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Catalytic Conversion of Glucose into 5-Hydroxymethyl Furfural Over Cu–Cr/ZSM-5 Zeolite

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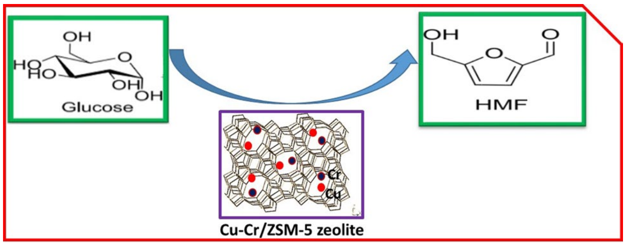
Abstract

Cu–Cr/ZSM-5 zeolite catalyst is successfully synthesized by loading Cu and Cr ions in the ZSM-5 zeolite particles using ion-exchange method. The as-obtained zeolite shows impressive efficiency when applied to the transformation reaction of glucose into 5-hydroxymethyl furfural (HMF). Technical conditions that influence HMF yield including solvent, catalyst dosage, reaction temperature, and reaction time are investigated. According to the results, suitable conditions leading to the highest yield of HMF of 50.4% are established. The synthesized Cu–Cr/ZSM-5 catalyst shows promising performance and can be considered as a potential catalyst for direct conversion of glucose to HMF. Biomass materials other than glucose might be of interest for further investigations.

Graphic Abstract

Cu–Cr/ZSM-5 zeolite catalyst was prepared and applied for conversion of glucose to 5-hydroxymethyl furfural (HMF).



Keywords 5-Hydroxymethyl furfural · Glucose · Cu–Cr/ZSM-5 zeolite · Biomass derivatives

1 Introduction

5-Hydroxymethyl-furfural (HMF) is an important immediate compound in chemical industry. HMF can be produced from lignocellulose and transformed into value-added chemicals or biofuels that help decreases the dependence of chemicals on fossil fuels [1, 2]. Production of HMF from biomass or cellulose derivatives such as glucose is, therefore, a state-of-the-art direction that contributes significantly to both science and industry.

The conversion of biomass and derivatives for production of HMF has been investigated widely using different catalysts or catalytic systems [2–4]. Xue et al. [3] have summarized the conversion of glucose and cellulose to HMF over heterogeneous catalysts. According to that, HMF could be synthesized from cellulose and glucose over metal oxides, such as TiO_2, ZrO_2. The application of zeolites like H-ZSM-5 or bimodal-HZ-5 were also successfully used for the dehydration of cellulose in water. More works on HMF production over heterogeneous catalysts including zeolites,

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metal oxides and minerals have also been reviewed thoroughly by Perez et al. [4]. Chheda et al. [5] used inorganic acid solutions such as HCl, H_2SO_4, or H_3PO_4 for synthesizing HMF and furfural from biomass via hydrolysis and subsequent dehydration. Their results showed that conversion yield of glucose into HMF was 41% and 48% when the reaction was catalyzed with HCl and H_2SO_4, respectively. When using H_3PO_4, 43% of HMF was achieved over the raw material. Lima et al. [6] investigated into the conversion of polysaccharides to furans using liquid catalyst $CrCl_3$ and ionic liquid catalyst 1-alkyl-3 methyllimidazolium chloride ([BMIM][Cl]), resulting in high yield of HMF with approx. 91%. HMF was successfully prepared from fructose–glucose mixture using acid catalyst HCl in presence of acetone and water by Pedersen and co-workers [7]. HMF yield of approx. 70% was achieved accordingly. In 2015, a study on the conversion of glucose into HMF using acid salt $Hf(OTf)_4$ in presence of water and HCl by Junjie Li et al. [8] resulted in up to 60% of HMF. Focussing on effects of solvents used during the glucose-to-HMF catalytic reaction, Cunshan Zhou and partners [9] investigated the application of several catalysts $FeCl_3{\cdot}6H_2O$, $CrCl_3{\cdot}6H_2O$, and $AlCl_3$ in presence of different solvents including H_2O, DMSO, and [BMIM][Cl]. The highest yield of HMF of 54.4% was achieved when using $CrCl_3{\cdot}6H_2O$ in DMSO. According to Su et al. [1], the conversion of cellulose into HMF using liquid catalysts such as mixture of $CuCl_2$ and $CrCl_2$ could yield in HMF of 57.5%, in which concentration of HMF in the product was up to 96%. However, the application of liquid catalysts has many drawbacks in catalyst recycling and reproducing, as well as economic and environmental issues.

