Full Length Article

Production of renewable toluene from biomass-derived furans via Diels-Alder and dehydration reactions: A comparative study of Lewis acid catalysts

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HIGHLIGHTS

- Lewis acids are more efficient to convert MF to toluene than Brønsted acids.
- MF oligomerization and alkylation are significantly retarded with Lewis acids.
- The toluene yield is a function of the Lewis acid strength in the metal chlorides.
- Alkali-exchanged Y zeolites, Li- and Na-Y are effective for toluene production.
- A high yield of toluene up to 70% is achieved with $AlCl_3$ and zeolite Na-Y.

GRAPHICAL ABSTRACT
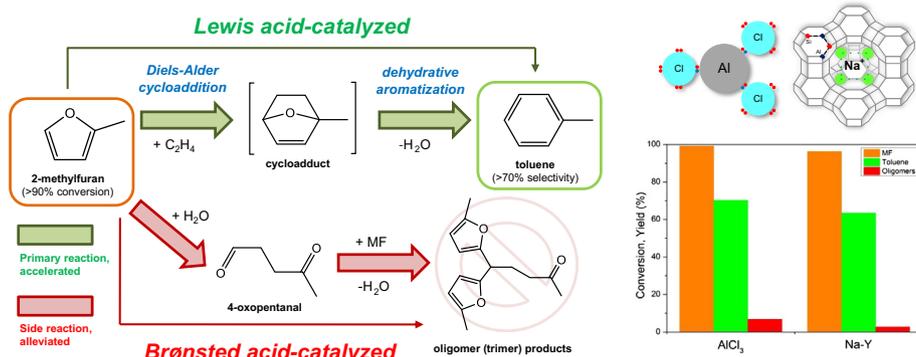
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ABSTRACT

The Diels–Alder cycloaddition of biomass-derived furans and subsequent dehydrative aromatization are potentially valuable processes for the sustainable production of aromatic chemicals from biomass. In this paper, we have investigated the catalytic activity of a series of homogeneous and heterogeneous Lewis acid catalysts in connection with the conversion of biomass-derived 2-methylfuran (MF) and ethylene to toluene. We have used a number of Lewis acid metal chlorides, cation-exchanged Y zeolites, Sn- and Zr-containing beta zeolites to understand the role of acid sites and activity correlation in the MF reaction. The Lewis acid catalysts of $AlCl_3$ and Na-Y zeolite demonstrated superior selectivity for toluene production with regard to the Brønsted acidic zeolites of H-Beta and H-Y, which have proven to be effective for the conversion of 2,5-dimethylfuran (DMF) to p-xylene. The high toluene selectivity of the Lewis acid catalysts was mainly attributed to their ability to retard side reactions, such as oligomerization and alkylation, as well as to accelerate the cycloaddition of MF and ethylene. In the case of Brønsted acidic zeolites, the side reactions were significantly enhanced, resulting in lower selectivity to toluene. The catalytic activity of the Lewis acidic metal chloride catalysts was correlated with an empirical scale of Lewis acid strength, showing that the strongest Lewis acid, $AlCl_3$, gave the highest toluene yield of ~70% at 250 °C after 24 h. Similarly, of the alkali cation-exchanged Y-zeolites investigated here, Li- and Na-Y were more active than K- and Cs-Y due to the smaller size of the cations, resulting in stronger Lewis acidity. Na-Y was also more active than Sn- and Zr-Beta, which have framework Lewis acidic sites, demonstrating its superiority for catalyzing the cascade of Diels-Alder and dehydrative

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aromatization reactions of MF. A remarkable toluene yield of ~65% was achieved with Na-Y at the nearly complete MF conversion (>96%) under optimal reaction conditions.

1. Introduction

The production of benzene, toluene and xylenes (BTX), which have many applications in the chemical industry, such as fuels, solvents, and precursors for polymers, requires a sustainable process that utilizes carbohydrates in biomass as promising alternative resources for petroleum-based feedstocks [1–4]. BTX aromatics are particularly utilized as precursors in the production of polystyrene, polyurethane, and polyethylene terephthalate (PET), for whose demand has increased globally [5]. Recently, a thermochemical route to produce renewable BTX aromatics from biomass-derived furans (i.e., 2,5-dimethylfuran (DMF), 2-methylfuran (MF), furan) and ethylene via Diels-Alder cycloaddition and subsequent dehydration reactions, has been proposed using solid Brønsted and Lewis acid catalysts [6–17]. Because ethylene can also easily be obtained by the dehydration of bio-ethanol [18], this route can be considered as a fully sustainable process for the production of BTX chemicals. The selective production of renewable *p*-xylene from DMF has been reported for microporous catalysts such as H-Beta zeolite [7], and for mesoporous materials such as mesoporous beta zeolite with a nanosponge-like morphology (NSP-BEA) [12], and silica-alumina aerogel (SAA) [11] catalysts with 70–90% *p*-xylene selectivity and greater than 90% DMF conversion. In contrast, with regard to toluene production from MF, only limited work has been done, mainly using solid Brønsted acid catalysts. Moreover, the highest toluene yields reported with an H-Beta zeolite are still very low (<46%), rendering much room for improvement of the process of toluene production [6,7].

