



An Effective and Inexpensive Hf/ZSM-5 Catalyst for Efficient HMF Formation from Cellulose

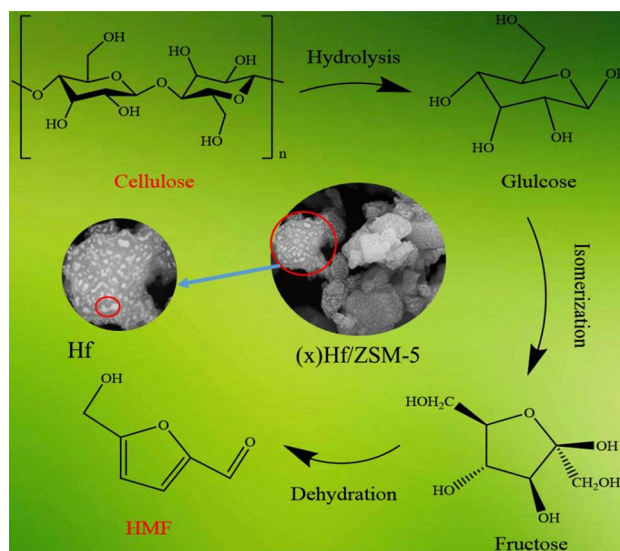
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Abstract

The production of 5-hydroxymethylfurfural (HMF) from cellulose is of great significance for the high-value utilization of biomass, although this route currently faces the challenge of low efficiency. In the present work, a series of effective (x)Hf/ZSM-5 catalysts were developed for HMF production from cellulose, and analyzed by BET, XRD, SEM, ICP, NH₃-TPD, Py-FTIR techniques. Driven by the (5)Hf/ZSM-5 catalyst, HMF with a yield of up to 67.5% and 17.2% of furfural are simultaneously obtained from cellulose in the H₂O_(NaCl)/THF biphasic system. Moreover, after four consecutive cycles, (5)Hf/ZSM-5 catalyst still maintained part of its catalytic activity. The 67.5% HMF yield achieved herein is one of the highest yields achieved in the conversion reaction using cellulose as a substrate, and the catalytic performance of the H₂O_(NaCl)/THF system containing the (5)Hf/ZSM-5 catalyst is even comparable to that of the expensive ionic liquid system. This result reflects the application prospect of (5)Hf/ZSM-5 catalyst in the future industrial production process of HMF.

Graphic Abstract



Keywords Cellulose · HMF · Furfural · Hf/ZSM-5 · Solid acid

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1 Introduction

The issues of energy scarcity and environmental problems caused by the rapidly rising resource consumption have received considerable critical attention [1]. Therefore, in

order to meet the requirements of sustainable development, studies on catalytic conversion of renewable biomass resources to high-value chemicals have been widely conducted [2, 3]. HMF, which is identified as one of the most important biomass platform chemicals because of its active functional groups, has the ability to be further transformed into high value-added chemical products such as 2,5-furandicarboxylic acid [4], 2,5-dimethylfuran [5], levulinic acid [6] and dihydroxymethylfuran [7]. Therefore, using biomass resources as a substrate to prepare HMF products with high yield and high selectivity is extremely valuable.

Notably, many efforts have been devoted to the area of catalytic conversion of biomass into HMF. High-yield HMF products can usually be realized in the catalytic conversion of simple biomass-derived monosaccharides such as fructose and glucose [7, 8]. However, as the main ingredient of the food industry, the proportion of monosaccharides that can be distributed for the HMF synthesis is quite limited. Therefore, the abundant and cheap cellulose is logically the most suitable substrate for the production of HMF [9]. The robust crystal structure of cellulose is the main difficulty hindering its efficient conversion. Referring to the previous studies, there is now a general consensus that acidic catalysts promote the degradation of cellulose [10, 11]. It is widely recognized that the conversion of cellulose to HMF is a synergistic reaction catalyzed by Brønsted and Lewis acid. This process successively undergoes the depolymerization of cellulose catalyzed by Brønsted acid to form glucose, the isomerization of glucose catalyzed by Lewis acid to produce fructose, and the subsequent dehydration of fructose catalyzed by Brønsted acid to generate HMF [12]. In response to this catalytic mechanism, a variety of effective acidic bifunctional catalysts were employed in the process of catalyzing the synthesis of HMF from cellulose. Nakajima et al. [13] received 12% HMF yield by using sole $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ as Lewis acid solid catalyst, and the yield rose to 48% through adding H_3PO_4 as Brønsted acid sites. Swift et al. [14] reported that vary two types of acid sites (e.g. in Sn-BEA and HCl) promoting the HMF formation and a plateau of HMF yield reached through adding Brønsted acid sites.

