Biomass-Derived Aromatics by Solid Acid-Catalyzed Aldol Condensation of Alkyl Methyl Ketones

Phillip Reif, Hannah Rosenthal, and Marcus Rose*

Cyclotrimerization of biomass-based alkyl methyl ketones exhibits great potential as a route to biomass-derived aromatics by a sustainable valorization of biorefinery streams. In this study, acetone is used as a model reagent to screen solid acid catalysts for the aldol condensation reaction to the aromatic trimer mesitylene. From a broad catalyst screening promising activity is shown by the cation exchange resin Purolite CT275DR, the beta-zeolite H-BEA 35, and aluminosilicate Siralox 70/170 HPV which are used to further investigate reaction parameters. Acetone conversion and mesitylene yield increase with temperature and time, while yield of the intermediate mesityl oxide decreases. This effect is also found for higher quantities of catalyst acid sites and is accompanied with an increased side product formation which negatively affects total product selectivity. Analyzing the reaction progress shows a significant drop in catalyst productivity after an initial start-up phase. This observation is linked to a deactivation of the catalyst which involves water that is formed during the condensation reaction of acetone. Obtained results confirm the general viability of the aromatization of alkyl methyl ketones and can be considered the first step to an alternative sustainable route to biomass-derived aromatics compared to other currently discussed routes.

1. Introduction

With a global annual production of 103 Mio. t (2012) for benzene, xylene, and toluene (BTX), aromatics are an important intermediate in chemical industry used for a wide array of products.[1] Obtained via catalytic reforming of naphtha, they are precursors for monomers used in the polymer industry, e.g., *p*-xylene for polyethylene terephthalate and styrene for polystyrene, and other commodity products such as solvents, plasticizers, and adhesives.[2] In the context of climate change and limitation of fossil resources, their wide application in consumer products drives a growing demand for their sustainable production. To meet this demand, strong research efforts have been made to obtain aromatics from renewable biomass over the past years. Among these catalytic fast pyrolysis, the utilization of the abundant but structurally complex lignin-fraction of wood by depolymerization and the selective Diels–Alder cycloaddition of biomass-derived furan derivatives with alkenes to specific aromatic compounds present the most fundamental routes.[3] Thermochemical or chemocatalytic processing of lignin via (catalytic) fast pyrolysis gives a bio-oil containing a heterogeneous mixture of over 300 compounds.[4] In addition to separating the aromatic compounds from the bio-oil, it is necessary to deoxygenate them via hydrotreating, associated with enormous challenges, to insert them in downstream processes developed for aromatics.[5] Due to the heterogeneous structure of lignin which strongly depends on its biomass source, a selective depolymerization to specific aromatics which substitute petroleum-sourced ones can only be expected in the long run.[6] High separation costs and overall low yields decrease the route's economic viability to date.[3] By catalytic treatment of pyrolysis vapors with acidic zeolites such as ZSM-5 at temperatures above 400 °C broad fractions of monoaromatic compounds can be obtained.[7] Selective formation of specific aromatics is achieved via Diels–Alder cycloadditions with subsequent aromatization through dehydrogenation or dehydration.[2] As biomass-based dienes, furan derivatives produced from 5-hydroxymethylfurfural (HMF), e.g., 2,5-dimethylfuran (DMF), are suitable. They are reacted with biomass-based dienophiles, e.g., acrolein, ethylene, or propylene, to Diels–Alder adducts. For the formation of *p*-xylene from DMF and ethylene, yields of over 90% have been reported.[8] However, the mass production of the precursor HMF, often envisioned as a biomass-derived platform chemical,[9] has not been established yet due to its challenging high reactivity. An economically viable route to aromatics via Diels–Alder cycloaddition therefore also depends on mass-scale availability of HMF and other furanic derivatives.

In order to overcome the limitations posed on existing routes to biomass-derived aromatics, facile accessibility to suitable feedstock and integration into an infrastructure for value added chains are advantageous. Such a platform for biomass-derived intermediates was devised by the Dumesic group who converted aqueous solutions of sugars to monofunctional hydrocarbons such as ketones and alcohols and thus reduced the primary oxygen content by 80%.[10] As a valorization step for ketones

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produced by this process, acid-catalyzed aldol condensation with subsequent hydrogenation to alkanes was proposed. It was also mentioned that in the absence of hydrogen, selectivity is shifted to the more stable aromatics which are formed by self-condensation of three ketone molecules under water formation. Based on this principle, the Bell group showed the formation of cyclic, acyclic and aromatic trimers from n-alkyl methyl ketones via base-catalyzed aldol condensation in the context of bio-based aviation fuels.[11] Moreover, accessibility of C_3–C_7 methyl ketones from biomass via hybrid biological/chemical and purely chemical pathways was outlined, e.g., acetone from the 100-year old acetone-butanol-ethanol fermentation process in which butanol and ethanol are produced as byproducts.

In contrast to these approaches on the hydrodeoxygenation of nonaromatic trimers to branched, cyclic alkanes, it is also feasible to increase the aromatics yield and thus, create a route to biomass-based aromatics that has not attracted any attention in the recent past. Besides greater utilization of biorefinery streams, the route benefits from its simplicity of a single reaction step and does neither require hydrogen for deoxygenation nor expensive precious metal catalysts, which immensely contributes to lower costs. Conceived as a sustainable drop-in solution for petroleum-sourced aromatics, the cyclotrimerization of alkyl methyl ketones via acid- or base-catalyzed aldol condensation of alkyl methyl ketones to 1,3,5-substituted C_6-aromatics is highly promising. The reaction proceeds via Michael addition and 1,6-aldol condensation reactions over dimers to trimer condensates which but the aromatic can further oligomerize, thus spanning a rather complex reaction network (**Figure 1**).[11] Alkylation chemistry to obtain direct replacement of BTX-aromatics is established and well known and can help shifting the product spectrum into the desired direction.

