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ORIGINAL PAPER

Efficient Production of 5-Hydroxymethylfurfural from Carbohydrates Catalyzed by Mesoporous Al–B Hybrids

Wenfeng Zhao[1] · Tingting Yang[1] · Hu Li[1] · Yemin Lu[1] ·
Jian He[1] · Yanxiu Liu[1] · Song Yang[1,2]

Abstract A series of hydroxylated mesoporous aluminum–boron catalysts with different Al/B molar ratios were synthesized through a sol–gel method, and were characterized by XRD, FT-IR, NH_3-TPD, SEM and N_2 adsorption–desorption techniques. It was demonstrated that hydroxylated Al_2B_3 containing more Lewis acidity showed superior activity to the other Al–B catalysts in dehydration of glucose to 5-hydroxymethylfurfural (HMF) with a high yield of up to 39.9 % and glucose conversion of 92.1 % at 140 °C for 2 h. The synergistic effect of Lewis and Bronsted acid sites in Al_2B_3 catalyst was demonstrated to be crucial for efficient conversion of glucose to HMF.

Introduction

5-Hydroxyfurfural (HMF), recognized to be one of the top ten biomass-derived chemicals by the Department of Energy (U.S.), has been widely applied as a valuable

✉ Song Yang
   jhzx.msm@gmail.com

1 Center for Research and Development of Fine Chemicals, State-Local Joint Engineering Laboratory for Comprehensive Utilization of Biomass, State Key Laboratory Breeding Base of Green Pesticide and Agricultural Bioengineering (Ministry of Education), Guizhou University, Guiyang 550025, China

2 School of Pharmacy, East China University of Science and Technology, Shanghai 200237, China

platform molecule in production of biofuels and fine chemicals [1–8]. A large quantity of renewable biomass derivatives (e.g., glucose, sucrose, fructose and inulin) can be used to produce HMF. Relatively high HMF yields have been achieved from fructose promoted by a series of acidic catalysts [9]. From the economic point of view, glucose is more readily available from nature and shows great potential in large-scale production of value-added chemicals [10, 11]. Therefore, increasing efforts are being made for the upgradation of glucose.

A variety of homogeneous and heterogeneous catalysts such as $Hf(OTf)_4$ [12], metal phosphates [13], SO_3H-functional ionic liquids [14, 15], MCM-41 silica [16], hydroxylated AlF_3 [17], sulfated mesoporous carbon [18], Sn-based catalyst [19–21], and graphene oxide-ferric oxide [22] were designed for dehydration of glucose to HMF. Although both heterogeneous and homogeneous acids can efficiently catalyze glucose being converted to HMF, homogeneous catalysts always contain some unavoidable drawbacks such as difficulty in separation, equipment corrosion and environmental pollution [23]. Generally speaking, heterogeneous catalytic materials are able to overcome these shortcomings from homogeneous acids. In general, the procedure for glucose degradation to HMF involves two catalytic steps involving Lewis acid-catalyzed isomerisation of glucose to fructose, and subsequent dehydration over Brønsted acid to produce HMF [24, 25].

The combination of aluminum with boron species was demonstrated to be capable of creating mesoporous architecture and additional acid sites. Importantly, the resulting mixed oxides were effective for various reactions such as methanol dehydration, Beckman rearrangement, oxidation, and esterification [25–33]. In the present study, a series of hydroxylated mesoporous Al–B catalysts with different molar ratios of B/Al were prepared from aluminium

isopropoxide and phenylboronic acid by a sol–gel method, which were testified to have large pore volume, and remarkably high surface area and enhanced Lewis acidity. The as-prepared catalysts were further used to produce HMF from carbohydrates especially glucose, wherein several important reaction parameters including molar ratio of Al/B, reaction time and temperature, catalyst dosage, and type of solvents were studied to optimize HMF production.

