

## One-pot synthesis of high fructose corn syrup directly from starch with $\text{SO}_4^{2-}/\text{USY}$ solid catalyst

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**Abstract**—An efficient process was developed for the conversion of starch directly into high fructose corn syrup (HFCS) by using  $\text{SO}_4^{2-}/\text{USY}$  solid catalyst in water. The  $\text{SO}_4^{2-}/\text{USY}$  catalyst was found to act as a bifunctional catalyst with high activity for both hydrolysis of starch and isomerization of glucose, achieving a one-step preparation path of HFCS from starch. An optimal HFCS yield, containing 58.34% glucose and 27.84% fructose (mass fraction), was obtained at 150 °C for only 1 h.

Keywords: Starch, HFCS,  $\text{SO}_4^{2-}/\text{USY}$  Catalyst, Hydrolysis, Isomerization

### INTRODUCTION

Efficient catalytic processes for isomerization of glucose into fructose have been a focus of numerous studies owing to the high demand of fructose. First, glucose-fructose syrups are widely used sweeteners [1-3]. Additionally, recent investigations on the production of bio-fuels, commodities and fine chemicals confirmed fructose as a superior substrate compared to glucose [4-9]. Despite the fact that enzymatic process has high performance, the commercial biotechnological process for isomerization requires costly enzymes along with highly pure substrates [10]. The reaction temperature, pH, feed purity and flow rate need to be carefully controlled [3,10]. Intensive investigations have undertaken to develop an alternative chemo-catalyst for glucose-fructose isomerization [11-13]. Promising catalytic activity of different bases [14-17] and Lewis acids [11] was uncovered, though the performance of the chemo-catalysts is inferior to enzymatic catalysts in terms of fructose yield. Many researches show that the chemical catalysis method has the advantage of low cost and a wider range of reaction conditions despite some existing problems that need to be resolved. Generally, the conversion of starch to fructose by chemical method involves two main steps: The starch is hydrolyzed into glucose, then the glucose is isomerized to fructose. To integrate the hydrolysis and isomerization steps into one-step, acidic catalysts for isomerization usually are used [17]. Because of the disadvantages of liquid acid, such as difficult recycling and high-erosion, solid acid catalyst has gained growing attention, with its remarkable advantages of retrievability, anti-corrosion, easy separation with products and non-pollution [13,18-21].

In this paper, we report the preparation of fructose directly from starch in a one-pot reaction with  $\text{SO}_4^{2-}/\text{USY}$  solid acid catalyst.

Loading sulfuric acid on USY can increase its surface acid catalytic activity. The hydrolysis and isomerization steps are integrated into a one-pot conversion using a single solid catalyst, which can perform two steps consecutively.

### EXPERIMENTAL

#### 1. Chemicals and Materials

Soluble starch was purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). USY molecular sieve, H $\beta$  MCM-41,  $\text{SiO}_2$ , Silica Gel, H-USY, HY, H-ZSM-5 was obtained from the Catalyst Plant of Nankai University. Sulfuric acid was supplied by West Long Chemical Co. Ltd.

#### 2. Catalysts Preparation

Ready-made USY, H $\beta$  MCM-41,  $\text{SiO}_2$ , Silica Gel and a certain concentration of  $\text{H}_2\text{SO}_4$  were stirred until the mixture was uniform. After impregnating for 3 h, the upper liquid was removed and dried. Then the catalysts were calcinated at 550 °C for 6 h.

#### 3. Catalytic Reaction Procedure

5 wt% starch, catalyst, and deionized water were loaded into a 50 mL reaction kettle. Zero time was taken as soon as the temperature of the reaction vessel rose to reaction temperature and kept constant. The reaction mixture was stirred magnetically at 400 rpm. At the end of reaction, the reactor was cooled to room temperature, and the solid catalyst was separated from the solution by centrifugation. The solution was diluted by deionized water, then was filtered and subjected to glucose, fructose and 5-HMF analysis.