Solid catalysts have several advantages over inorganic (liquid) acid catalysts [7, 8]. First of all, solid catalysts are recycleable and possess high selectivity leading to fewer by-products formed during the catalytic reactions. Second, the reusability of solid catalysts helps reduce energy consumption for the process. Another overview on the developments and catalytic applications of sulfonic-acid-based mesostructures (SAMs) has been presented by Doustkhah et al. [10]. Over ten most popular precursors for the sulfonation of mesoporous structures have been listed, such as fluoro-based sulfonic acid precursors (F-SAPs), phenylsulfonic acid siloxane-based precursors (Ph-SAPs), sulfonic acid-based carbon mesoporous materials. More works on sulfonated solid acid catalyst for preparation of furfural from different sources of biomass have also been conducted by Wang et al. [11, 12].

Among several different sorts of solid acid catalysts, zeolite ZSM-5 is one of the most popular ones, which is effective in organic syntheses [13–17]. Study on zeolite-catalyzed conversion of carbohydrates into hydroxymethylfurfural (HMF) has been performed popularly and still drawn much attention. The production of furfural from D-xylose and xylan was investigated using over sulfonated carbon-based catalyst [11], or sulfonated sporopollenin [12]. Hu et al. [18] reported the zeolite-promoted transformation of glucose to 5-HMF in ionic liquid. Jiménez-Morales et al. [19] developed a process for selective dehydration of glucose forming 5-HMF on acidic mesoporous tantalum phosphate catalyst. The selective dehydration of glucose to HMF in a biphasic medium (water/methylisobuthylketone) using different catalysts based on mesoporous MCM-41 silica containing ZrO_2 was also performed by Jiménez-Morales's group [20]. In another publication, Fang et al. [21] presented an application of Cr-exchanged montmorillonite K-10 clay as a solid catalyst for the conversion of carbohydrates into HMF. SAPO-34 catalyst was prepared by Zhang et al. [22] and used as catalyst to convert glucose into HMF in the biomass-based solvent γ-valerolactone (GVL). The nano-sized mesoporous Al_2O_3–B_2O_3 catalysts with different molar ratios of Al/B and sizes were prepared and applied as solid acids to the catalytic conversion of glucose to 5-hydroxymethylfurfural (HMF) [23].

It is well-known that metal ions once are present in zeolite catalyst structure, they are able to improve catalytic activity of the zeolite material, which is reflected by enhancements in its pore and surface structure [17]. Among many available metal catalysts, Cu and Cr ions are proved to be most effective. These catalysts have shown good performance in the conversion of cellulose or glucose into HMF resulting in high conversion yield. However, Cu and Cr ions are used in form of salt solutions, which makes the catalyst difficult to recover and reuse [1]. The motivation of this work was, therefore, to take fully advantages offered by both zeolitic catalyst and metal catalyst for preparation of solid acid Cu–Cr/ZSM-5 zeolite catalyst and applying it to the conversion of glucose into HMF.

Herein, we reported a promising solid acid catalyst, Cu–Cr/ZSM-5 for transformation of glucose derived biomass into HMF with outstanding advantages. In such processes of biomass conversion that is mentioned above, solvent also plays an important role. Among a variety of solvents that can be used, DMSO and THF/H_2O are most effective ones [9]. Therefore, in this work, these solvents were used for comparison and evaluation. The results provide a new direction and contribute significantly to HMF synthesis from biomass and biomass derivatives.

2 Experimental

2.1 Materials

Chemicals were all analytical grades and mostly purchased from Sigma Aldrich such as: $CrCl_3{\cdot}6H_2O$, $CuSO_4{\cdot}5H_2O$, glucose, DMSO, THF.

2.2 Synthesis of Cu–Cr/ZSM-5 Catalyst

Mesoporous zeolite ZSM-5 was synthesized according to the work of Su et al. [1] using CTAB as mesoporogen. Gel liquor consisting of several components with following ratio was prepared: $TEOS/TPAOP/NaAlO_2/KOH/H_2O/CTAB = 8/1.05/0.1/0.85/64/500/5$. The gel liquor was poured into a closed 1 L autoclave. It was placed in a roaster, which was set at 175 °C for a specific time depending on case study. After the reaction time, products in form of micro-nano size solid particles were separated by centrifugation and washed for several times with distilled water. The obtained zeolite ZSM-5 was dried at 100 °C and calcined at 550 °C for 8 h.

