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Highly effective transformation of carbohydrates

to 5-Hydroxymethylfurfural with Almontmorillonite as catalyst

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Graphical abstract



We prepared the catalysts through the ion-exchange of natural calcium montmorillonite with an aqueous aluminum trichloride solution. Al³⁺ was a good Lewis acid catalyzing the isomerization of glucose to fructose, and the partially hydrolyzed Al–OH groups acted as Brønsted acid for the dehydration of fructose to HMF, which can be extracted by THF with a high yield.

Highlights

• A series of Al-mont-n were prepared with ion-exchange method for conversion of

carbohydrates to HMF.

- The catalytic activity is dependent on the concentrations of Al³⁺ ion.
- A high yield of HMF (80.4%) was produced from glucose.
- 60.1 % and 81.6 % yield of HMF were obtained from the dehydration of starch and

inulin, respectively.

ABSTRACT

Aluminum ion-exchanged Ca-montmorillonite with different concentrations of aluminum ion were prepared and applied in the conversion of carbohydrates to 5-hydroxymethylfurfural (HMF). It was found that two types of acid sites were present in the catalyst, Lewis acid sites for isomerization of glucose and Brønsted acid sites for dehydration of fructose. With Al-mont-10 as catalyst, the yield of HMF converted from glucose was 80.4 % in a biphase system (THF: NaCl solution) at 180 °C for 2.5 h. Further, the catalyst also shows excellent catalytic performance in the conversion of starch and inulin, and the yield of HMF reached 60.1 % and 81.6 % under identical conditions, respectively.

KEYWORDS: biomass, energy, carbohydrates, 5-hydroxymethylfurfural, catalysis

INTRODUTION

The increasing carbon dioxide emission, diminishing fossil fuel supply and growing environmental concerns have increased the widespread focus on renewable resources over steadily depleting source. Carbohydrates, a renewable resource, can be transformed into biofuels and diverse high value-added chemicals. 5-Hydroxymethylfurfural (HMF), the product of carbohydrates, is one of the versatile and important building blocks for the synthesis of compounds such as 2,5-furan dicarboxylic acid, levulinic acid, formic acid and so on, which enables HMF to be widely applied in industry, sustainable supply of energy and pharmaceutical intermediates, as well as its derivatives.^[1]

A variety of carbohydrates can be converted into HMF. Among them, glucose has gradually become a major ingredient due to its low cost and its abundance on Earth. Most researchers believe that the conversion of glucose to HMF consists of two steps: isomerization of glucose to fructose catalyzed by Lewis acid sites or base and dehydration of fructose to HMF.^[2-4] It was generally assumed that dehydration of fructose catalyzed by Lewis acid sites was faster than isomerization of glucose catalyzed by Brønsted acid sites under aqueous conditions and thus isomerization took place prior to dehydration.^[5]

The homogeneous catalyst exhibits good catalytic performance, such as ionic acids (CrCl₂, CrCl₃) as catalysts, and the yield of HMF ranges from 60 % to 70 %.^[5-7] Further research has led to the capture of aluminum in our eyes, because the content of aluminum is abundant in the earth's crust, and partially hydrolyzed Al-OH groups can act as Brønsted acid sites catalyzing the dehydration of fructose. However, the difficulty in separating Al³⁺ from the solution limits the application of homogeneous catalysts. Therefore, the supports were studied to load Al³⁺ ion. In the numerous researches on supports, it is found that chromium-exchanged and erbium-exchanged montmorillonite K-10 has shown a good catalytic performance in catalyzing carbohydrates into HMF and lactic acid^[9-11] because montmorillonite has a significant cation-exchange ability, good adsorption capacity, flexible acidity, and expansible interlayer space.^[12,13] In addition, it possesses both Lewis and Brønsted acid sites, making it an alternative catalyst in acid-catalyzed organic transformations.^[9,14,15] To date, cation-exchanged montmorillonite K10 have been used as effective environmentally benign heterogeneous catalysts and promising acidic supports for many chemical reactions.^[16-20]

In this work, aluminum montmorillonite (Al-mont) catalysts were prepared through ionexchange of natural calcium montmorillonite (Ca-mont) with an aqueous solution of aluminum

trichloride. And the samples were characterized by XRD, ICP, N₂-TPD, NH₃-TPD, Py-IR and so on. Moreover, the catalyst also showed a good performance when using different disaccharides and polysaccharides as substrates.