As model reagent for studying the cyclotrimerization reaction to produce aromatics, acetone was chosen as its production in biorefinery processes is already realized and it is the simplest of all available alkyl methyl ketones. Therefore, only one aromatic trimer condensate as main product can be formed: mesitylene (Mes). Hence, our objective was the selective formation of mesitylene despite the many possible side reactions. While acid- and base-catalyzed self-condensation of acetone have been proposed and studied in the past nearly one century ago, little focus was given to optimizing the aromatic yield or applying technically suitable solid catalysts.[12] Common understanding
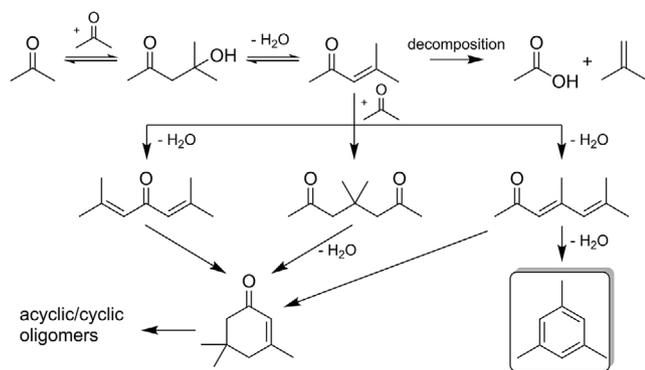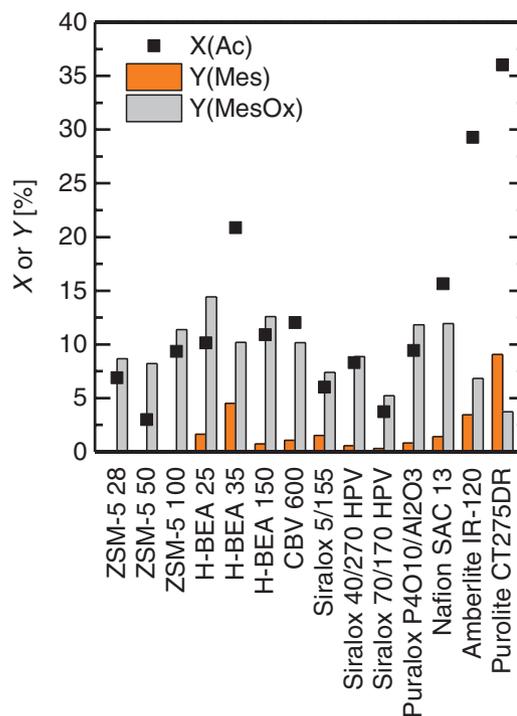
is that base catalysts favor mesityl oxide (MesOx) formation and the consecutive reaction toward isophorone while acids promote mesitylene formation.[13] Consequently, solid acid catalysts were studied to increase the aromatic yield of the self-condensation of acetone in liquid phase. In this work, suitable solid catalysts for acetone to mesitylene conversion, influence of reaction parameters, and reaction kinetics are presented.

2. Results and Discussion

2.1. Screening of Solid Acid Catalysts

More than 16 solid acid catalysts were initially screened for the selective aromatization of the model reagent acetone to mesitylene. The screening focused on heterogeneous catalysts due to their intrinsic advantages of simple product removal and susceptibility to wide reaction conditions. Moreover, in prior tests with homogeneous acids, e.g., p-toluenesulfonic acid, strongly acidic, phase-separated product mixtures of an organic and an aqueous phase occurred. These limited characterization by gas chromatography (GC) as acids can damage the GC column and reported yields can be altered by processing of the product mixture. Based on literature, three classes of solid acids were chosen for screening: different types of zeolites, amorphous aluminosilicates, and acid cation resins.[14] Additionally, Nb_2O_5 was tested.[15] Employed catalysts are commercially available in order to facilitate possible scale-up in a later process development.

To assess the catalyst activity for liquid-phase acetone aromatization, initial reaction conditions were mild at 130 °C and 3 h. For these, acetone conversion X_{Ac} was in almost all cases

Figure 1. Simplified reaction scheme of the consecutive aldol condensation reactions of acetone to the trimeric products mesitylene and isophorone.
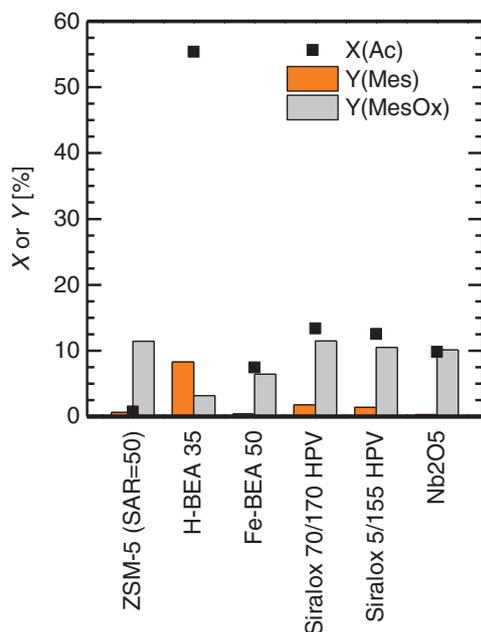

Figure 2. Results of X_{Ac}, Y_{Mes}, and Y_{MesOx} for selected solid acid catalysts screened in the condensation reaction of acetone at 130 °C and 3 h.