Chrome and copper ions were introduced to the ZSM-5 structure by ion exchange method. ZSM-5 in powder form was well stirred in a mixed solution of 2 M $CrCl_3$ and 2 M $CuSO_4$ at room temperature for 3 h. Solid product was then washed with distilled water for several times before it was separated from the solution by centrifugation. The product was subsequently dried at 105 °C for 8 h and calcined at 550 °C for 5 h. Structural properties and features of the final product were characterized by modern analytical techniques such as XRD, IR, SEM–EDS.

2.3 Conversion of Glucose into HMF Using the Synthesized Catalyst Cu–Cr/ZSM-5

The catalytic reaction was taken place in a 150 mL pressurized reactor. 0.5 g (o.d.) of glucose was placed in a beaker. A specific amount of catalyst together with 20 mL of solvent were added. The mixture was then treated with ultrasound for 15 min before it was transferred to the reactor. The reactor was placed in a glycerin bath, which was set at 120–140 °C and kept there for 2–8 h according to experimental design. After reaction time, the reactor was cooled down to room temperature. Products were separated from each other by centrifugation. The liquid part was collected and stored in a glass bottle at 4 °C for sugar analysis using an HPLC (High Performance Liquid Chromatogaphy) Agilent 1200 system located at the Laboratory of Food Technology (HUST). Working conditions were set as follows: temperature 5–50 °C, humidity 5–96%, and using GLP/GMP compliance as standard. The system is equipped with a G1322A vacuum pump; an Aminex HPX-87P column; the stationary phase was in lead form with particle size of 9 µm, 8% cross linkage; mobile phase was ionized water, which was filtered through a 0.45 µm filter and degassed, working well at pH 5–9. Obtained data were analyzed with an Agilent 2D LC ChemStation software (G2170BA).

The solid catalyst was recovered by washing with distilled water, ethanol and subsequently dried at 105 °C. HMF yield and glucose conversion were calculated according to Hu et al. [18].

$$\text{Glucose conversion } (\%) = \left(1 - \frac{\text{Mole of glucose in products}}{\text{Starting mole of glucose}}\right) \times 100$$

$$\text{HMF yield } (\%) = \frac{\text{Mole of HMF in products}}{\text{Starting mole of glucose}} \times 100$$

3 Results and Discussion

3.1 Characterization of the Synthesized Cu–Cr/ZSM-5 Catalyst

Structure of Cu–Cr/ZSM-5 was characterized with XRD. The result is shown in Fig. 1.

According to Fig. 1, the XRD pattern of Cu–Cr/ZSM-5 zeolite product coincides with that of the parent ZSM-5 zeolite. Comparing the two spectra, it can be seen that the structure of ZSM-5 remains intact either with Cu or Cr exchanged into its structure. Cu–Cr/ZSM-5 with high crystallinity as observed at peaks $2\theta = 7 \div 10$ and $22 \div 25$ is unchanged after the ion exchange of H with Cu and Cr inside the ZSM-5 zeolite structure (see Fig. S1, Electronic Supporting Information). In addition, new peaks appearing at the $2\theta = 42$, 43, and 50; and $2\theta = 36$, 38, 48, and 59 are assigned to Cr_2O_3 and CuO, respectively (see more Figs. S2 and S3, Electronic Supporting Information) [24]. This indicates that Cu–Cr/ZSM-5 zeolite is successfully synthesized. The obtained zeolite product is highly crystallined with MFI zeolite structure.

IR spectra of the sample revealed all typical bands of an MFI type zeolite. The bands observed at 450 cm^{-1} and 550 cm^{-1} reflect internal vibrations of TO (tetrahedrons) and vibrations of the secondary building units, respectively [13, 17]. Asymmetric stretching vibration of framework Si–O–Si or Si–O–Al bonds corresponding to the band at 1099 cm^{-1} was also observed [25]. The IR spectra of Cu–Cr/ZSM-5 zeolite in Fig. 2 showed the presence of a peak at about 660 cm^{-1} for the Cr containing samples that were tentatively ascribed to asymmetric vibration of the $(Si–O–Cr)_n$ groups [13, 17]. The absorption peak at 695 cm^{-1} could be attributed to vibrational modes of CuO structures [26].

