of 310–400 °C, the framework began to collapse and ligand decomposed. Compared to the catalysts without -Cl (313 °C), the initial thermal decomposition of the catalysts with -Cl initiates at a higher temperature, followed by a significant weight loss in the range of 380–400 °C. TGA (a) and DTG (b) curves (Fig.3) show that the skeleton of PTA@MIL-101-NH<sub>2</sub>-Cl(4) began to collapse at 385 °C, and the weight loss at this stage was about 44%, and PTA@MIL-101-NH<sub>2</sub>-Cl(8) began to collapse at 395 °C, the loss of weight at this stage is about 52%. The above data show that the catalysts is stable at about 350 °C, which is consistent with the data reported in the literature [26]. It is indicated in Fig. 3(a) that the water content of PTA@MIL-101-NH<sub>2</sub> is larger than that of other samples, mainly due to the residual amount of solvent and the difference in air humidity. Comparing the TGA (a) and DTG (b) curves of three samples, the thermal stability of the catalysts were found in the following order: PTA@MIL-101-NH<sub>2</sub>-Cl(8) > PTA@MIL-101-NH<sub>2</sub>-Cl(4) > PTA@MIL-101-NH<sub>2</sub>. It is indicated that good thermal stability can still be maintained after grafting the chlorine groups in the MIL-101 structure. And the grafting of chlorine groups improved the thermal stability of MIL-101 to a certain extent.

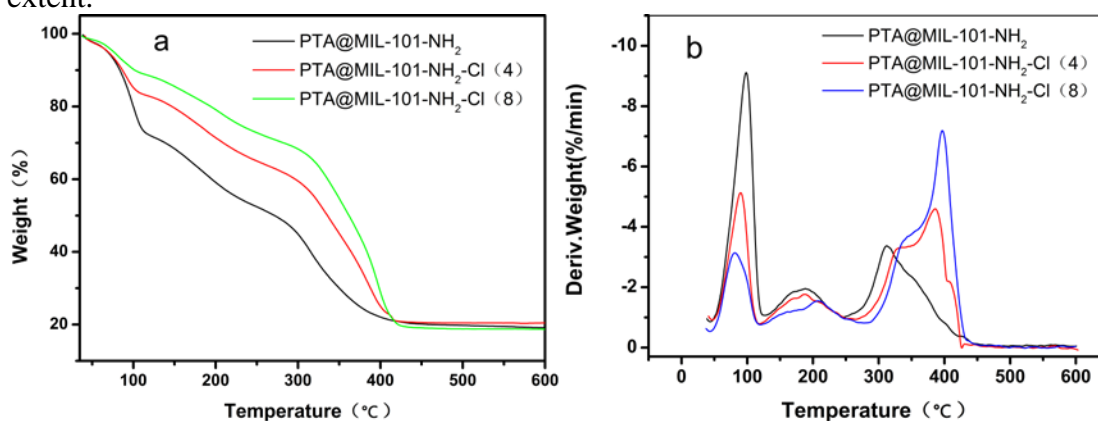


Fig. 3 (a) TG-curves of samples with various TA-Cl; (b) DTG-curves of samples with various TA-Cl. (TA-Cl = 0 mmol, 2 mmol, 4 mmol, 6 mmol,)

### The Effect of -Cl Content on Selective Conversion of Cellulose

Cellulose was simulated by cellobiose. The selective adsorption performance of the catalyst was investigated by comparing the adsorption performance of the same molar amount of glucose and cellobiose. With the prolongation of time, the remaining amount of glucose and cellobiose in different adsorption systems showed a decreasing trend, and the remaining amount of glucose far exceeded the remaining amount of cellobiose, indicating that the catalysts with and without -Cl had the ability to adsorb glucose and cellobiose and had the stronger ability to adsorb cellobiose. Both the non-adsorbed glucose and cellobiose amount of PTA@MIL-101-NH<sub>2</sub>-Cl were smaller than the ones of PTA@MIL-101-NH<sub>2</sub>. It illustrated that the catalysts with -Cl have stronger adsorption performance of glucose and cellobiose than the catalysts without -Cl. Chlorine-containing catalyst can adsorb glucose, cellobiose by the formation of hydrogen bonds O-H...Cl with the contribute of

the strong electronegative group -Cl[4]. Cellobiose have more -OH than glucose which results in the higher cellobiose adsorption than glucose.