Experimental Section

Material

Glucose (>99 %) was purchased from Sigma–Aldrich Corporation, F68 [HO(C₂H₄O)ₘ(C₃H₆O)ₙH] and aluminum isopropoxide (>99.5 %) were bought from Zhejiang Maya reagent Company. Other reagents procured from Shanghai Aladdin Industrial Corporation were of analytical grade without any purification, unless otherwise noted.

Catalyst Preparation

A series of hydroxylated aluminum–boron catalysts with different B/Al molar ratios were synthesized via a sol–gel process. In a typical procedure, Pluronic F68 (1.0 g) was added into a mixture containing absolute ethanol (20 g), and kept stirring at 40 °C for 1 h. Then, a certain amount of aluminium isopropoxide (1.02 g) was added. After stirring for 4 h, phenylboronic acid (0.91 g) was slowly dropped into the above mixture. Upon completion, the resulting solution was further stirred for another 1 h. The catalyst (Al₂B₃) could be obtained through ultrasound treatment for 40 min, drying in vacuum at 40 °C for 3 days, 80 °C for another 3 days, and then calcined at 400 °C for 6 h. Other boron–aluminum catalysts (Al$_x$B$_y$: x & y denote the mole of B and Al, respectively) with molar ratios of 1/1, 2/1, 2/1, and 2/3 were also prepared through the identical method. For comparison, P-Al (Al₂P₃) and P-Zr (Zr₂P₃) catalysts were synthesized, according to previously reported procedures [28].

Catalyst Characterization

NH₃-TPD measurements of those prepared catalysts were conducted using an AutoChem 2920 chemisorption analyzer. FT-IR spectra were recorded on an IR prestige-21 FT-IR instrument (KBr disks). Scanning electron microscopy (SEM) image was performed using a FESEM XL-30 (Philips) electron microscope. X-ray diffraction (XRD) measurements were carried out using a D/Max-3c X-ray

diffractometer with Cu Ka ($\lambda = 0.154$ nm), scanning from 5° to 90° and using an operating voltage and current of 40 kV and 30 mA, respectively.

Catalytic Dehydration of Carbohydrates to HMF

All kinds of sugar conversion experiments were conducted in a pressure tube (15 mL) under magnetic stirring condition, unless otherwise mentioned. In a typical procedure, glucose (50 mg), catalyst (20 mg) and DMSO (1.0 g) were added into the pressure tube. The resulting mixture was stirred at 500–700 rpm and heated by a controllable oil bath for a specific time. The zero time of the reaction was recorded when the pressure tube was submerged into the oil bath. After filtration, the solution was decanted into volumetric flask (25 mL) using de-ionized water as diluent. The liquid products in the mixture were quantitatively analyzed by high performance liquid chromatography (HPLC).

Analytical Method

HMF yield and glucose conversion were analyzed by using HPLC (Agilent 1100, USA), which was fitted with a LiChrospher C18 column and an ultraviolet detector at 284 nm, and equipped with an Aminex HPX-87H column (Bio-Rad, Richmond, CA) and a refractive index (RI) detector. The column oven temperature was set at 65 °C, while the mobile phase was CH₃CN/H₂O (V/V = 80/20) at a flow rate of 1.0 mL/min. The molar concentrations of glucose and HMF were verified according to the external standard method. Glucose conversion rate (X, mol%) and HMF yield (Y, mol%) were calculated as follows:

$$X\,(\%) = [1 - (\text{mole concentration of glucose in products})/ \\ (\text{mole concentration of initial glucose})] \times 100\,\%$$

$$Y\,(\%) = (\text{mole concentration of HMF})/ \\ (\text{mole concentration of initial glucose}) \times 100\,\%$$