Moreover, the intensity of the band at 3450 cm^{-1} of Cu–Cr/ZSM-5 zeolite is weaker than that of the parent ZSM-5 zeolite. It can be explained that the Cu and Cr species migrated the zeolite framework and occupied H^+ position resulting in decreasing of the intensity of this band [27].

This result is also consistent and confirmed by SEM and EDS images, which are presented in Fig. 3. As seen from SEM image (Fig. 3a), particle size of the Cu–Cr/ZSM-5 zeolite is about 400 nm. On the one hand, the Cu–Cr/ZSM-5 zeolite shows high crystallinity, while its shape and size are relatively uniform. On the other hand, the particles are

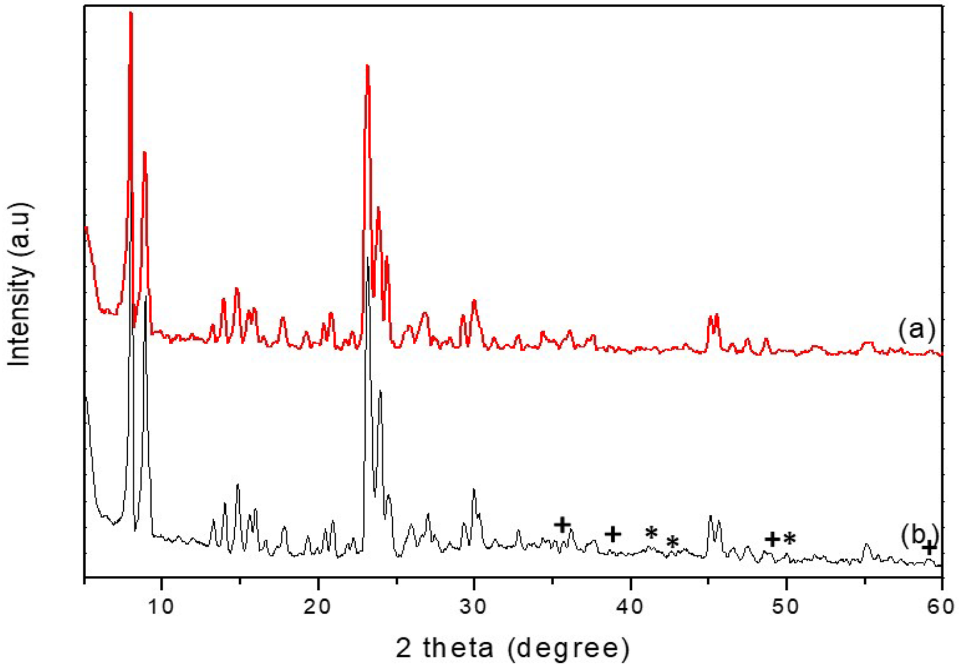

Fig. 1 XRD spectrum of (a) parent ZSM-5 and (b) Cu–Cr/ZSM-5; (+) and (*) indicate peak of CuO and Cr_2O_3, respectively

