



Liquid phase aromatization of bio-based ketones over a stable solid acid catalyst under batch and continuous flow conditions

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ABSTRACT

Herein, we describe a one-step process for renewable aromatics from biomass-derived ketones over solid acid catalysts under liquid phase batch and flow conditions. The ion exchange resin was highly active for aromatics due to high acidic strength but leaching of acidic sites caused low stability. In contrary, zeolite HY showed a lower activity but higher stability in batch by regenerability and was stable in flow for 250 min-on-stream. HY is further applicable for the conversion of higher ketones (butanone and pentanone). This work contributes towards an industrially important aromatic production from biogenic ketones and thus an economical and sustainable process.

1. Introduction

Aromatics are highly demanded commodity chemicals from petroleum resources. For instance, *p*-xylene, mesitylene, etc. are used for the production of high-volume polyethylene terephthalate, solvents, fuel components, and other chemical intermediates [1,2]. The high octane number of aromatics provides additional advantages in the use as octane enhancer [3]. While having unique features for a wide range of industrial applications, the expanded use of aromatics is challenging due to diminishing fossil resources and global concerns of CO₂ emissions. Therefore, utilization of renewable resources for the sustainable production of aromatics is a key challenge to satisfy growing industrial demands. To overcome this, aromatic production from biomass-derived furanics has been studied over solid acid catalysts [4]. In this process, aromatic skeletons are produced in high yields by tandem Diels-Alder cycloaddition followed by dehydration. However, low yields of furanics from sugars are the main obstacle for large-scale aromatic production [5].

The development of a single-step process for aromatics from biomass-derived platform chemicals will bring significant advances. Therefore, aromatics production from biogenic alkyl methyl ketones is considered an industrially relevant pathway. A variety of chemo-catalytic and biotechnological routes have been proposed from biomass to alkyl methyl ketones such as decarboxylation of levulinic acid to 2-butanone or ABE-fermentation to acetone and consecutive alkylation to 2-pentanone [6]. The aromatic mesitylene can be synthesized via self-

condensation from acetone using conventional Brønsted acid catalysts, e.g., H₂SO₄ or HCl [7]. However, one serious drawback of the process is the energy-inefficient separation or removal of inorganic byproducts, e.g., gypsum (produced by neutralization treatment) from the reaction solution [8]. Heterogeneous catalysts, e.g., ion exchange resins, zeolites, metal oxides, have been reported as an alternative for aromatics at 300–450 °C [9–11]. In general, the high reaction temperature and in situ generated water restrict the continuous process due to the formation of heavy coke and subsequent catalyst deactivation [12–14]. Recently, we showed that the liquid phase conversion of acetone to mesitylene can also take place at lower reaction temperatures of around 150 °C over solid acid catalysts [15]. However, a deeper understanding of the catalyst stability under various reaction conditions is essential for further scale-up. Thus, designing suitable high-performance recyclable heterogeneous catalysts becomes crucial for the efficient catalytic conversion of renewable ketones into aromatics. Additionally, this pathway can also be used for byproduct valorization of the conventional phenol synthesis via the cumene process where large volumes of acetone are produced, thus increasing its potential for value addition [16].

Herein, we have investigated the efficient conversion of various biomass-derived alkyl methyl ketones to aromatics over a stable and reusable solid acid catalyst in liquid phase batch and flow conditions. Heterogeneous acid catalysts can efficiently catalyze the aromatization of alkyl methyl ketones in multiple steps (Scheme 1). Since the conversion of alkyl methyl ketones to aromatics is a complex phenomenon involving several intermediates [6], such as dimers, trimers, tetramers,