<16% (**Figure 2**) and only significantly higher for the catalysts H-BEA 35 (21%), Amberlite IR-120 (29%), and Purolite CT275DR (36%). Of interest for the selective aromatization is the product distribution, and here specifically the yields for mesitylene Y_{Mes} and mesityl oxide Y_{MesOx}. For the ZSM-5 zeolites, Y_{Mes} below 0.1% were found irrespective of their silica-to-alumina ratio. The consecutive reaction from formed mesityl oxide ($Y_{MesOx} < 10\%$) to mesitylene is thus not catalyzed by ZSM-5 zeolites under reaction conditions. Slightly higher activities were observed for the different aluminosilicates which yielded up to 1.5% mesitylene for Siralox 5/155. The overall best performance based on conversion and mesitylene yield was shown by the sulfonated ion exchange resins. For Purolite CT275DR, Y_{Mes} not only exceeded Y_{MesOx} by more than 5% but also the highest Y_{Mes} of 9% was found. Promising results were also obtained for the second-best performing catalyst H-BEA 35, a beta zeolite in proton form, with an Y_{Mes} of 4.5%. Interestingly, other beta zeolites with higher or lower silica-to-alumina ratios were significantly less active for the consecutive reaction.

In this assessment of the activity, potentially formed side products, such as isophorone, were not considered. While for the Purolite-catalyzed reaction significant amounts of isophorone (4%) were detected, this is not the case for the aluminosilicate catalysts (0–0.8%) under reaction conditions (see Figure S2, Supporting Information). As catalysts were screened for the aromatization reaction of acetone, the yield of mesitylene was the main criterion.

Differences in conversion and yield of three different catalysts were assessed for their statistical significance in later experiments (see Figure S2, Supporting Information). Repeating identical experiments multiple times gives standard deviations of ≈2% and 0.2% for conversion and yields, respectively. A comparable statistical error is therefore assumed for the screening experiments.

Figure 3. Results of X_{Ac}, Y_{Mes}, and Y_{MesOx} for solid acid catalysts of lesser activity screened in the condensation reaction of acetone at 160 °C and 6 h.

Catalytic activity is strongly influenced by the reaction conditions. Therefore, five catalysts that showed lesser activity at aforementioned reaction conditions were tested at an elevated temperature of 160 °C and prolonged reaction time of 6 h. Results are depicted in **Figure 3** and also include Nb_2O_5 and Fe-BEA 50 which both showed a negligible activity under previous conditions so that they were not listed earlier.

Despite the harsher conditions, catalytic activity for the acetone aromatization did not increase for most catalysts and mesitylene yields were generally lower than 0.6%. One notable exception is the significant increase in Y_{Mes} from 0.3 to 1.8% for the aluminosilicate Siralox 70/170 HPV which was also highly selective as over 99% of acetone was converted to either mesitylene or mesityl oxide. The substantial influence of reaction conditions is marked by the significant increase in activity of H-BEA 35 for which Y_{Mes} exceeded Y_{MesOx} and over 55% acetone was converted. Latter is a sign of decreased selectivity and increased side product formation as the desired product yields did not increase similarly. It must be mentioned in the discussion of the screening experiments that in some cases X_{Ac} was lower than the actual products yield. This is likely caused by errors in measurement of the highly volatile compounds acetone and cyclohexane, the internal standard, due to losses by either adsorption on the catalyst surface or vaporization. Assessment of the reactor blank activity shows that even at an elevated temperature of 220 °C less than 1% of acetone is converted and no significant amounts of products are detected (see Figure S3, Supporting Information). However, it is also demonstrated that the measurement of very low conversions is error-prone and subject to a significant statistical error.
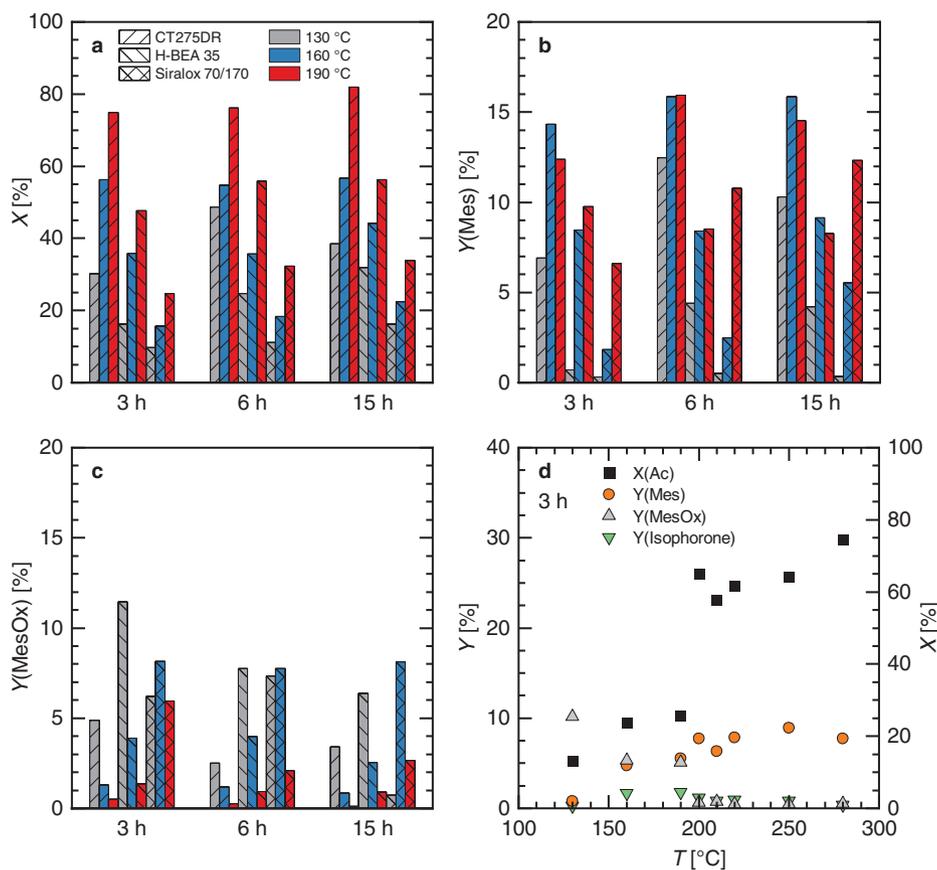
Noticeable are the differences in the activity of the various zeolites for the condensation reaction to mesitylene. This could be a result of their different pore sizes as first data on the acid site densities from temperature-programmed NH_3-desorption (NH_3-TPD) measurements shows only little difference (see Figure S4, Supporting Information).

