

Direct Conversion of Cellulose Into 5-HMF By Transition-Metal Doped Montmorillonite Catalyst In Water

Ebru Tunç

Eskişehir Technical University

Emir Zafer Hoşgün

Eskişehir Technical University

Halit L. Hoşgün

Bursa Technical University

Berrin Bozan (✉ bbozan@eskisehir.edu.tr)

Eskişehir Technical University <https://orcid.org/0000-0002-3112-5784>

Research Article

Keywords: Cellulose, 5-HMF, Solid acid, Transition metals, Montmorillonite, Hydrothermal

Posted Date: November 10th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-1023161/v1>

License:   This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Abstract

In this study, transition metal doped montmorillonite catalyts (Cr-MMT, Cu-MMT, Fe-MMT and Zn-MMT) were successfully synthesized by hydrothermal method and evaluated for the conversion of cellulose to 5-HMF in the water media. Metal-MMT catalyts were characterized by XRD, BET, Ammonia-TPD and pyridine-FTIR to investigate the properties of the samples. Using Cr-MMT, an efficient conversion of cellulose to 5-HMF was achieved in the water system, affording a conversion yield 93.47% and 5-HMF yield 9.07% within 6 h at 200°C.

1. Introduction

Lignocellulosic biomass is a promising resource for the production of fuels, chemicals and energy products. It is a cost-effective, environmentally friendly and renewable resource and the best alternative to fossil fuels. Cellulose is the main component of lignocellulosic biomass and depolymerization of cellulose leads to simple C6 sugar monomers (glucose), which are suitable for subsequent upgrading to platform chemicals (Kumar et al. 2021). Hydroxymethylfurfural (HMF) is one of the most attractive cellulose-derived biochemical. HMF can be synthesized by acid-catalyzed dehydration of fructose, glucose, sucrose, or cellulose. The conversion of cellulose to HMF is challenging due to its chemical structure, which makes the polymer insoluble in many conventional solvents and depends on a favorable catalyst that acts synergistically with a suitable reaction medium (Yu and Tsang 2017).

There are numerous studies in the literature on the conversion of lignocellulosic biomass and cellulose in the presence of homogeneous acid catalyts or enzymes. However, these two types of catalyts have some disadvantages. Enzymatic reactions are slower and the cost of enzymes is high. Homogeneous acid catalyts are effective for biomass conversion, but they tend to corrode and are difficult to separate and reuse from the reaction mixture (Xue et al., 2016). Solid acid catalyts are an attractive alternative to homogeneous acids as they are safer and more environmentally friendly according to green chemistry principles. The use of different solid acid catalyts for cellulose conversion has been investigated in various studies. Among these heterogeneous catalyts, metal oxides are most commonly used due to their property-tunable solid acids (Lanzafame et al. 2012, Shao et al. 2021). Shirai et al reported that the maximum 5-HMF yield was obtained over Al-SBA-15 catalyts (Shirai et al. 2017). Lanzafame et al investigated several solid acid catalyts such as zeolites (H- BEA, H- MOR), sulfated zirconia on mesoporous silica (SBA-15) for the conversion of cellulose. Among these catalyts, microporous zeolite showed the highest catalytic activity for the formation of glucose and 5-HMF from cellulose, which is attributed to the presence of shape selectivity effects that limit the polymerization of glucose to humin species (Lanzafame et al. 2012). In the conversion of cellulose, Brønsted acid is known to promote the hydrolysis of cellulose to sugars, while Lewis acid is essential for the conversion of carbohydrates to 5-HMF (Yu et al. 2018). It is believed that the strong Brønsted and Lewis acid of the catalyts could efficiently increase the hydrolysis reaction rate, which also promotes the further reactions such as the conversion of glucose to 5-HMF. Therefore, bifunctional catalyts (Lewis acid/Brønsted acid ratio balanced) are ideal for the production of HMF from cellulose (Kassaye et al. 2016).

Montmorillonite is a type of clay with a three-layered structure of acidic silica minerals that is available on the market at low cost (Fang et al. 2014). Some studies have been reported on the production of HMF and furfural using montmorillonite. Li et al. synthesized tin on montmorillonite (Sn-MMT) to convert xylose and corncob hydrolysate into furfural. The maximum furfural yield of 76.79% with conversion efficiency of 93.13% and furfural selectivity of 82.45% was obtained at 180 °C for 30 min using xylose as raw material in SBP/NaCl-DMSO system (Li et al. 2015). Fang et al. prepared metal (Al, Cr, Zn, Cu, Fe) exchanged K-10 clay. K-10 clay-Cr proved to be the best catalyst for the conversion of glucose. Glucose was converted to 5-HMF at 120 °C after 2 h using the solvent system [BMIM]Cl-DMSO, yielding 56.3% (Fang et al. 2014). But none of the previous researches have investigated Lewis metal-MMT solid catalysts for the conversion of cellulose to HMF. Moreover, the use of organic solvents or ionic liquids as solvents is both expensive and unsuitable for environmental pollution. Therefore, the conversion of a solid acid catalyst and cellulose in hot water seems to be the most attractive option for one-step catalytic glucose and 5-HMF production without isolation of intermediates (Gromov et al. 2017).

In this study, solid acid catalysts were synthesized by applying different transition metals (Cr^{+3} , Cu^{+2} , Fe^{+3} , and Zn^{+2}) onto montmorillonite clay by wet impregnation and the effects of these solid acid catalysts on the conversion of cellulose to 5-HMF were investigated. In addition, the effects of various reaction parameters on cellulose conversion and product distribution were investigated.

2. Material And Methods

2.1 Material

Microcrystalline crystalline cellulose, glucose, xylose, 5-HMF, furfural, levulinic acid, formic acid, K10-montmorillonite, $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were obtained from Sigma-Aldrich. Aminex HPX 87H column was purchased from Bio-Rad Laboratories (California, USA). All chemicals used were of analytical grade and were obtained from Sigma-Aldrich.

2.2 Catalyst preparation

The doped montmorillonite catalysts were prepared by impregnation with metal nitrates (10 wt%). The nitrate salts of metals were dissolved in ethanol-water mixture (50-50% v:v) and montmorillonite was added to the solution and mixed for 24 hours. The collected clay was washed with deionized water, dried under vacuum at 40°C and calcined at 400°C for 4 hours. 5Cr-MMT, 10Cr-MMT, 15Cr-MMT were prepared by the same method by adding different amounts of chromium (5%, 10%, 15% by weight).