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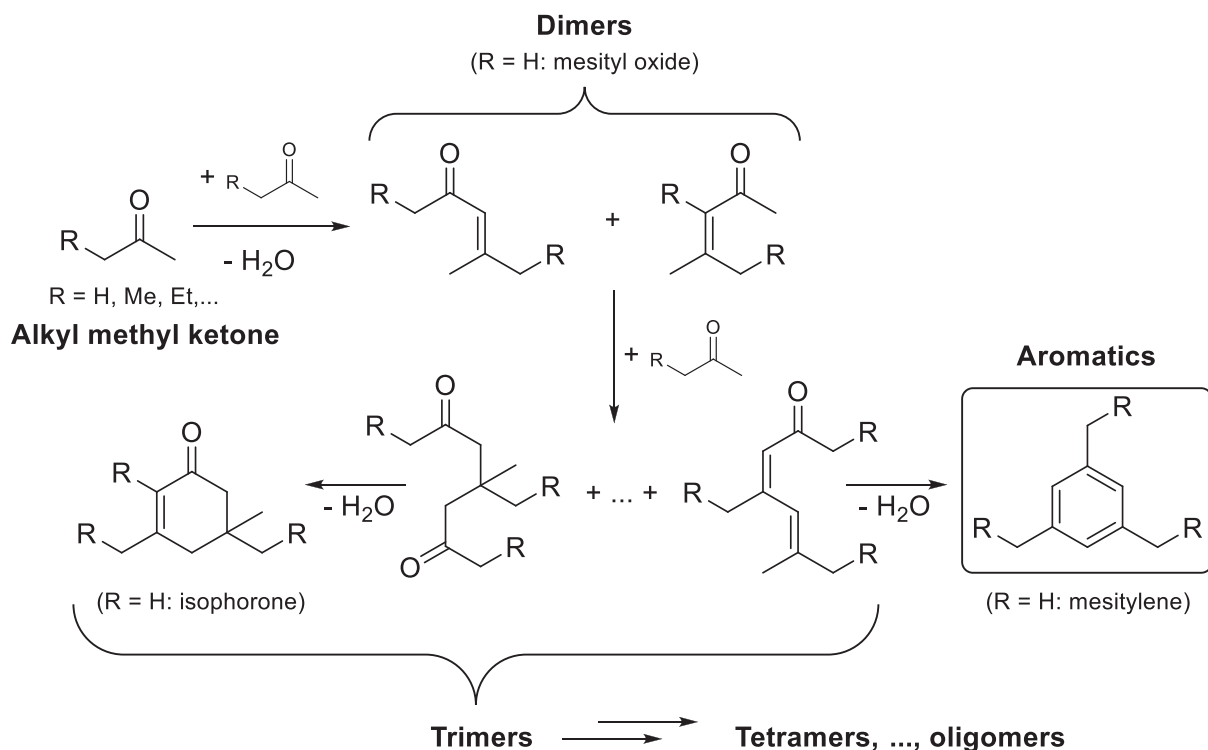
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Scheme 1. Simplified reaction scheme for the acid-catalyzed self-condensation of alkyl methyl ketones to aromatics without depicting possible positional isomers.

and oligomers, the formation of linear/branched chains was also studied together with aromatics. The interplay between structural features and acid sites for the solvent-free transformation of various alkyl methyl ketones to their corresponding aromatics is evaluated.

2. Experimental

2.1. Catalysts and Reagents

As starting materials acetone (99.9%), 2-butanone (99.5%), and 2-pentanone (99.5%) were purchased from Sigma-Aldrich and used as received. For GC-quantification, 1,4-dioxane (99.5%, Carl Roth), mesityl oxide (97%, Sigma-Aldrich), mesitylene (99%, Acros Organics), isophorone (97%, Sigma Aldrich), and triethylbenzene (97%, Sigma-Aldrich) were used.

Cation exchange resin Purolite CT275DR (also denoted as Purolite) was supplied by Purolite® and beta-zeolite H-BEA 35 by Clariant. Zeolite HY-60 was obtained from Alfa-Aesar. All catalysts were used as received.

2.2. Catalytic reaction studies

2.2.1. Catalytic testing in batch reactor

Catalytic reactions in batch experiments were typically performed by adding 150 mL ketone and 2.5 wt% catalyst to the autoclave (300 mL, Parr) which is then pressurized with 30 bar Ar and heated to the reaction temperature while stirring at 1000 rpm [15]. After completion of the reaction, filtered samples of the reaction mixture were analyzed using gas chromatography (Shimadzu GC-2010 Plus) with a capillary column (Restek RTX-5 Amine) and 1,4-dioxane as an internal standard. Furthermore, the identification of products was confirmed by GC coupled with mass spectrometry (Shimadzu GCMS-QP2010SE). For the higher ketones 2-butanone and 2-pentanone, products were quantified based on the concept of the effective carbon number (see SI).

For kinetic experiments, the amounts of aromatics and oligomers were monitored from the initial stage of the reaction by sampling of the

reaction solutions in specific intervals maintaining a constant Ar pressure for the remaining experiment.