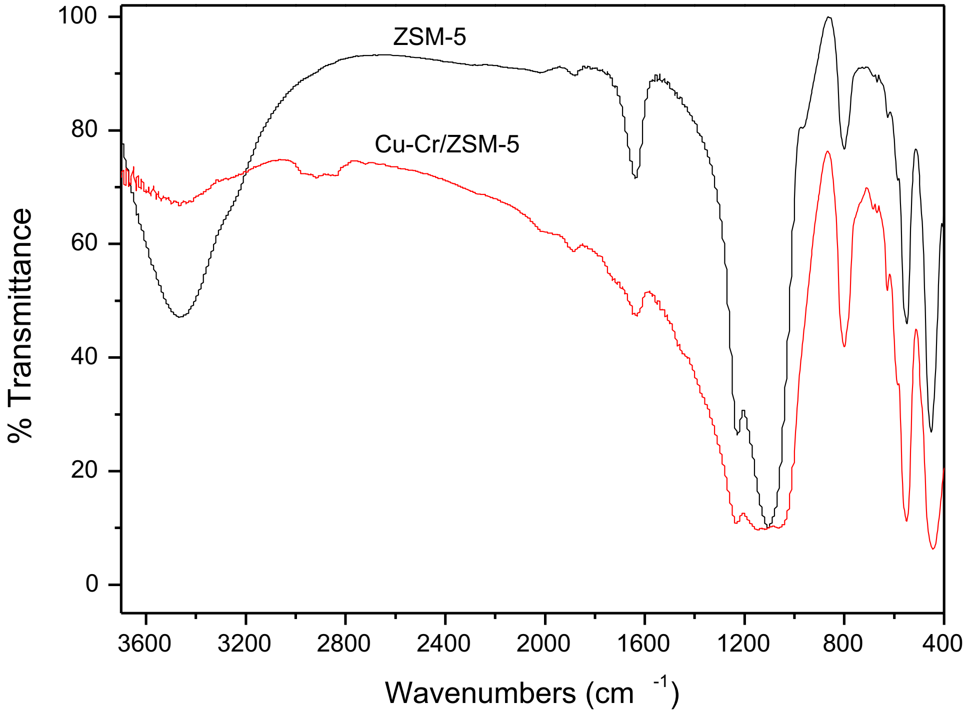

Fig. 2 IR spectra of parent ZSM-5 and Cu–Cr/ZSM-5 zeolite catalyst

orthorhombic, which is a typical configuration of ZSM-5 structure.

In addition, a variety of elements including O, Al, Si, Cr, and Cu are present as observed in EDS spectrum (Fig. 2b) of the Cu–Cr/ZSM-5 zeolite. The Cu–Cr/ZSM-5 consists of approx. 0.2 wt% of Cr, 0.6 wt% of Cu, 45.6 wt% of Si, and 1 wt% of Al. On the other hand, Si/Al ratio in the parent ZSM-5 zeolite is 48, no Cu and Cr detected. This indicates that Cr and Cu ions are successfully introduced to the ZSM-5 structure. The ions are present on the surface or inside pores by replacing H^+ ions. This result is consistent with and complements the analyzed XRD and IR data. It, therefore, can be concluded that the Cu–Cr/ZSM-5 zeolite is successfully synthesized by ion exchange method.

Calculation of BET data (Fig. S4, Electronic Supporting Information) shows that the surface area of Cu–Cr/