H-ZSM-5 zeolite is a well-known microporous material, has the advantages of available pore structure, high surface area and favorable thermal and hydrothermal stability. Furthermore, H-ZSM-5 zeolite itself processing both Lewis and Brønsted acid sites, and the acidity can be easily modified by metal modification (inside or outside the framework) [15, 16], wherefore ZSM-5 based catalyst is frequently used in the formation of HMF. Moreno-Recio et al. [17] utilized H-ZSM-5 zeolite as a catalyst to catalyze glucose conversion, and obtained 42% HMF yield at 195 °C for 30 min. Under the catalysis of bimodal H-ZSM-5 zeolite, Nandiwale et al. [18] used cellulose as a substrate to achieve a

considerable yield of 46% HMF products. The comparison of some C_6 substrates to prepare HMF is summarized in Table S1. Meanwhile, in the few studies, the excellent performance of hafnium (Hf) element as the active center in the formation of furan-based platform compounds has attracted our attention. Hu et al. [19] reported that extremely 98% yield of HMF was obtained from fructose over Hf-MOF catalyst at 100 °C for 60 min. Xu et al. [20] used silica supported hafnium phosphide (HfP/SiO_2) as catalyst, achieving 85% furfural yield from xylan at 180 °C for 60 min in the water_(NaCl)/THF biphasic system. Therefore, considering the excellent catalytic performance of H-ZSM-5 and Hf element, we have developed an idea to combine the beneficial effects of the two through a simple impregnation method to prepare a catalyst suitable for the production of furan-based platform compounds.

To the best of our knowledge, Hf modified H-ZSM-5 catalysts have not been synthesized and used in the production of HMF from cellulose. In the present work, after screening by reaction conditions, the optimal 67.5% HMF yield was obtained through using (5)Hf/ZSM-5 in $\text{H}_2\text{O}_{(\text{NaCl})}$ /THF system at 190 °C for 120 min, one of the highest HMF yields achieved so far in using cellulose as a substrate. In addition to HMF, furfural, another useful and important chemical, was also generated in the (5)Hf/ZSM-5-catalyzed cellulose conversion process, and the highest yield is 18.3%. Moreover, the inherent structure of the (5)Hf/ZSM-5 catalyst remained unchanged after four cycles. These satisfactory results indicate the industrial application prospects of the Hf/ZSM-5 catalyst.

2 Experimental

2.1 Materials

Cellulose (microcrystalline, 435, 236-250G) was obtained from Sigma-Aldrich (Shanghai China). 5-hydroxymethylfurfural (HMF) and furfural standard products were purchased from Aladdin (Shanghai, China). Hafnium chloride (HfCl_4) was supplied by Sigma Reagent (Shanghai, China). Tetrahydrofuran (THF) and NaCl were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). The H-ZSM-5 zeolite was obtained from The Catalyst Plant of Nankai University Catalyst Co., Ltd. in Tianjin, China. The bought H-ZSM-5 was calcined in muffle at 550 °C for 2 h to assure its protonic form (H^+ cation), and all purchased chemicals were used without further purification.

2.2 Catalyst Preparation

(x)Hf/ZSM-5 catalysts were synthesized by a simple wetness impregnation method. The typical synthesis procedure

was as follows: 2 g H-ZSM-5 and 0.036 g (1 wt%) HfCl₄ were mixed in 20 mL deionized water and stirred at room temperature for 12 h. After stirring, the mixture was dried by evaporation at 80 °C, and then be put into an oven overnight. Finally, the target catalyst was obtained through calcining at 550 °C for 3 h in the air atmosphere and masticating into powder. The (x)Hf/ZSM-5 catalysts with different Hf element loading (1 wt%, 3 wt%, 5 wt%, 7 wt%, 10 wt%) was denoted as (1)Hf/ZSM-5, (3)Hf/ZSM-5, (5)Hf/ZSM-5, (7) Hf/ZSM-5 and (10)Hf/ZSM-5 respectively. The actual Hf content in the catalysts was determined by ICP-AES and the results are collected in Table 1.

2.3 Catalyst Characterization

The elemental analysis of the samples was tested by ICP-AES (Perkin OPTIMA 5300DV).

N₂ adsorption–desorption isotherms were recorded at –196 °C on an automatic 3H-2000PS1 gas sorption system (BeiShiDe Instrument Technology Co., Ltd., Beijing, China). The specific surface area was calculated by Brunauer–Emmett–Teller (BET) equation, and the pore volume and pore size distribution were measured by Barrett–Joyner–Halenda (BJH) method. Prior to analysis, the catalysts were degassed under vacuum at 200 °C for 12 h to remove moisture and volatile impurities.

The XRD patterns were determined by X-ray diffractometer (XRD, Rigaku Ultima IV), employing Cu–K α radiation ($k=0.154$ nm, 40 kV, 40 mA) with a rate of 10°/min, scanning range from 5° to 80°.

Scanning electron microscope (SEM, Inspect F50, FEI, USA) images were obtained to assess the morphology, microstructure of samples and the element distribution.

The NH₃-temperature-programmed desorption (NH₃-TPD) was carried out to estimate the acidity of (x)Hf/ZSM-5 catalysts, using a TP-5076 catalyst analyzer (Xianquan Industrial and Trading Co., Ltd., Tianjin, China). In a typical process, 100 mg catalyst was firstly degassed at

200 °C in He flow (40 mL min⁻¹) for 1 h. Next, after the catalyst cooling to 50 °C, NH₃ was adsorbed for 0.5 h through exposing the catalyst to NH₃ atmosphere. Then, the catalyst was purged with He flow for 1 h to remove the physisorbed NH₃. Finally, desorption of NH₃ was conducted in He flow (40 mL min⁻¹) from 50 to 700 °C (10 °C min⁻¹).