More analysis and characterization are required for optimizing the catalytic activity due to the complex cyclotrimerization reaction of three acetone molecules inside a zeolite pore and the various effects present in zeolite catalysis, such as acid strength and density and pore and channel size.

Overall, the catalysts H-BEA 35, Siralox 70/170 HPV, Amberlite IR-120, and Purolite CT275DR were the most promising candidates for the acid-catalyzed aldol condensation to mesitylene based on the screening results. Due to the chemical similarity of the two strongly acidic, sulfonated cation exchange resins, the subsequent screening of the reaction conditions time and temperature focused on the more active Purolite catalyst as well as the two aluminosilicates. An explanation for the higher activity of Purolite could be its higher weight capacity of 5.2 eq kg^{-1}[16] compared to 2.2 eq kg^{-1} calculated for Amberlite[17] which results in a higher concentration of catalytically active sites on the Purolite surface.

2.2. Influence of Reaction Parameters

The three selected catalysts were subject to a variation in reaction temperature (130, 160, and 190 °C) and reaction time

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Figure 4. Results for the three selected catalysts Purolite CT275DR, H-BEA 35, and Siralox 70/170 HPV in the reaction parameter screening for a) acetone conversion, b) mesitylene yield, and c) mesityl oxide yield at different reaction times, respectively. d) Results of the temperature variation for H-BEA 35 at 3 h.

(3, 6, and 15 h). For all catalysts conversion of acetone increased continuously with reaction temperature while Y_{MesOx} declined as it reacts to consecutive products (**Figure 4**a). Differences in activities of the catalysts become apparent by taking into account the maximum acetone conversion as more than 82% of acetone are converted with Purolite CT275DR at 190 °C after 15 h, considerably more than for H-BEA 35 (56%) and Siralox 70/170 HPV (34%). This could be attributed to the higher quantity of acid sites per catalyst mass for Purolite CT275DR. Since equal amounts of catalysts were employed, a higher site density increases the total number of acid sites present in the reaction system. For a just comparison of activities, catalysts are required to be dried precedingly and added according to their amount of acid sites. However, the type and strength of acidity need to be addressed as well in further characterization.

A continuous increase in Y_{Mes} with temperature is only observed for Siralox 70/170 HPV, particularly from 160 to 190 °C which implies that it requires a high temperature due to a higher activation barrier to become active for catalyzing the aromatization reaction. In case of H-BEA 35 and Purolite CT275DR, Y_{Mes} does not further increase but remains constant from 160 to 190 °C. Maximum yields for mesitylene (H-BEA 35: 10%, Siralox 70/170 HPV: 12.5%, Purolite: 16%) and mesityl oxide (H-BEA 35: 12.3%, Siralox 70/170 HPV: 8%, Purolite: 5%) are in a comparable range (Figure 4b,c). The

decrease of Y_{MesOx} with reaction temperature can be explained with mesityl oxide being a reaction intermediate of which less is yielded when consecutive trimerization reactions are promoted. On the other hand, the observed rise in X_{Ac} for higher reaction temperatures is caused by an increasing formation of side products which compete with the formation of mesitylene. As side products water, isobutylene from the decomposition of intermediate products,[15] trimer condensates phorone and isophorone as well as higher oligomers such as acyclic and aromatic tetramer condensation products were identified through GC-mass spectrometry (MS) analysis (see Figure S5, Supporting Information). Depending on the catalyst, 90–95% of the total product amount detected in GC-analysis can be assigned to the main products for the studied reaction temperatures of 160–190 °C. As such 88–99% of the product yield consists of mesitylene, mesityl oxide and isophorone for 160 °C (see Figure S2, Supporting Information). Nevertheless, errors in conversion and yield occur due to the high volatility of acetone and the reaction intermediates and the likely formation of carbonaceous deposits. Concluding, catalyst selectivity decreases with increasing temperature and increasing quantity of acid sites as mesityl oxide is increasingly converted to undesired by-products instead of mesitylene.