According to the above analysis, in the cellulose hydrolysis reaction, the chlorine-containing catalyst selectively adsorbs the cellulose through the formation of hydrogen bonds of -Cl and cellulose[27].The formation of hydrogen bonds can improve the contact frequency of the cellulose to achieve the directional hydrolysis of cellulose.

It is indicated in Fig.4 that the adsorption ratio of cellobiose and glucose increases with the addition of TA-Cl. With the increase of TA-Cl, the proportion of cellulosic and glucose adsorption increased rapidly , When the addition of TA-Cl more than 6mmol, the proportion of cellulosic and glucose adsorption is basically unchanged.This is because -Cl can form hydrogen bonds with -OH to promote the adsorption of cellobiose, but when the TA-Cl content is overmuch, it will cause the catalyst pore structure changes and inhibit the adsorption capacity.

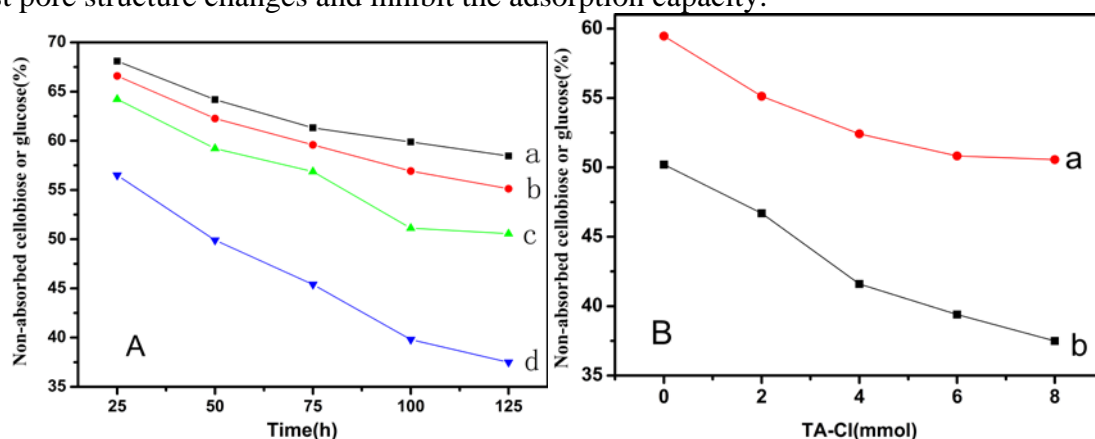


Fig. 4 A. The glucose (a) and cellobiose (b) adsorption curve of PTA@MIL-101-NH<sub>2</sub> and glucose (c) and cellobiose (d) adsorption curve of PTA@MIL-101-NH<sub>2</sub>-Cl.  
B. The effect of grafting -Cl on The adsorption of. glucose (a) and cellobiose (b). Conditions: temperature, 180 °C,time, 11h,