Pyridine adsorption infrared spectroscopy (Py-FTIR) was applied to detect the Lewis and Brønsted acidic sites of the catalysts through a Frontier Fourier Transform Infrared Instrument. After evacuating at 400 °C and 0.06 Pa for one hour, the sample was next exposed to pyridine vapor for one hour at room temperature, and finally outgassed at 150, 250 and 350 °C. The IR spectra were recorded at a resolution of 4 cm⁻¹ in the range of 1700 cm⁻¹ to 1400 cm⁻¹.

The GC–MS was used for by-products analyzing. A GC (Agilent Technologies 7890A) was used at a rate of 10 °C min⁻¹ from 40 to 280 °C, and MS analysis (Agilent Technologies 5975C) employed a Triple-Axis Detector.

2.4 Typical Procedure of Catalytic Test

In a typical process, 100 mg cellulose, 50 mg (1)Hf/ZSM-5, 200 mg NaCl and solvent (H₂O/THF, 1/4 mL) were mixed together into a 15 mL pressure-resistant glass tube, heating and stirring in oil bath mixer. Start timing once the specified temperature was reached and stop heating upon predefined time. After reaction, the mixture should be cooled to room temperature and then separated by centrifugal filtration for further analysis.

2.5 Product Analysis

Quantitative analysis of HMF and furfural in the liquid phase was determined by HPLC (Shimadzu LC-2010AHT) with a XDB-C18 column at ultraviolet wavelength of 280 nm at 35 °C, and the mobile phase was a mixed solution with 70 vol% methanol and 30 vol% water flowing at a speed of 0.5 mL min⁻¹ (the legend of HPLC is shown in Fig. S1). The yields

Table 1 Physicochemical properties of H-ZSM-5 and (x) Hf/ZSM-5 catalysts

Catalysts	S _{BET} ^a (m ² /g)	V _{pores} ^b (cm ³ /g)	D _{mean} ^c (nm)	Hf (wt%) ^d	Si (wt%) ^d	Hf/Si
H-ZSM-5	343.3	0.270	2.62	–	–	–
(1)Hf/ZSM-5	326.6	0.233	2.61	0.85	2.5	0.3
(3)Hf/ZSM-5	305.6	0.224	2.96	2.5	2.6	1.0
(5)Hf/ZSM-5	304.7	0.208	2.97	4.3	2.8	1.5
(7)Hf/ZSM-5	296.2	0.199	3.15	5.7	2.4	2.4
(10)Hf/ZSM-5	280.9	0.187	3.20	7.9	2.6	3.0
Recycled (5)Hf/ZSM-5	167.8	0.134	3.30	2.1	1.4	1.5

^aBET surface area was determined from N₂ adsorption isotherm

^bVolume of pore was determined from single point desorption method

^cAverage pore size was determined from the desorption average pore diameter(4 V/A by BET)

^dDetermined by ICP-AES

of HMF and furfural were defined according to the following equations:

$$\text{HMF yield from cellulose (mol\%)} = \frac{\text{moles of HMF produced}}{\text{moles of glucose units}} \times 100$$

$$\text{Furfural yield from cellulose (mol\%)} = \frac{\text{moles of furfural produced}}{\text{moles of glucose units}} \times 100$$

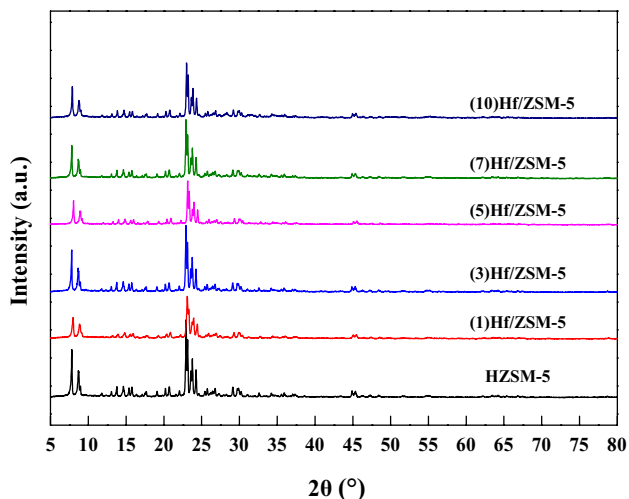


Fig. 1 XRD patterns of H-ZSM-5 and (x)Hf/ZSM-5 catalysts

3 Results and Discussion

3.1 Characterization of the Catalysts

The ICP results were shown in Table 1, testifying the actual Hf loading of catalysts were close to expected value.

The XRD patterns of the parent H-ZSM-5 zeolite and synthesized (x)Hf/ZSM-5 catalysts are shown in Fig. 1. It can be seen from Fig. 1 that the diffraction peaks displayed by the (x)Hf/ZSM-5 catalysts are consistent with the parent H-ZSM-5 zeolite, indicating the introducing of Hf element had no significant effect on the framework of catalysts. Meanwhile, diffraction signals of bulk hafnium oxide species were not detected, suggesting no accumulation and sintering of Hf element occur during preparation, and Hf element in (x)Hf/ZSM-5 catalysts was uniformly dispersed into the zeolitic framework.

