

Research Article

Catalytic Transfer of Fructose to 5-Hydroxymethylfurfural over Bimetal Oxide Catalysts

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Direct conversion of fructose into 5-hydroxymethylfurfural (HMF) is achieved by using modified aluminum-molybdenum mixed oxide (S-ALMo) as solid acid catalysts. The synthesized catalyst was characterized by powder XRD, nitrogen adsorption-desorption isotherm, NH₃-TPD, and SEM. As a result, the presence of strong acidity, mesostructures, and high surface area in the S-ALMo catalyst was confirmed by nitrogen adsorption-desorption isotherm and NH₃-TPD studies. A study by optimizing the reaction conditions such as catalyst dosage, reaction temperature, and time has been performed. Under the optimal reaction conditions, HMF was obtained in a high yield of 49.8% by the dehydration of fructose. Moreover, the generality of the catalyst is also demonstrated by glucose and sucrose with moderate yields to HMF (24.9% from glucose; 27.6% from sucrose) again under mild conditions. After the reaction, the S-ALMo catalyst can be easily recovered and reused four times without significant loss of its catalytic activity.

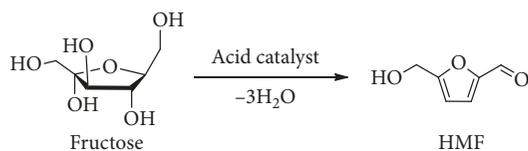
1. Introduction

With diminishing fossil fuel and degradation of the environment, catalytic routes to the production of fuels and chemicals from sustainable sources have aroused much concern over past decades [1–4]. An abundant renewable and carbon-neutral biomass resource is a promising alternative to petroleum for the production of fuels and chemicals [5]. In recent years, many chemicals have been successfully synthesized from biomass, and among the various platform molecules, 5-hydroxymethylfurfural (HMF) is considered a flexible chemical platform owing to their versatile functions and benign properties [6, 7], and it can be further oxidized into 5-ethoxymethylfurfural (EMF), 2,5-diformylfuran (DFF), and 2,5-furandicarboxylic acid (FDCA) [8–10]. Therefore, extensive investigations have been performed for the transformation of carbohydrates into HMF [11–13].

As a sustainable precursor for biofuel chemistry, HMF is obtained mainly by dehydration of monosaccharide,

disaccharide, and polysaccharide, using homogeneous acids (such as H₂SO₄ and HCl) or heterogeneous acid as catalysts (Scheme 1). However, the major drawback of homogeneous acid suffered from problems of equipment corrosion, product separation, and difficult recycle and reuse. In turn, solid acid catalysts were found to be efficient, are easy to separate, and have reusability and lower catalyst loading; some of them that can be produced with methods that have a low environmental impact have received significant attention in recent years; and several types of solid acid catalysts include metal salts [14], acidic resins [15], solid organo-catalyst [16], ionic liquids [17], sulfonated graphene quantum dots [18], and zeolites [19].

Metal oxides as heterogeneous acid catalyst typically possess Lewis and Brønsted acid sites that have shown a heterogeneous pathway for biodiesel production, dehydration, hydrolysis, isomerization, etc. Single metal oxide has appeared as a kind of catalyst for catalytic performance in acid-catalyzed reaction due to low-cost and their good



SCHEME 1: Synthesis of HMF from fructose dehydration.

thermal stability. But, the single metal oxide is often associated with distinct disadvantages such as low catalytic activity, repeated poor usability, tough experimental conditions, which limit their applications. Recently, the original idea of preparing the mixed metal oxide solid catalysts were to enhance acid strength, increase the surface area, and strengthen the stability of these catalysts in comparison with single metal oxide for various organic reactions [20, 21]. However, in few studies, mixed metal oxides were used in dehydration of carbohydrates to HMF. Very recently, we have already reported that AlMo oxides are solid acids which exhibit unique acidic properties and good stability in the esterification reaction. Based on the above discussion, we report within this paper that modified aluminum-molybdenum mixed oxide in the presence of stearic acid is used as a solid catalyst for the synthesis of HMF from fructose. The catalyst was characterized using various analytical techniques such as powder XRD, NH_3 -TPD, nitrogen adsorption-desorption isotherm, and SEM. The effect of reaction temperature, reaction time, and catalyst dosage on HMF yield along with catalyst reusability was investigated.

2. Experimental

2.1. Materials. Aluminum isopropoxide ($\text{C}_9\text{H}_{21}\text{AlO}_3$, 98%), MoCl_5 (99.6%), stearic acid (>99%), fructose, glucose, sucrose, and dimethylsulfoxide (DMSO) were purchased from Sinopharm Chemical Reagent Co., Ltd; HMF of reagent grade (99%) were purchased from Shanghai Aladdin Industrial Inc. All other chemicals were of analytical grade and used as received, unless otherwise noted.

