Journal of Corrosion and Materials
www.corromat.com

J. Corros. Mater. (2023) 2(2), 142–157.

Accessible Acid-Site Retention in Solvent-Free Acetone Aromatization over Mesoporous Amorphous Silica-Alumina

Stefan Berger[1,*]

[1] *Department of Chemistry, Leipzig University, Leipzig, Germany.*

*Corresponding author: stberger@rz.uni-leipzig.de

(Received: 23 September 2023. Received in revised form: 30 November 2023. Accepted: 18 December 2023. Published online: 30 December 2023.)

Abstract

Conversion of bio-based acetone to mesitylene via catalytic reactions is an effective pathway that can transform biocompatible ketones directly to sustainable alkyl aromatics; however, there are many processes involved in acetone transformation to mesitylene, namely, C-C coupling, dehydration, cyclization, aromatication, and carbonaceous deposition growth, which should be optimized for the reaction to take place. Solvent-free continuous conversion of acetone to mesitylene over commercially available amorphous silica-alumina catalysts depends greatly on the presence of active acid centers throughout operation time. The composition of Siralox 30 includes 30 wt% SiO_2, a mesoporous structure, a specific BET surface area of 199 m^2 g^{-1}, a total pore volume of 0.59 cm^3 g^{-1}, average pore diameter of 12.3 nm, and acidity of 0.30 mmol NH_3 g^{-1}. Acetone conversion rises from approximately 17% to 63% between 200 °C and 300 °C at 75 bar, with mesitylene selectivity having its maximum near 260 °C. Mesitylene yield of approximately 10.1% can be obtained using Siralox 30 at 260 °C and $W/F = 12.5$ g_{cat} h mol^{-1}, remaining stable for over 50 hours on stream. On the contrary, spent Siralox 30 keeps virtually all its mesoporous volume, while HY-5 demonstrates considerable reduction in microporous surface area and about 20 wt% weight loss. Durable acetone aromatization therefore depends on a retained Brønsted-Lewis acid environment in open mesopores rather than on maximum fresh surface area or maximum acid-site concentration.

Keywords: acetone aromatization; mesitylene; amorphous silica-alumina; Siralox 30; solvent-free catalysis; Brønsted acidity; Lewis acidity; mesoporosity; catalyst deactivation; renewable aromatics.

1. Introduction

Production of renewable aromatics is challenging in catalytic terms, since aromatics are key chemical platform compounds while industrially they continue to be derived primarily from petroleum refinery feedstocks. Catalytic naphtha reforming remains an important conventional route associated with petroleum aromatics and therefore represents the fossil benchmark that renewable processes must challenge [1]. Benzene, toluene, isomers of xylene, trimethylbenzenes, and more complex alkyl aromatics are solvents, fuels, monomers, resins, and specialty chemicals. Integration of these compounds into existing chemical value chains sets a practical benchmark for success in renewable aromatics chemistry: the technology must deliver compounds which are capable of being separated and processed using existing infrastructure and decreasing our dependency on carbon sources which are non-renewable. Biomass conversion chemistry shows that renewable carbon can be transformed into fuels and platform chemicals through several catalytic paths [2]. Liquid-phase processing of biomass-derived oxygenates also illustrates the need to manage carbon efficiency and hydrogen balance [3]. Platform-molecule upgrading studies emphasize selectivity and catalyst durability during conversion to fuel additives and hydrocarbons [4]. Circular-economy analysis further underlines the significance of biomass as a renewable carbon source [5]. As such, finding a catalytically active compound is not enough to produce renewable aromatics: the catalytic environment must be able to maintain selectivity during constant exposure to highly reactive oxygenate intermediates and products of condensation.

A number of technologies have been proposed for producing aromatics from renewables, with varying strengths and weaknesses. Catalytic fast pyrolysis may lead to aromatics-rich vapors from renewable sources, but the product distribution will be wide and deactivation by coke accumulation is inevitable in zeolitic processes [6]. Diels Alder chemistry can allow synthesis of target aromatics such as xylenes from furans and olefins, but the use of appropriate furan intermediates and avoiding excessive dehydration are required [7]. Reviews of renewable aromatic routes similarly identify furan-based pathways as promising but demanding in selectivity and scale-up [8]. Hydrodeoxygenation routes may transform oxygenates to aromatics and hydrocarbons, but they often need significant amounts of hydrogen and should avoid ring hydrogenation and cracking [9]. Platform-molecule upgrading studies confirm that deoxygenation chemistry must balance oxygen removal, carbon retention, and product selectivity [4]. Ketone condensation is appealing in its potential to create aromatic rings out of C-C bond formation and deoxygenation. In ketone condensation, the oxygenated feed is not only deoxygenated: it is reorganized into an aromatic structure.

The particular relevance of the current chemistry lies in the use of acetone. Acetone was historically obtained from acetone-butanol-ethanol fermentation, and became additionally important with the development of gas-fermentation processes that allow producing acetone along with isopropanol from carbon oxides [10]. Acetone can undergo self-condensation to mesityl oxide and other C_6 structures, then condense more extensively and cyclize to mesitylene or 1,3,5-trimethylbenzene. Mesitylene is a valuable C_9 aromatic hydrocarbon, and a valuable model compound due to the need to achieve selective construction of an aromatic structure from the oxygenated starting molecule. Methyl ketone condensation has shown the possibility of producing branched fuel-range products from biomass-derived ketones [11]. Solid-acid-catalyzed aldol condensation has also been used to obtain biomass-derived aromatics from alkyl methyl ketones [12]. Studies of acetone conversion on aluminosilicates show that product formation depends heavily on acid and base functionality, pore size, and residence time [13]. Therefore, acetone-mesitylene transformation allows probing the ability of the material to facilitate a multi-step process without letting it turn into heavy hydrocarbons.

However, the key challenge of the mechanism lies in the fact that acetone cannot transform to mesitylene within one step only. The reaction leads to the generation of dimers including mesityl oxide, cyclic trimers such as isophorone, aromatic compounds like mesitylene, oligomers of different lengths and structures, and residual coke-like carbonaceous matter. Isophorone-related chemistry also has industrial relevance because isophorone derivatives can be incorporated into polymer systems [14]. Mesityl oxide can be considered as an intermediate that promotes a successful transformation if quickly upgraded, but can also become a source of heavier structures if lingering on an acid surface for too much time. The mesitylene is the desired product here, although this is not an inert product under strong acid environments. Therefore, excessive condensations and alkylation could be possible after mesitylene formation. Niobium oxide studies show that acetone aldol condensation depends strongly on the nature of oxide active sites [15]. Molybdenum nitride and carbide catalysts similarly demonstrate that acetone condensation routes change with catalyst chemistry [16]. Aluminosilicate studies clarify elementary steps in acetone condensation over different void structures [17]. One-pot conversion studies further show that acid and basic catalysts must be combined carefully to obtain mesitylene selectively [18]. The central design problem is therefore selectivity under sustained operation, not conversion alone.