2.3 Characterization

The X-Ray Diffraction (XRD) patterns of the catalysts were carried out on a Rigaku Ultima II in the range of 2θ from 5 to 80. The accelerating voltage and applied current were 40 kV and 15 mA, respectively. The

measurement of Brunauer-Emmett-Teller (BET) surface area, average pore width, and pore volume was performed using the Micromeritics Tristar II Surface Area and Porosity Instrument model. The pore size distributions and pore volume of the samples were calculated using the Barrett-Joyner-Halenda (BJH) method. Before analysis, all samples were degassed at 573 K for 24 h under vacuum. NH_3 -TPD was performed using a Micromeritics chemisorption instrument 2720 equipped with a TCD detector. The Bronsted and Lewis acid sites of the synthesized catalyst were determined by FTIR spectra (ThermoScientific Nicolet IS10 FTIR) of the adsorbed pyridine (Yu et al 2018). The ratio of Bronsted and Lewis acidity was calculated from the area under the peaks of the Bronsted (1540 cm^{-1}) and Lewis sites (1450 cm^{-1}).

2.4 Catalytic conversion of cellulose

The catalyst screening experiments were carried out in a 140 mL stainless steel high pressure reactor (PARR, USA) at a temperature of 180°C and for 2 hours. 5 g of cellulose was added to the reactor containing 500 mg of solid acid catalyst in 50 mL of water. The solution was kept liquid under N_2 atmosphere. At the end of the treatment, the treated slurry was collected and filtered with filter paper to separate the solid and liquid fractions for further analysis. Parametric studies with Cr-MMT catalysts were carried out in a 500 mL stainless steel reactor (PARR, USA). The desired amount of cellulose, distilled water and catalyst was added to the reactor. The reactions were carried out at a temperature of $160\text{-}220^\circ\text{C}$. Liquid samples were taken at different time intervals. The composition of the liquid products was analyzed by high-performance liquid chromatography (HPLC), which was mainly equipped with a Bio-Rad Aminex HPX-87H column ($300\text{ mm} \times 7.8\text{ mm}$) and a refractive index detector. The analytical column was operated at 60°C with $0.2\text{ }\mu\text{m}$ filtered $0.005\text{ M H}_2\text{SO}_4$ solution as the mobile phase. The flow rate of the mobile phase was 0.6 ml/min (Sluiter, et al 2008). The molar product yields were calculated using the initial mole content of cellulose.

$$\text{Cellulose Conversion (\%)} = \frac{\text{Converted cellulose concentration}}{\text{Initial cellulose concentration}} \times 100 \quad (1)$$

$$\text{5-HMF Yield (\%)} = \frac{\text{Produced 5-HMF}}{\text{Potential glucose amount in cellulose}} \times 100 \quad (2)$$

$$\text{Selectivity of 5-HMF (\%)} = \frac{\text{5-HMF yield}}{\text{Cellulose conversion}} \times 100 \quad (3)$$

3. Results And Discussion

3.1 Characterization of the catalyst

Figure 1 shows the XRD patterns of the doped and undoped MMT catalysts. Montmorillonite has three main diffraction peaks at $2\theta = 9, 19$ and 35 (Garade et al. 2010; Husin et al. 2015). The intense peak at $2\theta = 27$ could be attributed to quartz. XRD analysis shows that the metals are well dispersed over the MMT clay and do not penetrate into the MMT skeleton. Similar XRD patterns were observed for all catalysts.

The N₂ adsorption/desorption isotherms were used to analyze the porosity of the transition metal MMT catalysts. According to the IUPAC classification, all catalysts have the type IV with H3 hysteresis, indicating a typical mesoporous structure. All catalysts exhibited a maximum pore volume around 50Å diameter. The surface area, pore volume and average pore size of the samples are listed in Table 1. The BET surface area of montmorillonite was 230.4 m²/g. After the impregnation process, the surface area of the catalysts decreased due to the deposition of species, while the pore volume and pore diameter did not change significantly up to 10% Cr.

Table 1
Textural properties of MMT, Cr-MMT, Cu-MMT, Zn-MMT and Fe-MMT catalysts

	Surface Area (m ² /g)	Pore Volume (m ³ /g)	Average Pore size (Å)
MMT	230.4	0.2863	49.7
Cr-MMT	221.8	0.2821	50.9
Cu-MMT	214.0	0.2708	50.6
Zn-MMT	220.1	0.2784	50.6
Fe-MMT	223.3	0.2799	50.7
5Cr-MMT	214.4	0.2710	50.7
10Cr-MMT	221.8	0.2821	50.9
15Cr-MMT	204.6	0.2492	48.8

The NH₃- TPD profiles of MMT, Cu-MMT, Cr-MMT, Zn-MMT and Fe-MMT catalysts are shown in Figure 2. In the area under the TPD curve, there were two distinct desorption peaks which divided them into two acidic regions, namely weak and strong acidity in the ranges of 100°C to 200°C and 350°C to 600°C, respectively (Putluru et al. 2016; Liu et al. 2013). The total acidity of the catalysts, as measured by the amount of ammonia desorbed, ranged from 0.249 to 0.460 mmol/g (Table 2). Compared to MMT, impregnation with metals decreased the total acidity of the catalysts (Table 2), which could be due to the

metal species replacing or covering the acidic sites (He et al., 2019). However, the intensity of these two peaks increased with increasing Cr content, indicating that a larger number of acid sites were formed.

Table 2
Acid content and NH₃-TPD peak temperatures of MMT catalysts

	Weak acid		Strong acid		Total acid amount (mmol/g)	Lewis/Brønsted
	Peak temperature (°C)	Acid amount (mmol/g)	Peak temperature (°C)	Acid amount (mmol/g)		
MMT	157.2	0,001	536.2	0.459	0.460	0.82
Cr-MMT	155.6	0.014	571.8	0.299	0.313	1.08
Zn-MMT	189.1	0.026	543.3	0.380	0.386	0.89
Fe-MMT	182.2	0.014	556.7	0.309	0.323	0.87
Cu-MMT	194.6	0.012	550.5	0.304	0.316	0.87
5Cr/MMT	145.3	0.019	548.6	0.230	0.249	0.86
10Cr-MMT	155.6	0.014	571.8	0.299	0.313	1.08
15Cr-MMT	156.1	0.023	527.2	0.420	0.423	1.27

Brønsted and Lewis acid sites were evaluated by the pyridine adsorption method to determine the relationship between the acid type and the catalytic activity of the prepared catalyst (Yu et al. 2018). Brønsted acid sites are observed in the FTIR spectra with an absorption peak at 1540 cm⁻¹, while the absorption peak of Lewis acid sites is found at 1450 cm⁻¹ (Figure 3). The Lewis/Brønsted ratio (L/B) was calculated based on the area under the corresponding peaks (Cao et al. 2019) and is shown in Table 2. The L/B ratio was highest for the MMT catalyst modified with Cr among all metals.