#### 4. Products Analysis

Quantitative analysis of glucose, fructose and 5-HMF was by HPLC using an UltiMate 3000 RS pump, an aminex column HPX-87H column (Agilent), and Shodex Refractive Index 101 detector.  $\text{H}_2\text{SO}_4$  (5 mM) was used as the mobile phase at a flow rate of 0.6 mL/min, and the column temperature was maintained at 50 °C. All concentrations of carbohydrates were determined by comparison to standard calibration curves. All the data were based on repeated

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runs and the standard deviation was less than 2%. The yields of glucose (Y<sub>G</sub>), fructose (Y<sub>F</sub>) and HMF (Y<sub>HMF</sub>) were calculated as follows:

$$Y_G = \frac{W_G}{W_S} \times 100\%$$

$$Y_F = \frac{W_F}{W_S} \times 100\%$$

$$Y_{HMF} = \frac{W_{HMF}}{W_S} \times 100\%$$

The terms W<sub>G</sub>, W<sub>F</sub>, W<sub>HMF</sub> and W<sub>S</sub> represent the weight of glucose, fructose, HMF and starch, respectively.

### 5. Catalysts Characterization

X-ray diffraction (XRD) pattern of the catalysts involved using a BRUKER D8 Advance X-ray diffractometer with Cu K $\alpha$  radiation source with the following parameters: 40 kV, 40 mA, 2 $\theta$  from 5° to 70° at a scanning speed of 10°/min.

BET surface areas and pore structure were determined on a ASAP-2020 accelerated surface area and porosimetry system (Micromeritics); the samples were measured by N<sub>2</sub> adsorption-desorption isotherms at liquid nitrogen temperature. Prior to analysis, each sample was pretreated at 90 °C for 1 h to remove any adsorbed species on the surface.

Temperature-programmed desorption of ammonia (NH<sub>3</sub>-TPD) was measured on a Micromeritics Autochem II 2920 instrument (Micromeritics). A thermal conductivity detector was used for continuous monitoring of the desorbed ammonia and the areas under the peaks were integrated to estimate the amount of acid in the catalysts. The sample was heated to 600 °C (15 °C/min) and kept for 0.5 h in a flow of He gas (25 mL/min) to remove adsorbed species on the surface. The sample was cooled to 100 °C in a flow of He gas, then followed by adsorption of NH<sub>3</sub> in 10% NH<sub>3</sub> gas flow (balance He, 25 mL/min) for 1 h. After being flushed with He (25 mL/min) for 1 h to remove the physically adsorbed NH<sub>3</sub>, the TPD data was recorded from 100 °C to 500 °C with a ramp of 15 °C/min. Carbon and sulfur composition of the catalysts was carried out on a Vario EL III elemental analyzer (Elementar).

## RESULTS AND DISCUSSION

### 1. Evaluation and Screening of Catalyst

Testova [22] suggested that molecular sieves possessed Brønsted acid centers, which was similar to proton acid (a kind of inorganic acid). Loading sulfuric acid on a molecular sieve could strengthen Brønsted acid in the molecular sieve, leading to great enhancement in the acidity. Zhou [19,23] showed that MCM-41, SiO<sub>2</sub> and silicon aluminum oxide as carriers loaded with sulfuric acid had strong Lewis acidity. In the experiment, a variety of solid acid catalysts were screened. As shown in Table 1, SO<sub>4</sub><sup>2-</sup>/USY catalyst performed excellently in efficiency among them with 62.08% glucose yield and 22.82% fructose yield. In particular, SO<sub>4</sub><sup>2-</sup>/MCM-41 performed excellently in glucose conversion efficiency with the yield of 102.32% (In theory, the complete hydrolysis of 0.9 g starch can produce 1 g glucose, which gets 111% mass yield of glucose), while MCM-41 had no catalytic effect. After being impregnated with sulfuric acid solution, the acidity of catalysts was enhanced, which made the starch almost all hydrolyze to glucose. However,

**Table 1. The conversion of starch to HFCS by using solid acid catalysts<sup>a</sup>**

Catalyst	Yield (%)		
	Glucose	Fructose	
USY	Na <sub>2</sub> O=0.05, Si/Al=11	0.36	0
H-USY	Na <sub>2</sub> O=0.05, Si/Al=11	21.56	0.69
SO <sub>4</sub> <sup>2-</sup> /USY	Na <sub>2</sub> O=0.05, Si/Al=11	62.08	22.82
H $\beta$	Si/Al=50	25.81	0.63
SO <sub>4</sub> <sup>2-</sup> /H $\beta$	Si/Al=50	65.90	15.00
MCM-41	100%SiO <sub>2</sub>	0	0
SO <sub>4</sub> <sup>2-</sup> /MCM-41	100%Si	102.32	3.37
SO <sub>4</sub> <sup>2-</sup> /SiO <sub>2</sub>	/	75.22	0.59
SO <sub>4</sub> <sup>2-</sup> /Silica Gel	/	62.00	13.45
HY	Si/Al=5	1.53	0
H-ZSM-5	Si/Al=25	4.84	0