Zeolite micropores have been seen as highly appealing for such a reaction chemistry due to their capacity to generate crystalline acid sites and facilitate dehydration, condensation, and aromatization reactions. However, there are some challenges associated with deactivating zeolites by coke formation as a combination of chemical and diffusion processes in acid catalysis [19]. Early acetone-conversion studies over zeolites showed that activity can decline rapidly when condensation products block pore access [20]. Catalyst-morphology studies confirm that acetone transformation into mesitylene depends on how the pore system handles larger intermediates [21]. Zeolite pore-structure research in transalkylation also illustrates how diffusion restrictions can alter catalytic behavior for aromatic molecules [22]. This challenge becomes even worse for the process of acetone aromatization since mesitylene, isophorone, and oligomeric products are much larger and less diffusible compared to acetone itself. Consequently, it is quite possible to develop a catalyst with plenty of acid sites in its fresh form, which will no longer be practically effective due to pore blockage.

On the other hand, amorphous silica-alumina could provide an entirely new direction since it can incorporate both types of acidic sites in its structure along with the development of mesoporous structure. Indeed, incorporation of silica into alumina not only affects the number of acid sites but also their type and acidity. Infrared and NMR studies identify silanols, coordinatively unsaturated aluminum species, Si-O-Al moieties, and hydrogen-bonded hydroxyls in amorphous silica-alumina [23]. Acidity characterization further shows that amorphous silica-alumina cannot be treated as a simple mixture of silica and alumina [24]. Silica-doped alumina studies connect acid-site properties with silica/alumina ratio and calcination temperature [25]. Atomic-scale NMR analysis sheds additional light on Brønsted acid sites in amorphous silica-alumina [26]. Microcalorimetric studies reveal that acidity depends on modified oxide surfaces and dopant character [27]. Low-temperature FTIR work confirms that mixed alumina-silicas can show enhanced surface acidity [28]. Brønsted acid sites based on penta-coordinated aluminum species add another structural origin for acidity [29]. Bifunctional support studies likewise show that support acidity in silica-alumina can govern catalytic performance [30]. Earlier liquid-phase aromatic isomerization over silica-alumina also illustrates the relevance of this catalyst family to alkyl-aromatic chemistry [31]. Such heterogeneity could become an asset in situations where the desired reaction involved two types of acidic interactions, i.e., the Lewis sites for initial condensation and Brønsted sites for dehydration, cyclization, and aromatization. The practical requirement is to place this chemical balance in a pore network large enough to prevent catastrophic pore blockage.

The importance of acetone as a renewable feedstock for aromatics synthesis stems not only from its renewability but also from the simplicity of its structure. As a result of being a relatively small ketone, unlike bigger oxygenates, the carbonyl present in acetone is easily accessible to aldol coupling reactions, while the water produced in the dehydration process is the main by-product of the process. The above difference is what distinguishes ketone aromatization from other deoxygenation processes that rely mainly on hydrogenation and deoxygenation of complex feeds. However, such chemical simplicity presents

the issue of selectivity, since acetone can go through various condensation sequences and produce numerous products. Hence, the reaction conditions have to favor C_6 intermediate formation over further formation of the C_9 ring and unrestricted growth of the alkyl chain. Studies on methyl ketone condensation identify control of oligomer size and branching as essential for useful yields [11]. Biomass-derived aromatics from alkyl methyl ketones also require selective solid-acid-catalyzed aldol condensation rather than conversion alone [12]. For acetone aromatization, selectivity becomes even more crucial, as opposed to a mixture of oligomers, the goal here is obtaining an aromatic molecule.

In addition, the presented catalytic system highlights the problem of optimization in catalysis, where focusing on single parameter often leads to poor results. Acidic catalysts can be described in terms of total acid density, individual acid sites' acidity, or porosity and crystallinity of the material. However, in case of ketone aromatization, all of these characteristics need to be considered together with kinetics and deposits' properties. The product molecule is bigger than the initial ketone; intermediates may be available for further coupling and produce higher molecular weight products; and some products are more mobile and/or more strongly adsorbed on the catalyst. A strong acid site needed for dehydration can lead to oligomerization of intermediates. Porosity which facilitates shape-selective reactions in other hydrocarbons can lead to trapping of bulky molecules in certain pore systems. Accessible acidity is therefore a working property of the catalyst under reaction conditions rather than a static property measured only before reaction.

Solventless continuous acetone aromatization over amorphous silica-alumina catalysts relies on maintenance of available acid sites during catalyst use. Thus, Siralox 30, despite having lower fresh specific surface area and total acid concentration than HY-5, retains almost its entire mesoporous surface during reaction and remains active for more than 50 h. This demonstrates a clear interrelation between the durability, selectivity and process operation of such a catalyst – the most effective is not the one consuming acetone faster, but the one able to retain a favorable ratio between mesitylene formation rate and heavy product formation rates, along with maintaining available acid sites.

Materials and methods

Commercial amorphous silica-alumina Siralox series was used as the main series of catalysts. The series included alumina-rich, medium, and silica-rich materials containing from 1 to 70 wt% SiO_2. Gamma-alumina and silica were used as reference oxides, enabling analysis of silica-alumina series with respect to the two composition end-members. Commercial Siralox catalysts were calcined in air at 550 °C for 6 hours with a heating rate of 2 K min^{-1} and an air flux of 100 NmL min^{-1}. Zeolite catalyst, HY-5, was prepared via triple NH_4NO_3 exchange at 60 °C for 1 hour and subsequent calcination in air at 550 °C for 6 h. 99% acetone was employed directly without pre-purification. Gas chromatographic calibration was based on the use of acetone, mesityl oxide, mesitylene, isophorone, 2-butanone and 1,3,5-triethylbenzene standards, with FID responses accounted for according to effective carbon number concepts where required [32].