EXPERIMENTAL SECTION

Materials. 5-Hydroxymethylfurfural (HMF, 95 %) was purchased from Aladdin (China), Calcium montmorillonite (Ca-mont) was purchased from Changchun Third Party Pharmaceutical Technology Co. Ltd. (China). The remaining chemicals including EtOH, NaCl, tetrahydrofuran (THF), AlCl₃·6H₂O, FeCl₃, ZnCl₂, Zr(NO₃)₄·5H₂O, glucose, fructose, cellulose, starch, saccharose and inulin were purchased from Sinopharm Chemical Reagent Co. Ltd..

Catalyst preparation. Two catalysts having different mass ratios of metal to Ca-mont were prepared using the reported ion-exchange method. The first one is 4 g Ca-mont was immersed in 100 mL of an aqueous solution of AlCl₃ at 80 °C for 12 h with stirring, then washed with deionized water after filtered and dried at 80 °C overnight. The products were named as Almont-n. "n" refers to the concentration of AlCl₃ aqueous solution (0.002, 0.004, 0.006, 0.008, 0.010 mol L⁻¹). The second one is the same way, but the mass ratio of metal to Ca-mont is 1:2. Fe-mont, Zn-mont, Zr-mont were prepared in the way. Two kinds of catalysts were characterized and tested under the same reaction.

Catalyst characterization. XRD X-ray diffraction (XRD) pattern of the catalysts were carried out using D/MAX 2550 Advance X-ray diffractometer with Cu K α radiation source operated at 30 kV and 20 mA, and data were collected in the 2 θ range of 10°–80° with a step of 0.02° at a scanning speed of 10° min⁻¹. The morphology of the samples was investigated by transmission electron microscopy (TEM; Te

cnai F20) and scanning electron microscopy (SEM; Jeol JSM-6700F). Inductively coupled plasma (ICP) analysis was evaluated at ambient temperature on OPTIMA 3300DV (Perkin Elmer company). Measurement of N₂ physisorption was performed on the Asap2420 surface adsorption apparatus. Before the measurement, samples were degassed at 200 °C for 6 h. The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) approach. The temperature programmed desorption of ammonia (NH₃-TPD) experiment was obtained using a Micromeritics AutoChem II 2920 automated chemisorption analysis unit with a thermal conductivity detector (TCD) under helium flow. To remove the physically adsorbed NH₃ from the sample, the samples were purged in N₂ flow for 2 h. Desorption of NH₃ was carried out from 100 °C to 500 °C at a heating rate of 10 °C min⁻¹. Pyridine adsorption fourier-transform infrared (Py-IR) test were recorded on a Jasco FT/IR-410 in air at ambient temperature using 420 Herschel series in KBr dispersion. The samples were treated at 350 °C for 1h and then raised to 150 °C and 350 °C, respectively, at a temperature increase rate of 10 °C min⁻¹.

Products analysis. HMF in the products was analyzed on the TRACE ISQ GC-MS (Thermo Scientific Co, TR-wax-ms column 30.0 m×320 μ m×0.25 μ m). The operating conditions for GC–MS were as follows: Initial temperature 60 °C (2 min), Gradient Rate 10 °C min⁻¹, and final temperature 230 °C (2 min). Sample volume: 0.2 μ l. MS: EI source. Mass range: 30-300. Carbohydrate conversions were determined by HPLC with RI detection (Agilent 1200 series, 30 cm Agilent Zorbax Carbohydrate, acetonitrile/water=75:25 as eluent, flow rate is 1.5 mL · min⁻¹, the column temperature was maintained at 30 °C). The conversion of monosaccharides (glucose and fructose) and polysaccharides was calculated on a carbon-basis.