Figure 2 displays the SEM images of H-ZSM-5 and (x)Hf/ZSM-5 catalysts. In all samples, (x)Hf/ZSM-5 catalysts showed a well-defined hexahedral morphology, consistent with the structure of crystalline H-ZSM-5 zeolite particles. Additionally, the obvious attachment appeared with introduction of Hf element, indicating Hf element was successfully loading on the surface of H-ZSM-5 zeolite. And from the result of SEM-EDS (Fig. S2), the Hf element shown was uniformly dispersed on (x)Hf/ZSM-5 catalysts. These results are consistent with the above-mentioned XRD analysis.

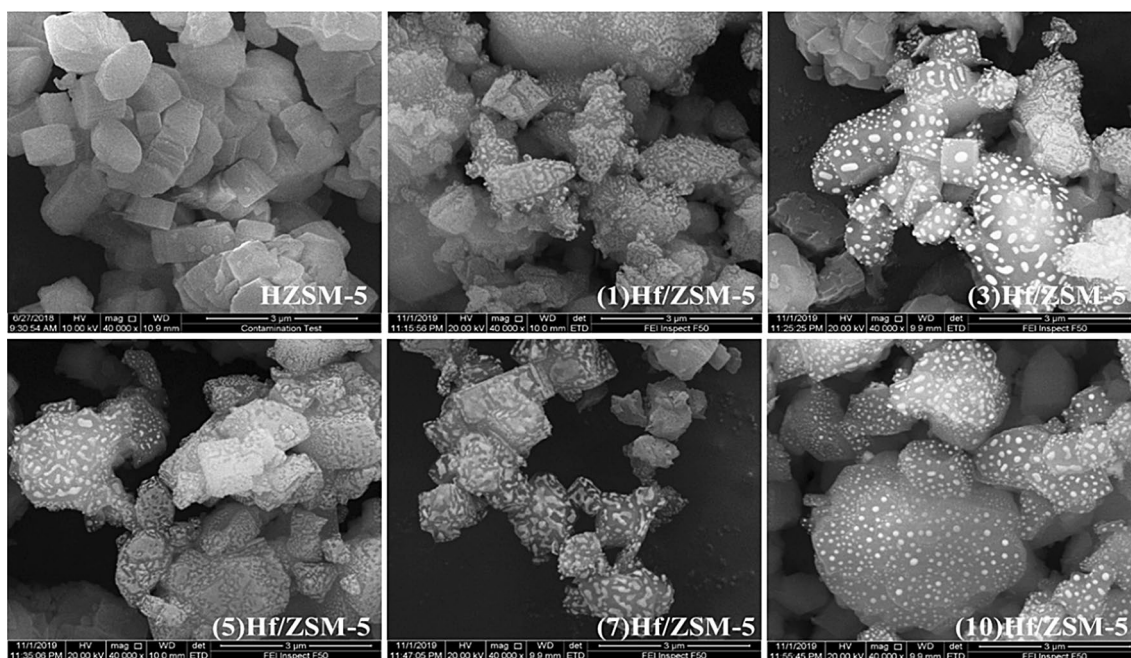


Fig. 2 SEM images of H-ZSM-5 and (x)Hf/ZSM-5 catalysts

Figure S3 shows the N_2 adsorption–desorption isotherms of H-ZSM-5 and (x)Hf/ZSM-5, all samples exhibited type IV isotherms with a clear hysteresis loop, showing a typical adsorption of microporous H-ZSM-5 and the presence of mesoporous structure [21]. It can be found from Table 1 that as the Hf element content continues to increase, the specific surface area (from 320.6 to 280.9 m^2/g) and pore volume (from 0.233 to 0.187 cm^3/g) of the corresponding (x)Hf/ZSM-5 catalysts gradually decrease. The reason for this result is that the introduced Hf species blocked the pores and channels of the parent H-ZSM-5 zeolite [22]. Accompanied by the gradual increase in the average pore diameter of the (x)Hf/ZSM-5 catalysts (from 2.61 to 3.30 nm), this phenomenon is caused by the existence of excessive available mesopores due to the blocking of micropores [19, 23].

In order to evaluate the acidic characteristics of the (x)Hf/ZSM-5 catalysts, NH_3 -TPD analysis technology was employed and the analysis results are shown in Fig. 3. There were two desorption peaks observed in parent H-ZSM-5 zeolite around 190 °C and 450 °C, corresponding with weak and moderate acid sites respectively [24]. With the initial introduction of Hf element (1 wt% and 3 wt%), desorption peaks at 670 °C, which are attributed to strong acid sites, appeared in the correspondingly formed (1)Hf/ZSM-5 and (3)Hf/ZSM-5 catalysts. Unexpectedly, after the loading of Hf element was further increased (5 wt%, 7 wt% and 10 wt%), the strong acid sites in the corresponding (5)Hf/ZSM-5, (7)Hf/ZSM-5 and (10)Hf/ZSM-5 catalysts disappeared. The result indicates that the (x)Hf/ZSM-5 catalysts with low loading of Hf species can derive some strong acid sites due to their high dispersibility. For (x)Hf/ZSM-5 catalysts with high Hf loading, due to the partial agglomeration of active Hf species, the strong acid sites formed are covered or disappeared. Similar phenomena have also appeared in other reported literatures [22–24].