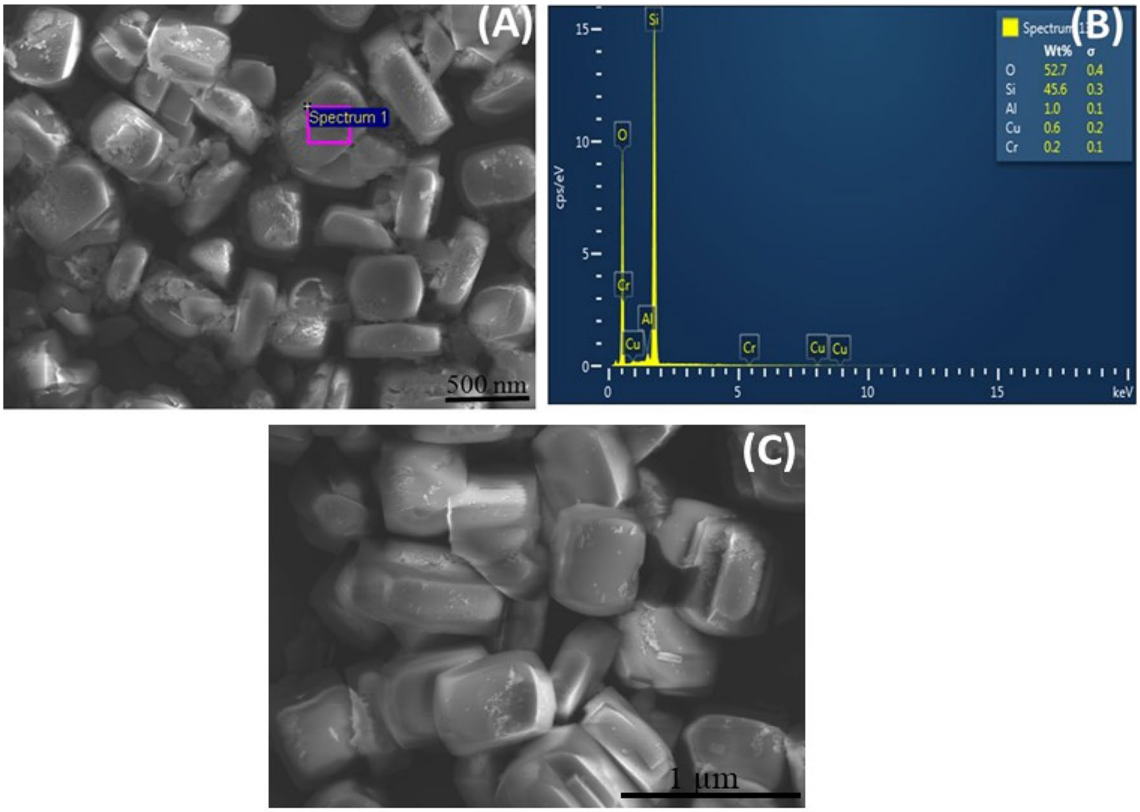

Fig. 3 SEM image (**a**) and EDS spectrum (**b**) of Cu–Cr/ZSM-5; SEM image of the parent ZSM-5 (**c**)

ZSM-5 (456 $m^2 g^{-1}$) is slightly smaller than that of the parent ZSM-5 (487 $m^2 g^{-1}$). Similarly, the pore size of Cu–Cr/ZSM-5 (5.0 nm) is also slightly smaller than that of the parent ZSM-5 (6.1 nm). This indicates that Cu and Cr ions are dispersed on the surface and/or mitigated into ZSM-5 pores.

NH_3-TPD (see Fig. S5, Electronic Supporting Information) was used to characterize the concentration and strength of acid sites by the amount of desorbed NH_3 and the location of desorption peak. It is known that total amount of ammonia desorbed (mmol/g) could correspond to the number of acid sites of catalysts. The result showed that acidity of the parent ZSM-5 zeolite is relatively high with acid concentration of 0.3 mmol/g, which is comparable to the results reported in the literature [14]. The acidity of catalyst after loading of metal ions is improved with the acid concentration of the Cu–Cr/ZSM-5 is around 2.35 mmol/g.

3.2 Application of the Synthesized Cu–Cr/ZSM-5 Catalyst for Conversion of Glucose into HMF

The conversion of glucose into HMF includes two steps: isomerization of glucose to form fructose and followed by dehydration of the fructose producing HMF. This reaction is often catalyzed by inorganic acids. In order to determine catalytic activity of the as-synthesized zeolite, Cu–Cr/ZSM-5 catalyst was applied to a conversion reaction of glucose instead of using traditional catalysts. Factors influencing the yield of HMF by catalytic conversion of glucose including solvent, temperature, catalyst dosage, and time are investigated to find the most suitable reaction conditions.

The main purpose of using solvents is to dissolve reactants making them able to contact well with each other as well as with catalyst if available, and therefore facilitate the reaction. In this work, DMSO and THF/H_2O solvents were used alternately, while other parameters were kept constant. After the reaction, the catalyst was separated from the main product by centrifugation. The product was subject to HPLC analysis for determination of the conversion effiency. Influence of solvent on the HMF yield is illustrated in Fig. 4.

As can be seen from Fig. 4, the conversion efficiency is improved remarkably when switching solvent from THF/H_2O to DMSO or in other words solvent influences obviously HMF yield. The HMF yield when using THF/H_2O is 11.4%, while it is 2.5 times higher (28%) when DMSO was used. Hydrogen bonds formed between the acidic site of the Cu–Cr/ZSM-5 and THF, H_2O are believed to be the reason that leads to this phenomenon. These hydrogen bonds would reduce the acidity and catalytic activity of acidic zeolite catalyst. In addition, low solubility of the reaction mixture in THF/H_2O due to low polarity of the two components also