3.2 Comparison of the performance of the catalysts under constant reaction conditions

In this work, the conversion of cellulose under hydrothermal conditions in the presence of MMT doped with transition metals as a solid acid catalyst was investigated. First, the performance of the different transition metal-MMT catalysts (Cr, Cu, Zn, Fe) was evaluated under constant conditions, at 180 °C for 2 h in water as reaction medium. To understand the role of catalyst in the conversion of cellulose, an idle run (without catalyst) was carried out by treating cellulose with water.

The process of HMF synthesis from cellulose involves the steps of hydrolysis, isomerization and dehydration. During the process, levulinic acid and formic acid are formed from HMF. Further hydration of HMF to levulinic acid and polymerization of HMF by itself to form humins have been the bottlenecks in

selective production of HMF from biomass conversion (He et al. 2019; Rout et al. 2016). The cellulose conversion results and yields of HMF, levulinic acid, and formic acid are shown in Figure 3. In the blank sample, the HMF yield was only 0.8%, with a low cellulose conversion of 8%. However, after addition of the catalysts, cellulose conversion of up to 15.4% was achieved, with the highest HMF yield (2.5%). The highest cellulose conversion and HMF yield was observed with Cr-MMT, followed by Zn-MMT, Cu-MMT and Fe-MMT. 5-HMF was further rehydrated to levulinic acid and formic acid. The maximum selectivity achieved using Cr loaded MMT catalyst as (16.5 %), followed by Zn-MMT (15.2 %), Cu-MMT (12.4 %), Fe-MMT (10.9 %) and blank (10.1%). These results were similar to the study reported by Zhou et al. (2016). They prepared metal loaded Bentonite catalyst with different type of metals and tested them for 5-HMF production from glucose. Among the metals studied, they found that Cr showed the highest catalytic activity (Zhou et al. 2016).

Both 5-HMF yield and selectivity was affected by Lewis/ Brønsted acid ratio. The highest HMF yield (2.56%) and selectivity (16.7%) was obtained with the catalyst (Cr-MMT) have lowest total acidity and highest Lewis/Brønsted acid ratio (Table 2). Generally, the isomerization of glucose into fructose is usually completed in an alkaline reaction system (Binder and Raines, 2009; Su et al. 2009), the dehydration of fructose to HMF requires an acidic environment (Nie et al., 2020).

Since Cr-MMT catalyst showed the highest cellulose conversion, 5-HMF yield and selectivity, the effects of various reaction parameters such as Cr loading, reaction time, reaction temperature and catalyst amount on the conversion of cellulose to 5-HMF were further investigated.

3.3 The effect of Cr loading.

The amount of catalyst plays an important role in the kinetics of production and needs to be optimized to achieve maximum selectivity for the desired product. Experiments were carried out varying the catalyst loading in the range of 5 to 10 wt% and the results are shown in Figure 4. All reactions were carried out at 180°C for 6 hours using a 1:2 catalyst:substrate ratio in water, and the results are shown in Figures 4 and 5. The cellulose conversion increased from 30.86–36.81% by increasing the amount of Cr from 0 to 10%. When the amount of Cr was further increased to 15%, the cellulose conversion decreased by 30.15%. The yield of 5-HMF production increased for all the synthesized catalysts with the increase in reaction time from 30 min to 360 min. The maximum 5-HMF yield (4.19%) was obtained at 360 min using 10Cr-MMT catalyst. However, when the amount of Cr was further increased from 10–15%, the 5-HMF yield decreased.

Although water used as the reaction medium in this study, the yield of 4.19% for 5-HMF is compatible with literature. For example, Kassaye and co-workers reported a 5.1% 5-HMF yield at 180°C using sulfated zirconia catalyst and ionic liquid from cellulose (Kassaye et al., 2016).

Figure 4 shows the product distribution obtained as a result of 6 h catalytic cellulose conversion reaction. The increase of Cr content from 5 to 10% resulted in an increase of all products (glucose, 5-HMF, levulinic

acid, formic acid). However, the yield of the products decreased slightly when Cr loading increased to 15%. A similar trend was also observed in cellulose conversion. This could be due to the decrease in surface area and pore volume of the catalyst when Cr loading was increased from 10–15%.

3.4 Effect of the reaction temperature and reaction time

Reaction temperature and reaction time are two important factors which greatly affect the dehydration of glucose. To evaluate how the reaction temperature affected the production of HMF, the treatments were performed keeping all other parameters constant. Temperature range of 160–220°C was tested to determine the optimal reaction temperature. As shown in Figure 5, the reaction temperature and reaction time had a great impact on the cellulose conversion as well as yield of the reaction products. Cellulose conversion increased from 17.85–87.32% sharply as the reaction temperature was raised from 160°C to 220°C for 6 h. 5-HMF yield increased from 0.65–4.41% with an increased temperature from 160°C to 200°C. However, further increase in the temperature to 220°C, the HMF yield and selectivity first increased to the maximum values of 10.88 % and 11.51%, respectively, and then decreased with an increase in reaction time (Figure 6). The reason for this phenomenon might be explained that the side reactions (i.e., rehydration) increased with the reaction time at high temperatures, which led to the generation of soluble polymers and insoluble humin (Nandiwale et al. 2014; Zi et al. 2015). At this temperature, longer reaction times resulted in the generation of more levulinic acid and formic acid. At low reaction temperatures (200°C), the HMF yield was as high as 6.74%, with a 4.95% levulinic acid yield and a 8.51% formic acid yield after 6 h.

3.5 Effect of initial cellulose loading

The ratio of cellulose to catalyst is a critical parameter for high cellulose conversion due to the solid-solid interaction between catalyst and cellulose. Adding an excess amount of catalyst to the cellulose conversion system can increase glucose conversion. There might be many reasons for these interactions. Chemical and van der Waals interactions between the cellulose and the catalyst, the outer surface of the catalyst, and the morphology of the catalyst (Lanzafame et al. 2012). For the above reasons, we optimized the ratio of cellulose to catalyst. The effect of initial cellulose loading on 5-HMF production was studied by varying the amount of cellulose in the range of 1.25–5.0 g with 2.5 g of catalyst at a temperature of 200°C for 6 hours. An increase in the initial amount of cellulose resulted in a decrease in the catalyst/substrate ratio (Figure 7). A lower initial amount of cellulose (1.25 g) increased the initial formation rate of 5-HMF at 120 minutes. After 2 hours, there was no significant change in 5-HMF yield with 2.5 g and 1.25 g of initial cellulose (Figure 8). However, there is a significant difference in 5-HMF yield when the initial amount of cellulose was increased to 5 g. Similar results were found by Su et al. 2018. When they decreased the ratio of catalyst to cellulose, their product yields decreased as much as our results, and they explained the reason for this situation as insufficient catalytically active sites formed between the solid acid catalyst and the substrate as a result of mass transfer resistance (Su et al., 2018). On the other hand, although a cellulose conversion was as high as 93.47%, only 30% of the reaction

products was identified. These products in the solution could be soluble polymers and humic substances derived from the decomposition or self-polymerization of glucose (Qi et al., 2011).

