

Efficient and One-pot Production of 2,5-dimethylfuran (DMF) from Fructose Using Bi-Functionalized Mesoporous Silica Nanocatalysts

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Abstract

Due to the recent demand for green and economical alternatives to traditional fossil fuels, this research dedicates itself to the synthesis of DMF from fructose. The usage of a solid acid catalyst is crucial for this reaction owing to the benefits these heterogeneous catalysts provide. For this experiment, bi-functionalized mesoporous silica nanoparticles (MSN) in a THF system have shown desirable results in one-pot reaction under mild conditions (75 °C, 15 hr). And, the maximum DMF yield is 65.50%.

Keywords: biofuel, biomass, mesoporous silica nanoparticles (MSN), bi-functional.

1 Introduction

Previous studies demonstrate that using formic acid (FA) as the catalyst can achieve excellent yield of DMF (>95%) from HMF_[1]. In economic view, we utilized heterogeneous catalyst to replace homogeneous catalyst in the production of DMF. In my previous studies, we synthesized MSN functionalized with two kinds of acid groups (HSO₃-MSN and COOH-MSN), and it shows the efficient and subsequent production of DMF from fructose. According to my previous studies, HSO₃-MSN is more contributive to forming HMF, and COOH-MSN is best suited for forming DMF. Therefore, we tried to synthesize bi-functionalized MSN, and did the one-pot production of DMF from fructose using bi-functionalized MSN.

2 Experimental

The bi-functionalized MSN, fructose and tetrahydrofuran (THF) were mixed in a flask, and heated to reflux with continuous stirring at 75°C for 15hr. The resulting solution was diluted with water. Then, resulting solution was extracted with diethyl ether. THF and diethyl ether in the organic phase were removed by rotary evaporator. A crude product containing a mixture of DMF, intermediates, and HMF was obtained. And the water phase contained a mixture of partial HMF, intermediates, and unconverted fructose.

3 Results and discussion

First, MSNs were grafted with two acid group, -HSO₃ and -COOH. The ratio of -HSO₃ to -COOH was 1:1. According to different post treatments of material synthesis adopted, the materials are labeled as “bif.-MSN(1-1):aci. only”, “bif.-MSN(1-1):oxi. only”, “bif.-MSN(1-1):aci.+oxi.”, and “bif.-MSN(1-1):oxi.+aci.”. “Acid.” and “oxi.” are the abbreviations of “acidification” and “oxidation”. We utilized these catalysts to synthesize the DMF from fructose in one-pot, and the results were shown in **Table 1**. Out of these four catalyst, it is suggested by the data that “bif.-MSN(1-1):oxi. only” is the most contributive to forming HMF (62.16% yield). Oxidation can convert the MP groups to -HSO₃ groups successfully. Fructose can be dehydrated by -HSO₃ groups. This is the reason why the yield of HMF using “bif.-MSN(1-1):oxi. only” is the highest in four catalysts. However, HMF cannot be hydrogenated to DMF by -HSO₃ groups. According to entry 1, “bif.-MSN(1-1):aci. only” is best suited for forming DMF. The yield of DMF is highest (65.50%). It indicates that CTES on MSNs were converted to -COOH groups by acidification, then -COOH groups can dehydrate the fructose partly and hydrogenate HMF simultaneously in one-pot reaction. The entry 3 and entry 4 show that adopting two post treatment (acidification and oxidation) is not good for DMF or HMF synthesis. These two post treatment would disturb each other, and -COOH groups and -HSO₃ groups cannot be obtained. According to the result, we found that -COOH groups of material are crucial for DMF synthesis from HMF. But the production of HMF depends on -HSO₃ groups, which were obtained by oxidation. Therefore, there is a perfect ratio between these groups, -HSO₃ groups and -COOH groups. In order to optimize the reaction result, we changed the ratio of acid functional groups. As shown as **Table 2**, the highest yield of DMF was achieved by “bif.-MSN(1-1):aci. only”. In

Table 1 synthesis of DMF from fructose with Bif.-MSN(1:1)