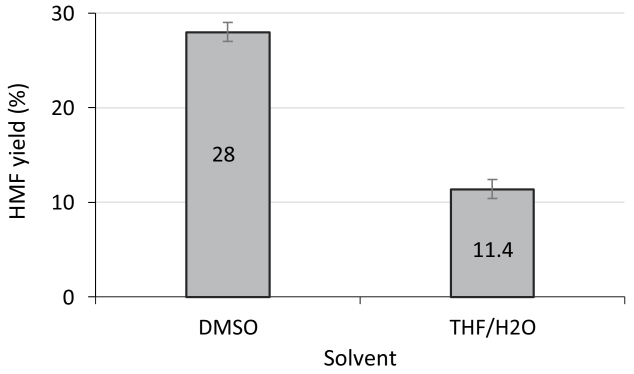

Fig. 4 Influence of solvent on glucose-to-HMF conversion efficiency (experimental conditions: glucose: 0.5 g, catalyst dosage: 30%; reaction time: 2 h; temperature: 130 °C; solvent volume: 20 mL)

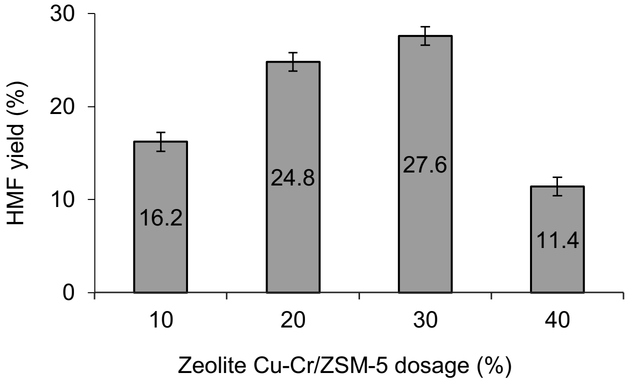

Fig. 5 Influence of catalyst proportion on HMF yield (experimental conditions: glucose: 0.5 g; temperature: 130 °C; solvent: 20 mL of DMSO, time: 2 h)

limits the interaction between the reactants resulting in low reaction efficiency. Furthermore, the presence of water may negatively affect the fructose dehydration for HMF formation. Possessing higher polarity than THF and H_2O, DMSO is a great solvent for dissolving reagents like glucose. Thanks to this property, DMSO facilitates the mixing of glucose molecules and catalyst. On the other hand, as an anhydrous solvent, DMSO can absorb water to promote the dehydration reaction resulting in high conversion efficiency. According to the obtained results, DMSO was chosen for further investigations including glucose hydrolysis for HMF [9].

It is well known that catalyst plays a very important role in organic syntheses. In this work, effect of catalyst loading on the acquisition of HMF obtained by glucose conversion using the Cu–Cr/ZSM-5 catalyst was investigated. Catalyst dosage was varied from 10 to 40% based on dried weight of the glucose, while other parameters were kept contstant. Influence of catalyst dosage on HMF yield is presented in Fig. 5.

It can be seen from Fig. 5, the Cu–Cr/ZSM-5 catalyst amount has influenced clearly the glucose conversion for HMF. Increasing the zeolite dosage from 10 to 20%, HMF yield is improved dramatically from 16.2 to 24.8%. However, as the dosage increases from 20 to 30%, the efficiency of HMF acquisition only rises insignificantly from 24.8 to 27.6%. When using higher amount of the catalyst, i.e. 40%, HMF yield decreased dramatically. The reason is clear as using a large amount of catalyst results in partial precipitation and deposition of the catalyst on the bottom of the reactor. It is, therefore, difficult for the glucose to approach. In addition, side reactions and adsorption into pores of catalyst particles can also reduce HMF yield. Considering both efficiency and economic issue, the catalyst dosage of 20% is chosen for further investigations.

According to thermodynamics law, temperature is one of the key factors that affect the performance of chemical transformation reactions. Therefore, in this work, reaction temperature was varied from 120 to 140 °C to study the effect of temperature on the conversion yield, while other conditions were maintained constant. Influence of reaction temperature on HMF yield is summarized in Fig. 6.

According data shown in Fig. 6, HMF yield clearly depends on reaction temperature. Increasing reaction temperature from 120 to 140 °C results in a significant increase in HMF yield from 14.4 to 38.5%, respectively. This can be explained by the thermodynamics theory. As temperature rises, diffusivity as well as number of effective collisions between reactant molecules and with acid sites of the catalyst are improved. Reaction temperature is, therefore, selected at 140 °C for further study.