Conclusion

In conclusion, Cr-MMT was the most effective catalyst among the other metal-MMT catalysts (Cu-MMT, Fe-MMT and Zn-MMT) investigated in this study. Cr-MMT catalyzed effectively conversion of cellulose to 5-HMF in the water media. Reaction temperature and reaction time had great impact on the conversion of the cellulose and 5-HMF yield. Maximum conversion of cellulose as high as 93.47% was obtained when reacting 1.25 g cellulose, 2.5 g catalyst Cr10-MMT, 50 ml water at 200°C for 6 h. Under these condition 5-HMF yield was 9.07%. Moreover, 5-HMF yield was depended on the total acid, and the ratio of Lewis/Brønsted acid. The highest 5-HMF yield and selectivity was obtained with the Cr-MMT which has lowest total acidity and highest Lewis/Brønsted acid ratio among the metal-MMT catalysts (Cu-MMT, Fe-MMT, Zn-MMT and Cr-MMT). Although the results showed that a low cost Cr-MMT catalyst was effective for the conversion of cellulose into the 5-HMF in the water media, reaction efficiency and selectivity still need to be improved.

Declarations

Acknowledgement:

This study was supported by Anadolu University Scientific Research Projects Commission under the grant no: 1502F080

References

1. Binder JB, Raines RT (2009) Simple chemical transformation of lignocellulosic biomass into furans for fuels and chemicals. *J Am Chem Soc* 131:1979–1985. <https://doi.org/10.1021/ja808537j>
2. Cao Z, Fan Z, Chen Y, Li M, Shen T, Zhu C, Ying H (2019) Efficient preparation of 5-hydroxymethylfurfural from cellulose in a biphasic system over hafnium phosphates. *Appl Catal B* 244:170–177. <https://doi.org/10.1016/j.apcatb.2018.11.019>
3. Fang Z, Liu B, Luo J, Ren Y, Zhang Z (2014) Efficient conversion of carbohydrates into 5-hydroxymethylfurfural catalyzed by the chromium-exchanged montmorillonite K-10 clay. *Biomass Bioenergy* 60:171–177. <https://doi.org/10.1016/j.biombioe.2013.12.002>
4. Garade AC, Kshirsagar VS, Jha A, Rode CV (2010) Structure–activity studies of dodecatungstophosphoric acid impregnated bentonite clay catalyst in hydroxyalkylation of *p*-cresol. *Catal Commun* 11(11):942–945. <https://doi.org/10.1016/j.catcom.2010.04.008>
5. Gromov NV, Taran OP, Semeykina VS, Danilova IG, Pestunov AV, Parkhomchuk EV, Parmon VN (2017) Solid Acidic NbO_x/ZrO₂ Catalysts for Transformation of Cellulose to Glucose and 5-

- Hydroxymethylfurfural in Pure Hot Water. *Catal Letters* 147(6):1485–1495.
<https://doi.org/10.1007/s10562-017-2056-y>
6. He X, Chen Y, Liu Y, Fang L, Chen Z, Ji H (2019) Distribution of Products from Catalytic Conversion of Cellulose Over Metal-Modified Hierarchical H-ZSM-5 in Aqueous Media. *Catal Letters* 149:2078–2088. <https://doi.org/10.1007/s10562-019-02795-7>
 7. Husin NFDC, Harun FW, Jumal J, Othman SS (2015) Preparation and Physicochemical Properties of Metal Complexes Immobilized on Montmorillonite K10 (MMT K10). *J Ind Eng Res* 1(5):8–13
 8. Kassaye S, Pagar C, Pant KK, Jain S, Gupta R (2016) Depolymerization of microcrystalline cellulose to value added chemicals using sulfate ion promoted zirconia catalyst. *Bioresour Technol* 220:394–400. <https://doi.org/10.1016/j.biortech.2016.08.109>
 9. Kumar A, Chauhan AS, Pralay Das S (2021) Lignocellulosic biomass and carbohydrates as feedstock for scalable production of 5-hydroxymethylfurfural. *Cellulose* 28:3967–3980.
<https://doi.org/10.1007/s10570-021-03764-3>
 10. Lanzafame P, Temi DM, Perathoner S, Spadaro AN, Centi G (2012) Direct conversion of cellulose to glucose and valuable intermediates in mild reaction conditions over solid acid catalysts. *Catal Today* 179(1):178–184. <https://doi.org/10.1016/j.cattod.2011.07.018>
 11. Li H, Ren J, Zhong L, Sun R, Liang L (2015) Production of furfural from xylose, water-insoluble hemicelluloses and water-soluble fraction of corncob via a tin-loaded montmorillonite solid acid catalyst. *Bioresour Technol* 176:242–248. <https://doi.org/10.1016/j.biortech.2014.11.044>
 12. Liu D, Yuan P, Liu H, Cai J, Tan D, He H, Zhu J, Chen T (2013) Quantitative characterization of the solid acidity of montmorillonite using combined FTIR and TPD based on the NH₃ adsorption system. *Appl Clay Sci* 80–81:407–412. <https://doi.org/10.1016/j.clay.2013.07.006>
 13. Nandiwale KY, Galande ND, Thakur P, Sawant SD, Zambre VP, Bokade VV (2014) One-pot synthesis of 5-hydroxymethylfurfural by cellulose hydrolysis over highly active bimodal micro/mesoporous H-ZSM-5 catalyst. *ACS Sustain Chem Eng* 2(7):1928–1932. <https://doi.org/10.1021/sc500270z>
 14. Nie Y, Hou Q, Bai C, Qian H, Bai X, Ju M (2020) Transformation of Carbohydrates to 5-Hydroxymethylfurfural with High Efficiency by Tandem Catalysis. *J Clean Prod* 274:123023.
<https://doi.org/10.1016/j.jclepro.2020.123023>
 15. Putluru SSR, Schilla L, Godiksen A, Poreddy R, Mossina S, Jensen AD, Fehrmann R (2016) Promoted V₂O₅/TiO₂ catalysts for selective catalytic reduction of NO with NH₃ at low temperatures. *Appl Catal B* 183:282–290. <https://doi.org/10.1016/j.apcatb.2015.10.044>
 16. Qi X, Watanabe M, Aida TM, Smith RL (2011) Catalytic conversion of cellulose into 5-hydroxymethylfurfural in high yields via a two-step process. *Cellulose* 18(5):1327–1333.
<https://doi.org/10.1007/s10570-011-9568-1>
 17. Rout PR, Nannaware AD, Prakash O, Kalra A, Rajasekharan R (2016) Synthesis of hydroxymethylfurfural from cellulose using green processes: A promising biochemical and biofuel feedstock. *Chem Eng Sci* 142:318–346. <https://doi.org/10.1016/j.ces.2015.12.002>