2.2.2. Catalyst stability in batch and flow conditions

Recycling of catalysts was carried out in the presence of 10 g acetone and 5 wt% catalyst in 45 mL batch reactors equipped with PTFE-inlets. After purging three times, reactors were pressurized with 40 bar Ar and heated to reaction temperature which was maintained for 3 h while stirring at 500 rpm. Afterwards, reactors were cooled down, filtered product samples were taken, and spent catalysts were separated from the reaction mixture. Before reuse in the next run, catalysts were washed with acetone and dried at 100 °C overnight. Calcination of spent zeolites was performed at 550 °C (6 h, 2 K min⁻¹) under 100 NmL min⁻¹ air flow.

Catalytic reactions in flow conditions were performed in a stainless-steel fixed-bed reactor (length of 300 mm, ID of 15.75 mm). A schematic diagram of the fixed-bed reactor used in this work is shown in Fig. S1. The reactor was loaded with 3 g of catalyst fixed in the center of the reactor by stainless-steel beads and quartz wool and two thermocouples were placed in the catalyst bed to monitor the accurate temperature. Bed volume was kept constant. The feed consisting of pure acetone was introduced into the heated reactor (100–190 °C) via an HPLC pump at a rate of 0.5 mL min⁻¹. The reactor pressure was maintained at 40 bar with a backpressure regulator. The product solution stream was analyzed via online GC (Shimadzu GC-2030) equipped with a MEGA-5 column and FID detector ($T = 40$ °C, 3 min, 10 K min⁻¹ to 250 °C, and isothermal for 1 min). Conversion and yield were determined based on relative response factors for the internal standard 1,4-dioxane.

2.3. Catalyst characterization

The density of acid sites on the fresh zeolite catalysts was determined by temperature-programmed desorption of NH₃ [15]. Samples (approx. 100 mg) were dried in N₂ flow at 600 °C (3 h), then NH₃ was adsorbed at 140 °C (2 vol% NH₃ in N₂, 20 mL min⁻¹) for 20 min. After desorption of the physisorbed NH₃, the sample was heated to 600 °C with 10 K min⁻¹ and NH₃ was detected by FT-IR. The strength of acid sites was classified