<sup>a</sup>Reaction conditions: 5% (w/w) starch in water, 30% (w/w) catalyst (catalyst/starch), 150 °C, 1 h, 400 rpm

MCM-41 contained neither Brønsted acid nor Lewis acid, which made it have no catalytic effect. It was noted that the fructose yield was very little for SO<sub>4</sub><sup>2-</sup>/MCM-41 and SO<sub>4</sub><sup>2-</sup>/SiO<sub>2</sub>; however, it was over 13% for SO<sub>4</sub><sup>2-</sup>/H $\beta$  and SO<sub>4</sub><sup>2-</sup>/Silica Gel. H $\beta$  had Brønsted and Lewis acid sites, and silica gel had Brønsted acid sites. Therefore, it was concluded that the Brønsted acid played the major role in the hydrolysis of starch; nevertheless, the Brønsted and Lewis acid contributed the isomerization of glucose to fructose. In addition, if sulfuric acid was loaded on the MCM-41 and SiO<sub>2</sub> and formed Brønsted acid sites, the isomerization effect would not perform so badly. It could be inferred that sulfuric acid was only absorbed on MCM-41 or SiO<sub>2</sub> and chemical bond with MCM-41 was not formed, leading to the loss of acid during the hydrolysis process of starch. The acid leached in the solution contributed the high yield of glucose.

### 2. Effect of Calcination Temperature on the Activity of Catalyst

Stability of sulfuric acid on the surface of catalyst carrier has a great effect on the catalytic efficiency. The calcination process facilitates the formation of a bond between sulfuric acid and the catalyst carrier to improve the stability of catalyst. Zhou [19,23] suggested that the appropriate pretreatment temperature of solid acids derived from sulfuric acid was 150-200 °C due to the boiling point of sulfuric acid was 338 °C. However, high temperature also made for bond formation between acid and catalyst. So, to estimate the effect of calcination temperature on different catalyst carriers, experiments were conducted at 180 °C and 550 °C, and the results are shown in Table 2. The effect of calcination temperature of different loaded zeolites on HFCS yields.

Table 2 shows that SO<sub>4</sub><sup>2-</sup>/MCM-41, SO<sub>4</sub><sup>2-</sup>/SiO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup>/Silica Gel all got very little glucose yield when the calcination temperature of catalysts was 550 °C. While relatively good glucose yields were obtained when the calcination temperature of catalysts was 180 °C. These indicated that most active component, sulfuric acid, may have evaporated from the surface of MCM-41, SiO<sub>2</sub> and silica gel during calcination at 550 °C, resulting in the poor catalytic efficiency in hydrolysis and isomerization reaction. The catalytic activity of SO<sub>4</sub><sup>2-</sup>/USY and SO<sub>4</sub><sup>2-</sup>/H $\beta$  at calcination temperature of

**Table 2. The effect of calcination temperature of different loaded zeolites on HFCS yield<sup>a</sup>**

Catalyst	180 °C		550 °C	
	Glucose yield (%)	Fructose yield (%)	Glucose yield (%)	Fructose yield (%)
SO <sub>4</sub> <sup>2-</sup> /USY	49.97	3.30	62.08	22.82
SO <sub>4</sub> <sup>2-</sup> /Hβ	49.49	18.36	65.90	15.00
SO <sub>4</sub> <sup>2-</sup> /MCM-41	102.32	3.37	21.91	0
SO <sub>4</sub> <sup>2-</sup> /SiO <sub>2</sub>	75.22	0.59	0	0
SO <sub>4</sub> <sup>2-</sup> /Silica Gel	62.00	13.45	2.1	0

<sup>a</sup>Reaction conditions: 5% (w/w) starch in water, 30% (w/w) catalyst (catalyst/starch), 150 °C, 1 h, 400 rpm