Result and Discussion

Characterization of Catalyst

XRD patterns show that all the Al–B catalysts consistently have a low crystallinity, as illustrated in Fig. 1. One broad band located at 16°–27° proved the existence of the boron component [33], while the band at 45° is roughly attributed to aluminium species [33, 34]. Those results indicated the presence of aluminum and boron components in the as-prepared catalysts. The structure of Al₂B₃ was further
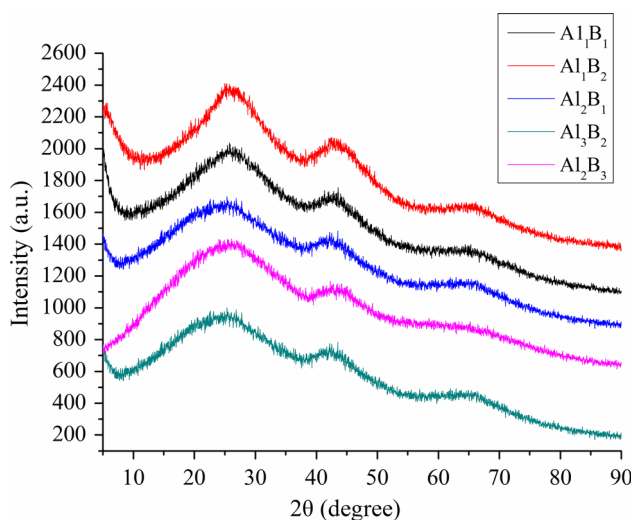
Fig. 1 XRD patterns of Al–B catalysts

examined by FT-IR spectrum (Fig. S1). A big peak in range of 3000–3500 cm^{-1} possibly belonged to hydroxyl group and water. The peak in the region of 1250–1450 cm^{-1} was characteristic of Al–O–B bond, while bands in the region of 900–1100 and 580–680 cm^{-1} were assigned to boron oxide and aluminum oxide, respectively [32]. Those results demonstrated that the Al–B mixed oxides were synthesized successfully.

The texture properties of the aluminum–boron catalysts were examined by N_2 adsorption–desorption and BJH pore-size distribution (Fig. 2). It can be seen that the N_2 adsorption–desorption isotherms of all aluminum–boron catalysts show a typical type IV patterns and the resulting hysteresis loops are assigned to H3-type, indicating the existence of mesopores structure in the as-prepared catalysts. In addition, the Al_2B_3 catalyst (Fig. 2) had broader pore size distribution and pore diameter, compared to another four catalysts, which may be responsible for its high catalytic performance. Furthermore, SEM image illustrates that the appearance of Al_2B_3 catalyst is fluffy (Fig. S2), further confirming the presence of porous structue, which is consistent with the results of N_2 adsorption–desorption (Fig. 2).

The acid properties of Al_2B_3 catalyst were evaluated by NH_3-TPD and pyridine-adsorbed FT-IR (Figs. S2 & 3). As shown in NH_3-TPD, two bands at 250 and 550 °C strongly illustrate that the acid centres of the Al_2B_3 catalyst are assigned to medium-strong and strong acid sites, respectively (Fig. S3). Two sharp absorption bands at around 1448 and 1622 cm^{-1} can be obviously observed from the pyridine-adsorbed FT-IR spectrum of Al_2B_3 (Fig. 3), which are characteristic of Lewis acid [35]. Brønsted acid sites are also existent, on the basis of the absorption peak at 1590 cm^{-1} [36]. Moreover, the peak at 1489 cm^{-1} can be
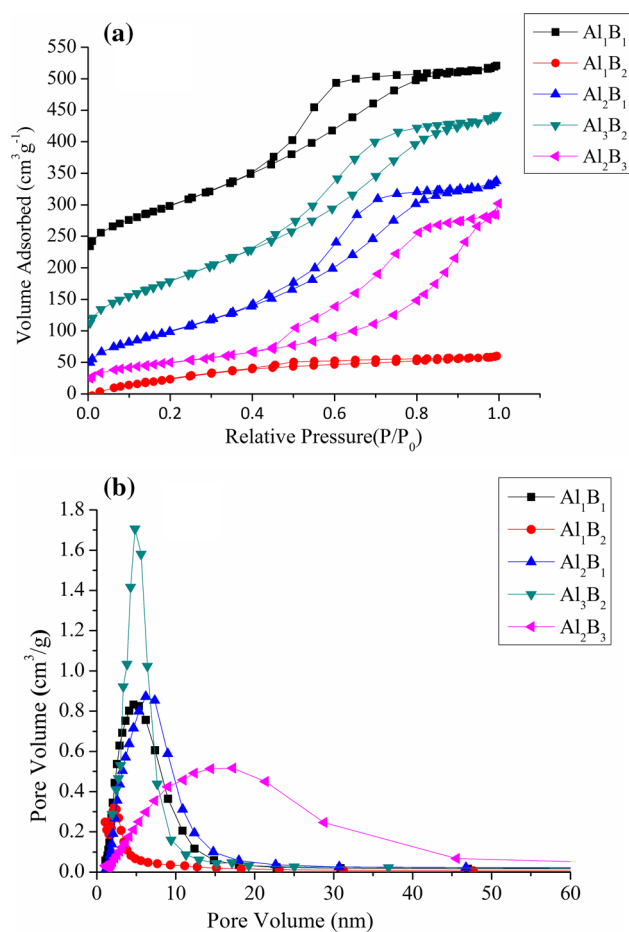