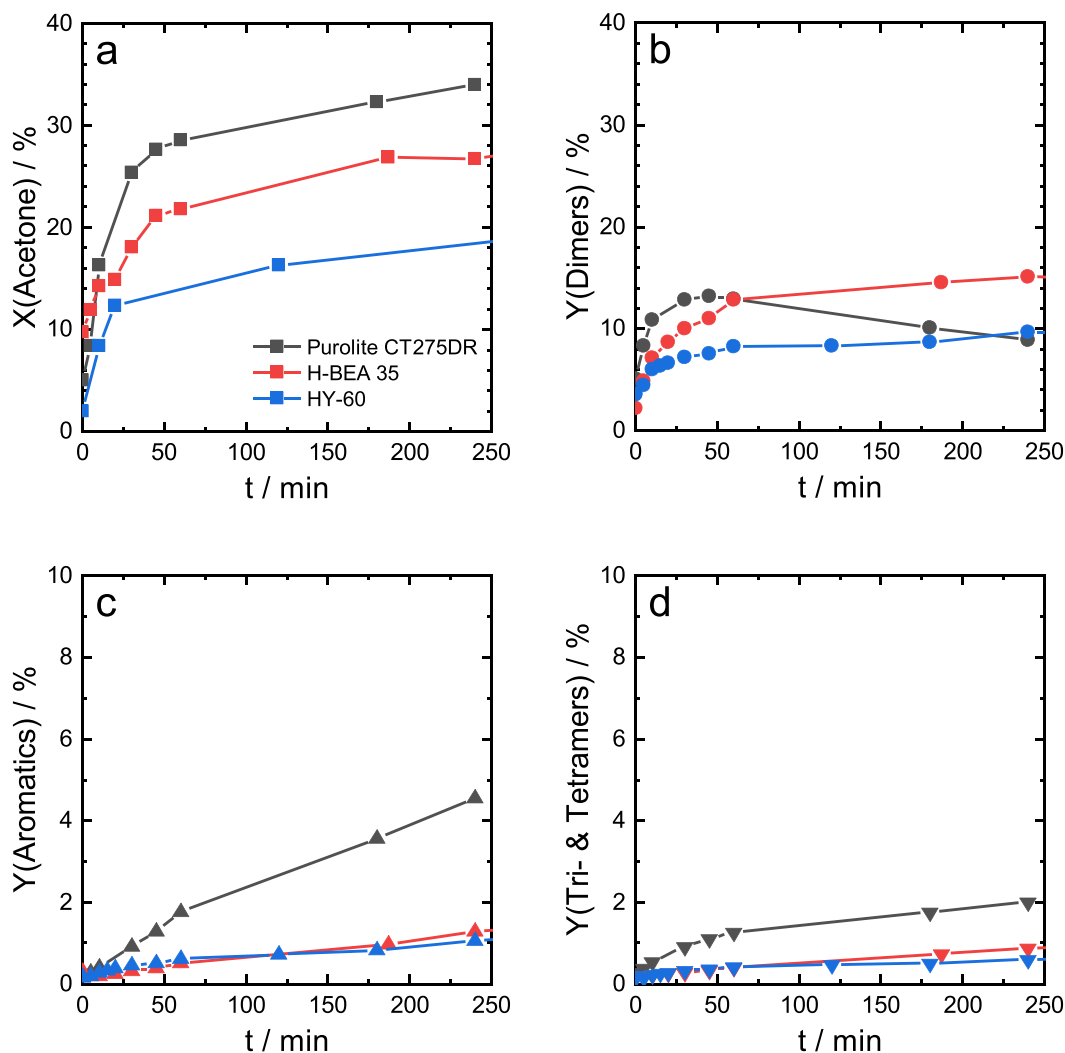


Fig. 1. Comparison of the batch reaction progress for Purolite CT275DR, H-BEA 35, HY-60 at 150 °C: acetone conversion (a) and molar product yields of dimers (b), aromatics (c), tri- and tetramers (d).

as follows: < 250 °C weak, 250–450 °C medium, and > 450 °C strong [17].

To evaluate the carbon deposition during ketone aromatization, thermogravimetric analysis (TGA, Netzsch STA 449 FE Jupiter) was performed. In the procedure, 20 mg of spent catalyst was placed in a TGA crucible and subjected to a TGA scan from 40 to 1000 °C (temperature ramp of 5 K min⁻¹) in synthetic air flow (100 NmL min⁻¹).

The sulfur content of the sulfonic ion exchange resin catalyst was determined by X-ray fluorescence (XRF) on an Epsilon 4 by Malvern Panalytical with Ag-cathode.

Powder X-ray diffraction (XRD) data of zeolites were obtained on a Bruker D2-Phaser using Cu-K- α radiation ($\lambda = 1.5406 \text{ \AA}$). The voltage of the radiation tube was 30 kV and the current 40 mA. Diffraction patterns were measured in the 2θ -range of 5–45° at 0.03° intervals and a step time of 2 s.

3. Results and discussion

3.1. Reaction progress of different solid acid catalysts for acetone conversion

In a prior catalyst screening, solid acid catalysts such as zeolites, ion exchange resins, and amorphous silica-alumina were examined for the direct conversion of acetone to mesitylene in the liquid phase at

130–160 °C [15]. It clearly indicated that the acidic catalysts Purolite CT275DR as well as H-BEA 35- and HY-zeolite had higher conversion and good selectivity towards mesitylene starting from acetone. To compare the previously observed activity behavior of Purolite CT275DR with other active catalysts, the reaction progress of the catalysts H-BEA 35 and HY-60 were assessed under identical conditions of 150 °C and 2.5 wt% of catalyst in a batch reactor (see Figure 1). While both types of catalysts converted acetone to the desired aromatics, Purolite CT275DR was superior in both acetone conversion and mesitylene yield which suggests that the Brønsted acid sites are apparently effective for the aromatization. Consistent with the reaction progress found for Purolite CT275DR, all three catalysts show a distinct behavior of two consecutive phases with a high initial activity in the first 20–30 min and a subsequent activity drop. This could be attributed to saturation of active sites by reactants and/or products, thus leading to a decrease in activity over time.