18. Shao Y, Ding Y, Dai J, Long Y, Hu Z-T (2021) Synthesis of 5-hydroxymethylfurfural from dehydration of biomass-derived glucose and fructose using supported metal catalysts. *Green Synth Catal* 2(2):187–197. <https://doi.org/10.1016/j.gresc.2021.01.006>
19. Shirai H, Ikeda S, Qian EW (2017) One-pot production of 5-hydroxymethylfurfural from cellulose using solid acid catalysts. *Fuel Process. Technol.* 159:280-286. <https://doi.org/10.1016/j.fuproc.2016.10.005>
20. Sluiter A, Hames B, Ruiz R, Scarlata C, Sluiter J, Templeton D (2008) Determination of sugars, byproducts, and degradation products in liquid fraction process samples. National Renewable Energy Laboratory, Technical Report NREL/TP-510-42623
21. Su J, Qiu M, Shen F, Qi X (2018) Efficient hydrolysis of cellulose to glucose in water by agricultural residue-derived solid acid catalyst. *Cellulose* 25(1):17–22. <https://doi.org/10.1007/s10570-017-1603-4>
22. Xue L, Cheng K, Zhang H, Deng W, Zhang Q, Wang Y (2016) Mesoporous H-ZSM-5 as an efficient catalyst for conversions of cellulose and cellobiose into methyl glucosides in methanol. *Catal Today* 274:60–66. <https://doi.org/10.1016/j.cattod.2016.01.055>
23. Xue Z, Ma MG, Li Z, Mu T (2016) Advances in the conversion of glucose and cellulose to 5-hydroxymethylfurfural over heterogeneous catalysts. *RSC Adv* 6:98874–98892. DOI:<https://doi.org/10.1039/C6RA20547J>
24. Yu J, Wang JY, Wang Z, Zhou MD, Wang HY (2018) Hydrolysis of cellulose promoted by silicalite-1 modified HY zeolite in 1-ethyl-3-methylimidazolium chloride. *Cellulose* 25(3):1607–1615. <https://doi.org/10.1007/s10570-018-1681-y>
25. Yu IKM, Tsang DCW (2017) Conversion of biomass to hydroxymethylfurfural: A review of catalytic systems and underlying mechanisms. *Bioresour Technol* 238:716–732. <https://doi.org/10.1016/j.biortech.2017.04.026>
26. Zhou J, Tang Z, Jiang X, Jiang R, Shao J, Han F, Xu Q (2016) Catalytic conversion of glucose into 5-hydroxymethyl-furfural over chromium-exchanged bentonite in ionic liquid-dimethyl sulfoxide mixtures. *Waste Biomass Valori* 7(6):1357–1368. <https://doi.org/10.1007/s12649-016-9525-1>
27. Zi G, Yan Z, Wang Y, Chen Y, Guo Y, Yuan F, Wang J (2015) Catalytic hydrothermal conversion of carboxymethyl cellulose to value-added chemicals over metal–organic framework MIL-53 (Al). *Carbohydr Polym* 115:146–151. <https://doi.org/10.1016/j.carbpol.2014.08.065>