### The Effect of -Cl content on Hydrolysis of Cellulose

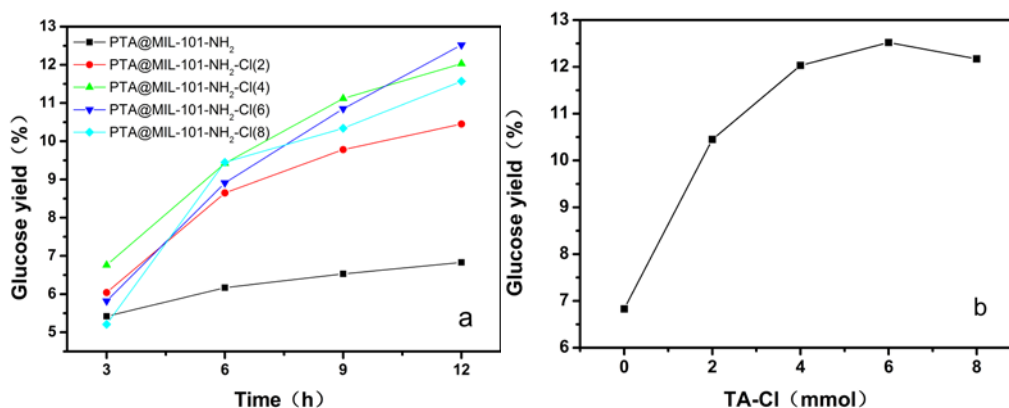


Fig. 5 (a) The glucose yield of samples with various TA-Cl.(b) The glucose yield of PTA@MIL-101-NH<sub>2</sub>-Cl(n),Conditions: temperature, 180 °C,time, 11h,(n=0 mmol, 2 mmol, 4 mmol, 6 mmol)

Glucose is the main product of cellulose hydrolysis. It is discussed that the glucose yield obtained by hydrolysis of cellulose under the condition of chlorine-containing catalyst and chlorine-free catalyst can analyze the effect of the presence of -Cl on the directional hydrolysis of cellulose. Fig.5 shows the glucose yield of the catalyst with different -Cl content under the same hydrolysis conditions. The yield of glucose obtained by hydrolysis of cellulose increased with the increase of the -Cl content of the catalyst, and the glucose yield increases first and then decreases with the increase of

the -Cl content of the catalyst. When the TA-Cl dosage is greater than 6mmol, the glucose yield has a downward trend. Indicating that high chlorine content is beneficial for obtaining higher glucose yields. This is because -Cl can be adsorbed by hydrogen bonding with the cellulose hydroxyl groups. In the same reaction system with the same amount of cellulose, the catalyst containing a higher amount of -Cl grafting can adsorb more cellulose to make more cellulose be able to contact with the catalyst and then hydrolysed by the PTA, ultimately get a higher glucose yield. Therefore, increasing the grafting capacity of -Cl can enhance the cellulose adsorption capacity of the catalyst, which is beneficial to the acid catalysis performance of the catalyst and promote the directional transformation of the cellulose. After grafting -Cl, the yield of glucose catalyzed by cellulose hydrolysis was 81% higher than that without -Cl. However, when the amount of -Cl graft was more than 6 mmol, because the total amount of organic ligands was fixed, the corresponding TA-NH<sub>2</sub> graft was reduced, resulting in a decrease in PTA loading, which reduced the degradation efficiency of the catalysts. The optimum TA-Cl dosage for catalyst synthesis was 6 mmol.

## Conclusion

In brief, this article has mainly studied the effect of grafting -Cl on the crystal structure, molecular structure and thermal stability of PTA@MIL-101-NH<sub>2</sub> and analyzed the mechanism of directional hydrolysis of cellulose catalyzed by strongly electronegative group -Cl. The catalysts still maintain the MIL-101 type crystal structure, after the grafting of the strong electronegative group -Cl, and the grafting of -Cl does not affect the electrostatic interaction between the basic group -NH<sub>2</sub> and PTA. The catalysts still maintained good thermal stability after grafting the chlorine groups in the MIL-101 structure. And the grafting of chlorine groups improved the thermal stability of MIL-101 to a certain extent. The presence of -Cl plays an important role in improving glucose production and realizing directional hydrolysis of cellulose. The catalyst can selectively adsorb cellulose through the formation of hydrogen bonds O-H...Cl between the hydroxyl groups of cellulose and -Cl to promote the selective conversion of cellulose to glucose. It can also weaken the internal hydrogen bonds of the cellulose molecules, make the crystalline structure of cellulose loose and easy to be Hydrolyze, and improve the hydrolysis efficiency of cellulose. After grafting -Cl, the yield of glucose catalyzed by cellulose hydrolysis was 81% higher than that before. High chlorine content is beneficial to increase glucose production and promote the directional transformation of cellulose.

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