A constant increase in acetone conversion and product yields of aromatics and oligomers is observed for all three acid catalysts. The considerably higher activity of Purolite CT275DR leads to a maximum in the yield of the dimer mesityl oxide of 13% after 50 min and a constant decrease afterward as the dimer reacts in consecutive reaction steps. H-BEA 35 shows the 2nd highest activity with a maximum acetone conversion of 26% (compared to 34% for Purolite CT275DR and 18% for HY) which can mainly be contributed to the dimerization step as it

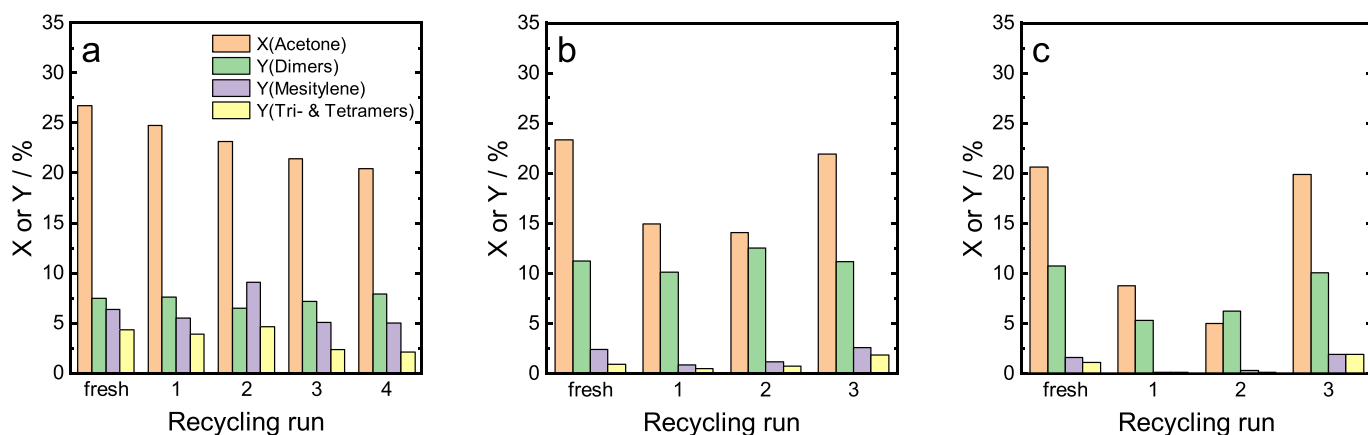


Fig. 2. Batch recycling experiments for Purolite CT275DR (a), H-BEA 35 (b), and HY-60 (c) at 150 °C (3 h), 5 wt% catalyst, 10 g acetone, 40 bar Ar. Recycled catalysts were calcined in air (550 °C, 6 h) from 2nd to 3rd cycle in figure (b) and (c).

shows a constant increase in dimer yield with a maximum of 15% at 240 min. Although the yield of total products for HY-60 is only 12%, the rates of formation for mesitylene and oligomers (tri- and tetramers) are comparable for both zeolites. Combined selectivity for mesitylene, tri- and tetramers (~20% for Purolite CT275DR and 8–9% for both zeolites at 240 min) slowly increases for all three catalysts over time (see Fig. S2). This results from the consecutive nature of the reaction where the conversion of intermediates such as mesityl oxide and trimeric phorones to secondary products, i.e., aromatics and oligomers, is fast compared to acetone conversion. Nevertheless, byproduct formation is observable for this reaction resulting in low quantities of less than 0.5% of the GC-area for acetic acid and isobutene from β -scission reaction (see Fig. S3) [18].

Acetone conversion and aromatics yield increase strongly for higher acid site densities which were determined via NH_3 -TPD for zeolites and given by the manufacturer for the cation exchange resin (see Fig. S4). Here, Purolite CT275DR exhibits the highest amount of acid sites due to its sulfonic acid groups on the surface which strongly correlates with its highest activity. The general increase in activity with increasing amount of acid sites is independent of their strength and can also be found for weak acid centers. This could also be shown by comparing zeolite HY-30 and HY-60 where an approximately 30% increase in aromatics yield was found for HY-30 which features 70% more acid sites (see Fig. S5). While the aromatization of acetone benefits from higher acid site densities, the structure of the catalysts also affects their activity. For instance, the narrow pore size of ZSM-5 (0.47 nm [19]) does not lead to aromatization products of acetone in the liquid and gas phase [11,15]. In the case of H-

BEA 35, the pore size (0.67 nm) is also smaller than the kinetic diameter of mesitylene (0.87 nm) and thus mostly external acid sites contribute to the aromatization [11]. All catalysts fit the criterion of being active for the aromatization of acetone but their suitability for a potential scale-up needs to be evaluated by stability performance as catalyst deactivation hinders an economical use.