Fig. 2 N_2 adsorption–desorption isotherms (a) and pore-size distribution curves (b) of Al_1B_1, Al_1B_2, Al_2B_1, Al_3B_2 and Al_2B_3 catalysts
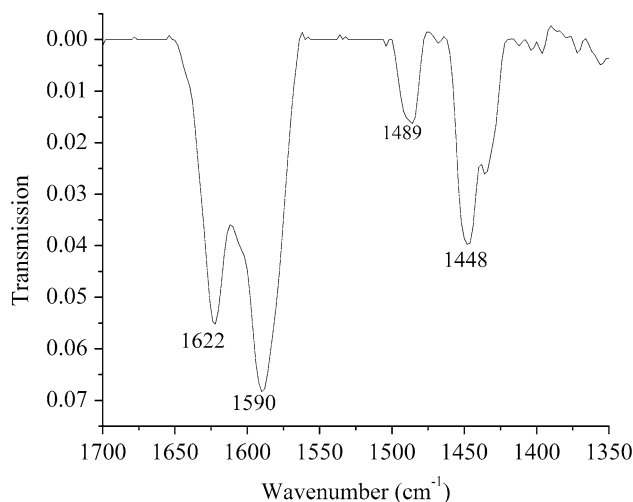

Fig. 3 Pyridine-adsorbed FT-IR spectrum of Al_2B_3 catalyst

attributed to pyridine-adsorbed Brønsted and Lewis acid sites [37], which clearly proves that the as-prepared Al_2B_3 catalyst containing both Brønsted acid and Lewis acid sites.

Effect of Catalyst Calcination Temperature on Production of HMF from Glucose

The effect of calcination temperature (400–700 °C) for Al_2B_3 with a constant calcination time of 6 h on conversion of glucose to HMF was initially investigated. As shown in Fig. 4, the catalyst calcined at 400 °C displays a relatively higher HMF yield (39.9 %), but further increasing calcination temperature from 400 to 700 °C leads to the gradual decrease of HMF yield (from 39.9 to 24.5 %). It's implied that the Al–B mixed oxide begins to cluster together at a high temperature of >400 °C, thus resulting in the decrease of its activity [38]. Hence, the Al_2B_3 catalyst used in this work was prepared by calcining at 400 °C for 6 h.