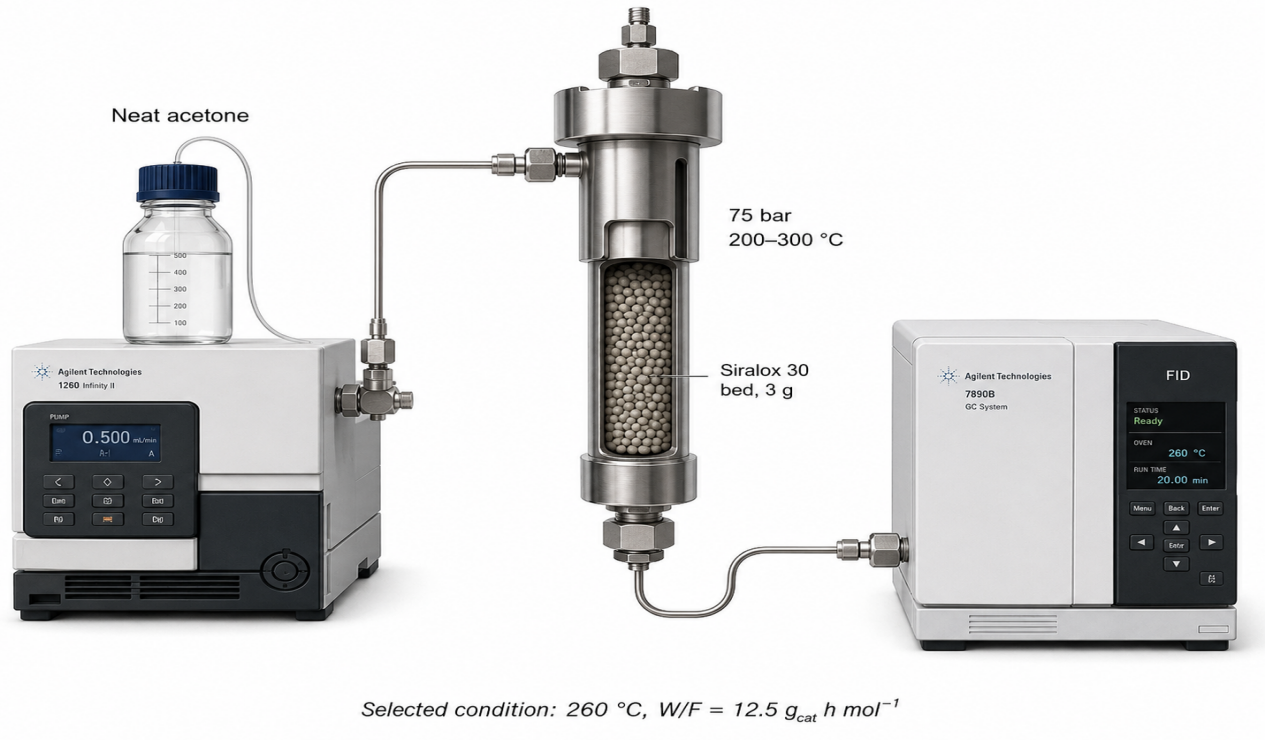


Figure 1: Continuous dense-phase acetone conversion setup.

The continuous conversion of acetone was carried out in an upward flow, fixed bed reactor made of stainless steel having inner diameter of 1.6 cm and height of 20 cm. The catalyst was loaded in the isothermal part of the reactor in a quantity of 3 grams. The catalyst particles were pressed, milled and screened to size of 100-200 μm for better mass transfer efficiency and obtaining a certain fraction of fixed bed particles. Pure acetone was used as the reactant feed using an HPLC pump. The reactor was run in the range from 200 to 300 °C with constant pressure of 75 bar, at which acetone appeared either in the form of a dense liquid or supercritical fluid depending on the temperature. The choice of 75 bar pressure was made according to the known data about the properties of acetone in dependence of pressure and temperature [33]. The reactor outlet was mixed continuously with a standard solution of 1,4-dioxane in 1-butanol, and products were analyzed by online gas chromatography equipped with a flame-ionization detector.

It is worth noting that the experimental setup in Figure 1 features the Siralox 30 bed within a pressure rated fixed-bed reactor system rather than in diluted batch setup. The significance of this lies in the fact that neat acetone, high pressure, and on-line GC-FID analysis are all defining parameters for the selectivity window in question. As far as the picture goes, it is clear now how it is necessary for the catalyst to incorporate both acidity and availability of pores for feeding and aromatic products formation.

Powdered X-ray diffraction was selected for characterization to determine the presence or absence of crystallinity for the samples pre and post-reaction. Nitrogen adsorption at 77K served to establish BET surface area, micropore area, mesopore area, pore volume, and average pore size of samples. Thermogravimetric analysis of spent catalyst was conducted using artificial air at temperatures between 40 and 1000 °C with heating rate of 5 K min^{-1}. Ammonia temperature programmed desorption was applied to determine total acid site concentration and to compare acidity using maximum temperature of NH_3 desorption peaks. The importance of NH_3 TPD method should be stressed here because although it shows the overall amount of acid sites, it does not tell by itself whether the acidic sites are available [34]. Thus, this interpretation combines both acidity and retained porosity.

The emphasis for this study was put on comparisons of performance that have validity during continuous operations. Values of conversion by itself are not considered as sufficient criteria for catalysts' efficiency since acetone consumption can rise when undesirable condensation occurs. Therefore, selectivity and yield of mesityl oxide were analyzed taking into account mesityl oxide behavior, mesitylene, isophorone production, heavy products generation, carbon balances, catalyst performance during its lifetime, and catalyst properties after use. Thus, we follow the main principle of reaction-network analysis according to which intermediates could be useful or not depending on their consumption via certain reactions or secondary transformation into byproducts. Data are presented accordingly, i.e., using intervals of operation rather than one-off activity figures.

The reaction network is summarized below using the abbreviations for the reactant and products. Namely, there are acetone, mesityl oxide and other C_6 dimers, mesitylene, isophorone and other cyclic trimers, as well as heavier oligomers/deposits. The initial dimerization reaction can be described as $2A \rightarrow D + H_2O$. Here A stands for acetone while D stands for dimers. The productive formation of aromatics is described by $D + A \rightarrow M + 2H_2O$. In this case, M stands for mesitylene. Finally, formation of the isophorone type of products takes place according to the following reaction equation: $3A \rightarrow I + 2H_2O$, where I stands for isophorone and others. Formation of the heavy products takes place according to reactions $D + A \rightarrow H$ and $M \rightarrow H$. These expressions show stoichiometric relationships between products rather than actual reactions; thus, mesityl oxide consumption goes up while mesitylene concentration rises, and heavies and unknown products become dominant at too high temperature or too long contact time.

An estimate of the retention-based descriptor for describing spent-catalyst stability relative to fresh properties is proposed. The ratio of BET surface areas of spent and fresh catalysts is termed the BET retention fraction, and the same is defined for the retention fraction of pore volume. The retention fraction of the surface deposit can be calculated as the product of BET retention and residual non-deposit fractions, $(S_{BET,spent}/S_{BET,fresh})(1 - m/100)$, where m is the spent-catalyst weight loss percentage. The above descriptor cannot serve as an alternative to kinetic analysis, but at least it provides the answer to the question of whether a promising fresh catalyst becomes practically inaccessible after treatment by reactive oxygenates and condensation products. Moreover, using this retention index will allow comparison of the high-surface microporous zeolite and low-surface mesoporous amorphous silica-alumina as catalytic materials.