3.2. Assessing catalyst stability in batch and flow reactor

The stability of catalysts for the acetone aromatization is studied in batch autoclaves at 150 °C (Figure 2). After each reaction, the catalyst was filtered and washed thoroughly with acetone to remove organic depositions from the surface and then reused for subsequent reaction cycles after drying. Although a slight decrease in acetone conversion was observed using Purolite CT275DR, mesityl oxide and mesitylene yields showed no significant activity loss up to four experimental cycles (Figure 2a). After the first cycle, the catalyst mass had increased by almost 10% which remained for the consecutive runs and is likely linked to carbonaceous deposits [15]. Deposition of polymeric species generally deactivates active sites on catalysts, but interestingly it was not observed in the case of Purolite CT275DR. Therefore, we studied the reaction solutions and spent catalyst by monitoring pH and sulfur content, respectively. Highly acidic pH-values were found for the product solutions which increased from 1 to 3.5 in consecutive runs. Also, the sulfur content in the fresh and spent catalyst showed a significant reduction of 35% which directly translates to a loss in catalytically active sulfonic sites. This type of deactivation behavior of the highly

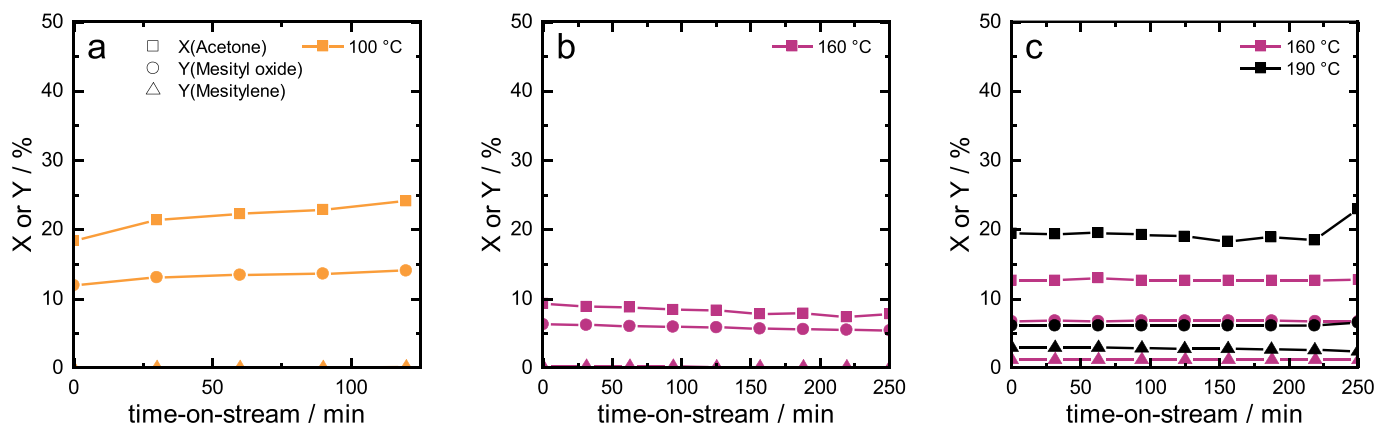


Fig. 3. Catalyst stability for acetone aromatization in liquid phase flow reactor for Purolite CT275DR (a), H-BEA 35 (b), and HY-zeolite (c). (square: acetone conversion, circle: mesityl oxide yield, and triangle: mesitylene yield).