Carbohydrate conversions and HMF yields were calculated according to the following equations:

Glucose conversion (mol %) = (moles of starting glucose - moles of remaining glucose) / moles of starting glucose \times 100

HMF yield (mol %) = moles of HMF produced/moles of starting glucose \times 100

For disaccharides and polysaccharides, HMF yields were defined as follows:

HMF yield (mol %) = moles of HMF produced/moles of hexose units \times 100

Carbohydrates conversion. The reactions were carried on in a stainless steel autoclave (40 mL) heated in a temperature-controlled oil bath. The mixture of carbohydrates, solvents (biphase: 15 mL THF as extract phase and 15 mL saturated NaCl solution as reaction phase) and catalyst were put in the Teflon-lined stainless steel autoclave (40 mL) equipped with a magnetic stirring bar. After reaction, the reactor was cooled to room temperature. The solid catalyst was removed by filtration and dried at 80 °C for the next run after washed with deionized water and ethanol.

RESULT AND DISCUSSION

Characterization of catalyst. X-ray diffraction patterns of Ca-mont, Al-mont before and after the reaction are examined and shown in **Fig. 1 and Fig. S3**. In fig. 1, that no different peaks appeared means the structure of montmorillonite has not changed.^[14] The peaks at 19.8°, 26.5° and 62.3° are attributed to quartz, and the peaks at 19.8°, 20.8° and 22.4° are ascribed to tridymite-O.^[14,16,17] In fig. 1b, all the peaks are also the main diffraction peaks of montmorillonite, and the intensity of the peaks increases as the loading of Al³⁺ in the montmorillonite increases (**Fig 1b**), indicating that although the samples still remain the layered structure similar to the Camont, the interlayer space is narrowed due to the treatment of ion exchanged.^[21] The peaks at

20.8° could be attributed to leaching of Al from the octahedral layers of the montmorillonite K10.^[9] Small angle XRD patterns of Ca-mont and Al-mont have been added to Fig. S3. In the revised manuscript, the corresponding expression is added as follows: "In Fig. S3, A main peak at $2\theta = 5.7^{\circ}$ corresponds to the (001) plane of Ca-mont. After insertion of Al3+ into the montmorillonite layers, the (001) peak was shifted from $2\theta = 5.7^{\circ}$ to $2\theta = 6.1^{\circ}$ and broadened in comparison to Ca-mont, indicating that the interlayer distance was expanded from 7.75 to 7.25 Å.[17] Changing the loading of Al-loading, the interlayer distance of montmorillonite did not change.

The NH₃-TPD results of Al-mont-10 was present in **Fig S1**. There are two desorption peaks, the lower temperature peak near the center of 150 °C is attributed to the peak of the weak acid sites, and the following higher temperature peak near the center of 350 °C is the peak of the moderate acid sites.^[18]

The results of ICP demonstrate that with the increase of the concentration of AlCl₃ solution, the concentration of aluminum ions in montmorillonite increases and the concentration of calcium ions decreases. (**Table 1**). When the concentration of AlCl₃ solution reaches to 0.006 mol L⁻¹ (Al-mont-6), only trace amounts of calcium ion exist in the catalysts.^[22-24] The concentrations of metal ion in other catalysts (such as Fe-mont, Zn-mont and Zr-mont) are shown in **Table S1**.

The type of acid sites in Al-mont catalysts was determined by Py-IR (**Fig 2**). The peak at 1540 cm⁻¹ indicates the identification of the Brønsted acid sites. The peak at 1450 cm⁻¹ is a characteristic of the Lewis acid sites. And the peak at 1490 cm⁻¹ is a mixed peak of the Lewis acid sites and the Brønsted acid sites. Moreover, the ratio of Brønsted/Lewis (B/L) acid was also

evaluated in Table 1. As the concentration of aluminum ion increases, an increase in the peak area means an increase in the acid content, which is in accordance with an increase in the yield of HMF. And the amount of Lewis acid sites that facilitated the initial isomerization of glucose to fructose has a similar variation tendency with conversion of glucose. However, due to the constant amount of water, the increased Al³⁺ could not be further hydrolyzed to Al-OH, resulting in a decrease in the B/L acid ratio from 0.023 for Al-mont-2 to 0.016 for Al-mont-10. ^[25,26]

Determination of optimal conditions for glucose conversion in a biphase system. Enhancing the yield of the desired product HMF requires an understanding of the effects of the different reaction factors on the conversion. For this purpose, six key factors were examined.