Results and discussion

The lack of correlation between fresh surface area and fresh acidity and durable catalytic performance

HY-5 and Siralox 30 differ the most from each other. The BET surface area of HY-5 is 778 m^2 g^{-1}, and its microporous surface area is 709 m^2 g^{-1}. Total acid concentration on the surface of this catalyst is 0.53 mmol NH_3 g^{-1}. On the contrary,

the surface area of Siralox 30 is much smaller and equals 199 $m^2\ g^{-1}$, and total acid concentration is 0.30 mmol $NH_3\ g^{-1}$. But it should be noted that all surfaces of Siralox 30 are mesoporous. Therefore, screening of the two catalysts with respect to fresh BET surface area and acid concentration would show that HY-5 is a stronger catalyst. But spent catalyst results show the opposite. HY-5 loses most of its microporous surface after acetone conversion, whereas Siralox 30 retains nearly its complete mesoporous texture.

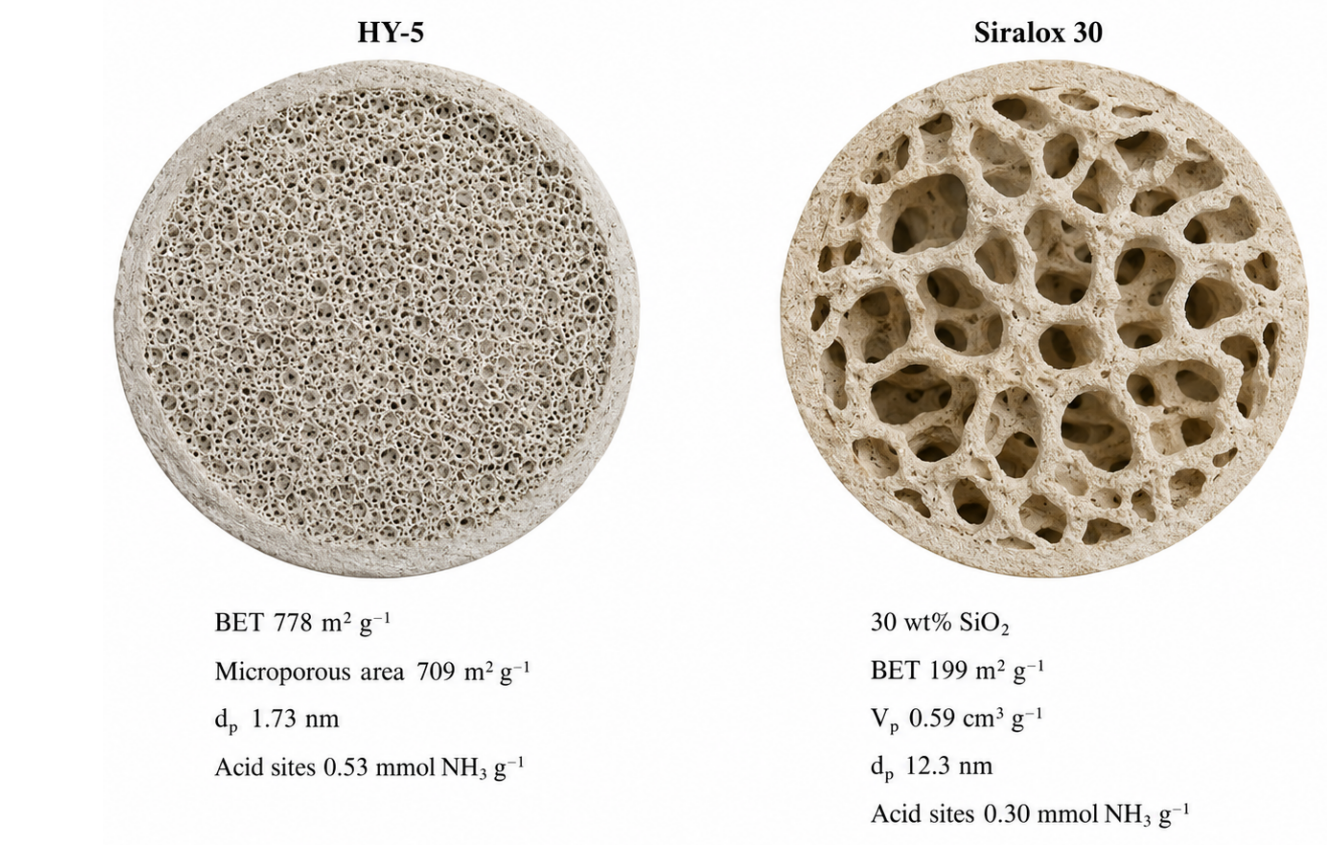


Figure 2: Fresh catalyst texture and acidity.

The cross-section data in Figure 2 differentiates between surface area and pore accessibility. Initially, HY-5 is the sample with higher surface area and acidity, but this surface area is mainly concentrated within a limited micropore range. Siralox 30 shows less number of acid sites and also a lower BET surface area; however, its macroscopic pore structure comprises bigger pores that make mesitylene, isophorone, and oligomer diffusion easier.

Table 1: Textural and acidic properties before and after acetone conversion.

Catalyst state	S_{BET} $m^2\ g^{-1}$	S_{micro} $m^2\ g^{-1}$	S_{meso} $m^2\ g^{-1}$	V_p $cm^3\ g^{-1}$	d_p nm	Acid sites mmol $NH_3\ g^{-1}$	Mass loss wt%
HY-5 fresh	778	709	69	0.34	1.73	0.53	–
Siralox 30 fresh	199	0	199	0.59	12.3	0.30	–
HY-5 spent	230	121	109	0.16	2.74	–	20.0
Siralox 30 spent	190	0	190	0.58	11.6	–	3.3

From Table 1, we can see that the surface area of the fresh HY-5 is around 3.9 times higher than that of fresh Siralox 30. On the other hand, after the reaction process, the BET surface area of HY-5 is reduced to just about 30% of its initial value and its pore volume only keeps at around 47% of its original value. Its micropore area is reduced from 709 to 121 $m^2\ g^{-1}$, which shows that the area which contributes significantly to the fresh surface area has become inaccessible. In contrast, Siralox 30 keeps its BET surface area and pore volume at about 95% and 98%, respectively. It experiences a change of pore diameter from 12.3 to 11.6 nm, and its weight loss is only about 3.3 wt%. In this way, the surface deposit retention indices can be calculated as being about 0.24 and 0.92, for HY-5 and Siralox 30, respectively. These derived values express the key materials conclusion: durable acetone aromatization is controlled by retained accessibility rather than by fresh surface area alone.