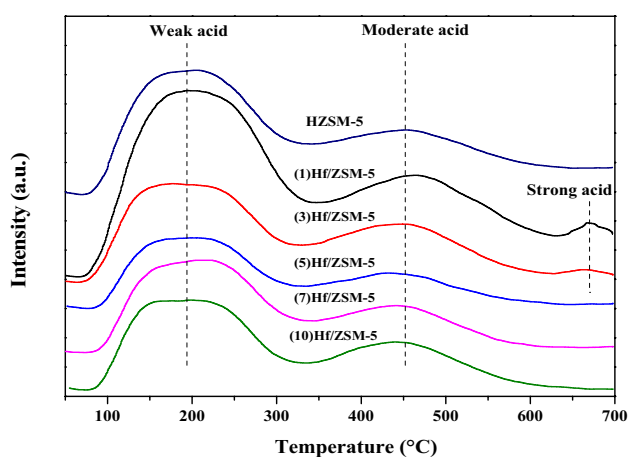


Fig. 3 NH_3 -TPD profiles of H-ZSM-5 and (x)Hf/ZSM-5 catalysts

Figure 4 presents results of Py-FTIR for the (x)Hf/ZSM-5 catalysts, the absorption bands attributed to Lewis and Brønsted acid sites are found at 1450 cm^{-1} and 1545 cm^{-1} , and another band observed at 1490 cm^{-1} is related to both Lewis and Brønsted acid sites. The quantitative analysis of catalyst acidity is summarized in Table 2. It can be clearly seen that, compared with the parent H-ZSM-5 zeolite, when Hf element is introduced, the total acidity of the formed (x)Hf/ZSM-5 catalysts drops suddenly. This result can be attributed to the active Hf species on the surface covering the acid sites of the H-ZSM-5 carrier itself [24, 25]. Then with the increase of Hf content, the total acidity of the series of (x)Hf/ZSM-5 catalysts gradually increased, indicating that the active Hf species itself is an acidic active center. Meanwhile, it can be seen from Table 2 that the ratio of the Brønsted to Lewis acid sites (B/L ratio) in the (x)Hf/ZSM-5 catalysts has a trend of first decreasing and then increasing, which demonstrates the acidity variation was tuned by adjusting Hf amount during preparation. Consequently, it is proven that (x)Hf/ZSM-5 catalysts possess both Lewis and Brønsted acid sites, and have the ability to be bifunctional catalysts for the transformation of cellulose into HMF.

3.2 Determination of Suitable Hf Content on (x)Hf/ZSM-5 for Cellulose Conversion

It can be seen from the above analysis that the acidic properties of (x)Hf/ZSM-5 catalysts could be easily tuned by altering the amount of Hf element. In order to seek a suitable acid catalyst for the conversion of cellulose to HMF, various (x)Hf/ZSM-5 catalysts with different Hf content have been investigated. A biphasic system consisting deionized water and THF was selected here as it has been proven to be beneficial for HMF formation [26]. As can be seen from Fig. 5, the HMF yield was less than 15% when there was no catalyst

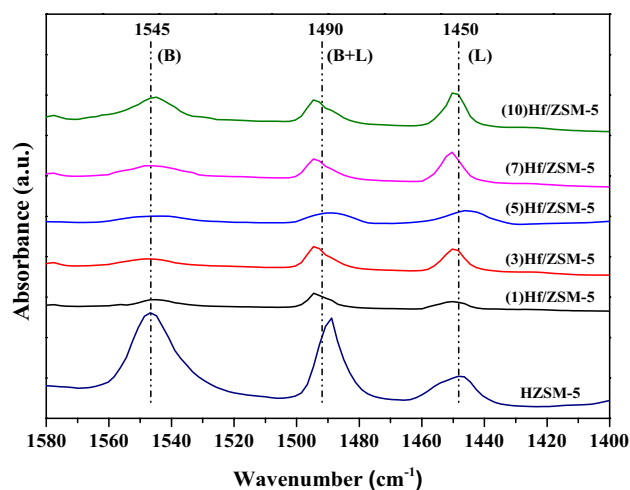


Fig. 4 Py-FTIR spectra of H-ZSM-5 and (x)Hf/ZSM-5 catalysts

Table 2 Acidity of H-ZSM-5 and (x)Hf/ZSM-5 catalysts

Catalysts	Leiwis acid sites ($\mu\text{mol/g}$)	Brønsted acid sites ($\mu\text{mol/g}$)	Total acidity ($\mu\text{mol/g}$)	Acid density ($\mu\text{mol/m}^2$) ^a	Ratio of Brønsted to Lewis
H-ZSM-5	153.9	918.13	1072.03	3.12	5.97
(1)Hf/ZSM-5	37.36	81.49	118.85	0.36	2.18
(3)Hf/ZSM-5	99.18	108.45	207.62	0.68	1.09
(5)Hf/ZSM-5	113.65	119.15	232.8	0.76	1.04
(7)Hf/ZSM-5	131.48	147.03	278.51	0.94	1.11
(10)Hf/ZSM-5	143.75	238.82	382.57	1.36	1.66

The amount of acid sites was determined by Py-FTIR at 150 °C

^aAcid density = (total acidity/ S_{BET})