A scheme for the production of toluene from biomass consists of four major steps, the hydrolysis of hemicellulose to xylose (C5 sugar), the dehydration of xylose to furfural, the hydrodeoxygenation of furfural to MF, and the Diels-Alder reaction of MF to toluene. Similar to the *p*-xylene production from DMF, toluene is produced via a cascade reaction of the Diels-Alder cycloaddition of MF and ethylene and dehydrative aromatization of the cycloadduct intermediate over solid acid catalysts. Green et al. recently expanded the reaction network for the conversion of MF to toluene, as depicted in Fig. 1 [6]. In addition to the Diels-Alder chemistry, a number of side reactions were identified. These side reactions include (1) the alkylation of toluene with ethylene (AT), (2) isomerization of the MF/ethylene cycloadduct (CI) and subsequent alkylation with ethylene (AC), (3) the self-Diels-Alder dimerization of MF (BF), (4) ring-opening hydrolysis of MF to 4-oxopentanal and subsequent alkylation with two MF molecules to form the MF trimer (OLI), and (5) the Diels-Alder condensation of MF and the MF/ethylene cycloadduct (OLI).

Because of the prevalence of numerous side reactions during the Diels-Alder cycloaddition of MF and ethylene, as shown in Fig. 1, the selective production of toluene is highly challenging. Unlike DMF, the absence of methyl groups at the α-carbon position of MF causes the more common occurrence of side reactions, such as dimerization and oligomerization reactions, contributing to a significant loss of carbon during the reaction and thus resulting in lower selectivity to toluene [6,7]. Also, it has been reported that Brønsted acids catalyze the hydrolysis of MF to 4-oxopentanal and the subsequent trimerization of 4-oxopentanal with two MF molecules [19,20]. This suggests that Brønsted acids may not be a suitable choice for the conversion of MF.

The use of Lewis acids has been known to be the most efficient way to enhance the Diels-Alder reaction rates [21–24]. However, in the case of conversion of furans to aromatics, Lewis acids have received very little attention because they are not as effective as Brønsted acids for catalyzing the second dehydration reaction. Although successful application of the Lewis acid zeolites of Sn- and Zr-Beta to this cascade reaction with oxidized 5-hydroxymethylfufural (HMF) or DMF has recently been reported, the role of Lewis acids in the Diels-Alder and dehydration reactions of furans is not well understood [25,26]. A systematic study of the reactions with well-defined Lewis acid catalysts would help understand how Lewis acids affect the catalytic chemistry and help design improved catalysts for the conversion of furans such as MF to value-added aromatics.

The objective of this paper is to study the role of acid sites and activity correlation in the conversion of MF to toluene via a combination of Diels-Alder and dehydration reactions. For this purpose, we investigated the catalytic activity of a series of homogeneous and heterogeneous Lewis acid catalysts, including various metal chlorides, cation-exchanged Y zeolites, and beta zeolites containing framework Sn or Zr. The activity correlation was explored based on the empirical scale of Lewis acid strength. The effects of reaction conditions such as initial ethylene pressure, reactant-to-catalyst (R/C) mass ratio, and reaction time on toluene production were also investigated. We were able to obtain a high yield of toluene up to 70% using $AlCl_3$ and Na-Y as Lewis acid catalysts under optimal reaction conditions.

2. Materials and methods

2.1. Materials

MF (98%) and *n*-heptane were purchased from Alfa Aesar and ethylene (99.9%) was purchased from Shinyang Sanso (Seoul, Korea). 1,4-Dioxane (⩾99%), *o*-xylene (⩾99%), and dimethylsulfoxide (DMSO, ⩾99.9%) were purchased from Sigma-Aldrich. Metal chlorides of $AlCl_3$, $CrCl_3$, $ZnCl_2$, $SnCl_4$, $YbCl_3$, VCl_3, $InCl_3$, $MgCl_2$, $LaCl_3$, and $NiCl_2$ were purchased from Sigma-Aldrich. The reagents for the ion exchange process such as $LiNO_3$, KNO_3, and $CsNO_3$ were purchased from Sigma-Aldrich. Na-Y (CBV100, SiO_2/Al_2O_3 = 5.1), H-BEA-25 (CP814E, SiO_2/Al_2O_3 = 25), and H-Y (CBV720, SiO_2/Al_2O_3 = 30) were purchased from Zeolyst, while Na-X (SiO_2/Al_2O_3 = 2) was purchased from Tosoh Corporation.

2.2. Catalyst preparation

The ion exchange of Na-Y (Si/Al = 2.55) (1 g basis) was performed in a 0.06 M solution of the corresponding nitrate or chloride salts at 80 °C for 24 h based on the method described elsewhere [27]. The Na-Y sample was also washed at a room temperature with 0.05 M $NaHCO_3$ solution for 1 h in order to preclude trace Brønsted acidity [10]. The cation-exchanged Y zeolites and the treated Na-Y catalyst were dried at 90 °C overnight and then calcined at 600 °C for 6 h with a ramp of 5 °C/min in a muffle furnace before catalytic testing.

Sn- and Zr-Beta were synthesized by using a modified seeding method, following the protocol reported by Fan et al. [28]. Silica-alumina aerogel (SAA) with SiO_2/Al_2O_3 = 2 (SAA-57) was prepared using a sol-gel method followed by CO_2 supercritical drying, based