2.2. Preparation of Aluminum-Molybdenum Mixed Oxides. Modified aluminum-molybdenum mixed oxides were prepared using stearic acid as a modifier by following the previous methods by our group [22, 23], and the catalyst was denoted as S-AlMo. For comparison, stearic acid-modified aluminum oxide was also prepared by the same method, and it was denoted as S-Al.

2.3. Characterization of Catalysts. The powder X-ray diffraction (XRD) patterns of the catalysts were obtained using a Rigaku D/max 2000 ultima plus diffractometer (monochromatic nickel filter, Cu K α radiation). The acidity of the catalysts was measured by temperature-programmed desorption (TPD) of ammonia (AutoChem 2920, Micromeritics, USA). Nitrogen adsorption-desorption isotherm was determined with ASAP 2020M volumetric adsorption analyzer (Micromeritics, USA). SEM was performed using a

field-emission scanning electron microscope (FESEM, XL-30, Philips) at 25 KV.

2.4. Catalytic Activity Measurement. Conversion of fructose was conducted in a batch glass tube heated in the oil bath with magnetic stirring condition. After catalysts and fructose were placed into the batch glass tube with the organic solvent DMSO, the reaction was started by heating the mixture to the given reaction temperature. As to the reaction media containing low boiling point or aqueous solvent, a sealed stainless steel autoclave was used under other same conditions. After the specified time, the resultant mixture was cooled to room temperature, and the solids were filtered off, then diluted with deionized water, and further analyzed by high-performance liquid chromatography (HPLC; Agilent 1100, USA) equipped with a LiChrospher C18 column and an UV detector (284 nm). The concentration of HMF was calculated based on the standard curve obtained with the standard substances. HMF yield was calculated according to the following equation:

$$\text{HMF yield (mol\%)} = \frac{\text{moles of HMF produced}}{\text{moles of starting fructose}} \times 100\% \quad (1)$$

3. Results and Discussion

3.1. Characterization of S-AlMo. The structural properties and acidity of S-AlMo sample prepared were characterized by powder XRD, nitrogen adsorption-desorption, NH_3 -TPD, and SEM (see Figure 1S). Powder XRD measurements showed that the S-AlMo sample has $\text{Al}_2(\text{MoO}_4)_3$ and crystalline MoO_3 peaks [24, 25] and was closely related to active sites for dehydration reaction. Nitrogen adsorption-desorption analysis showed that the sample gave type-IV isotherms with type H2 hysteresis loop in the high pressure region, characteristic of materials with mesostructure, indicating that stearic acid-modified aluminum-molybdenum mixed oxide catalyst could get the mesoporous structure, which was consistent with our previous work [13, 22, 23]. In addition, the Brunauer-Emmett-Teller (BET) surface area, pore volume, and average pore size were $49.82 \text{ m}^2 \cdot \text{g}^{-1}$, $0.17 \text{ cm}^3 \cdot \text{g}^{-1}$, and 14.19 nm, respectively. Compared with the S-Al sample, the Brunauer-Emmett-Teller (BET) surface area, pore volume, and average pore size were $21.73 \text{ m}^2 \cdot \text{g}^{-1}$, $0.03 \text{ cm}^3 \cdot \text{g}^{-1}$, and 5.68 nm, respectively. Moreover, there were two desorption profiles (100–200°C and around 750°C) over the temperature range of 50–800°C in the NH_3 -TPD profiles, suggesting the catalyst contains weak and strong acid sites on its surface; meanwhile, the acid concentration of S-AlMo sample (0.87 mmol/g) was higher than that of S-Al sample (0.78 mmol/g). SEM also allows us to get insights into the morphological data of catalysts, and the images reveal that the aggregation of small particles in irregular shapes formed a grainy structure.

3.2. Effect of the Type of Catalysts on Fructose Dehydration to HMF. In this study, we initially explored the effects of the

type of catalysts on the dehydration of fructose to HMF in DMSO at 140°C for 60 min (Figure 1). As shown in Figure 1, it is apparent that various catalysts have diverse effects on HMF yields, and it can be observed that the HMF yield is lower without adding the catalyst. However, the S-AlMo catalyst gives the highest HMF yield of 49.8%, and the S-Al catalyst gives the low HMF yield of 35.4%. These results are in good agreement with the characterization of NH₃-TPD, where a higher number of acid concentrations led to a better catalytic performance in dehydration reaction. Therefore, the S-AlMo catalyst was applied as the most active solid acid for the synthesis of 5-HMF from fructose.