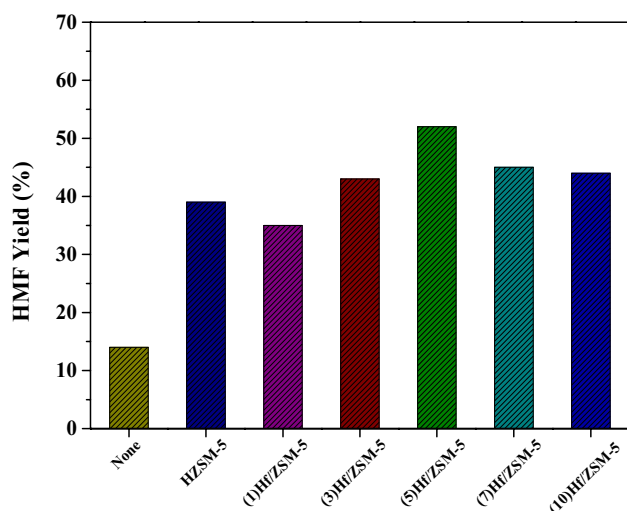


Fig. 5 HMF yield over no catalyst, H-ZSM-5 and (x)Hf/ZSM-5 catalysts. Reaction conditions: cellulose (100 mg), catalyst (50 mg), H₂O (1 mL), THF (4 mL), NaCl (200 mg), 180 °C, 180 min

in this reaction, which was intensely lower than that of possessing catalysts, suggesting the necessary of catalysts for high cellulose conversion. When (1)Hf/ZSM-5 catalyst (1 wt% Hf content) was used, only 35.5% HMF yield was provided, lower than that of unmodified H-ZSM-5 zeolite. The possible reason is that the adjustment of Hf element altered the acidic properties of catalyst, which could be proven by the sharp drop of total acidity from Py-FTIR results. Moreover, although Hf itself is active site (confirmed by NH₃-TPD results), the addition of Hf element still covered lots of original acid sites. While the Hf element in the (x)Hf/ZSM-5 catalyst increasing slowly, the catalytic efficiency improved and approached a plateau with increasing total acidity. The (5) Hf/ZSM-5 catalyst (5 wt% Hf content) exhibited the optimal catalytic performance in all (x)Hf/ZSM-5 samples, obtaining 52.0% yield of HMF, four times over than that with no catalyst. This result indicates that among the series (x)Hf/ZSM-5 catalysts, the (5)Hf/ZSM-5 catalyst has the most suitable acidic properties, including total acidity and B/L

ratio. This property makes the three processes of cellulose depolymerization release glucose, glucose isomerization to form fructose, and fructose dehydration to produce HMF under the catalysis of the (5)Hf/ZSM-5 catalyst, always in the optimal dynamic balance [14, 27]. Therefore, (5)Hf/ZSM-5 was screened as the optimal catalyst for the process of preparing HMF from cellulose.

3.3 Optimization of Reaction Parameters

3.3.1 The Effect of Reaction Temperature and Reaction Time on the HMF Yield

After determining the optimal Hf content, the effect of reaction temperature and reaction time on the catalytic conversion of cellulose was further discussed. Primarily, the reactions were monitored as a function of time from 1 to 5 h at different temperature range from 170 to 200 °C, every one hour and 10 °C as a step, settled in Fig. 6. It was obvious that the reaction temperature exhibited a significant effect on HMF yield. The three-step tandem for transportation of cellulose to HMF are endothermic [28, 29], thus higher temperature are beneficial to the formation of HMF. As shown in Fig. 6, when the reaction proceeded for 1 h, HMF yield increased with temperature rising from 25.2% (170 °C) to 57.4% (200 °C). However, when the reaction temperature was extended to 2 h, the HMF yield achieved at 190 °C was the highest, as high as 60.0%. Moreover, under this standard (190 °C, 2 h), further increasing the reaction temperature and prolonging the reaction time all resulted in a decrease in the HMF yield. This phenomenon implied that the violent reaction conditions provided excessive reaction energy, accelerating side reactions such as HMF rehydration and condensation occur more readily, led to a decrease in HMF yield and an augment of soluble polymer [30] and humins [31]. Therefore, the reaction conditions of 190 °C and 2 h were determined to be the most suitable after a comprehensive screening, which was also used as a test standard for the remaining parameter evaluation process.

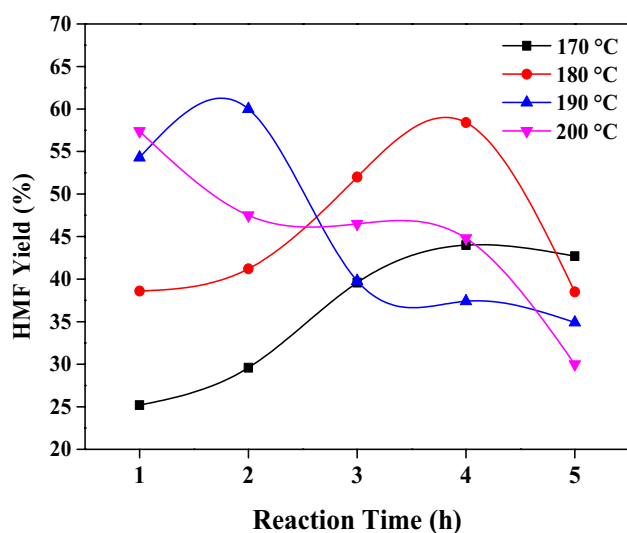


Fig. 6 Effect of reaction time at different temperatures on the HMF yield. Reaction conditions: cellulose (100 mg), (5)Hf/ZSM-5 (50 mg), H₂O (1 mL), THF (4 mL), NaCl (200 mg)