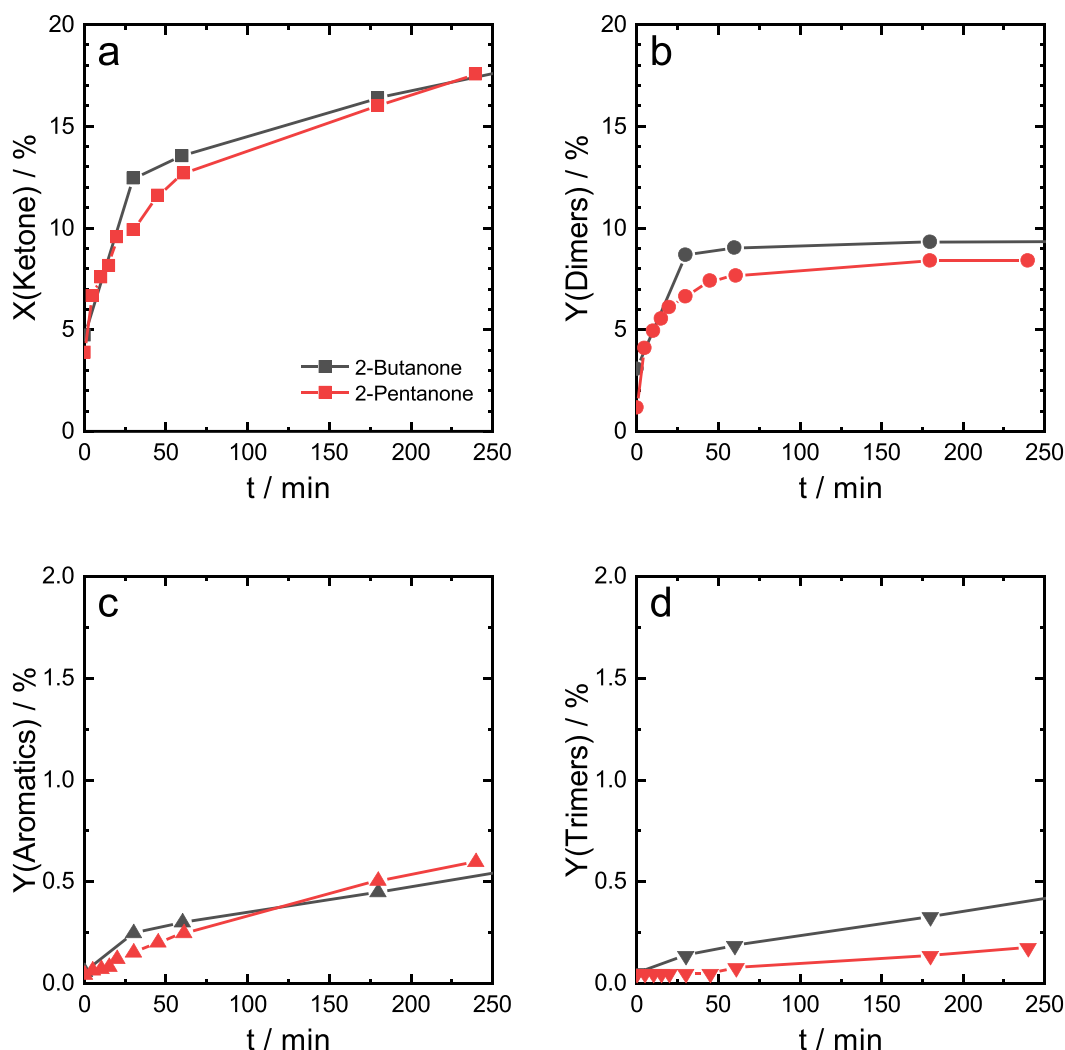


Fig. 4. Batch reaction progress for conversion (a) of 2-butanone and 2-pentanone with HY-60 at 160 °C and product yields of dimers (b), aromatics (c), and trimers (d).

active Purolite CT275DR catalyst was also observed in an esterification reaction by Saboya et al. [20] The finding can explain the concurrent decrease of active sites in the batch reactor responsible for constant acetone aromatization.

Figures 2b and 2c show a strong initial decrease in activity for both zeolites after the first cycle likely due to carbonaceous deposits (see Fig. S6). But an almost complete regeneration of active sites was achieved by simple calcination (550 °C, 6 h) which is widely practiced [21–23]. XRD analysis showed that the structural features remained unchanged after calcination (see Fig. S7). This means that all tested catalysts are generally recyclable according to their specific material properties. The observed leaching of active sites for Purolite CT275DR remains its biggest problem as it contradicts its use in a potential scale-up of continuous reaction conditions. For the latter, zeolite catalysts with regenerable activity have an advantage as automated regeneration processes such as implemented in fluid catalytic cracking exist in industry [24]. Furthermore, since neither precious metal catalysts nor hydrogen are involved in the deoxygenation reaction argon can be readily replaced with nitrogen for pressurizing the reactors to keep the reaction system in the liquid phase under batch reaction conditions and achieve similar yields (see Fig. S8).