Effect of different metal ions. A series of cation-exchanged Ca-mont were prepared for the conversion of glucose to HMF. It is apparent that Al-mont displayed the best catalytic activity in the conversion with a 71.7 % HMF yield at 180 °C for 2 h in a biphase system (saturated NaCl aqueous solution and THF).^[1] It is worth noting that Ca-mont without any treatment can also effectively catalyze the reaction, which may be due to trace amounts of Al³⁺ in the Ca-mont, showed in **Fig. 3**.

These results indicate that aluminum acts as an amphoteric metal, and the Al³⁺ ion loaded into the montmorillonite is an ideal Lewis acid sites that catalyzes the isomerization of glucose to fructose, while the partially hydrolyzed Al–OH groups acted as a Brønsted acid sites that catalyzes the dehydration of fructose to HMF, which is in accordance with Corma's reports in the MPV reaction. ^[27-29]

Therefore, in the following research, aluminum ion-loaded montmorillonite was intensively studied.

Effect of different concentrations of Al^{3+} ion. An experiment to modulate the concentration of aluminum ions was carried out. (Table 1) The concentration of Al^{3+} ions increases synchronically with the yield of HMF, which means that the effective constituent of the catalysts is Al^{3+} ions. Under the same conditions, the highest yield of HMF of 71.7 % was obtained by using Al-mont-10 with the highest concentration of Al^{3+} ion and the most acid content as a catalyst. However, as the concentration of Al^{3+} ion continues to increase, the yield of HMF does not change.

Effect of glucose loading. The effect of the glucose loading was demonstrated in Fig 4. It points out that as the glucose loading increases from 0.33 wt% to 1.61 wt%, there is no significant difference in the conversion of glucose, and the highest yield of HMF is 71.7 % with 1.29 wt% as glucose loading at 180 °C for 2 h. Continuing to increase glucose loading to 1.61 wt%, the yield of HMF remains nearly constant.

Effect of the Al-mont-10 catalyst loading. Subsequently, the effect of the Al-mont-10 catalyst loading were presented in Fig 5. It is apparent that the catalyst loading has a prominent influence on the conversion of glucose and the yield of HMF. By increasing the catalyst loading from 0.33 wt % to 1.29 wt %, the conversion of glucose (45.0 % and 92.1 %) doubles and the yield of HMF (22.5 % and 71.7 %) is more than three times that of the original at 180 °C for 2 h in biphase system. However, continuing to increase the catalyst loading from 1.29 wt % to 1.61 wt %, the conversion of glucose increases only a little while the yield of HMF decreases, which is attributed to the occurrence of more side-reactions caused by higher concentrations of HMF.^[30-32] Therefore, the optimal catalyst loading is 1.29 wt %.

Effect of reaction time and temperature. In order to examine the effect of reaction time and temperature on catalytic activity, a study has also been carried out. The results are summarized in Fig.6 and Fig.7. As the normal behavior of the catalytic reaction, a gradual increase in the conversion of glucose and the yield of HMF is observed with increasing reaction time as well as temperature up to 2.5 h and 180 °C respectively. From Fig.6, at initial time (1 h to 1.5 h), the HMF yield increased from 28.2 % to 35.0 % with 1.26 wt % glucose and 1.26 wt % catalyst in biphase system. By prolonging the reaction time to 2.5 h, the yield of HMF increased to the highest yield of 80.4 %, while the conversion of glucose increased slowly (from 92.1 % to 93.6 %). With the reaction time prolonged to 3 h, the conversion of glucose only increased a little but the yield of HMF declined a lot with the formation of humin.

The results from **Fig.7** strongly suggest that the reaction temperature markedly affects the conversion of glucose and the yield of HMF. As the reaction temperature increased, the conversion of glucose and the yield of HMF increased rapidly and reached 93.6 % and 80.4 % at 180 °C, respectively. Further raising the reaction temperature to 200 °C, the yield of HMF was reduced to 43.8 %, and the curve of the yield of HMF as a function of reaction temperature exhibited a volcano-type behavior, indicating that HMF was decomposed and carbonized at a high temperature.^[33] Therefore, 180 °C and 2.5 h were chosen as the optimum reaction conditions.