3.3. Effect of Different Solvents on Fructose to HMF Conversion. For determination of catalytic activity, the S-AlMo as the solid acid catalyst was carried out in different types of organic solvent. Four types of solvents (DMSO, DMA, DMF, and MIBK) were applied in the dehydration of fructose to HMF at 140°C for 60 min, and the results are summarized in Table 1. In DMSO solvent, the yield of HMF is 49.8% with fructose as raw material. In DMA, DMF, and MIBK solvents, the yields of HMF are 10.5%, 1.7%, and 0%, respectively (entries 1–3). This may be due to that DMSO could inhibit the occurrence of side reactions such as rehydration of HMF into levulinic acid and formic acid [26]. Above results show that the S-AlMo catalytic system could effectively transform fructose to HMF in the DMSO solvent. Hence, DMSO was selected as an organic solvent for the subsequent experiments in this work.

3.4. Effect of Reaction Time and Temperature on Fructose Dehydration to HMF. In order to get the highest HMF yield, the reaction conditions, such as reaction temperature and time, were optimized. The results are shown in Figure 2. In the case of fructose dehydration into HMF, the reaction temperature and time showed a critical role in the reaction with respect to the HMF yield. When the dehydration of fructose was conducted at 100°C, a low HMF yield of 8.7% was obtained after 120 min. Then, the reaction temperature was up to 120°C, HMF yield increased from 8.7% at 100°C to 46.9% at 120°C at the same of 120 min, and these results show that a relatively higher temperature promotes the formation of HMF. Further increasing the reaction temperature to 140°C, the maximum HMF yield (49.8%) of HMF is achieved after 60 min. Meanwhile, it was clear that the HMF yield had a slow decrease that further prolonged reaction time at 140°C, indicating that the product HMF was not very stable at a high temperature and a long time. It is possible due to the rehydration of HMF into levulinic acid (LA) or other byproducts [27–29]. Overall, a temperature of 140°C and time of 60 min were proper for fructose dehydration to HMF using the S-AlMo catalyst.

3.5. Effect of Catalyst Dosage on Fructose Dehydration to HMF. The effect of catalyst dosage on the fructose-to-HMF transformation was studied by varying the weight of the S-AlMo catalyst ranging from 5 to 40 mg (see Table 2). As

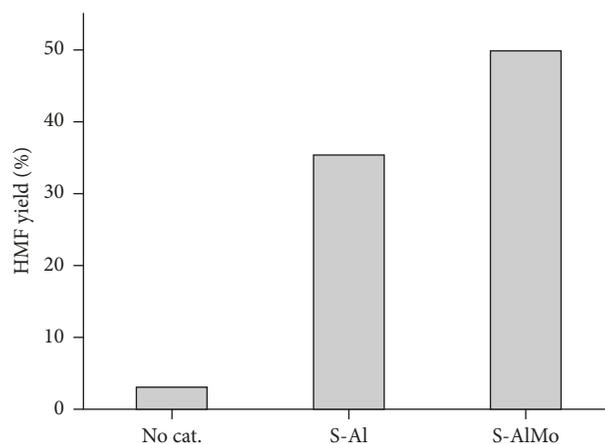


FIGURE 1: Effect of the type of catalysts on fructose dehydration to HMF. Conditions: fructose (50 mg), catalyst (20 mg), DMSO (1.0 g), $T=140^{\circ}\text{C}$, and $t=60$ min.

TABLE 1: Effect of different types of solvents on the acid-catalyzed dehydration of fructose to HMF^a.

No.	Solvent	Temperature ($^{\circ}\text{C}$)	Time (min)	HMF yield (%)
1	MIBK	140	60	Not detected
2	DMF	140	60	1.7
3	DMA	140	60	10.5
4	DMSO	140	60	49.8

^aConditions: fructose (50 mg), S-AlMo catalyst (20 mg), and solvent (1.0 g).