550 °C was higher than that at 180 °C, demonstrating that high temperature made for the interaction between sulfuric acid with USY and Hβ and formation of strong chemical bonds. While catalysts were calcined at 180 °C, owing to SO<sub>4</sub><sup>2-</sup>/Hβ and SO<sub>4</sub><sup>2-</sup>/Silica Gel owned Brønsted acid sites, a fructose yield of over 13% was obtained. Though sulfate acid was absorbed on the carriers such MCM-41, SO<sub>4</sub><sup>2-</sup>, and USY, the bonds between acid and carriers did not form, leading to the leaching of acid from catalysts. Therefore, these catalysts performed badly in isomerization of glucose. It could be concluded that the Brønsted acid sites made the isomerization take place, instead of the acid leaching from catalysts. Thus the effect of calcination temperature of SO<sub>4</sub><sup>2-</sup>/USY and SO<sub>4</sub><sup>2-</sup>/Hβ on HFCS yield, including the glucose yield and the fructose yield, was discussed in detail. The results are shown in Table 3.

The maximal yield of HFCS with 62.08% glucose and 22.82% fructose was achieved by using SO<sub>4</sub><sup>2-</sup>/USY at calcination temperature of 550 °C. Low calcination temperature did not facilitate the bond formation between sulfuric acid and USY, resulting in loss of sulfuric acid from catalyst surface during hydrolysis reaction. Therefore, catalysts, such as SO<sub>4</sub><sup>2-</sup>/USY, SO<sub>4</sub><sup>2-</sup>/MCM-41, SO<sub>4</sub><sup>2-</sup>/SiO<sub>2</sub>, obtained little fructose yield. However, SO<sub>4</sub><sup>2-</sup>/Hβ and SO<sub>4</sub><sup>2-</sup>/Silica Gel obtained relatively good fructose due to Brønsted acid sites owned by itself. While too high temperature would break the bond between sulfuric acid and USY and destroy the structure of USY as well, the activity of catalyst also dropped with the enhancement of calcination temperature. Hence, the optimum calcination temperature of catalyst was 550 °C for the preparation of SO<sub>4</sub><sup>2-</sup>/USY.

### 3. Effect of Sulfuric Acid Loading

The acid intensity of catalyst is also an important factor that

**Table 3. The effect of calcination temperature of SO<sub>4</sub><sup>2-</sup>/USY and SO<sub>4</sub><sup>2-</sup>/Hβ on HFCS yield<sup>a</sup>**

Catalyst	Yield (%)	Temperature (°C)			
		180	360	550	650
SO <sub>4</sub> <sup>2-</sup> /USY	Glucose	49.97	60.20	62.08	49.78
	Fructose	3.30	10.60	22.82	16.25
	5-HMF	0	0.73	3.31	2.60
SO <sub>4</sub> <sup>2-</sup> /Hβ	Glucose	49.49	63.05	65.90	49.65
	Fructose	18.36	16.32	15.00	10.30
	5-HMF	0	1.35	2.68	2.03

<sup>a</sup>Reaction conditions: 5% (w/w) starch in water, 30% (w/w) catalyst (catalyst/starch), 150 °C, 1 h, 400 rpm

affects HFCS yield. Therefore, 0.5 mol/L, 1.0 mol/L, 1.5 mol/L, 2.0 mol/L and 2.5 mol/L sulfuric acid were used as impregnation liquid of USY to estimate the effect of the sulfuric acid loading. The results are shown in Table 4. It was observed that the glucose yield was decreasing as the concentration of sulfuric acid growing. At the same time, the fructose yield increased with the increasing concentration of sulfuric acid from 0.5 to 1.5 mol/L, while it dropped quickly with the continual increase of sulfuric acid concentration from 1.5 to 2.5 mol/L, most likely because more sulfuric acid accelerated to produce more HMF and other byproducts [24]. The maximal yield of HFCS was 86.18% with 58.34% glucose and 27.84% fructose by using catalyst impregnated with 1.5 mol/L sulfuric acid.