Catalyst reusability. Since the reusability of heterogeneous catalyst is very important for industrial production, the reusability of the Al-mont-10 catalyst was tested and showed in **Fig 8**. After the reaction, although the catalyst was repeatedly washed with distilled water and alcohol, a large amount of humin still blocked a part of the active sites of the catalyst. After many attempts, it was found that ultrasound was able to partially remove humin with the retention of

catalyst structure. And after six cycles, the conversion of glucose and the yield of HMF dropped slightly to 71.4 % and 50.4 % respectively, indicating that the Al-mont-10 catalyst still partially retained its catalytic activity after six cycles. In order to explore the leaching and heterogeneity of the catalyst, the reaction of Al-mont-10 catalyzed glucose was carried out at 180 °C. (Fig. S4) The reaction was stopped after 1h, and then the reaction was continued after the catalyst was filtered off. As a result, the yield of the product did not increase, which confirmed that the active site of the catalyst was not dissolved in the solution, and the catalyst was heterogeneous.

Conversion of di/poly-saccharides with Al-Mont-10 as catalyst. In previous reports, HMF was only generated from the fructose, which led to the waste of glucose.^[31,34-36] The use of Al-mont-10 catalyst in the synthesis of HMF from glucose opens up the possibility of utilizing more complex carbohydrates, and several other feedstocks such as disaccharides (saccharose) and polysaccharides (starch, inulin and cellulose) were evaluated and the results were illustrated in **Fig.9**. Admirable results were obtained from four carbohydrates (fructose, glucose, saccharose and inulin) with 98.5 %, 80.4 %, 86.1 % and 81.6 % yield of HMF respectively. Among the four carbohydrates, the HMF yields from saccharose and inulin are located between fructose and glucose because saccharose is a disaccharide consisting of glucose and fructose, while inulin is also composed of chain-terminating glucosyl moieties and a repetitive fructosyl moiety linked by $\beta 2,1$ bonds. The facts proved once again that the reaction of glucose to fructose is the rate determining step in the reaction.^[37]

High yield of HMF (60.1 %) is also produced with starch (glucose α 1,4-polysaccaride) as substrate. However, from cellulose (glucose β 1,4-polysaccharide) which is an especially promising resource because of its low price and high availability from nonfood resources, the result was poor with only 2% yield of HMF under the same conditions. This could be due to the

low Brønsted acid sites in Al-mont-10 catalyst (see in **Fig. S1**) which effects the hydrolysis of cellulose to glucose.

CONCLUSION

In conclusion, a series of low-cost, easily prepared aluminum exchanged montmorillonite catalysts were synthesized and exhibited excellent catalytic performance in the conversion of glucose or carbohydrates to HMF. For glucose, the HMF yield reaches 80.4 % with Al-mont-10 as catalyst in biphase system (THF: NaCl solution) at 180 °C for 3 h. Especially, for starch and inulin, the yield of HMF reaches 60.1 % and 81.6 % under the same condition, respectively. It is attributed to appropriate Brønsted acid sites and Lewis acid sites in Al-mont-10 catalyst which can effectively catalyze the isomerization of glucose to fructose process and the dehydration of fructose to HMF in one-pot reaction. The separation of HMF (boiling point is 114-116 °C) and THF (boiling point is 67 °C) is also very easy, which makes the recycle of extraction phase possible.

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REFERENCE

- [1] B. Saha, M.M. Abu-Omar, Green. Chem. 16 (2014) 24-38.
- [2] R.L. Huang, W. Qi, R.X. Su, Z.M. He, Chem. Commun. 46 (2010) 1115-1117.
- [3] A. Takagaki, M. Ohara, S. Nishimura, K. Ebitani, Chem. Commun. (2009) 6276-6278.
- [4] M. Watanabe, Y. Aizawa, T. Iida, T.M. Aida, C. Levy, K. Sue, H. Inomata, Carbohyd. Res. 340 (2005) 1925-1930.
- Z4\ K-S-L hj d+D-Brde`ku`x+@-Mdmeth, Chem. Rev. 118 (2018) 505-613.
- [6] H.B. Zhao, J.E. Holladay, H. Brown, Z.C. Zhang, Science. 316 (2007) 1597-1600.
- [7] S.Q. Hu, Z.F. Zhang, J.L. Song, Y.X. Zhou, B.X. Han, Green. Chem. 11 (2009) 1746-1749.
- [8] E. Nikolla, Y.R. Leshkov, M. Moliner, M.E. Davis, ACS Catal. 1 (2011) 408-410.
- [9] Z.F. Fang, B. Liu, J.J. Luo, Y.S. Ren, Z.H. Zhang, Bismass. Bioenergy. 60 (2014) 171-177.
- [10] F.F. Wang, J. Liu, H. Li, C.L. Liu, R.Z. Yang, W.S. Dong, Green. Chem. 17 (2015) 2455-2463.
- [11] Y. Zhou, M. Wang, H. Yin, S. Ai. Microchimica Acta, 184 (2017) 3301-3308.
- [12] A. Jha, A.C. Garade, M. Shirai, C.V. Rode, Appl. Clay. Sci. 74 (2013) 141-146.
- [13] H. Wang, C. Qi, W. He, M. Wang, W. Jiang, H. Yin, S. Ai, Bismass. Bioenergy. 99 (2018)281-288.
- [14] G.B.B. Varadwaj, S. Rana, K. Parida, Chem. Eng. J. 215-216 (2013) 849-858.