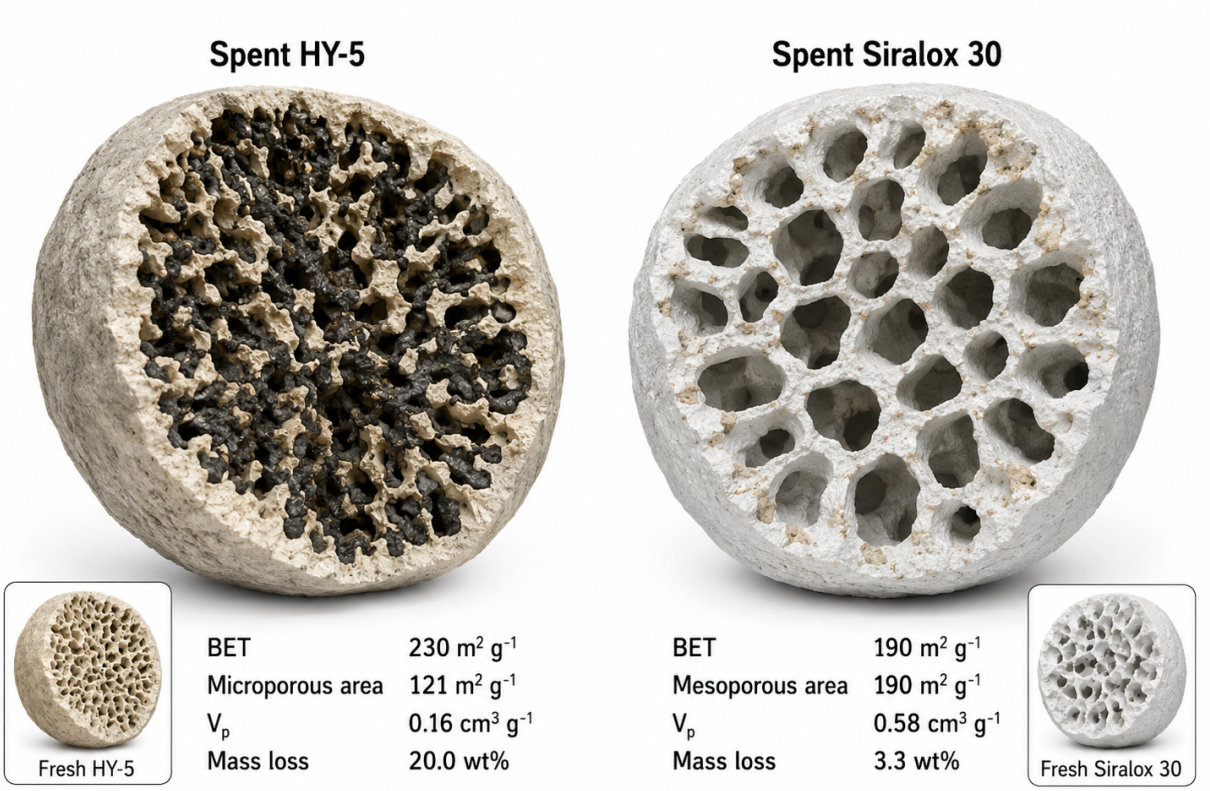


Figure 3: Spent-catalyst accessibility after acetone conversion.

A difference between retained and fresh surfaces also alters the definition of catalyst economy. Even a catalyst with a large amount of internal surface may need frequent regeneration or large amounts of the catalyst itself if a substantial portion of the surface is rendered unavailable by short treatment. On the contrary, having smaller internal surface but keeping access to the acid centers can be more advantageous for the use of a catalyst in a continuous operation. The relevance of retaining surface accessability is especially important when it comes to solvent-free process where the catalyst bed is permanently exposed to organic substances. Therefore, HY-5 comparison can be seen as more than just a control experiment since it illustrates how the failure of a catalyst should be prevented when aromatic compounds and oligomers are synthesized from acetone.

The comparison of spent catalysts (Figure 3) shows that even though the initially higher surface area is beneficial for the production of olefinic products, a microporous acid catalyst loses that benefit after a long contact time during the conversion of oxygenates to aromatics. The significant drop in HY-5 surface area and 20 wt% loss of catalyst mass indicate the substantial accumulation of deposits inside the pores. Zeolite-deactivation literature explains how coke formation can remove the advantage of a highly developed microporous surface [19]. Acetone-to-mesitylene studies further show that catalyst morphology affects deactivation and product selectivity [21]. As opposed to this, Siralox 30 does not display such behavior because of an additional open structure formed by acid sites in the mesopores. The surface area of Siralox 30 is smaller than that of HY-5; however, it stays accessible after reactions. In the process producing mesitylene, isophorone, and oligomers from acetone, retained accessibility plays a bigger role than maximizing the starting area.

A solvent-free dense-phase reaction produces a narrow productive operating range

The idea of operating a solvent-free process relates catalyst architecture to reaction severity. In this case, neat acetone is fed to the Siralox 30 fixed bed under 75 bar pressure, resulting in mesitylene, mesityl oxide, isophorone, and condensed compounds. In this process, separation of products is easier than usual since there is no inert solvent present to extract. Dense-phase acetone promotes mass transfer between the fluid phase and solid catalyst surface, while the continuous flow limits secondary reactions of bulky compounds. This process makes sense only if pores within the catalyst structure are sufficiently open for leaving the reaction zone to occur prior to the secondary condensation.

The process setup illustrated in Figure 1 cannot be considered simply as reactor design. On the contrary, the picture represents the idea of selectivity where low conversion, product extraction, and mesoporous transport are considered as complementary factors. Under selected conditions of 260 °C and $W/F = 12.5$ g_{cat} h mol^{-1}, mesitylene production rate amounts to 10.1% yield and catalyst stays active for more than 50 hours. Nevertheless, the chosen conditions are not those of

maximum conversion. They correspond to those at which the reaction network is pushed far enough for mesitylene formation, but not too far for secondary oligomerization to become the preferred channel. This point is key to the understanding of the temperature and time-on-stream results.

Temperature determines the balance between acetone conversion and aromatic selectivity

Temperature greatly influences the degree of acetone conversion but not necessarily its mesitylene selectivity at the corresponding maximum. Acetone conversion over Siralox 30 at 75 bar increases from about 17% at 200 °C to about 63% at 300 °C. Selectivity towards mesitylene behaves differently. The value starts at about 11% at 200 °C, then grows to reach a maximum value of about 38% at 260 °C before decreasing at higher temperatures. Selectivity towards mesityl oxide, on the other hand, shows an opposite trend and decreases from about 29% at 200 °C to about 3% at 300 °C. This opposing behavior suggests that mesityl oxide is a central intermediate whose accumulation declines as the downstream aromatization pathway becomes more active.