Assessing the influence of reaction time on the self-condensation of acetone shows that the main reaction progress occurs

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in the first 3 h and approaches maximum values for conversion and yields afterward. A general increase of X_{Ac} and Y_{Mes} and decrease of Y_{MesOx} over time is only apparent for H-BEA 35 and Siralox 70/170 HPV at 130 and 160 °C and is less pronounced for higher temperatures. Reaching the equilibrium of the reaction or catalyst deactivation over time could explain the observed behavior. Deactivation could be either caused by pores blocked by formed by-products or buffering of the acidic protons of the catalyst by the water formed as by-product of the condensation reaction. As catalyst conversion increases with time and temperature total product yields for mesitylene and mesityl oxide do not increase similarly. This is likely due to promoted catalyst deactivation for higher temperatures and longer reaction times. Fast recycling combined with reactivation of the catalyst could potentially yield significant product amounts.

The polymeric nature of cation exchange resins limits their use to temperatures of ≈180 °C in case of Purolite CT275DR due to the insufficient thermal stability. In order to gain insight into the influence of higher reaction temperatures the beta-zeolite H-BEA 35 was tested in a temperature range from 200 to 280 °C. For H-BEA 35 a significant increase in conversion from 26% to 65% is observed for a 10 °C increase in temperature from 190 to 200 °C (Figure 4d). The greater acetone conversion is accompanied by only a minor increase in Y_{Mes} whereas the yield of the intermediate product mesityl oxide decreases to below 0.5%. For the higher temperature reactions tested, phase separation of the product mixture occurred. The two separating phases had to be resolubilized by adding 30 wt% of 1,4-dioxane as phase solubilizer for GC analysis. Regarding a future process development based on the cyclotrimerization of alkyl methyl ketones, the phase separation that occurs during the reaction could be used to separate water from the desired products, the aromatics, thus shifting the reaction equilibrium. The influence of water on the catalytic activity of the reaction system and the effects on catalyst stability and activity has to be assessed in advance though.
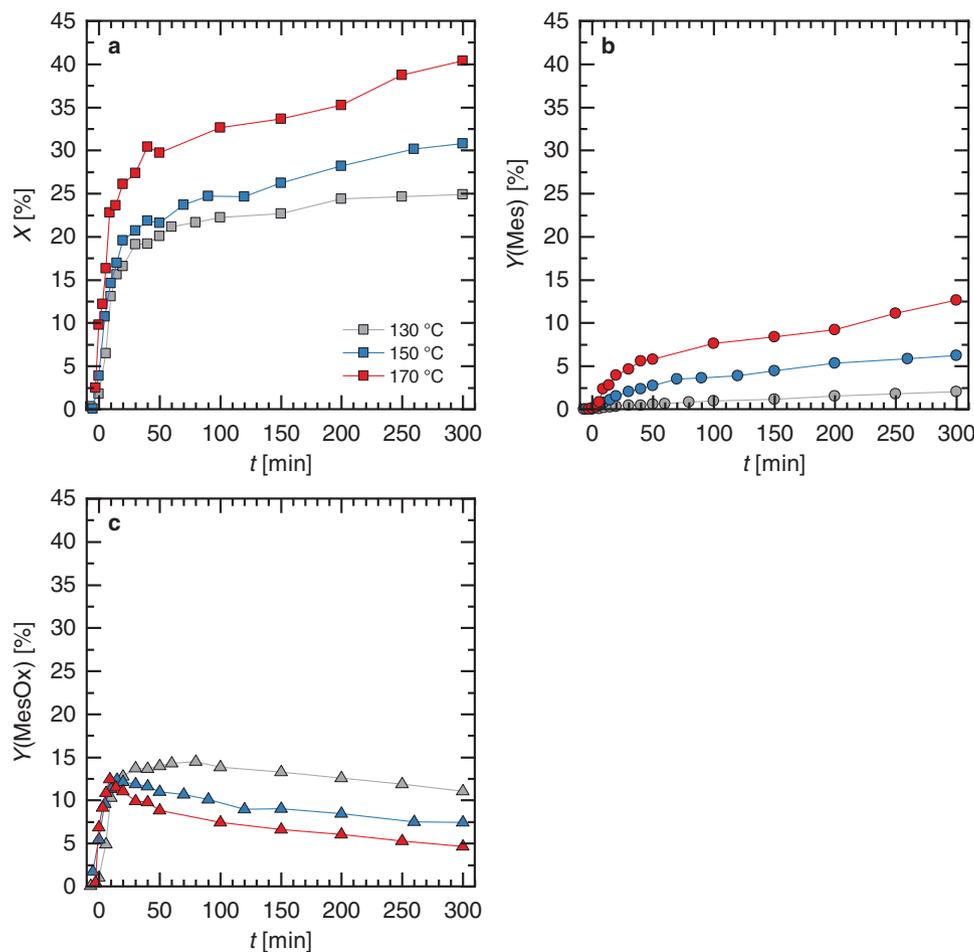
As mentioned above, formation of undesired by-products increases drastically with temperature while selectivity to mesitylene declines. Above 200 °C decomposition of intermediate products is becoming increasingly pronounced as shown by the presence of acetic acid in the reaction mixture. This emphasizes once more the complexity of the reaction in terms of possible side reactions and desired product selectivity. Albeit a generally increased formation of side products, isophorone yield similarly to mesityl oxide yield decreases with higher temperatures and can only be detected in traces above 200 °C. Due to the microporous nature of zeolites, reaction pressure can potentially influence the acetone condensation reaction. But a variation of the autoclave pressure from 40 to 145 bar showed only a negligible pressure dependence for the H-BEA 35 catalyst at 160 °C (Figure S6, Supporting Information). A slight increase in Y_{Mes} and decrease in X_{Ac} and Y_{MesOx} is observed for pressures of 95 bar and higher.