[15] J.B. Binder, R.T. Raines, J. AM. CHEM. SOC. 131 (2009) 1979–1985.

- [16] K. Shimizu, T. Higuchi, E. Takasugi, T. Hatamachi, T. Kodamab, A. Satsuma, J. Mol. Catal. A-Chem. 284 (2008) 89-96.
- [17] V.V. Bokade, G.D. Yadav, Appl. Clay. Sci. 53 (2011) 263-271.
- [18] J.J. Wang, J.W. Ren, X.H. Liu, J. X. Xi, Q.N. Xia, Y.H. Zu, G.Z. Lu, Y.Q. Wang, 14 (2012) 2506-2512.
- [19] B.S. Kumar, A. Dhakshinamoorthy, K. Pitchumani, Catal. Sci. Technol. (2014) 2378-2396.
- [20] B. Tyagi, C.D. Chudasama, R.V. Jasra, Spectrochim. Acta. A. 6 (2006) 273-278.
- [21] S.D. Miao, Z.M. Liu, B.X. Han, J.L. Zhang, X. Yu, J.M. Du and Z.Y. Sun, J. Mater. Chem. 1 (2006) 579–584.
- [22] Y. Duan, M. Zheng, D.M. Li, D.S. Deng, L.F. M, Y.L. Yang, Green. Chem. 19 (2017)5103–5113.
- [23] R. Ramos, A. Grigoropoulos, N. Perret, M. Zanella, A.P. Katsoulidis, T.D. Manning, J.B. Claridge, Matthew J. Rosseinsky, Green. Chem. 1 (2017) 1701-1713.
- [24] K. Gupta, R.K. Raia, S.K. Singh, Inorg. Chem. Front. 4 (2017) 871-880.
- [25] A.A. Marianoua, C.M. Michailofa, A. Pineda, E.F. Iliopoulou, K.S. Triantafyllidisa,
- A.A. Lappasa, Appl. Catal. A-Gen. 555 (2018) 75-87.
- [26] X. Li, K. Peng, X. Liu, Q. Xia, Y. Wang, ChemCatChem. 9(2017) 2739-2746.

- [27] I.J. Morales, M.M. Recio, J.S. González, P.M. Torres, A.J. López, Appl. Catal. B-Environ.164 (2015) 70-76.
- [28] M. Boronat, A. Corma, M. Renz, J. Phys. Chem. B. 110 (2006) 21168-21174.
- [29] A. Corma, M.E. Domine, L. Nemeth, S. Valencia, J. AM. CHEM. SOC. 124 (2002) 3194-3195.
- [30] Y.R. Leshkov, J.N. Chheda, J.A. Dumesic, Science, 312 (2006) 1933-1937.
- [31] J.N. Chheda, Y.R. Leshkov, J.A. Dumesic, Green. Chem. 9 (2007) 342-350.
- [32] C.Y. Fan, H.Y. Guan, H. Zhang, J.H. Wang, S.T. Wang, X.H.Wang, Biomass. Bioenergy.35 (2011) 2659-2665.
- [33] Z.S. Ma, H.L. Hu, Z.Q. Sun, W.T. Fang, J. Zhang, L.F. Yang, Y.J. Zhang, L. Wang, ChemSusChem. 10 (2017) 1669-1674.
- [34] B.M. Kabyemela, T. Adschiri, R.M. Malaluan, K. Arai, Ind. Eng. Chem. Res. 38 (1999)2888-2895.
- [35] J.H. Dai, L.F. Zhu, D.Y. Tang, Xi. Fu, J.Q. Tang, X.W. Guo, C.W. Hu, Green. Chem. 19 (2017) 1932–1939.
- [36] C. Carlinia, M. Giuttaria, A.M.R. Gallettia, G. Sbranaa, T. Armarolib, G. Busca, Appl, Catal. A-Gen. 183 (1999) 295-302.
- [37] H. Tang, N. Li, F. Chen, G.Y. Li, A.Q. Wang, Y Cong, X.D. Wang, T. Zhang, Green Chem.19 (2017) 1855-1860.