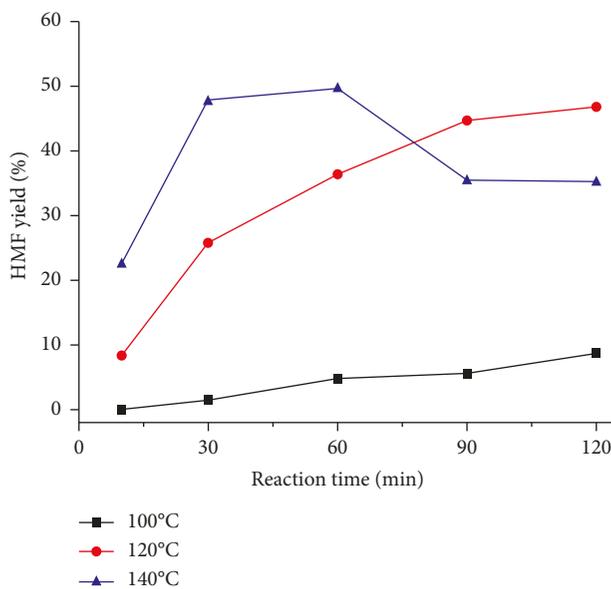


FIGURE 2: Effect of reaction time and temperature on fructose dehydration to HMF with S-AlMo catalyst. Reaction conditions: fructose (50 mg), S-AlMo catalyst (20 mg), and DMSO (1.0 g).

shown in Table 2, an initial steep increase in the yield of HMF is observed when the dosage of the catalyst is increased up to 20 mg, and a maximum yield (49.8%) can achieve. Continuing to increase catalyst dosage, the yield of HMF smoothly decreases; this may be due to excess catalyst

TABLE 2: Effect of catalyst weight on the acid-catalyzed dehydration of fructose to HMF^a.

No.	Catalyst weight (mg)	Temperature (°C)	Time (min)	HMF yield (%)
1	5	140	60	27.5
2	10	140	60	39.8
3	20	140	60	49.8
4	30	140	60	28.9
5	40	140	60	26.6

^aReaction conditions: fructose (50 mg) and DMSO (1.0 g).

dosages that not only provides large active sites in this reaction system, which would accelerate the synthesis of HMF, but also promotes more side reactions such as the formation of levulinic acid and humins [30, 31]. Thus, we have considered 20 mg as the optimized catalyst amount of S-AlMo for fructose dehydration to HMF at 140°C for 60 min reaction time in this work.

3.6. Effect of Water Amount in the System. The influence of water amount in DMSO on dehydration of fructose to HMF is also investigated. As displayed in Figure 3, surprisingly, the addition of water clearly led to a serious decrease of the HMF yield. When the deionized water was increased from 0 to 0.6 mL, the HMF yield decreased from 49.8% to 4.4%. It was possible that water impaired the poisoning of acid sites, causing the declined catalytic activity of S-AlMo and giving a low HMF yield. To some extent, these findings were in good agreement with the results reported by Qi et al. [32].

3.7. Synthesis of HMF from Sugars Catalyzed by S-AlMo Catalyst. Additionally, the developed method was also used to the synthesis of HMF with sugars as raw material, and the results are demonstrated in Table 3. The moderate HMF yield at 24.9% and 27.6% was obtained from glucose and sucrose in the DMSO system, respectively. The experiment results indicated that the S-AlMo catalyst with the presence of basic sites (eg., Al₂O₃ moieties) as well as acidic sites (eg., Al₂(MoO₄)₃ and MoO₃) was similar to the result reported by Li et al. [33].

3.8. Catalyst Recycling Experiments. The reusability of the solid acid catalyst is very important to the low-cost and environmentally friendly biomass transformation. Thus, recycling of the S-AlMo catalyst was tested, and the dehydration of fructose into HMF was used as a model reaction. After the reaction, the catalyst was separated by filtration, washed, and dried prior to being reused in the next run. Then, the recovered S-AlMo catalyst was used to catalyze the dehydration of fructose to 5-HMF over four successive reactions under the same reaction conditions (Figure 4). As shown in Figure 4, no significant loss in the yield of HMF was observed over four cycles (49.8% in the first cycle versus 36.6% in the fourth cycle), and the slight loss of activity with respect to the first reaction cycle could be attributed to partial oligomeric products adhering to the surface of the catalyst [31, 34]. These results clearly indicated that the S-AlMo catalyst could be reused without

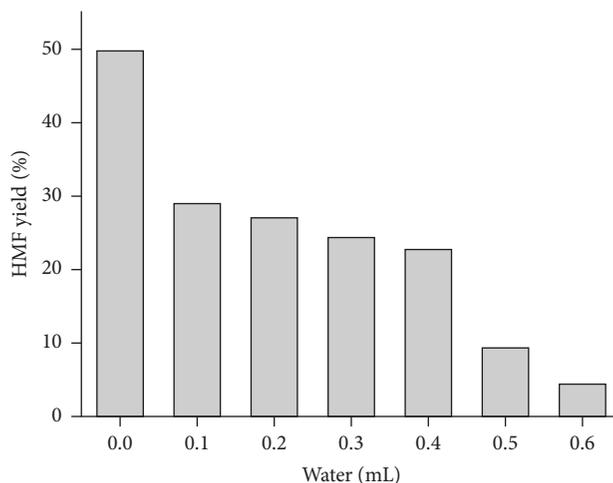


FIGURE 3: Effect of water added into system on the degradation of fructose. Reaction conditions: fructose = 50 mg, S-AlMo catalyst = 20 mg, DMSO = 1.0 g, $T = 140^{\circ}\text{C}$, and $t = 60$ min.