2.3. Reaction Kinetics

For a better understanding of the reaction and the influence of reaction time on intermediates and product formation, the progress of reaction was followed by taking samples of the reaction mixture in a batch reactor over the course of a total reaction time of 300 min. A 300 mL stirring autoclave that features a sampling line was used to study the time-resolved reaction progress at 130, 150, and 170 °C. Reaction temperatures were limited to 170 °C to accommodate for the maximum operating temperature of the catalyst. Furthermore, maximum Y_{Mes} were obtained at 160 °C. The reaction had to be scaled-up by a factor of 30 based on the acetone volume due to the larger reactor. The catalyst amount was reduced to 2.5 wt%. As catalyst the cation exchange resin Purolite CT275DR was investigated since it showed the highest activity in the screening of reaction parameters and required lower temperatures for activation than Siralox 70/170 HPV. Since the reactor was loaded with catalyst and starting material acetone prior to heating up, a first sample was taken when the final reaction temperature was reached. This marked the start of the reaction and was set as 0 min. The data obtained from following the reaction progress support the results found in the parameter screening: acetone conversion increases with time and temperature (**Figure 5**). More interesting is the fact that the reaction progress can be subdivided into two consecutive phases: in the first 20 min the reaction is very fast and X_{Ac} and Y_{MesOx} increase linearly. 20–30 min into the reaction, Y_{MesOx} goes through a maximum. This is especially pronounced for higher reaction temperatures. Two explanations are feasible: 1) The formation of water or by-products limits the further course of the reaction or 2) the reaction kinetics of the initial acetone condensation step and the consecutive reaction, i.e., growth/aromatization of mesityl oxide, are different. For the latter reason it is conceivable that the initial step is of second order as a bimolecular reaction occurs while in the second case the reaction is of first order regarding the concentration of mesityl oxide and acetone. At 130 °C a slower formation with a later maximum of mesityl oxide is observed. Formation of the consecutive reaction product mesitylene starts delayed as its intermediate must be formed first and Y_{Mes} is only significant after 10 min. Characteristic for this 20 min long start-up phase where almost two thirds of acetone are converted is the steep slope for X_{Ac}. In the subsequent second phase acetone conversion slows down immediately which is marked by a significant decrease of the slopes for X_{Ac} and Y_{MesOx} since the reaction to its consecutive products increases. However, X_{Ac} and Y_{Mes} steadily increase over the full reaction time of 300 min. It can be concluded that no equilibrium state is reached during the reaction time. Over the course of the reaction not only the yields are shifted from mesityl oxide to mesitylene but also the overall selectivity decreases as formation of side products increases which is the main contributor to the rising acetone conversion. During the start-up phase at 130 °C acetone, diacetone alcohol, mesityl oxide, phorone, isophorone, and mesitylene are detected via GC-MS with their sum representing 99.9% of the total GC area. Higher reaction temperatures lead to longer heat-up phases. Thus, formation of side products and mesitylene are already observed at $t = 0$ min.

Concerning the reaction temperature, reaction progresses run almost parallel when monitored by X_{Ac} and Y_{Mes} for 130–170 °C, especially during the start-up phase. In the reaction parameter screening a maximum for Y_{Mes} was obtained

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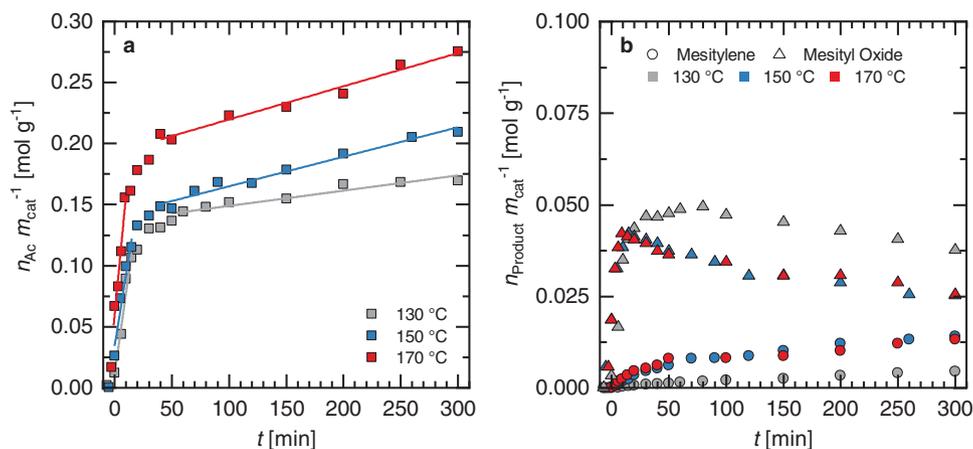SYSTEMS**
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Figure 5. Time-resolved a) acetone conversion, b) mesitylene yield, and c) mesityl oxide yield for the acetone condensation reaction with Purolite CT275DR at 130, 150, and 170 °C (straight lines connect the measured points just for clarity and to indicate trends).

at 160 °C. Although this is not replicated in the time-resolved experiments, the general trend of a constant increase of X_{Ac} with reaction temperature is confirmed.