Figures

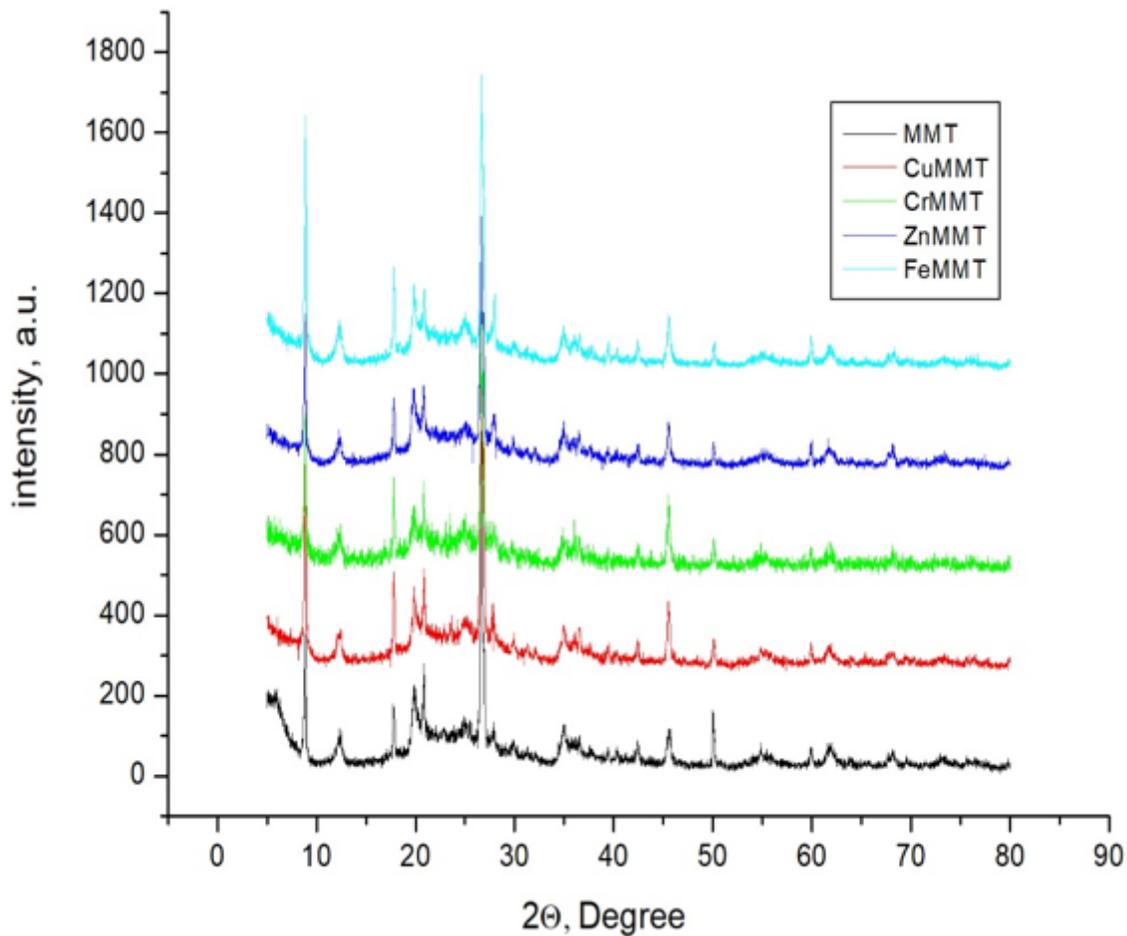


Figure 1

XRD patterns of MMT, Cr-MMT, Cu-MMT, Zn-MMT and Fe-MMT catalysts

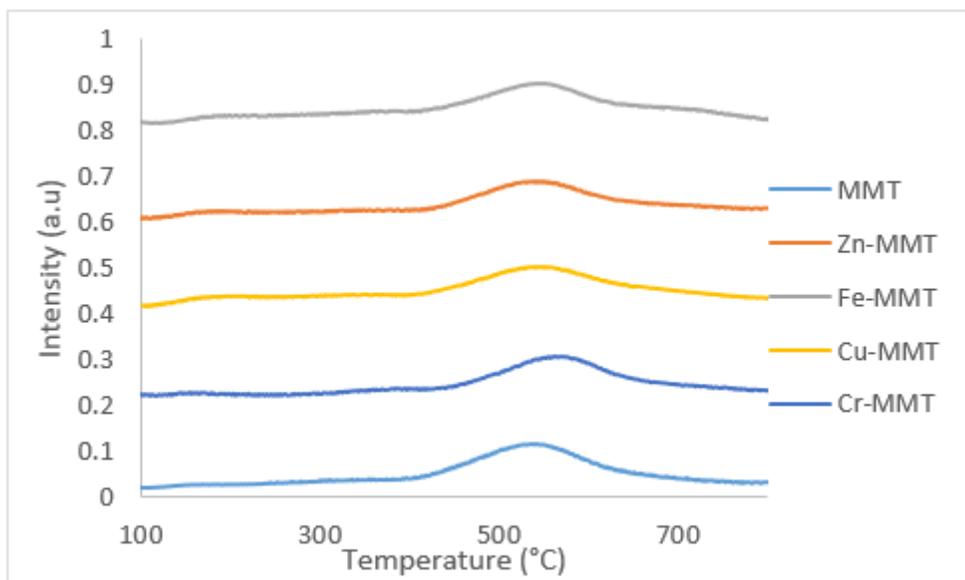


Figure 2

NH₃-TPD Patterns of Transition-Metal Doped Montmorillonite Catalysts (Zn-MMT, Fe-MMT, Cu-MMT and Cr-MMT)

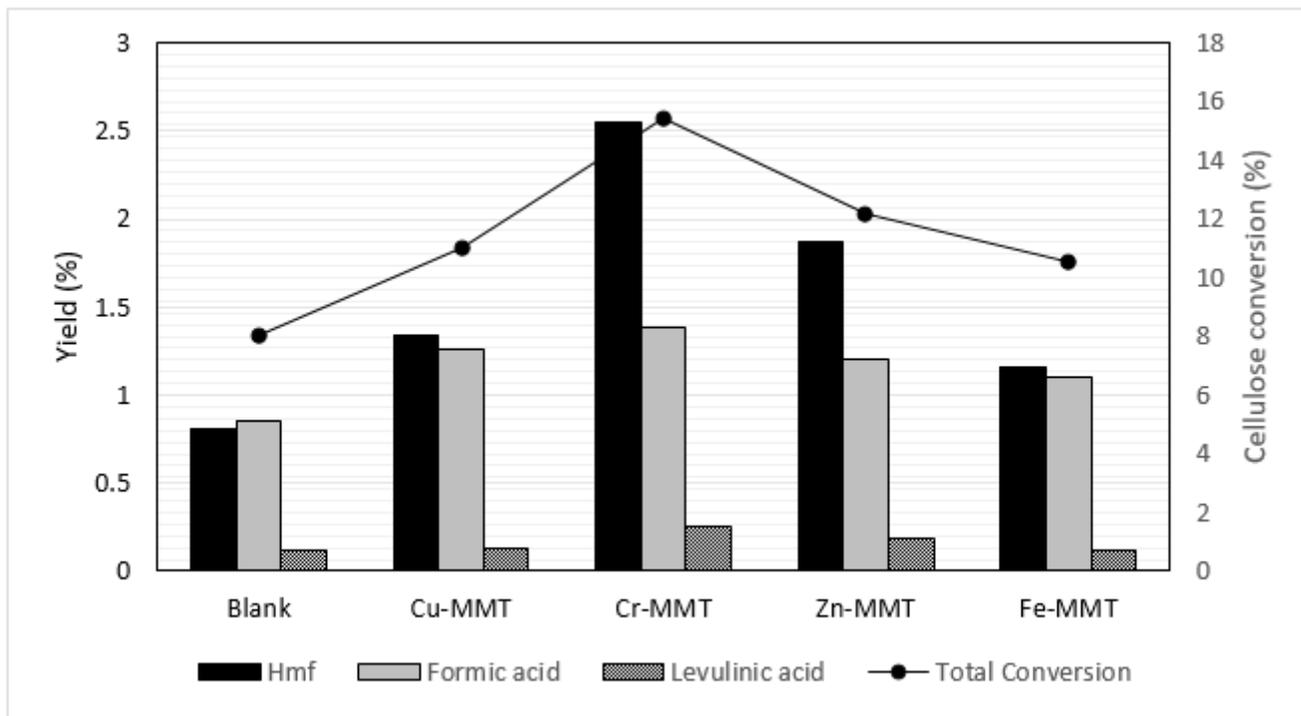


Figure 3

Cellulose conversion yield over Cr-MMT, Cu-MMT, Zn-MMT and Fe-MMT catalysts (Reaction conditions: 180oC, 2 h, 5 g cellulose, 50 mL water, 0.5 g catalyze, 200 rpm)