TABLE 3: Synthesis of HMF from sugars in DMSO system with S-AlMo catalysts^a.

No.	Substrate	Temperature (°C)	Time (min)	HMF yield (%)
1	Fructose	140	60	49.8
2	Glucose	140	180	24.9
3	Sucrose	140	180	27.6

^aSugars (50 mg), S-AlMo catalyst (20 mg), and DMSO (1.0 g).

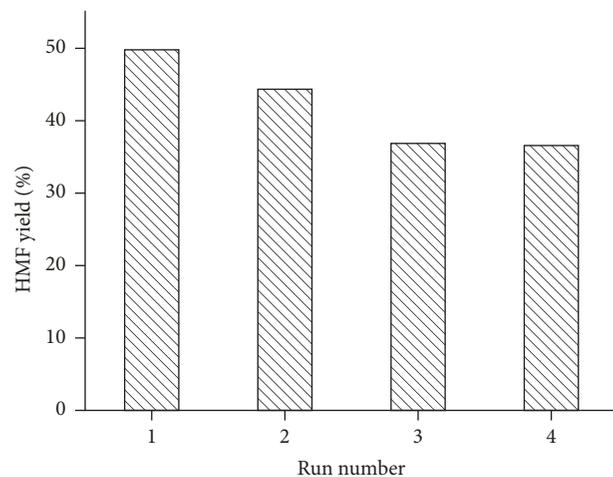


FIGURE 4: Recyclability study of S-AlMo catalyst for fructose dehydration reaction. Reaction conditions: fructose = 50 mg, S-AlMo catalyst = 20 mg, DMSO = 1.0 g, $T = 140^{\circ}\text{C}$, and $t = 60$ min.

significantly losing its catalytic activity. Therefore, the catalyst is capable under mild reaction condition.

4. Conclusions

In conclusion, stearic acid-modified aluminum-molybdenum mixed oxide is an efficient solid acid catalyst for direct conversion of fructose into HMF. The S-AlMo catalyst exhibited excellent textural properties (e.g., strong acidic sites, mesostructures, and large surface area) and better catalytic activity for dehydration reaction. HMF was obtained with a good yield of 49.8% by the dehydration from fructose, and the moderate HMF yield of 24.9% and 27.6% were also obtained from glucose and sucrose, respectively. Moreover, the catalyst can be recycled and reused for four cycles without significant loss in the HMF yield. Therefore, the S-AlMo catalyst would have promising potential for other acid-catalyzed chemical reactions.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Authors' Contributions

Qiuyun Zhang and Xiaofang Liu contributed equally to this work.

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Supplementary Materials

The structural properties and acidity of S-AlMo sample prepared were characterized by powder XRD, nitrogen adsorption-desorption, NH₃-TPD, and SEM (Figure 1S). Powder XRD measurements showed that the S-AlMo sample have Al₂(MoO₄)₃ and crystalline MoO₃ peaks [24, 25] and was closely related to active sites for dehydration reaction. Nitrogen adsorption-desorption analysis showed that the sample gave type-IV isotherms with type H2

hysteresis loop in the high pressure region, characteristic of materials with mesostructure, indicating that stearic acid-modified aluminum-molybdenum mixed oxide catalyst could get the mesoporous structure, which was consistent with our previous work [13, 22, 23]. In addition, the Brunauer-Emmett-Teller (BET) surface area, pore volume, and average pore size were 49.82 m²·g⁻¹, 0.17 cm³·g⁻¹, and 14.19 nm, respectively. Compared with the S-Al sample, the Brunauer-Emmett-Teller (BET) surface area, pore volume, and average pore size were 21.73 m²·g⁻¹, 0.03 cm³·g⁻¹, and 5.68 nm, respectively. Moreover, there were two desorption profiles (100–200°C and around 750°C) over the temperature range of 50–800°C in the NH₃-TPD profiles, suggesting the catalyst contains weak and strong acid sites on its surface; meanwhile, the acid concentration of the S-AlMo sample (0.87 mmol/g) was higher than that of the S-Al sample (0.78 mmol/g). SEM also allows us to get insights into the morphological data of catalysts, and the images reveal that the aggregation of small particles in irregular shapes formed a grainy structure. (*Supplementary Materials*)

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