2.3.1. Catalyst Conversion Activity and Productivity

The preceding observations are clarified by investigating the catalyst conversion activity which is defined as the amount of converted acetone n_{Ac} per catalyst mass m_{cat} and time t and determined via linear regression of the data in the two reaction phases (see **Figure 6**a). These two phases can be clearly distinguished by the abrupt change in catalyst conversion activity around 20 min. While for 130 and 150 °C the converted amount of acetone per catalyst mass in the start-up phase is 6–7 and 9.8 mmol g^{-1} min^{-1} at 170 °C, a drastic decline is noted for the second phase when the conversion activity drops below 0.3 mmol g^{-1} min^{-1}. The sudden decrease in catalyst activity is also observable in the formation of products, particularly for mesityl oxide (see Figure 6b). Productivity for both mesityl oxide and mesitylene after the start-up phase flattens and is significantly reduced for the remainder of the reaction. On the one hand this shows that temperature has a major influence on

catalyst conversion activity. On the other hand, this represents a decrease in activity of more than 95% which can be an indicator for a drastic inhibition of the reaction caused by catalyst deactivation or change in reaction order due to the mechanism and concentration dependence as described above. However, the catalyst is not completely deactivated since mesitylene productivity monotonically increases with time. Plausible explanations for catalyst deactivation could be blocking of the catalyst pores by formed reaction and side products, such as oligomers but also water of which three molecules are formed for every molecule of mesitylene. A water film on the catalyst surface can lead to inhibition of the acidic surface centers by creating a buffer solution with H_3O^+-ions which would decrease the acidic strength considerably. Additional mass transfer limitations posed by an aqueous acidic phase would further contribute to a decrease in catalyst activity. Besides water, oligomerization products formed by the high quantity of acid sites in the pores can mechanically block pores and thus hinder access to a substantial number of catalytically active centers. In fact, Podrebarac et al. assumed heavier side products to be the cause for the observed deactivation of an Amberlite IR-900 anion exchange resins in hydroxide form when investigating the conversion of acetone to diacetone alcohol and mesityl oxide.[18] For the studied Purolite CT275DR

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Figure 6. a) Converted amount of acetone n_{Ac} and b) formed products mesitylene and mesityl oxide per catalyst mass m_{cat} to determine the catalyst activity of Purolite CT275DR.

catalyst, an increase in catalyst mass of 9.3% is observed after reaction at 160 °C for 3 h (see Table S1, Supporting Information). At low reaction temperatures under 200 °C carbonaceous deposits on acid catalysts are nonpolyaromatic and stem mainly from condensation and rearrangement steps.[19] Besides coke formation on the catalyst surface, nondesorbed reaction products such as mesitylene can add to the catalyst mass. Their strong adsorption to the catalyst's acid sites can contribute to the catalyst deactivation. Further investigations of the species adsorbed on the catalyst surface must be conducted to understand in more detail what causes the decrease in activity and to what extent catalyst deactivation occurs.

2.4. Influence of Water on the Reaction

Formation of an acidic aqueous phase on the catalyst surface could cause catalyst deactivation and would imply a change from heterogeneous to homogeneous catalysis. To further address the influence of water on the reaction progress of the acetone self-condensation, the catalyst and reagent acetone were dried before the reaction to remove residual water and compared to untreated conditions. Additionally, an experiment with a molecular sieve (3 Å) was performed to remove the water formed during the reaction. The results for the reaction progress of the two variants in comparison to the one under standard conditions without dried reactant or additives are displayed in **Figure 7**.

Notably, under dry conditions higher acetone conversions were obtained which is supported by an activity increase of 1.6 times in the start-up phase illustrated by a much steeper slope. Albeit, this increase does not transfer to the second phase where the curves of dry and standard conditions run parallel. Removal of residual water from Purolite CT275DR and acetone increases the initial acidic strength of the catalyst, thus preventing the immediate formation of a buffer solution which can lead to catalyst deactivation. Since the shifted equilibrium further accelerates the reaction in the start-up phase, formation of water increases rapidly as does the decrease in catalyst activity. Based on the assumption that water is the limiting factor in the reaction, in situ removal of water should result in a higher

catalyst activity. Using a 3 Å molecular sieve, progress of the start-up phase is highly similar to the one under dry reaction conditions. But the reaction does not proceed past 100 min as displayed by the constant conversion and yield curves. Inside the pores of the molecular sieve ion exchange of Na^+- or K^+-ions with H_3O^+-ions can occur and is facilitated by water formation during the reaction which increases ion mobility in the reaction system. Consequently, catalytically active H_3O^+-ions are removed from the reaction mixture and catalyst activity is diminished. Using a molecular sieve is therefore not suitable for the investigation of a water-free system for the aldol condensation reaction of acetone.

As an alternative means to study the catalyst deactivation which occurs during the start-up phase, fresh catalyst was added after 50 min. This resulted in acetone conversion and mesitylene yield increasing further (Figure S7, Supporting Information). Instead of an increase in Y_{MesOx} which would be expected based on the reaction progress without addition of
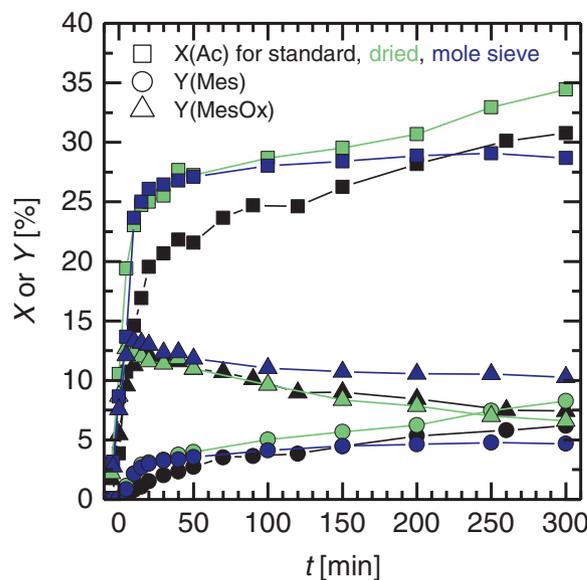
Figure 7. Comparison of the reaction progress for the catalyst Purolite CT275DR under dry (acetone and catalyst dried prior to reaction) and standard conditions and the addition of a mole sieve to the reaction.