Effect of Reaction Temperature and Time

Figure 5 indicates that the reaction temperature obviously affects HMF production from glucose over Al_2B_3. With the increase of reaction time from 1 to 8 h, the yield of HMF raised from 0 to 42 % at 120 °C. On the other hand, as the reaction temperature was further elevated to 140 °C, the HMF yield increased to 39.9 % in only 2 h. At a high temperature of 160 °C, HMF yield could reach 36.9 % within 1 h, but was decreased after reacting for 2 h. It was proposed that relatively high temperature and long reaction time caused the degradation of HMF to form by-products such as levulinic acid [30]. Therefore, the optimal reaction temperature (140 °C) and time (2 h) with the presence of Al_2B_3 were utilized for subsequent studies.
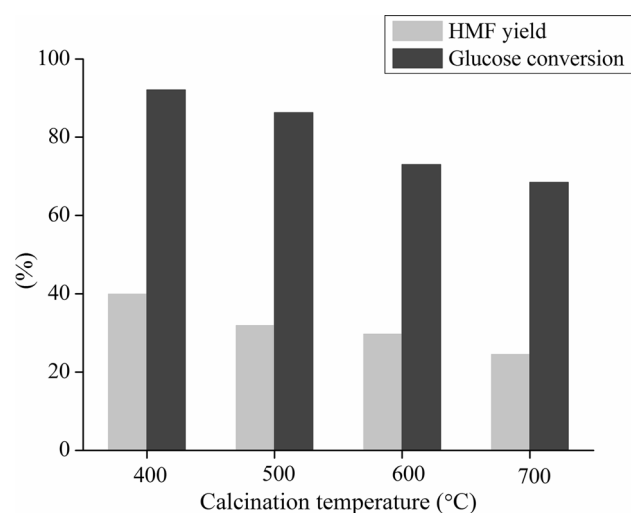

Fig. 5 Effect of reaction temperature and time on HMF production from glucose (Reaction condition: 1 g DMSO, 50 mg glucose, and 20 mg Al_2B_3)

Effect of the Molar Ratio of B/Al

Figure 6 displays the influence of the molar ratio of B/Al (i.e., 1:1, 1:2, 2:1, 2:3 and 3:2) on synthesis of HMF from glucose. The optimum molar ratio of B/Al for glucose dehydration was found to be 3:2, and a relatively high HMF yield of 39.9 % could be achieved at 140 °C for 2 h. The relatively larger pose size of Al_2B_3 (Fig. 2) was demonstrated to facilitate the access of substrate to active sites [39], which could be partially resposible for its superior activity to other Al–B catalysts. To examine the effect of acidity on glucose-to-HMF conversion in DMSO, the catalytic performance of Al_2P_3, Zr_2P_3 and Al_2B_3 was also investigated. It was clear to see that the catalytic

Fig. 4 Effect of Al_2B_3 calcination temperature on conversion of glucose to HMF (Reaction conditions: 50 mg glucose, 20 mg Al_2B_3, 1 g DMSO, 140 °C and 2 h)
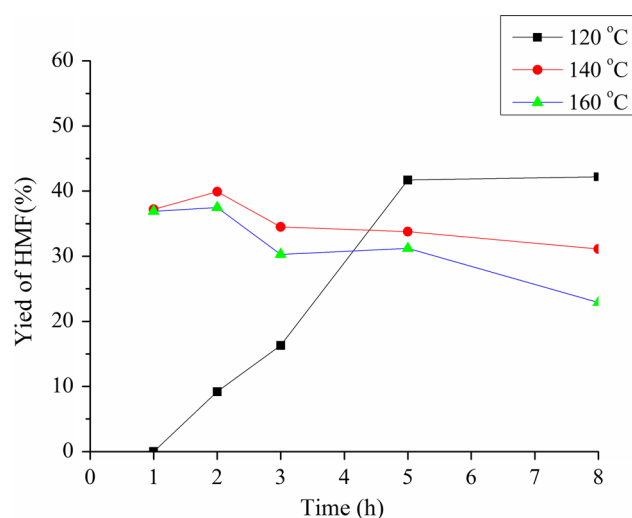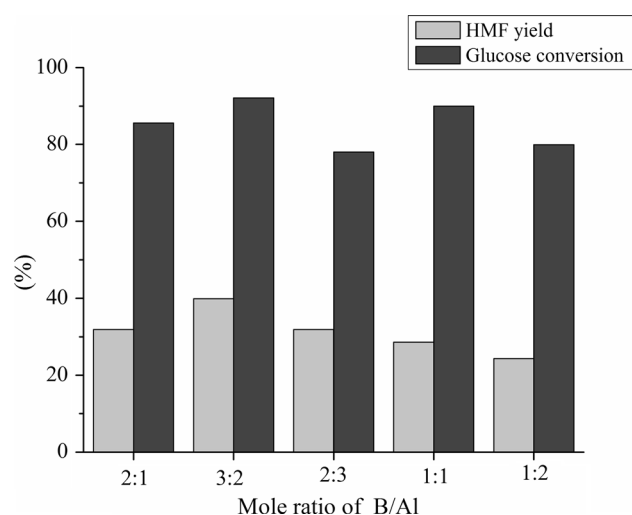