### 4. Effect of Reaction Temperature

As can be seen from Table 5, the yield of glucose and fructose initially increased and then dropped quickly with the reaction temperature rise. Only 8.86% yield of glucose could be obtained at 130 °C, and almost no fructose was produced. It was concluded that hydrolysis of starch catalyzed by SO<sub>4</sub><sup>2-</sup>/USY needs higher reac-

**Table 4. The effect of sulfuric acid loading on HFCS yield<sup>a</sup>**

The loading amount of H <sub>2</sub> SO <sub>4</sub> (mol/L)	Yield (%)		
	Glucose	Fructose	5-HMF
0.5 SO <sub>4</sub> <sup>2-</sup> /USY	65.81	6.45	0
1.0 SO <sub>4</sub> <sup>2-</sup> /USY	62.08	22.82	3.31
1.5 SO <sub>4</sub> <sup>2-</sup> /USY	58.34	27.84	3.72
2.0 SO <sub>4</sub> <sup>2-</sup> /USY	39.58	22.26	4.37
2.5 SO <sub>4</sub> <sup>2-</sup> /USY	28.64	19.83	6.02

<sup>a</sup>Reaction conditions: 5% (w/w) starch in water, 30% (w/w) catalyst (catalyst/starch), 150 °C, 1 h, 400 rpm

**Table 5. The effect of reaction temperature on HFCS yield<sup>a</sup>**

Temperature (°C)	Yield (%)		
	Glucose	Fructose	5-HMF
130	8.86	0.06	0
140	48.32	13.54	1.03
150	58.34	27.84	3.72
160	30.28	17.17	6.93
170	15.22	13.32	5.61

<sup>a</sup>Reaction conditions: 5% (w/w) starch in water, 30% (w/w) catalyst (catalyst/starch), 1 h, 400 rpm

**Table 6. The effect of reaction time on HFCS yield<sup>a</sup>**

Time (min)	Yield (%)		
	Glucose	Fructose	5-HMF
20	25.46	3.04	0
40	55.4	11.57	0.88
60	58.34	27.84	3.72
80	47.73	21.04	5.63
100	44.29	19.54	7.67
120	40.64	17.06	9.29

<sup>a</sup>Reaction conditions: 5% (w/w) starch in water, 30% (w/w) catalyst (catalyst/starch), 150 °C, 400 rpm

tion temperature. The maximal HFCS yield of 86.18% was at 150 °C. While the HFCS yield declined when the reaction temperature further rose, which may be ascribed to the degradation of fructose to HMF and other unknown compounds.

### 5. Effect of Reaction Time

Experiments were conducted at 150 °C with different reaction time to study its effect on the HFCS yield. As shown in Table 6, the yields of glucose and fructose increased first and then decreased slightly with prolonged reaction time. The maximal yield of glucose and fructose reached to 58.34% and 27.84% in 1 h.

### 6. Effect of Catalyst Amount

The influence of catalyst amount on the conversion process of starch to glucose and fructose was investigated. It can be seen from Table 7, catalyst amount increased, the yield of glucose and fructose increased first and then decreased slightly. More amount of catalyst provided more acid sites for the conversion of starch to fructose. Meanwhile, more sites also stimulated the degradation of fructose to HMF and other unknown compounds [25,26]. The maximum glucose yield of 67.03% was achieved by using 20% (w/w)  $\text{SO}_4^{2-}/\text{USY}$  (catalyst/starch), but the fructose yield was only 12.57%. The maximum yields of fructose and HFCS were obtained by using 30% (w/w)  $\text{SO}_4^{2-}/\text{USY}$ ; continual increase in catalyst amount resulted in the low yields of glucose and fructose, which could be ascribed to the degradation of product into byproducts.

### 7. Catalyst Recycling

Long-term stability and recyclability are extremely important characteristics of solid catalysts to reduce production cost greatly for future industrial application. After the reaction,  $\text{SO}_4^{2-}/\text{USY}$  catalyst was separated and collected from the solution, then was recycled in a new experiment under the same reaction condition. Three

**Table 7. The effect of catalyst amount on HFCS yield<sup>a</sup>**

The mass fraction of catalyst (g)	Yield (%)		
	Glucose	Fructose	5-HMF
10	26.22	2.23	0
20	67.03	12.57	1.16
30	58.34	27.84	3.72
40	57.1	20.69	4.96
50	51.41	21.21	5.48
60	48.92	20.39	7.48
70	45.76	19.98	8.17