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fresh catalyst, a decrease occurred, implying that mesityl oxide is converted to the consecutive product mesitylene. No change in the two step behavior of the reaction is apparent when adding the fresh catalyst, thus, disproving the theory of the influence of water on the two reaction steps and on the other hand proving the dependence on the higher reaction order of the initial condensation reaction and the subsequent further reaction of mesityl oxide and acetone of lower reaction order. The increase observed for X_{Ac} and Y_{Mes} of ≈10% is less prominent compared to the initially added catalyst. This indicates that the deactivation of the catalyst is caused by species in the reaction mixture, e.g., water or oligomers that are formed during reaction.

3. Conclusion

As suitable solid acid catalysts for catalyzing the aldol condensation reaction of acetone to mesitylene we identified the beta-zeolite H-BEA 35, the cation exchange resin Purolite CT275DR, and the aluminosilicate Siralox 70/170 HPV. Regarding the influence of reaction time it was noted that in the first 3 h of reaction the majority of acetone was converted. Mesitylene yield increased with higher reaction temperatures and longer reaction times which also increased formation of side products. Latter was also emphasized by higher surface acid group densities of the catalysts, negatively affecting the total product selectivity. Progress of the reaction was found to take place in two phases with an initial 20 min long start-up phase characterized by high catalyst acetone conversion activity and a subsequent phase which was marked by an immediate apparent decrease in activity probably due to the subsequent reaction of lower reaction order. Water plays a role in the deactivation of the catalyst and thus presents a challenge for future optimization of the reaction to aromatics.

The investigated self-condensation of acetone to mesitylene demonstrates the potential of an innovative route to aromatics via cyclotrimerization of alkyl methyl ketones. A comparison with other more established routes is not yet permissible due to the early stage of the research that requires further optimizations of the catalyst selectivity and studying the cyclotrimerization reaction of longer alkyl methyl ketones, such as 2-butanone. The results present a first step toward a better understanding of the required reaction conditions and will be followed by investigation of the kinetics in a continuous reactor setup.

4. Experimental Section

All materials were used as received without further purification. Acetone (≥99.5%) and 1,4-dioxane (≥99.5%) were purchased from Carl Roth, cyclohexane (≥99.9%) from Sigma-Aldrich. Catalysts were either supplied by their manufacturer or commercially available and were used as received. Nb_2O_5 (98.5%) was purchased from Alfa Aesar.

Screening of Catalysts and Reaction Parameters: A 45 mL batch autoclave (Parr MRS 5000 series) equipped with a polytetrafluoroethylene-inlet and magnetic stirring bar (500 rpm) was loaded with acetone (3.950 g, 68 mmol) and solid acid catalyst (0.198 g, 5 wt%). Cyclohexane (1.431 g, 17 mmol) was added as internal standard in the catalyst screening experiments. Reactors were purged twice with argon during which the stirring speed was set to 100 rpm. They were then pressurized with argon (25 bar) and heated to the specified reaction temperature and time at a speed of 500 rpm. The reactors were cooled down in an ice-water bath before the product solution was filtered and analyzed by GC and GC/MS. In reaction parameter screening experiments, 1,4-dioxane (30 wt%) was added as internal standard and phase solubilizer.

Kinetic Experiments: Acetone (150 mL, 2.0 mol) and catalyst Purolite CT275DR (2.96 g, 2.5 wt%) were added to a stirred tank reactor from Parr featuring a sampling line. The purged reactor was pressurized with argon (20–40 bar) and heated to the specified reaction temperature. For the duration of reaction (300 min), the reaction mixture was stirred at 1000 rpm and samples (1–2 mL) were taken in regular intervals.

Acetone Condensation under Dry Conditions: Analogous to the reaction procedure for the temporal reaction progress of the acetone condensation, the reaction proceeded either in the presence of a molecular sieve (3 Å, 6.14 g) or with predried acetone and catalyst. Reactant acetone was dried over a molecular sieve (3 Å) and catalyst Purolite CT275DR was dried at 80 °C under vacuum.

Product Characterization via GC: Samples for GC analysis were usually prepared by adding 70 wt% of the filtered product solution to 30 wt% of the internal standard 1,4-dioxane. In reactions in which cyclohexane was added initially, filtered product solutions were used directly. Quantitative analysis was performed with a Shimadzu GC-2010 Plus with flame ionization detector and qualitative analysis with a GCMS-QP2010SE, both equipped with a Macherey-Nagel Optima WaxPlus column.

NH_3-TPD: Zeolitic acid sites were quantified by temperature-programmed desorption of adsorbed NH_3. Catalyst samples (100 mg) were initially calcined for 1 h at 600 °C under N_2-atmosphere to remove residual water. Subsequently, at 140 °C the sample was loaded with NH_3 (2 vol% NH_3 in N_2, 20 mL min^{-1}) for 20 min, followed by desorption of the physiosorbed NH_3 in N_2-flow (100 mL min^{-1}). Afterward, the sample was heated to 600 °C (10 K min^{-1}, 100 mL min^{-1} N_2) and desorbed NH_3 was detected by Fourier-transform-IR.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Conflict of Interest

The authors declare no conflict of interest.

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