3.3.2 The Effect of Catalyst Dosage and Substrate Concentration on the HMF Yield

It is anticipated to obtain a satisfactory HMF yield in a low catalyst dosage and high cellulose concentration, hence the effect of catalyst dosage and initial substrate on the cellulose conversion process was studied and the results are correspondingly summarized in Figs. 7 and 8. When the dosage of (5)Hf/ZSM-5 catalyst was 2.5 wt%, the yield of HMF reached maximum value of 67.5%, further increases in the catalyst dosage (5.0 wt%, 7.5 wt%, 10.0 wt%) led to a decrease in HMF yield. It is because there are excessive available active sites in the system, which accelerate

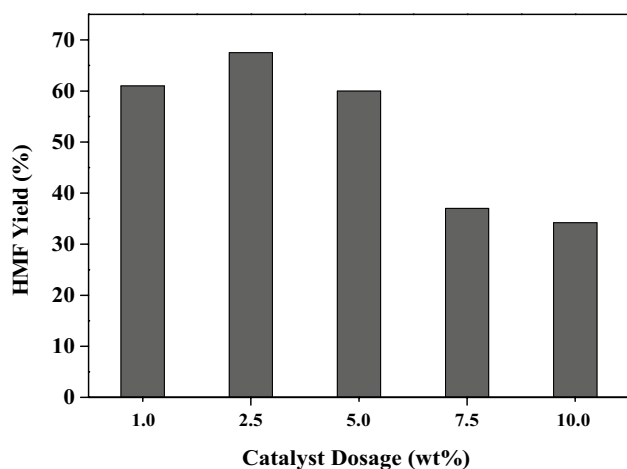


Fig. 7 Effect of catalyst dosage on the conversion of cellulose to HMF. Reaction conditions: cellulose (100 mg), H₂O (1 mL), THF (4 mL), NaCl (200 mg), 190 °C, 120 min

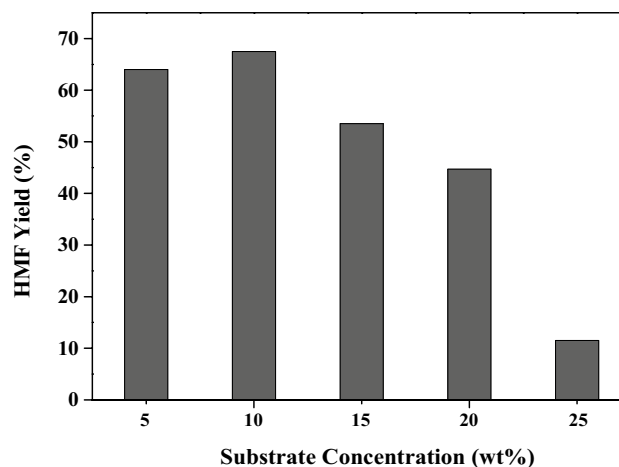


Fig. 8 Effect of substrate dosage on the conversion of cellulose to HMF. Reaction conditions: (5)Hf/ZSM-5 (25 mg), H₂O (1 mL), THF (4 mL), NaCl (200 mg), 190 °C, 120 min

the occurrence of side reactions such as fragmentation of furan compounds, the condensation between products and reactants or intermediates, and promote the formation of humins and soluble polymers [32, 33].

It can be seen from Fig. 8 that when the initial concentration of cellulose is 5 wt% and 10 wt%, the obtained HMF yields are at a high level, corresponding to 64.0% and 67.5%, respectively. As the substrate concentration further increased to 15 wt% and 20 wt%, the realized HMF yields dropped to 53.5% and 44.7%. To make matters worse, the cellulose with a concentration of 25 wt% gives only 11.5% of the low-level HMF yield. The swift decline of HMF yield in agreement with literature reported [34], that high initial cellulose concentrations probably contribute to more sugar monomers and intermediates in reaction system, which increase side reactions between these molecules and HMF. Therefore, for the (5)Hf/ZSM-5-catalyzed conversion of cellulose to HMF, the appropriate catalyst dosage and substrate concentration were determined to be 2.5 wt% and 10 wt%, and the optimal HMF yield achieved under these conditions was an impressive 67.5%.

3.4 Analysis of By-Products

In the (5)Hf/ZSM-5-catalyzed cellulose conversion process, in addition to achieving a satisfactory HMF yield, another valuable result appeared. That is, another high value-added chemical furfural is also generated simultaneously and the yield range is as high as 16.7–18.3% (Table 3). The formation of furfural from cellulose may be due to the retro-aldol reaction of fructose intermediates in the catalytic process, which results in the production of xylose [35]. It can be seen from Table 3 that a furfural yield of 17.2% was achieved under the reaction conditions of 190 °C for 2 h. It means

Table 3 Effect of reaction temperature and time on the yields of furfural

Entry	Temperature/°C	Time/min	Furfural yield/%
1	190	60	16.7
2	190	120	17.2
3	190	180	17.7
4	190	240	18.3
5	190	300	18.3
6	170	120	17.5
7	180	120	17.5
8	200	120	17.1

Reaction conditions: cellulose (100 mg), (5)Hf/ZSM-5 (50 mg), H₂O (1 mL), THF (4 mL), NaCl (200 mg)

that the total yield of furyl products simultaneously achieved under this condition is 84.7% (HMF: 67.5%, Furfural: 17.2%). For microcrystalline cellulose with a complex structure and high degree of polymerization, it is particularly rare to achieve such a high furan-based product yield through catalytic conversion, which further confirms the excellent catalytic performance of the prepared (5)Hf/ZSM-5 catalyst.