In order to further understand the suitability of the selected catalysts for industrial importance, stability tests were performed in a flow reactor in the liquid phase at a weight hourly space velocity (WHSV) of

8 h^{-1} (see Figure 3). Given the lower thermal stability of Purolite CT275DR it was tested at 100 °C to see its potential activity in a low-temperature continuous aromatization process. Although significant acetone conversion (up to 25%) and dimer formation (14%) were observed, no mesitylene was formed. An increase in reaction temperature to mimic previous batch experiment conditions at 150 °C led to agglomeration of the catalyst bed which ultimately blocked the flow reactor. The thermal degradation at elevated temperatures is intrinsic to the resin material, and thus renders it not suitable for flow conditions in the case of acetone aromatization.

The activity of the beta-zeolite in the flow reactor was very low with an acetone conversion below 10% and marginal formation of mesitylene observed at 160 °C (Figure 3b). The insignificant activity can likely be attributed to the dependence on external acid sites in the case of the beta-zeolite which are not active or too low in number for significant aromatization under the tested reaction conditions. This is in line with a previous study by Faba et al. [25] For HY-zeolite, on the other hand, a conversion of 12% and constant aromatics formation of 1.8% was found at 160 °C. An increase in temperature to 190 °C led to a significant increase in catalyst activity and mesitylene yield of 2.8%. Under the tested reaction conditions, the HY-catalyst was stable for more than 250 min-on-stream.

Given the stability in the flow reactor and the successfully applied regeneration under batch conditions, HY-zeolite can be considered as an

adequate catalyst for a potential industrial application of the aromatization of acetone in the liquid phase for both batch and flow reactors. An advantage of the liquid flow reactor is that no additional inert gas is required for pressurization or as carrier gas which can reduce costs.

3.3. Testing the HY-catalyst for higher alkyl methyl ketones in a batch reactor

While acetone is the simplest alkyl methyl ketone for the self-condensation reaction to biomass-derived 1,3,5-C₆-aromatics, longer-chain alkyl methyl ketones such as 2-butanone and 2-pentanone can also be obtained in good yield from biomass [6,26,27]. Testing the suitability of the HY-zeolite with these higher ketones can extend its applicability for the formation of further alkyl aromatics. Batch experiments under reaction conditions similar to the one with acetone as starting material were therefore performed with 2-butanone and 2-pentanone (see Figure 4).

For both higher ketones, the time course experiments show a fast initial conversion of up to 10–15% in the first 50 min which is comparable with the acetone conversion activity of HY-60. Conversion then steadily increases over time to approximately 17–18% at 240 min. Dimer and aromatics formation is also observed and yields of both products increase with ketone conversion and time. For the intermediate dimer, a maximum yield is obtained within 50 min from when it remained constant. Yields of the aromatics and trimer products of the consecutive reaction of the dimers with another ketone molecule are constantly increasing over time. This shows that the catalyst remains active despite the larger molecular size of the compounds (kinetic diameter of 2-butanone: 0.52 nm [28]; 2-pentanone: 0.59 nm [29]). Considering the acetone conversion, dimer formation is comparable while yields of the consecutive products are roughly halved. This can likely be attributed to the lower overall reactivity of the higher alkyl methyl ketones compared with acetone due to steric hindrance.

4. Conclusions

Stable and efficient one-step conversion of ketones, a biomass-derived raw material, is realized using HY-zeolite as an acid catalyst at 150 °C. HY-zeolite is not only a suitable catalyst for the batch reactor but also showed high stability in the continuous liquid phase production of aromatics, e.g., mesitylene, in the flow reactor. Facile catalyst recovery and reusability of HY-zeolite in batch and flow conditions are essential for the establishment of a new environmentally benign process for alkyl methyl ketone aromatization.

Larger pores and a higher amount of acid sites are advantageous in the condensation reaction of ketones to aromatics in the liquid phase and determine catalyst activity and stability. While zeolite H-beta was more active in the batch reactor, a much higher activity of zeolite HY is observed in the flow reactor. The overall highest batch activity was found for the cation exchange resin Purolite CT275DR. However, it was not deemed suitable for a potential industrial application as it showed leaching of strong acid sites in recycling experiments and did not show substantial aromatization activity at 100 °C in the flow reactor. Further increasing the temperature (150 °C) eventually led to thermal degradation of the ion exchange resin in flow conditions.

Credit author experiments

Phillip Reif performed the experiments. Phillip Reif, Navneet Kumar Gupta and Marcus Rose contributed to the design and implementation of the research. All authors analyzed the results and wrote the manuscript.

Declaration of Competing Interest

The authors declare no conflict of interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.catcom.2022.106402>.

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