<sup>a</sup>Reaction conditions: 5% (w/w) starch in water, 150 °C, 1 h, 400 rpm

different methods were used to recycle  $\text{SO}_4^{2-}/\text{USY}$  catalyst, without calcination, with calcination and regeneration by impregnation in sulfuric acid for 3 h followed by calcination at 550 °C for 3 h. The results are shown in Table 8. It was found that the used  $\text{SO}_4^{2-}/\text{USY}$  catalyst without calcination in the reaction caused an obvious decrease of the HFCS yield in subsequent runs. Surprisingly, the appearance of catalyst had undergone a great change from white powder to dark brown granular. The probable reason was the unreacted starch and byproducts absorbed on the surface of catalyst, which could be removed by calcination. Meanwhile, the HFCS yield was also declined by using  $\text{SO}_4^{2-}/\text{USY}$  with calcination as catalyst, its catalytic activity higher than that without calcination. Gratifyingly, it can be seen that the regenerated catalyst still retained excellent catalytic activity after the fourth cycle.

### 8. Characterizations of Catalysts

Impregnated with sulfuric acid, USY would form bonds with sulfuric acid molecules. Owing to strong acidity, sulfuric acid may have an impact on the structure of USY. The surface structure of USY and  $\text{SO}_4^{2-}/\text{USY}$  was characterized by XRD technique to estimate the effect of the sulfuric acid on the structure of catalysts. The results indicated that the crystallization structure of  $\text{SO}_4^{2-}/\text{USY}$  was nearly the same as that of USY, and its characteristic diffraction peaks were consistent with USY (Fig. 1). However, the intensity of the diffraction peaks decreased, indicating that the crystallinity of the  $\text{SO}_4^{2-}/\text{USY}$  decreased. Because USY contained a certain amount of aluminum, it usually partly dissolved out during the molecular sieve immersed in sulfuric acid solution, leading to the skeletal defect of USY, partial amorphous increased and the crystallinity decreased.

To gain an insight into the microstructure of catalyst, the sur-

**Table 8. The effect of reused time of three different methods on the HFCS yield<sup>a</sup>**

Reused time	Glucose yield (%)			Fructose yield (%)			5-HMF yield (%)		
	A	B	C	A	B	C	A	B	C
1	58.34	58.34	58.34	27.84	27.84	27.84	3.70	3.70	3.70
2	37.53	48.30	57.72	15.23	20.92	27.15	0	0.52	3.35
3	18.62	38.12	57.66	8.12	15.87	26.88	0	0	3.08
4	9.34	20.40	57.49	2.32	9.32	26.67	0	0	2.86

<sup>a</sup>Reaction conditions: 5% (w/w) starch in water, 30% (w/w) catalyst (catalyst/starch), 150 °C, 1 h, 400 rpm. A represents without calcination; B represents with calcination; C represents with regeneration

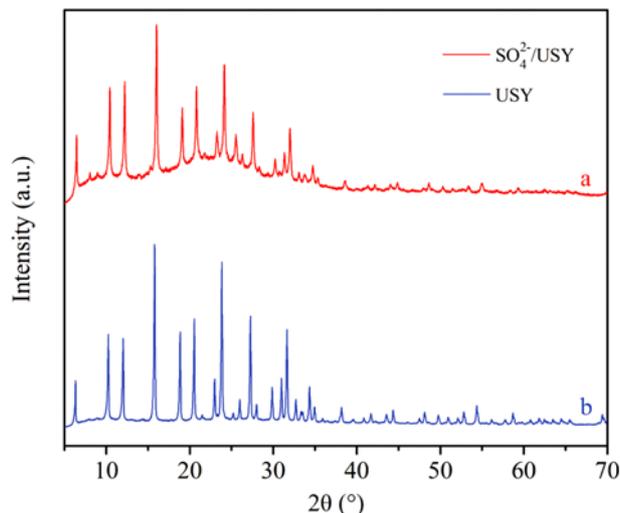


Fig. 1. XRD patterns of SO<sub>4</sub><sup>2-</sup>/USY (a) and USY (b).