After the reaction was completed, the organic phase (THF) and the water phase in the biphasic system were separated, and the by-products dissolved therein were detected. The GC–MS analysis result of the organic phase showed that the soluble by-products formed in the cellulose conversion catalyzed by (5)Hf/ZSM-5 were C₄–C₁₅ molecular fragments and polymers, such as C₄H₈O₂, C₇H₁₄O, C₁₂H₁₀O₅ and C₁₅H₂₄O. In the aqueous phase, glucose, as a cellulose depolymerization monomer, was detected with negligible yield (<4%). Apart from these soluble by-products, humins as insoluble by-products has also been found, which can be directly observed from the dark brown organic phase and brown substances on the catalysts after the reaction (Fig. S4). All these detected by-products directly proved the existence of side reactions such as resinification, fragmentation and condensation during the formation of HMF from cellulose.

3.5 Catalytic Stability of (5)Hf/ZSM-5

The reusability of heterogeneous catalysts is one of its most important advantage, can not only evaluate the structural stability of (5)Hf/ZSM-5, but also one of the criteria for large scale HMF production. After each cycle, the (5)Hf/ZSM-5 catalyst was recovered by centrifuging, washing with deionized water and ethanol three times respectively, drying at 80 °C overnight and calcining in air at 450 °C for 3 h to eliminate the effects of residual carbon deposition. As shown in Fig. 9, with increasing number of cycles, the catalytic performance of (5)Hf/ZSM-5 lowered gradually, resulting in a

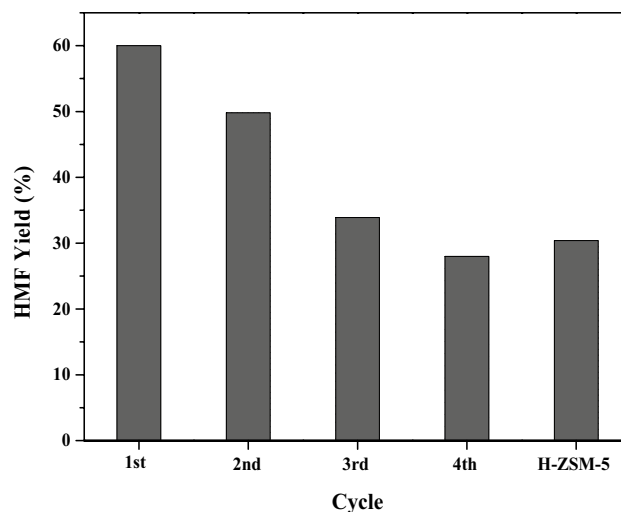


Fig. 9 The recycled (5)Hf/ZSM-5 catalyst and the parent H-ZSM-5 catalyst for HMF production from cellulose. Reaction conditions: cellulose (100 mg), catalyst (50 mg), H₂O (1 mL), THF (4 mL), NaCl (200 mg), 190 °C, 120 min

32% loss of HMF yield after four cycles of use (from 60.0% to 28.0%). Compared with the 14.1% HMF yield obtained in the blank control experiment without catalyst addition, the forth recycled (5)Hf/ZSM-5 could still achieve approximately twice of that number, implying the partial remaining of catalytic activity.

In order to recognize the reasons of catalyst deactivation, the texture and acidity properties of recycled (5)Hf/ZSM-5 catalyst have been analyzed. As can be seen from Table 1, sharply reduced specific surface area and pore volume indicate the collapse of pore structure. Meanwhile, the loss of Hf element proves the leaching of active sites [20]. Therefore, it is reasonable to believe that the collapse of the framework and the loss of active components are the causes of the degradation of the performance of the (5)Hf/ZSM-5 catalyst, and these phenomena usually occur with high probability under severe hydrothermal conditions (190 °C).

4 Conclusion

In summary, a series of (x)Hf/ZSM-5 catalysts were successfully synthesized by simple impregnation method, among which the (5)Hf/ZSM-5 catalyst exhibited an excellent catalytic performance for HMF production from cellulose. Under the optimal conditions, an outstanding 67.5% HMF yield could be achieved using (5)Hf/ZSM-5 as catalyst in H₂O/THF (1/4 mL) system at 190 °C for 120 min. At the same time, furfural in the high-yield range, soluble C₄–C₁₅ molecules and insoluble humus were detected and identified as by-products. Furthermore, after four cycles of use, the

framework structure and catalytic performance of the (5) Hf/ZSM-5 catalyst are partially maintained, confirming the potential of (5)Hf/ZSM-5 in conversion cellulose to HMF and further application.

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