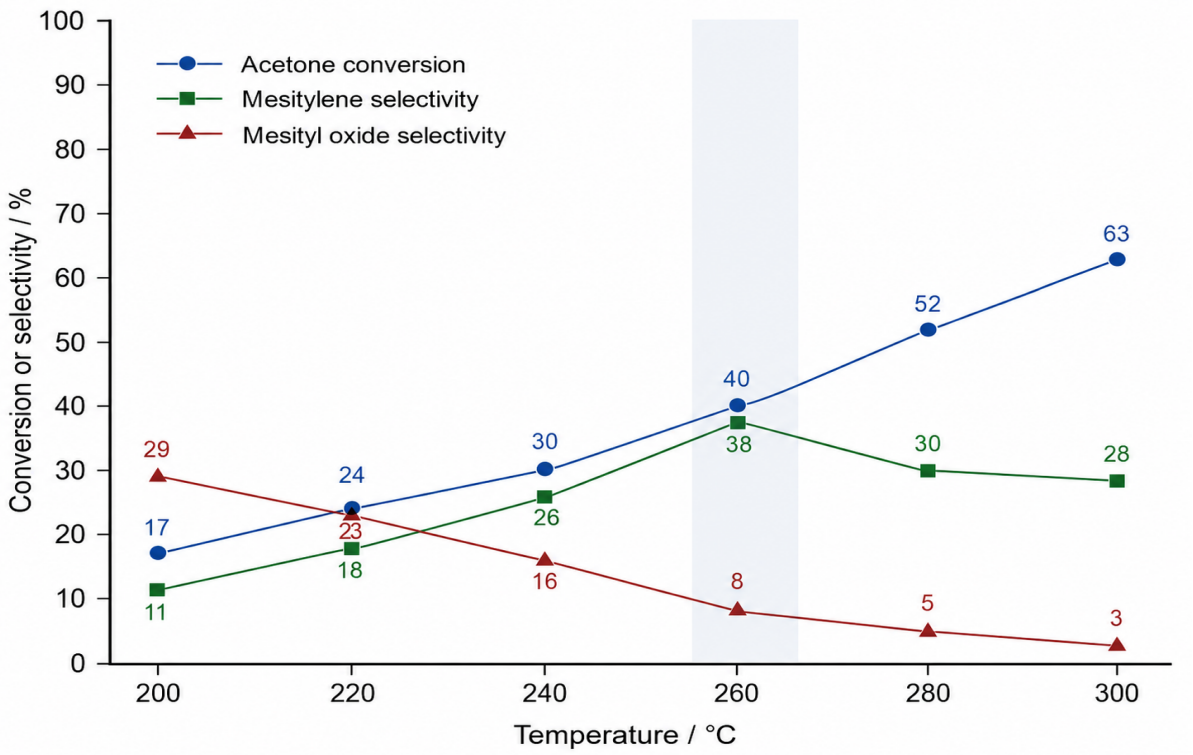


Figure 4: Temperature-dependent conversion and selectivity.

It is evident from the curve depicted in Figure 4, that the activation of acetone and selective formation of mesitylene have different requirements regarding the severity level. The relatively low temperature is inadequate for achieving an efficient conversion of the dimeric mixture into an aromatic product, hence mesityl oxide dominates. Near 260 °C, a catalyst acquires the ability to consume mesityl oxide and make mesitylene the major output compound. Beyond 260 °C, the conversion increases further while selectivity goes towards the direction of non-detected or even more heavyweight products. The product selectivity value at 260 °C is around 66% whereas carbon balance is estimated as being equal to 91% for acetone-to-mesitylene conversion. Hence, it could be concluded that increasing the temperature enhances both selective and non-selective reactions. Therefore, the effective operation condition corresponds to the one when selective reactions become fast enough without making heavier products dominate.

The temperature response can be conveniently interpreted using the concept of dividing the reaction into three severity domains. At low temperatures, the catalyst demonstrates a sufficient activity to produce dimers. Yet, the catalyst lacks sufficient capacity for producing aromatics due to its inability to efficiently convert dimers into mesitylene. In the intermediate range, the C_6 pool is produced with such rapidity, that increases the aromatic selectivity. The production of strongly retained heavy products is insignificant at these conditions. High temperature allows for an efficient conversion of acetone; however, it becomes less selective. Thus, the mesitylene selectivity maxima at around 260 °C corresponds to a point of intersection of these domains. It cannot be regarded as a thermodynamically determined maximum applicable to all catalysts; rather it represents a specific point determined for Siralox 30 by means of acid strength, acid site density, dense-phase feedstock, and mesoporous transport characteristics.

This behavior was also observed in the condensation of acetone previously, wherein the product distribution was dependent on whether the acidic environment promoted the formation of dimers, cyclic trimers, aromatics, or heavier oligomers [35]. Elementary-step analysis of acetone condensation over aluminosilicates explains why acid-site configuration affects this distribution [17]. One-pot mesitylene synthesis further shows that acid and base functions can shift the network among competing products [18]. It is thus not surprising that the strength of acidity alone is not sufficient. Acidity may promote dehydration and cyclization reactions, yet it may also promote subsequent condensation of dimers and aromatics. Therefore, the optimal temperature is more a point of network selectivity where the rate of productive aromatization exceeds carbon growth, rather than merely kinetic acceleration. The interpretation is significant for the scaling of the process, as it implies that one should not run the reaction until complete conversion of acetone is reached.

Contact time controls intermediate residence and secondary condensation

A plot of contact time for mesitylene formation at 260 °C yields the corresponding residence-time optimum to the temperature optimum. An increase of the W/F ratio results in higher values of acetone conversion and mesitylene yield because there is more time for the dimers formed from acetone to be subjected to condensation, cyclization, dehydration, and aromatic stabilization steps in the catalyst bed. Mesitylene yield achieves a value of around 10.1% when $W/F = 12.5$ g_{cat} h mol^{-1}, which corresponds to a WHSV of 4.66 h^{-1}. Further increases of W/F did not lead to an appreciable increase in mesitylene yield even though the acetone conversion increased.