Figure Caption

Table 1. Chemical composition and physicochemical properties of different catalysts by the first method.

Figure 1. XRD patterns of catalysts.

Figure 2. Pyridine-adsorbed FT-IR spectra on different catalysts.

Figure 3. Effect of different metal ion catalysts on the yields of HMF (Reaction conditions: 30 mL of reaction solution, THF: NaCl solution = 50:50 v/v, 0.4 g glucose (1.29 wt %), 0.4 g catalyst (1.29 wt %), 180 °C, 2 h)

Figure 4. Effect of the glucose loading on the yield of HMF and the conversion of glucose (Reaction conditions: 30 mL of reaction solution, THF: NaCl solution = 50:50 v/v, 0.4 g Almont-10 (1.29 wt %), 180 °C, 2 h).

Figure 5. Effect of the Al-mont-10 catalyst loading on the yield of HMF and the conversion of glucose (Reaction conditions: 30 mL of reaction solution, THF: NaCl solution = 50:50 v/v, 0.4 g glucose (1.29 wt %), 180 °C, 2 h).

Figure 6. Effect of reaction time on the yield of HMF and the conversion of glucose (Reaction conditions: 30 mL of reaction solution, THF: NaCl solution = 50:50 v/v, 0.4 g glucose (1.29 wt %), 0.4 g Al-mont-10 (1.29 wt %) 180 °C.

Figure 7. Effect of reaction temperature on the yield of HMF and the conversion of glucose (Reaction conditions: 30 mL of reaction solution, THF: NaCl solution = 50:50 v/v, 0.4 g glucose (1.29 wt %), 0.4 g Al-mont-10 (1.29 wt %), 2.5 h.

Figure 8. Reusability of Al-mont-10 catalyst. (Reaction conditions: 30 mL of reaction solution, THF: NaCl solution = 50:50 v/v, 0.4 g glucose (1.29 wt %), 0.4 g Al-mont-10 (1.29 wt %), 180 °C, 2.5 h).

Figure 9. The yields of HMF from various carbohydrates. (Reaction conditions: 30 mL of reaction solution, THF: NaCl solution = 50:50 v/v, 0.4 g glucose (1.29 wt %), 0.4 g Al-mont-10 (1.29 wt %), 180 °C, 2.5 h).

Enter	Catalysts _	ICP(ppm) ^[a]		BET(m ²	B/L ratio	Con(%)	Yield(%
		Ca	Al	_ g ⁻¹) ^[b]	B/L ratio Con(70)) ^[c]	
1	Ca-mont	30.45	10.82	51.70			
2	Al-mont-2	1.413	12.55	40.20	0.023	49.7	21.7
3	Al-mont-4	1.123	12.97	43.08	0.023	49.2	36.0
4	Al-mont-6	0.8010	13.19	42.27	0.021	87.3	55.2
5	Al-mont-8	0.7864	15.40	44.40	0.019	88.6	58.5
6	Al-mont- 10	0.7702	27.17	50.41	0.016	92.1	71.7

[a] Calculated by ICP.

[b] measured by N2-physisorption.

[c] Reaction conditions: 30 mL of reaction solution, THF: NaCl solution = 50:50 v/v, 0.4 g glucose (1.29 wt %), 0.4 g catalyst (1.29 wt %), 180 °C, 2 h

Table 1



Fig 1



Fig 2







Fig 4







Fig 6







Fig 8



Fig 9