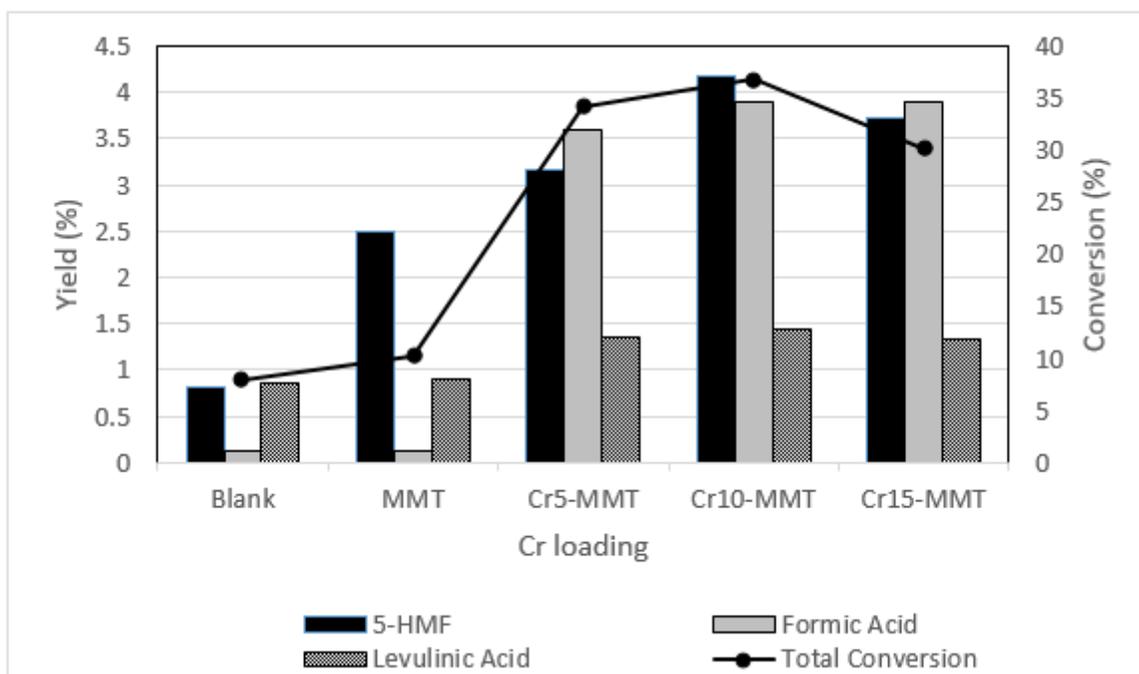


Figure 4

Effect of catalyst loading on the conversion of cellulose and 5-HMF yield (1/50 solid to liquid, 2.5 g Cr10-MMT, 6 h, 180 °C).

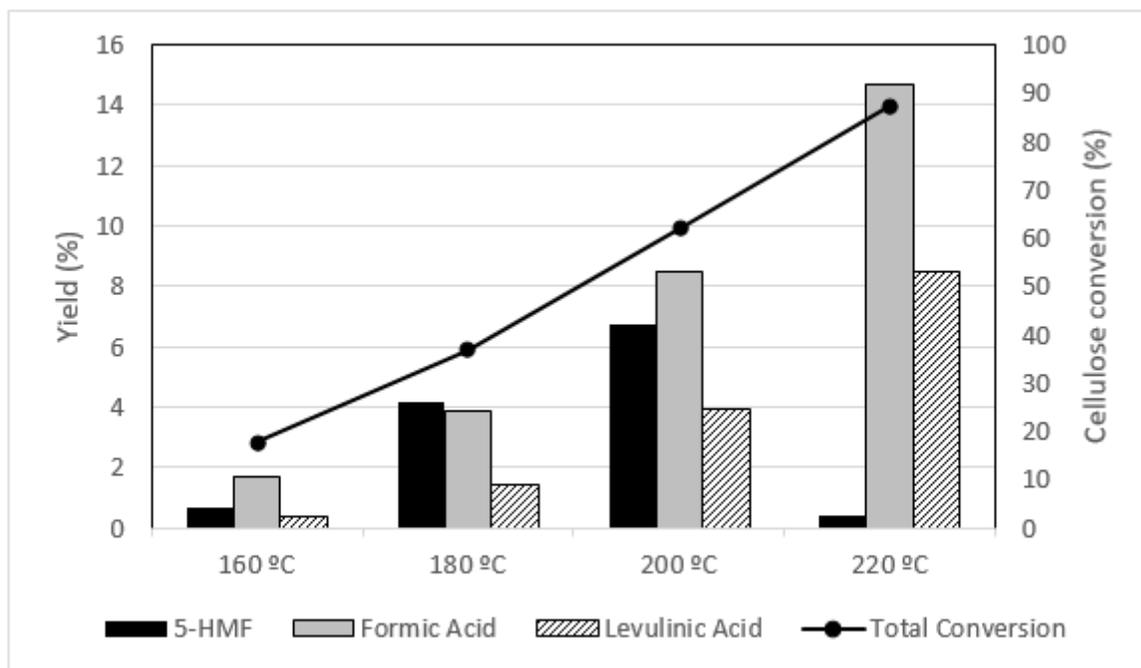


Figure 5

Effect of the reaction temperature on the reaction products and cellulose conversion (2.5 g Cr10-MMT, 6 h).

