

Catalytic conversion of xylan into furfural over sulfonic acid-functionalized graphene oxide

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Abstract: Sulfonic acid functionalized graphene oxide (GO-SO₃H) was found to be superior for the production of furfural from xylan with 79% of furfural yield. GO-SO₃H was successfully recycled after each reaction, and it shows its reusability without significant loss in catalytic activity. Presence of oxy-functional groups not only strengthen the -SO₃H in GO-SO₃H but also help to enhance the substrate sorption capacity, which was probably not allow to leached it out into the reaction medium.

Keywords: Xylan decomposition, Graphene Oxide, Furfural

1. Introduction

Utilization of renewable biomass for the chemical production has been a growing interest in the current bio-based industries [1-3]. Furfural has been identified as one of the most promising platform chemical directly derived from biomass, because it is having potential in the productions of value-added chemicals, fuels, and intermediates [2]. One step chemical conversation of hemicellulose (xylan) to furfural in presence of acid functionalized catalysts is very important in the bio-refinery. Many researchers have made considerable efforts to use Brønsted acids instead of Lewis acids as catalysts for chemical conversion of hemicellulose [3]. In this regards, homogenous acid catalysts are utilized for the furfural production from hemicellulose and C5 sugars [3], however, these processes faces some limitations such as catalyst separation, environmental issues, toxicity, corrosiveness etc. There are also reports of eco-friendly routes using solid-acid catalysts, but the yields are often low, even if an excess of catalyst is used [1]. Last decade, graphene has attracted much interest because of its outstanding electronic and mechanical properties [4]. Graphene oxide (GO) are graphene sheets that contain high densities of hydrophilic functional groups such as hydroxyl, carboxyl, and epoxy groups. These hydrophilic groups provide means for incorporation of sulfonic acid groups as Brønsted acid sites through sulfonation, and the sulfonated GO could become a promising candidate of solid acid catalyst for xylan decomposition to industrially important chemicals, or other useful chemical reactions [4]. Here, we report that a new SO₃H-grafted GO (GO-SO₃H) is one of the best solid acid catalysts for the chemical conversion of xylan to furfural.

2. Experimental

The GO-SO₃H catalyst was prepared by sulfonation of GO using chlorosulfonic acid in chloroform. The details of the catalysts preparation is published in the previous article [4]. The structural characteristics and morphology of the catalysts were determined using different characterization techniques such as, XRD, XPS, FTIR, Pyridine-FTIR, CHNS elemental analysis, SEM, TEM etc. Xylan decomposition was performed in a 200-mL stainless-steel reactor. In a typical experiment, 10.0 g of xylan and a catalytic amount (0.5 g) of GO-SO₃H in 200 mL of deionized water were loaded in an autoclave; all reactions were carried out at 175 °C to 200 °C for 2 h with a stirring speed of 1000 rpm. Identification of products and quantitative analysis of products were carried out by HPLC and LC/MS.

3. Results and discussion

GO-SO₃H and C-SO₃H (Sulfonated carbon) catalysts were successfully synthesized and detail investigation on GO-SO₃H surface and its physicochemical properties were demonstrated in previous report [4]. The catalysts were tested in the conversion of xylan to yield furfural. The catalytic results are presented in Table 1. At first, around 15% of furfural yield was obtained without any catalysts and it was probably due to formation of hydronium ion from water under the tested reaction conditions. Among the tested catalyst (displayed in table 1), GO-SO₃H catalyst exhibited remarkable activity for furfural synthesis and it was found to be much more active and stable under tested reaction conditions. High yield of furfural (79%) was obtained after 90 min of reaction. Superior activity of GO-SO₃H over tested catalysts was attributed due to the difference between their structures and types of acid sites. From the IR and XPS study (not provided here), strong bonding between the SO₃H species and carbon in GO-SO₃H and AC-SO₃H was conformed. Such strong bonding should help minimize leaching in an aqueous reaction medium. GO-SO₃H has a higher density of Brønsted acid sites as compare to others (conformed though pyridine FTIR study). GO-SO₃H has much larger pores and, consequently, much easier for the sizable furfural to diffuse in and out [4]. The catalytic properties of Zr(SO₄)₂ can be explained similarly. Its relatively low catalytic activity is due to its small pore size, and its low selectivity for furfural due to the fact that most of its acid sites are Lewis acid sites typically found in Zr(SO₄)₂. As observed before, possible synergistic effects of -SO₃H with other functional groups (COOH and OH) may contribute to the high activity in GO-SO₃H. The reusability of GO-SO₃H catalyst was carried out up to three cycles; it showed excellent performance without significant loss in its catalytic activity. Nevertheless, Char formation and deposition is very serious issue in the biomass conversion processes [4]. More importantly, we did not observed any char formation and leaching of sulfur in the reaction medium.

Table1. Catalytic activity for xylan decomposition to furfural

Catalysts	Surface area (m ² /g)	Acidity (mmol/g)	Time (min)	Conv. (%)	Yield (%)
Blank run	-	-	120	15	8
Zr(SO ₄) ₂	86	1.2		84	63
C-SO ₃ H	753	2.7		83	65
GO-SO ₃ H	217	3.8		86	73
			90	84	79

Reaction condition: Temp. 190 °C, Xylan 10 gm in 200 ml water, Catalyst 0.5 g.

4. Conclusions

GO-SO₃H was found to be very promising candidate for the selective synthesis of furfural from initial biomass xylan. Presence of Brønsted acid (SO₃H sites) together with other oxy functional groups was important in such types of biomass conversions processes. Moreover, it can help to strengthen the -SO₃H bonding and do not allow leaching out into the reaction mixture. GO-SO₃H has showed excellent catalytic performance and produced maximum 79% of furfural yield from xylan without any char formation. The catalyst was recycled very easily and reused it up to three times with minimal loss in its activity.

References

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