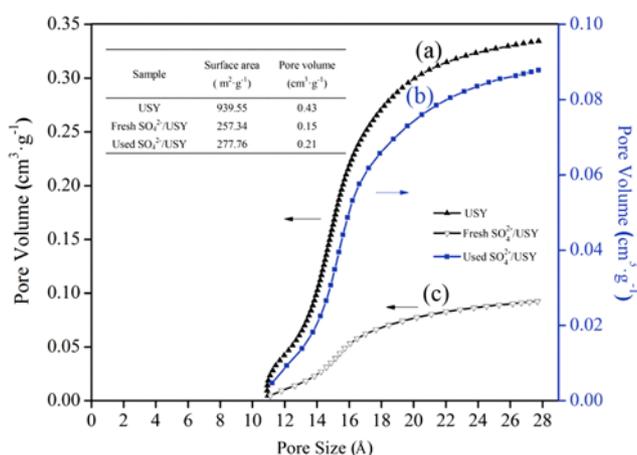


Fig. 2. The pore volume distribution profiles of samples: USY (a), fresh SO<sub>4</sub><sup>2-</sup>/USY (b) and used SO<sub>4</sub><sup>2-</sup>/USY (c).

face area and pore volume of USY, fresh and used SO<sub>4</sub><sup>2-</sup>/USY were characterized by physical adsorption technique. Compared with USY, the surface area and pore volume of SO<sub>4</sub><sup>2-</sup>/USY decreased (Fig. 2), which suggested that sulfuric acid penetrated into the pores of USY and adsorbed on the surface of USY. Meanwhile, the surface area and pore volume of used SO<sub>4</sub><sup>2-</sup>/USY increased slightly compared with fresh SO<sub>4</sub><sup>2-</sup>/USY, which suggested some sulfuric acid lost during reaction. The pore volume distribution profiles are shown in Fig. 2. Clearly, the pore volume of zeolite sharply decreased from 0.43 cm<sup>3</sup>·g<sup>-1</sup> to 0.15 cm<sup>3</sup>·g<sup>-1</sup>. Compared with the fresh SO<sub>4</sub><sup>2-</sup>/USY, the pore volume increased slightly. These results certified that the structure of catalyst was not changed and there was only a little sulfuric acid lost during reaction.

The acidity variations of USY, fresh SO<sub>4</sub><sup>2-</sup>/USY and used SO<sub>4</sub><sup>2-</sup>/USY were characterized by NH<sub>3</sub>-TPD technique. NH<sub>3</sub>-TPD profiles are shown in Fig. 3. It can be seen clearly that the amount of desorbed NH<sub>3</sub> from USY was apparently higher than that of the fresh and used SO<sub>4</sub><sup>2-</sup>/USY, which revealed that the USY had a large enough surface area and acid sites to adsorb NH<sub>3</sub>. After being loaded

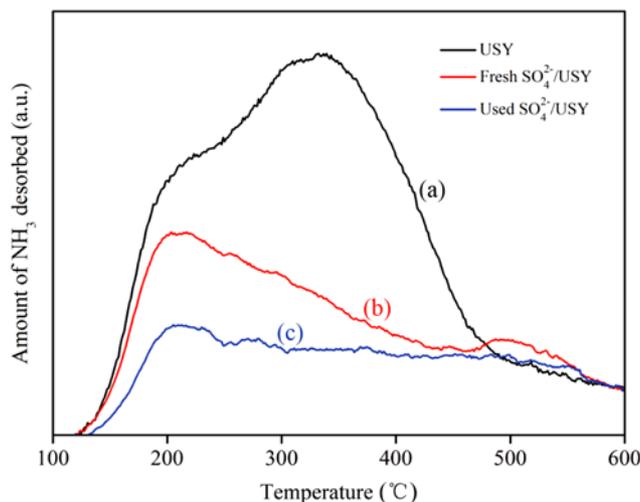


Fig. 3. NH<sub>3</sub>-TPD profiles of USY (a), fresh SO<sub>4</sub><sup>2-</sup>/USY (b) and used SO<sub>4</sub><sup>2-</sup>/USY (c).