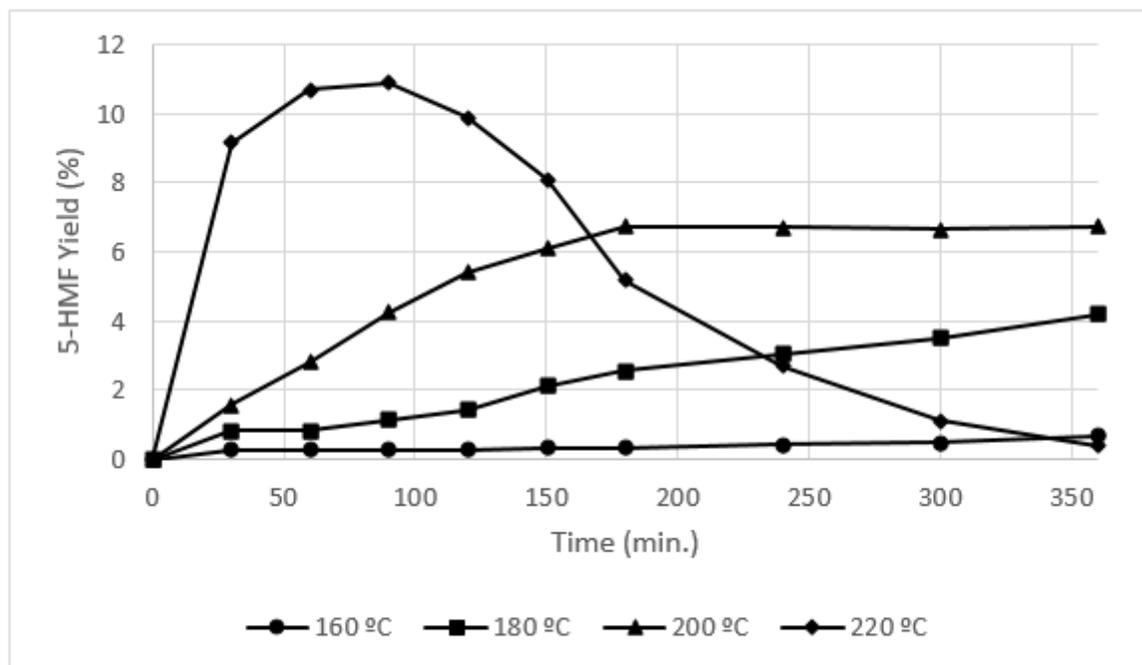


Figure 6

Effect of the reaction temperature and reaction time on the 5-HMF yield (2.5 g Cr10-MMT, 6 h).

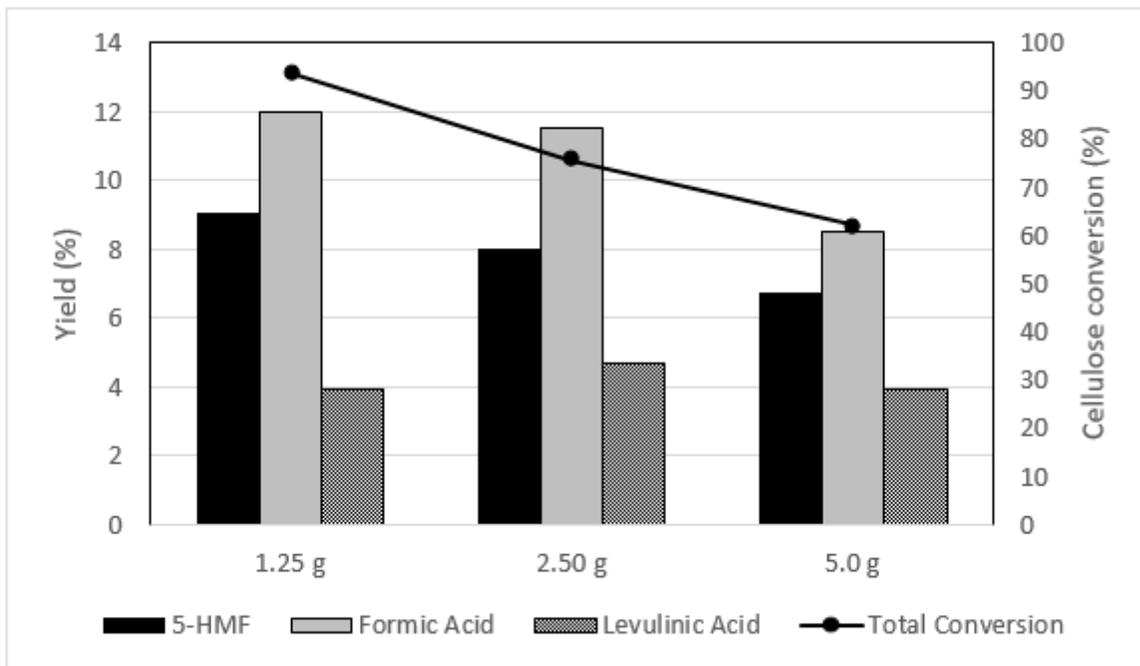


Figure 7

Effect of the cellulose loading on reaction products and cellulose conversion (2.5 g Cr10-MMT, 200oC, 6 h).

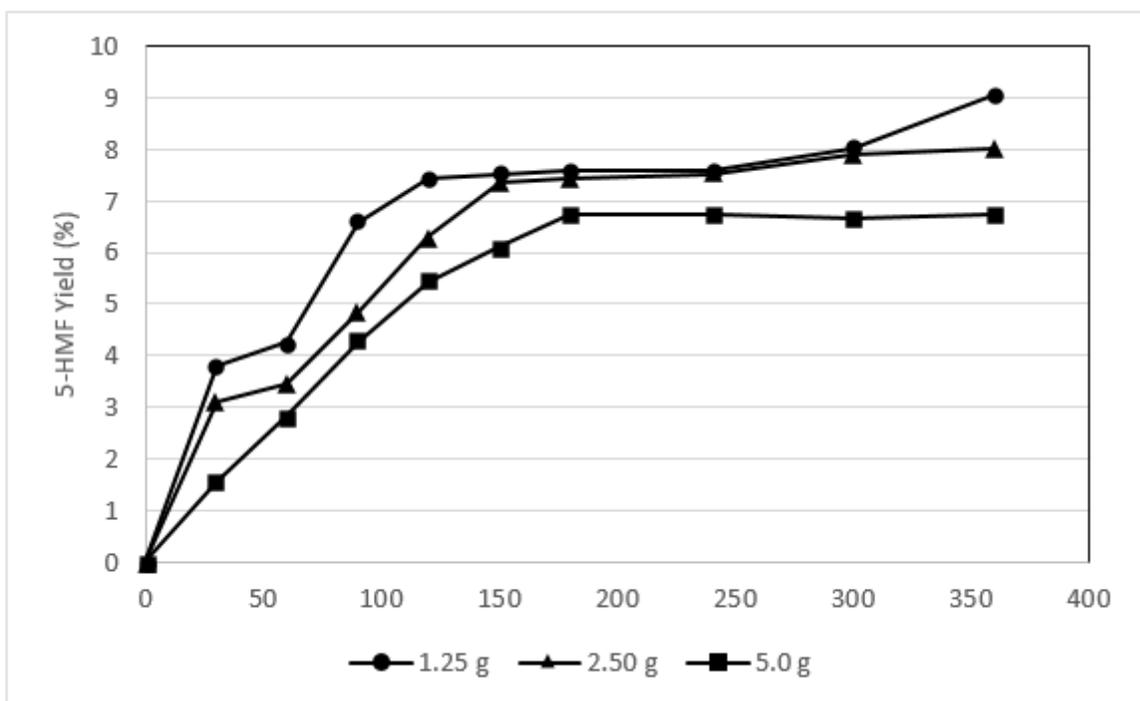


Figure 8

Effect of the cellulose loading on the 5-HMF yield (2.5 g catalyst Cr10-MMT, 200oC, 6 h).