Fig. 6 Effect of B/Al molar ratio on conversion of glucose to HMF (Reaction conditions: 50 mg glucose, 20 mg catalyst, 1 g DMSO, 140 °C, and 2 h)

activity of Al_2P_3 and Zr_2P_3 was inferior to that of Al_2B_3 (Table S1), demonstrating that the higher acid strength and density of Al_2B_3 led to its enhanced efficiency in catalyzing conversion of glucose to HMF (Fig. S3).

Effect of Catalyst Dosage

Figure 7 shows the influence of catalyst amount (i.e., 0, 10, 20, 30, 40 and 50 mg) on converting glucose to HMF. It's found that only 8 % HMF yield with 47 % glucose conversion was obtained in DMSO with the absence of any catalyst. When 10 mg Al_2B_3 was used to catalyze conversion of glucose, 39.5 % yield of HMF was obtained at 140 °C for 2 h. Further increasing the catalyst amount to 20 mg afforded a slightly increased HMF yield (39.9 %). However, the HMF yield did not continue to rise but decline by 4 % when 30 mg Al_2B_3 was employed. Excess amount of catalyst was likely to cause catalyst aggregation to hinder the mass transfer, thus decreasing the activity of the Al_2B_3 catalyst. Therefore, 20 mg catalyst was chosen as the best dosage.

Catalytic Degradation of Glucose to HMF in Various Solvents

The type of solvents was reported to have significant effect on producing HMF from sugars. In this regard, dimethyl formamide (DMF), dimethyl sulfone (DMSO), 1-ethyl-3-methyl imidazolium chloride ([EMIM][Cl]), water/[EMIM][Cl], methyl isobutyl ketone (MIBK)/water, and DMSO/acetonitrile (MeCN) were used to investigate the effect of solvent on HMF production from glucose. As shown in Fig. 8, DSMO exhibits the superior activity, and
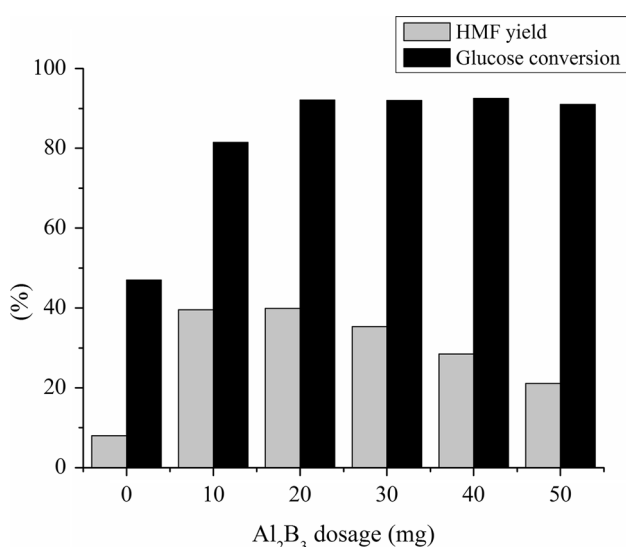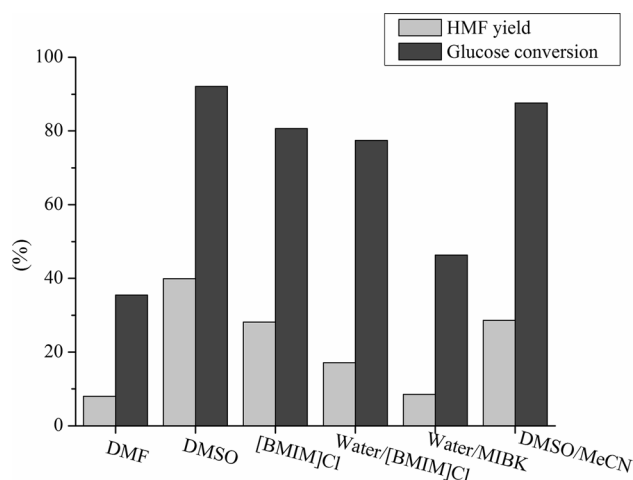
Fig. 8 Effect of various solvents on glucose-to-HMF conversion catalyzed by Al_2B_3 (Reaction condition: 50 mg glucose, 1 g solvent, 20 mg Al_2B_3, 140 °C, and 2 h)