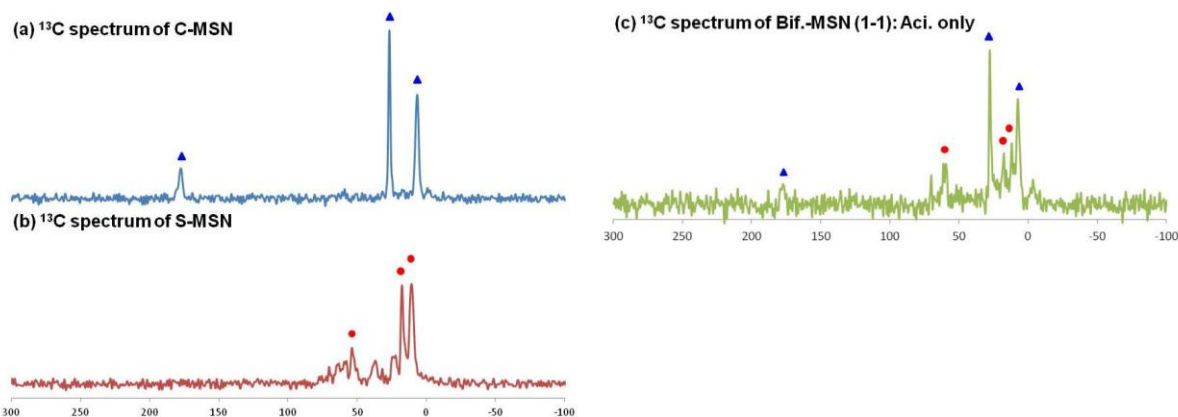
Entry	fructose	Amount of catalyst (g)	Conversion	Yield		
			(mol%)	(mol%)		
MP:CTES = 6mmole:6mmole			fructose	HMF	DMF	
1	0.25g	Bif.-MSN (1-1): Aci. only	0.3g	96.52	3.60	65.50
2	0.25g	Bif.-MSN (1-1): Oxi. only	0.3g	95.73	62.16	27.19
3	0.25g	Bif.-MSN (1-1): Aci.+Oxi.	0.3g	28.24	2.60	0.37
4	0.25g	Bif.-MSN (1-1): Oxi.+Aci.	0.3g	36.33	1.26	0.37
5	0.25g	S-MSN 0.15g + C-MSN 0.15g		96.00	6.70	66.61

Reaction conditions : fructose (0.25g); catalyst(0.3g); THF (10mL); 75°C; 15hr

Table 2 synthesis of DMF from fructose with Bif.-MSN which is in different ratio of acid group

Entry		Amount of catalyst (g)		Conversion (mol%)	Yield (mol%)	
		12mmole in total (MP:CTES)		fructose	HMF	DMF
1	0.25g	Bif.-MSN (1-1): Aci. only	0.3g	96.52	3.60	65.50
2	0.25g	Bif.-MSN (1-1): Oxi. only	0.3g	95.73	62.16	27.19
3	0.25g	Bif.-MSN (1-2): Aci. only	0.3g	97.54	2.46	53.13
4	0.25g	Bif.-MSN (1-2): Oxi. only	0.3g	49.55	2.34	0.34
5	0.25g	Bif.-MSN (2-1): Aci. only	0.3g	80.99	3.19	0.37
6	0.25g	Bif.-MSN (2-1): Oxi. only	0.3g	76.29	2.00	0.45

Reaction conditions : fructose (0.25g); catalyst(0.3g); THF (10mL); 75°C; 15hr

**Figure 1** ^{13}C NMR spectra of (a) C-MSN [COOH-MSN], (b) S-MSN [HSO₃-MSN], (c) Bif.-MSN [1-1]: Aci. only

entry 3 (Table 2), the ratio of –COOH groups on “bif.-MSN(1-2):aci. only” is higher than which on “bif.-MSN(1-1):aci. only”, however, there is not enough –HSO₃ groups to dehydrate fructose. Because the acidity of –COOH groups is much lower than –HSO₃ groups. Consequently, HMF is not adequate for hydrogenation, and the yield of DMF is lower. Finally, in order to prove that –HSO₃ groups and –COOH groups exist simultaneously on “bif.-MSN(1-1):aci. only”. We proceeded the ^{13}C NMR analysis, as shown as Figure 1. It shows that “bif.-MSN(1-1):aci. only” possesses two functional groups(–HSO₃ and –COOH groups) indeed. We also did the experiment that using the mixture of HSO₃-MSN and COOH-MSN proceeded the fructose conversion in one-pot at the same reaction condition(75°C, 15hr). The result shows the same yield with “bif.-MSN(1-1):aci. only” (entry 5 in Table 1).

4 Conclusion

Bi-functional Mesoporous Silica Nanocatalyst,”

bif.-MSN(1-1):aci. only”, possesses two functional groups(–HSO₃ and –COOH groups). Moreover, it can dehydrate the fructose to HMF and hydrogenate HMF to DMF simultaneously. And, the maximum DMF yield (65.50%) was obtained. We summarized that utilizing ” bif.-MSN(1-1):aci. only” catalyst can achieve efficient one-pot production of DMF from fructose with high DMF yield. In economic view, this catalyst does not only decrease the reaction time, but also save the cost.

5 Acknowledgments

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6 References

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