To investigate the effects of reaction time on the conversion of glucose into HMF, the conversion reaction was carried out for different periods of time ranging from 2 to 8 h. Other conditions such as solvent, catalyst dosage, and temperature were kept constant. As seen from Fig. 7, both

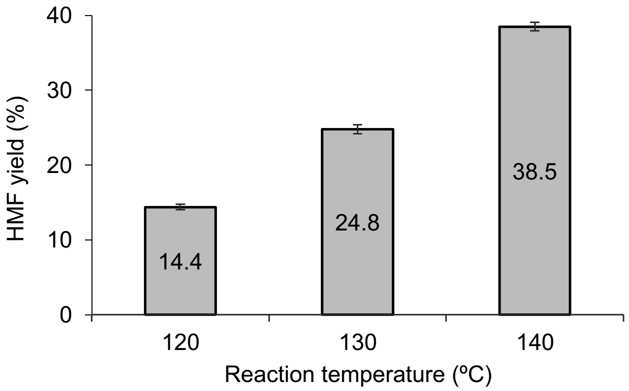

Fig. 6 Influence of reaction temperature on HMF yield (experimental conditions: glucose: 0.5 g; catalyst dosage: 20%; solvent: 20 mL of DMSO, reaction time: 2 h)

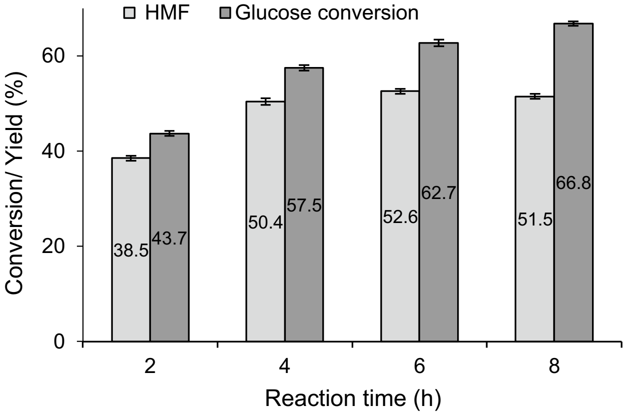

Fig. 7 Influences of reaction time on yield of HMF and glucose conversion (experimental conditions: glucose: 0.5 g; catalyst dosage: 20%; solvent: 20 mL of DMSO; temperature: 140 °C)

HMF yield and glucose conversion yield are improved when lengthening the reaction time. However, when conducting the reaction for longer than 4 h, HMF yield tends to decrease slightly. HMF yield reaches the highest yield of 52.6% after 6 h of reaction. In case of glucose, the conversion yield keeps rising from 43.7 to 66.8% when increasing the reaction time from 2 to 8 h. Looking closely to the data, both HMF yield and glucose conversion rises sharply when increasing reaction time from 2 to 4 h. After 4 h of reaction with 50.4% of HMF achieved, this parameter seems to remain constant, which can be considered as a sign of saturation. Formation of by-products during the reaction and decomposition of HMF forming humin or other compounds can be the reason of this phenomenon. Therefore, 4 h is chosen as suitable reaction time for the catalytic conversion.

Furthermore, the synthesized Cu–Cr/ZSM-5 zeolite was subject to several runs of the glucose conversion reaction to examine its reusability and durability. Reaction conditions were kept constant at 140 °C for 4 h, and 20 wt% of catalyst loading in DMSO solvent. Results show that Cu–Cr/ZSM-5 solid catalyst can be reused effectively for at least 6 times with only modest decrease in catalytic activity. After the sixth run, the obtained amount of reducing sugars is about 49.6%, quite close to the first run with about 50.4% of HMF. This indicates that the Cu–Cr/ZSM-5 is highly stable in such catalytic reactions and is more resilient to catalytic deactivation.

4 Conclusions

Cu–Cr/ZSM-5 zeolite is successfully synthesized with high crystallinity, while the MFI specific structure of ZSM-5 zeolite is retained unchanged. The Cu–Cr/ZSM-5 shows high catalytic activity and efficiency in the glucose conversion. In addition, suitable conditions for the acquisition of HMF from glucose have also established. The suitable parameters are as follows: dosage of Cu–Cr/ZSM-5 zeolite catalyst: 20% based on dried weight of glucose; reaction temperature: 140 °C; reaction time: 4 h; using DMSO as solvent. Under these conditions, approx. 50.4% of HMF is achieved from glucose. The obtained results show that Cu–Cr/HZSM-5 zeolite can be considered as a promising catalyst for conversion of glucose to HMF as well as for lignocellulosic processing.

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