39.9 % yield of HMF can be obtained. The unique function of DMSO on preventing the formation of byproducts (e.g., levulinic acid and humins) in the reaction systems is helpful to improve the yields of HMF, illustrating that DMSO can be chosen as the optimum solvent.

Synthesis of HMF from Various Sugars with Al_2B_3

To expand the substrate scope, other biomass-derived sugars including fructose, inulin, sucrose and cellobiose were also applied as feedstock to produce HMF in the presence of Al_2B_3 (Fig. 9). Relatively high HMF yields of 45.5, 40.2, 50.1 and 36.4 % could be achieved from fructose, inulin, sucrose and cellobiose, respectively. Notably,
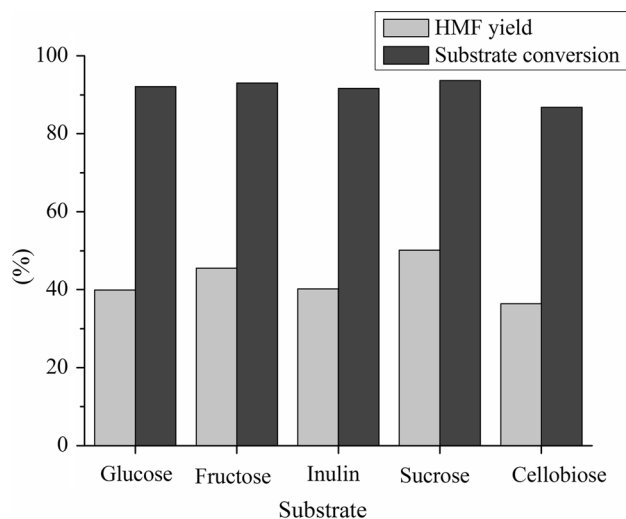
Fig. 7 Influence of Al_2B_3 dosage on conversion of glucose to HMF (Reaction conditions: 50 mg glucose, 1 g DMSO, 140 °C, and 2 h)

Fig. 9 Catalytic production of HMF from various carbohydrates with Al_2B_3 (Reaction condition: 50 mg substrate, 20 mg Al_2B_3, 1 g DMSO, 140 °C, and 2 h)

a little higher HMF yield was obtained from sucrose than that from fructose. It's proposed that humins are much easier to be formed from fructose than sucrose during the reactions [40]. These data indicated that the Al–B catalyst containing Lewis and Brønsted acid sites was more helpful for converting sugars that contain glucose units to HMF.

Recycling Experiment

After each cycle of reactions, the used catalyst was separated from the reaction mixture by centrifugation, successively washing with water, acetone and ethanol for three times, and drying at 80 °C overnight. The recovered catalyst was used for the next cycle in producing HMF from glucose. Figure 10 demonstrates that the catalyst can be reused for at least 5 times with only slight decrease in catalytic activity. No obvious changes in the structure and acid density (0.8 vs. 0.6 mmol/g) of the fresh and recovered (after five cycles) Al_2B_3 catalysts are observed, as illustrated by IR spectra and NH_3-TPD patterns (Fig. 11), which clearly indicate the good stability of Al_2B_3 in the reations. Two possible reasons are speculated to be responsible for the decreased catalytic activity of Al_2B_3 after five consecutive recycles: (1) the active sites of the catalyst are hindered by humins, and (2) part of active sites in the catalyst may be lost during filtration [17, 22, 32].