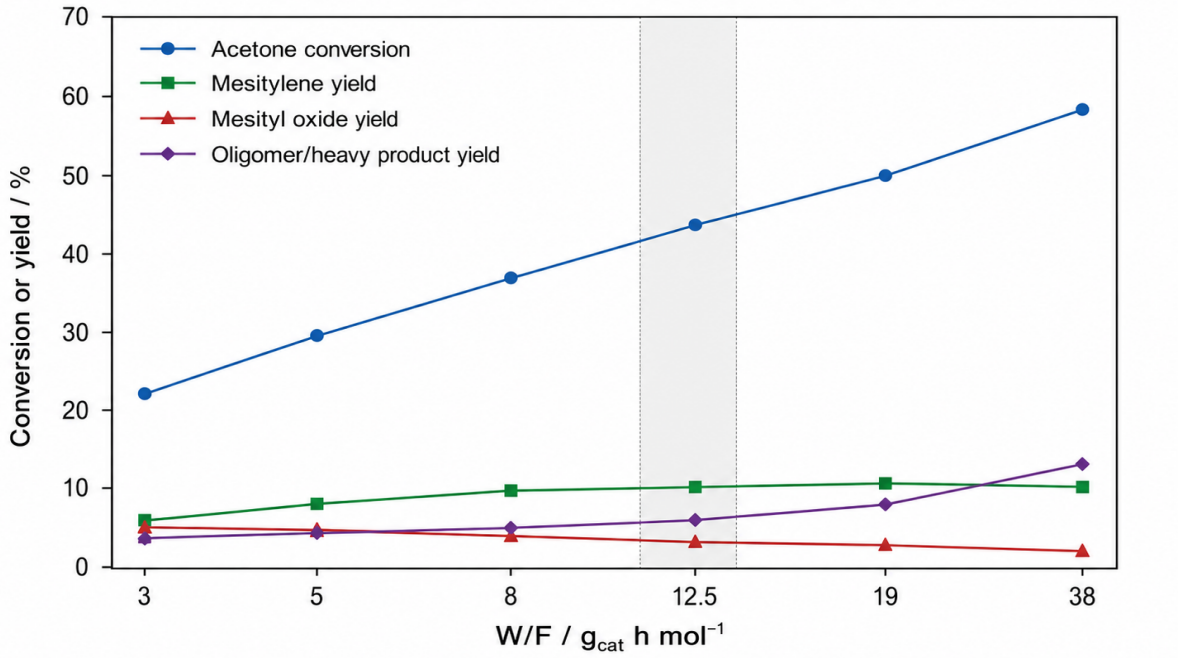


Figure 5: Contact-time response at 260 °C.

It becomes evident from the results presented in Figure 5 that contact time plays an important role in regulating both conversion and intermediate retention. For low contact times, acetone conversion remains low, and the formation of dimers does not result in sufficient upgrading of dimers to mesitylene. Excessive contact time ensures that dimers and aromatics have longer exposure to active sites, and consequently there is a higher chance of their participation in oligomerization or deposition reactions. It means that increased oligomerization and/or heavy hydrocarbon production under conditions of elevated values of W/F is not an accidental outcome but a necessary one resulting from a series of consecutive reactions. A selective process should avoid forcing single-pass conversion to the highest possible value when recycle of acetone and mesityl oxide can preserve carbon utilization with lower deactivation risk.

Table 2: Residence-time interpretation for Siralox 30 at 260 °C.

Contact-time region	Acetone behavior	Mesitylene behavior	Dominant effect
Low W/F	Incomplete conversion	Low yield	Dimer pool not fully converted
Near 12.5 g_{cat} h mol^{-1}	Moderate conversion	Useful maximum yield	Aromatization dominates
High W/F	Higher conversion	No clear gain	Secondary condensation increases

Residence time interpretation in Table 2 provides guidance in design of the continuous process. Too low W/F values are not desirable since the amount of feed conversion and the C_6 intermediates pool is still small. Too high W/F value are also undesirable since further conversion does not result in improved selectivity toward the target product yield. Intermediate W/F values correspond to sufficient residence time in order to allow the dimeric pool to pass through the aromatic pathway without significant mesitylene and dimers oligomerization. This approach confirms that the intermediate mesityl oxide should be considered as a recoverable intermediate rather than just a by-product. Mesityl oxide should be viewed as a feed stock intermediate, which can return into the reactor under conditions promoting its aromatic conversion over oligomerization.

Continuous operation at steady state for over 50 hours demonstrates long-term stability of the optimum

Operation in continuous mode with Siralox 30 at 260 °C, 75 bar, and $W/F = 12.5$ g_{cat} h mol^{-1} demonstrates the stability of the process for more than 50 hours. Acetone conversion remains in 40-45%, while mesitylene yield varies between 10-11%. There are no tendencies towards decrease in performance during the run. The particular significance of this result is associated with neat acetone feedstock used as the substrate for continuous conversion. The catalyst is thus operated under exposure to a high concentration of highly reactive oxygenate and continuously formed aromatics/oligomers.

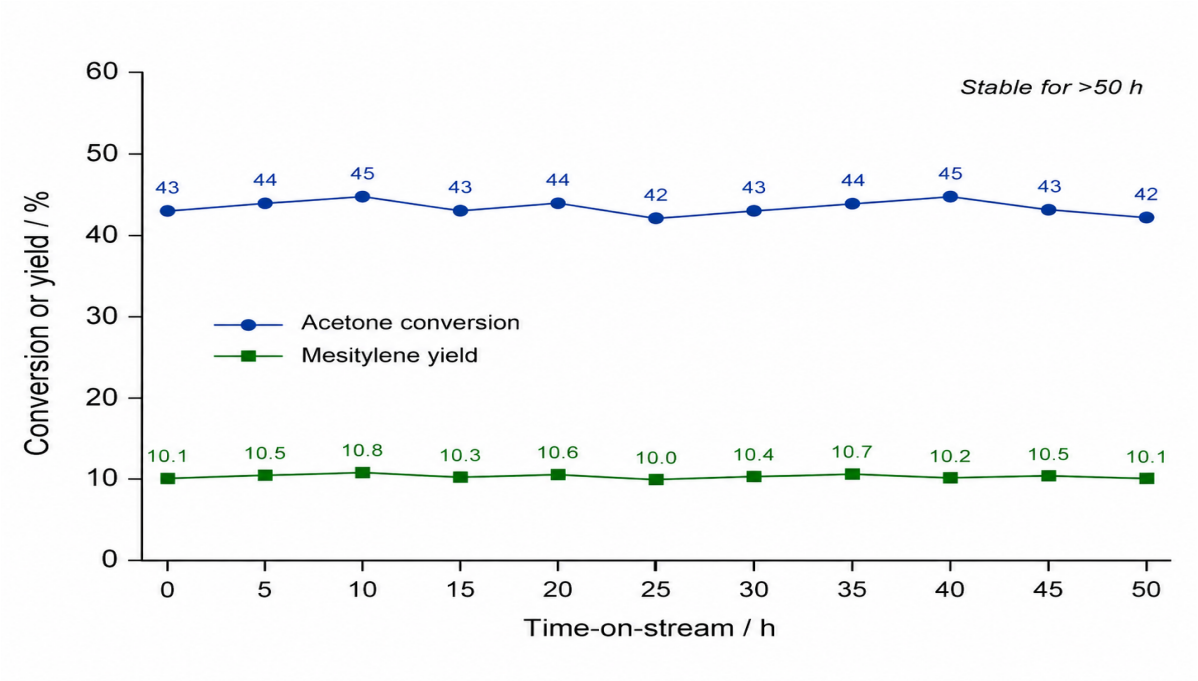


Figure 6: Stable operation over Siralox 30.

Figure 6 gives stability information relating to the operating window derived from kinetic results. The preservation of mesoporous surface area would be hard to achieve if active sites deactivated rapidly, or if deposits were created inside the transport pathway. The flat curve in Figure 6 indicates that the catalyst's operation remains stable despite being at full utilization. Brønsted acidity content on Siralox 30 catalyst is adequate for aromatization of C9 alkylbenzene. The catalyst does not exhibit extremely high density of acid sites and restricted microporosity. Hence, the products have enough opportunity to exit the active site before they react further to create non-mobile species. Therefore, there is no danger that the high initial catalyst's activity will lead to rapid deactivation due to inaccessible acid sites.

