ISGC 2022

N°51 / OC
TOPIC(s) : Biomass conversion / Homogenous, heterogenous and biocatalysis

Liquid-phase aromatization of biomass-derived ketones

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PURPOSE OF THE ABSTRACT

Aromatics such as benzene, toluene and xylene (BTX) are important precursors in industrial applications as solvents, plasticizers and monomers for the large-scale production of p-xylene (PET) and styrene (PS), etc.[1] Annually more than 103 Mio. t (2012) are produced globally via catalytic reforming of naphtha.[2] But limitation of fossil resources demands for sustainable routes from renewable resources such as biomass.[3] Current approaches for bio-based aromatics focus on biomass-derived furan derivatives as raw material or pyrolysis of lignocellulosic biomass. However, these processes are based on multiple reaction steps which suppress total yields and require complex separation due to the similar nature of by-products. Therefore, alternative processes for the direct valorization of biomass need to be developed. Herein, we present the one-step, solvent-free direct production of 1,3,5-substituted C6-aromatics by cyclotrimerization of biomass-derived alkyl methyl ketones which are accessible from chemocatalytic or biotechnological biorefinery processes, e.g., acetone from ABE-fermentation.[4,5] Starting with acetone as a model substrate, the consecutive aromatization via the dimer mesityl oxide to mesitylene was studied in liquid phase batch as well as flow conditions. Catalysts, reaction temperature and time were screened for maximum yield and selectivity to aromatics. The suitability of catalysts for aromatization of the higher alkyl ketones 2-butanone and 2-pentanone was also studied.[6]

Screening of solid acid catalysts (5 wt%) was performed in stirred batch autoclaves with acetone (10 g) at 130-190 °C (3-15 h). Time course of the reaction was studied in a batch reactor (2.5 wt% catalyst, 150 mL ketone) with a sampling line. Filtered product solutions were analyzed by GC and GC/MS with 1,4-dioxane (30 wt%) as internal standard and phase solubilizer. Catalyst stability was assessed in a fixed-bed reactor equipped with an online-GC at 130-230 °C at 40 bar and a WHSV of 8 h-1 using 3 g of shaped catalyst particles.

From a screening of 30 solid acid catalysts, ion exchange resin Purolite CT275DR, beta-zeolite H-BEA 35 and amorphous silica-alumina Siralox 70/170 were selected based on their mesitylene yield. The overall highest aromatics yield (15.8 % at 160 °C, 6 h) was found for Purolite compared to metal-oxides. However, increasing the temperature to 190 °C did not further increase product yields but formation of side products was favored. The reaction time course experiments led to identification of two consecutive phases with a high initial activity in the first 20-30 min and a subsequent activity drop (see Fig. 1).[4] This is marked by a maximum in the dimer yield, whereas acetone conversion and consecutive product yields constantly increase over time. It was found that the aromatization activity generally increases with acid site density but is not dependent on acid strength.[6] Reactions in continuous liquid flow revealed that Purolite was not thermally stable at elevated temperatures (150 °C) and that the majority of tested zeolites quickly deactivated once aromatization activity was observed. In contrast, the amorphous silica-alumina Siralox 70/170 HPV was highly stable for more than 35 h-on-stream at 230 °C and showed constant acetone conversion and mesitylene production (see Fig. 2). No significant catalyst deactivation was observed which is supported by the low mass loss of 6 % detected by TGA in synthetic air.

In conclusion, amorphous silica-alumina was found stable and efficient for the one-step conversion of biomass-derived ketones. The high stability of the catalyst under liquid phase conditions is essential for the establishment of a new environmentally benign process for alkyl methyl ketone aromatization.

FIGURES

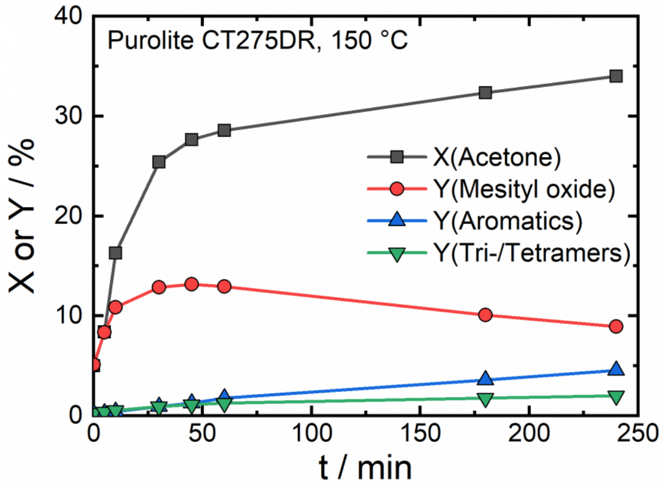

FIGURE 1

Reaction progress of acetone conversion in a batch reactor.

black squares: conversion of acetone
red dots: yield of mesityl oxide
blue upward triangles: yield of aromatics
green downward triangles: yield of tri-/tetramers

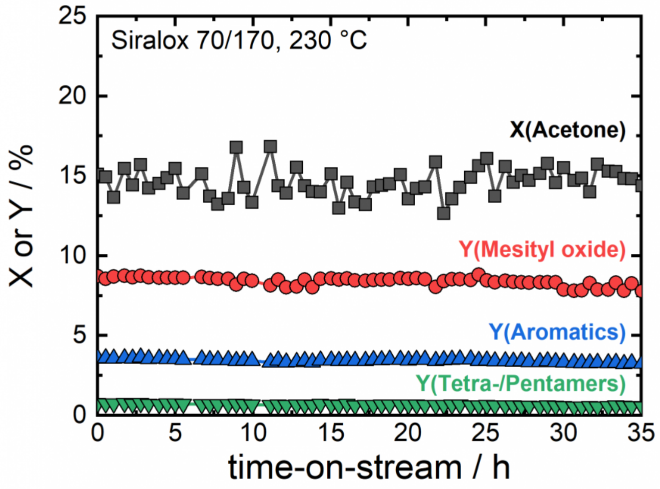

FIGURE 2

Continuous conversion of acetone in a liquid flow fixed-bed reactor.

black squares: conversion of acetone
red dots: yield of mesityl oxide
blue upward triangles: yield of aromatics
green downward triangles: yield of tetra-/pentamers

KEYWORDS

biomass-derived aromatics | liquid phase catalysis | ketone aromatization | acid catalyst

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