Conclusions

In this study, a series of aluminum–boron catalysts with different molar ratios and Bronsted-Lewis acid sites were prepared and employed for converting glucose to HMF in DMSO under mild reaction conditions. A relatively high
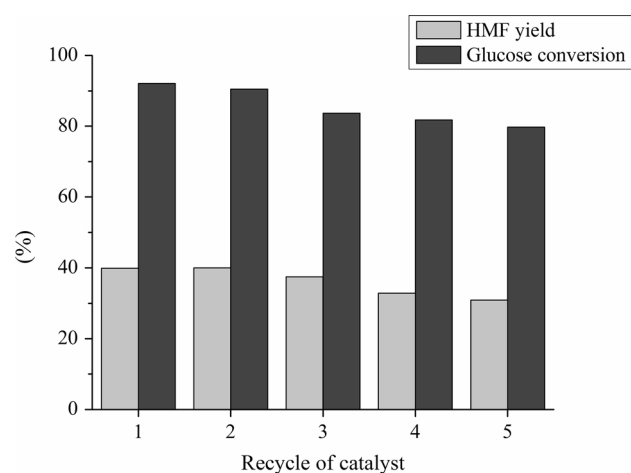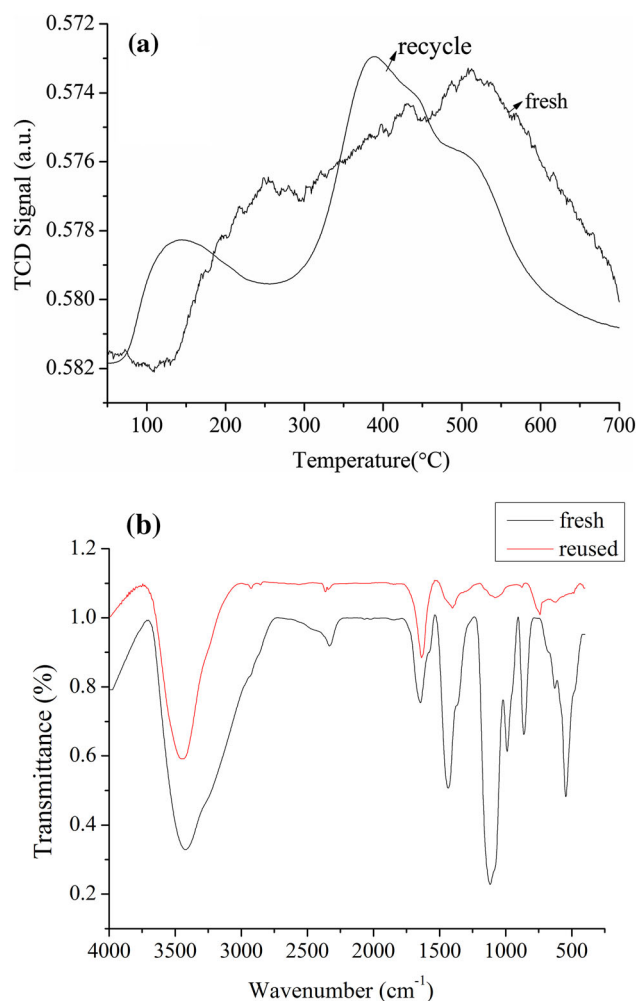

Fig. 11 NH_3-TPD patterns (**a**) and FT-IR spectra (**b**) of fresh and recycled Al_2B_3 catalysts

HMF yield of 39.9 % with glucose conversion of 92.1 % was obtained over Al_2B_3 at 140 °C for 2 h. Moreover, the catalyst was stable and could be recycled for at least five times without obvious loss in activity.

Fig. 10 Recycling study of Al_2B_3 in glucose-to-HMF conversion (Reaction conditions: 50 mg glucose, 20 mg Al_2B_3, 1 g DMSO, 140 °C, and 2 h)

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