by sulfuric acid, the surface and pore volume of USY declined sharply, leading to decrease in NH<sub>3</sub> adsorption capacity. It is consistent with the results of the physical adsorption characterization of the SO<sub>4</sub><sup>2-</sup>/USY that sulfuric acid penetrated into the pores of USY and occupied the pore volume. The amount of desorbed NH<sub>3</sub> was further reduced for used SO<sub>4</sub><sup>2-</sup>/USY, suggesting that some acid was lost during the reaction, which may be covered by humins [26] generated from the degradation of sugar, resulting in the decreasing amount of desorbed NH<sub>3</sub>. The other reason was the sulfate acid molecules were covered by humins. The catalytic activity increased by calcination; meanwhile, the yield of HFCS was enhanced correspondingly (Table 8). In addition, the desorption temperature of NH<sub>3</sub> from USY was in the range of 200–450 °C, which conformed to the characteristics of weak acid sites. Meanwhile, to view the previous experimental results, USY had little effect on conversion of starch into fructose, which accorded with the character of weak acid sites on USY. In addition, NH<sub>3</sub> was adsorbed on the surface of SO<sub>4</sub><sup>2-</sup>/USY and some ammonium salt formed, such as ammonium sulfate, ammonium hydrogen sulfate and ammonium pyrosulfate. There was an obvious characteristic peak at 180–300 °C for SO<sub>4</sub><sup>2-</sup>/USY. The decomposition temperature of ammonium sulfate ranged from 213 °C to 308 °C. These peaks may be explained by decomposition of ammonium sulfate at this temperature. However, the decomposition temperature of ammonium hydrogen sulfate and ammonium pyrosulfate ranged from 308 °C to 419 °C [27]; the small characteristic peak of desorbed NH<sub>3</sub> may be attributed to the decomposition of ammonium hydrogen sulfate and ammonium pyrosulfate. When the programmed temperature exceeded 420 °C, the peak of desorbed NH<sub>3</sub> changed slightly, which suggested that ammonium sulfate had almost completely decomposed.

The catalysts were characterized by carbon and sulfur elemental analysis to explain the reason for the decrease in catalytic activity. As seen in Table 9, the carbon content of the catalyst without calcination increased with the increasing reused times, while it remained unchanged for the catalyst with calcination. This suffi-

**Table 9. Carbon and sulfur contents of the reclaimed  $\text{SO}_4^{2-}/\text{USY}$  catalysts<sup>a</sup>**

Reused time	Carbon content (wt%)			Sulfur content (wt%)		
	A	B	C	A	B	C
1	0.08	0.08	0.08	3.02	3.02	3.02
2	0.89	0.06	0.06	2.42	2.21	2.96
3	1.77	0.07	0.08	1.74	1.24	2.90
4	2.96	0.06	0.05	0.92	0.68	2.85

<sup>a</sup>A represents without calcination; B represents with calcination; C represents with regeneration

ciently demonstrated that calcination could effectively remove the carbon deposited on the catalysts. Meanwhile, the sulfur content of the catalysts decreased with the increase of reused times, indicating that the loss of  $\text{SO}_4^{2-}$  occurred during the reaction, which led to the decrease of the catalytic activity. In addition, the high calcination temperature also resulted in the loss of sulfate acid. However, the sulfur content was approximately recovered to the original level and maintained stable activity after regeneration. Therefore, the catalytic activity of  $\text{SO}_4^{2-}/\text{USY}$  could be effectively regained by calcining (to removal carbon from the surface of catalyst) and subsequently impregnating in sulfuric acid (to increase  $\text{SO}_4^{2-}$ ).

### CONCLUSIONS

$\text{SO}_4^{2-}/\text{USY}$ , a bifunctional solid catalyst, was developed for producing HFCS directly from starch in a one-pot reaction. The optimal preparation conditions of catalyst were 1.5 mol/L  $\text{H}_2\text{SO}_4$ , 550 °C of calcination temperature. A good HFCS yield of 58.34% glucose and 27.84% fructose was obtained at 150 °C for 1 h. The catalysts were characterized by XRD analysis, physical adsorption analysis,  $\text{NH}_3$ -TPD analysis and elemental analysis to interpret the relationship between the property change and the decrease of catalytic activity. Brønsted acid played the major role in the hydrolysis of starch; nevertheless, the Brønsted and Lewis acid contributed the isomerization of glucose to fructose. A small amount of acid loss occurred during the reaction, but the structure of catalyst remained unchanged. Meanwhile, a high calcination temperature may result in the loss of acid at regeneration process. The activity of  $\text{SO}_4^{2-}/\text{USY}$  could be effectively recovered by calcining and regenerating.

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