This time-on-stream test shows that the operating point chosen for this experiment has sufficient tolerance to variation of conversion levels in practical situations. Even though conversions differ slightly during the experiment, the mesitylene yield stays almost constant. This is important because it shows that even a small fluctuation in reactor's conditions does not instantly affect the catalyst's performance in a negative way. The reason for that could be that real processes in industry hardly ever follow theoretical ideal models where the severity of a process remains constant throughout the entire time. Local temperature distribution, flow variations, and gradual change in adsorbed species' concentrations could all influence the severity in different ways.The constant profile demonstrates that the mesoporous surface of Siralox 30 offers some tolerance during operation in the sense that products can leave the region before a sequence favoring deposition is realized.

This stability observation further explains the utility of mesoporosity. Mesoporosity is often viewed as a passive transport characteristic, but here it is a requirement of selectivity and durability. The target molecule and side products are all more bulky than the feedstock, which means that if they develop within narrow pores, the likelihood of retention is greater and the

chances of additional reactions is greater. If the target species or other intermediates develop within a mesopore structure, then their retention at active centers is minimized due to reduced residence times. The fact that Siralox 30 exhibits stable behavior is a result of this pore size-acid strength-product mobility-deposition combination, which is consistent with findings from deactivation studies [19].

Homologous ketone transformation experiments test tolerance to larger products

Transformation of 2-butanone in the optimal acetone-aromatization process is helpful in determining if the Siralox 30 pores are capable of working with larger methyl ketones and their larger condensation products. While undergoing the transformation of 2-butanone, the Siralox 30 catalyst maintains its stability for over 40 hours. In terms of aromatic products, triethyl benzene isomers are obtained in around 5% yield, whereas the dimers constitute around 8% of the total products. The total product selectivity for dimers, aromatics, and trimers is found to be around 48%, with the carbon balance of 80%. Low amounts of propionic acid are detected as a side product.

Table 3: Performance indicators for homologous ketone conversion over Siralox 30.

Descriptor	Observed behavior
Feed molecule	2-butanone
Operating basis	Optimized acetone-aromatization condition
Dominant products	Dimeric products, approximately 8% yield
Aromatic products	Triethylbenzene isomers, approximately 5% yield
Total product selectivity	Approximately 48% for dimers, aromatics, and trimers
Carbon balance	Approximately 80%
Stability	More than 40 h on stream without severe deactivation
Minor side product	Propionic acid

The results given in Table 3 indicate that the catalyst works effectively on a larger ketone molecule under conditions different from the previous case. In fact, the reduced yield of aromatic molecules is explained by increased chemical resistance due to the presence of an alkyl group that is longer. Steric effects cause many isomers, making ring formation even more complicated. A much more critical conclusion from the study is that catalysts can function under the influence of bulkier C_8-C_{12} condensation products. Stability under such conditions confirms that the principle of open mesoporosity can be extended to the chemistry of aromatics synthesized from ketones. It is worth noting that the study does not provide complete proof for other ketone types; however, this material principle can be extended to them.

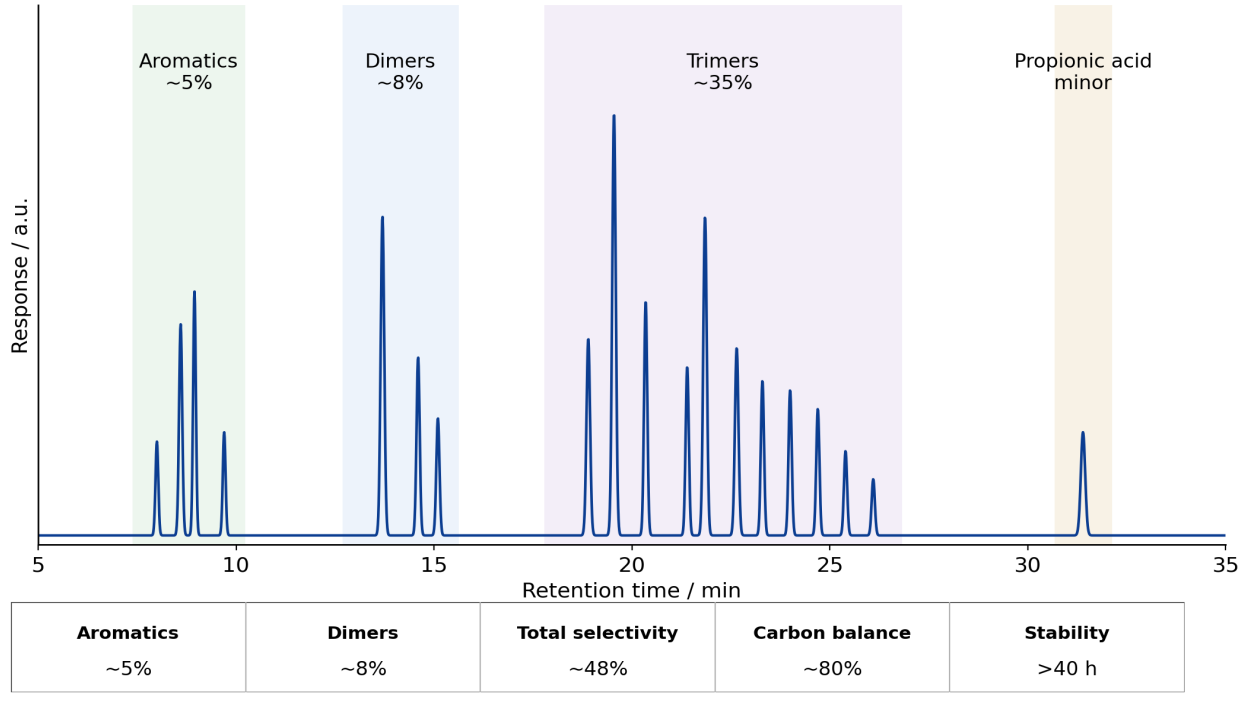


Figure 7: Homologous ketone conversion over Siralox 30.

The reason why it is still useful to conduct this homologous-feed study despite the lower aromatic yield relative to acetone can be seen from the product distribution in Figure 7. The product distribution consists mostly of dimers and trimers, whereas the triethylbenzene isomers have been obtained with an approximate yield of 5%. The stability observed beyond 40 h suggests that the mesoporous acid site is sufficiently large to accommodate bulky products of the ketones without losing accessibility.

Silica level determines acid activity and selectivity

The silica level is the main compositional parameter in the silica-alumina series of amorphous catalysts. The use of pure silica or alumina would be a poor choice in catalyzing the production of mesitylene. Aluminosilicates with a high content of alumina have a higher Lewis or amphoteric nature that is able to facilitate the initial condensation reaction leading to mesityl oxide or other dimers.

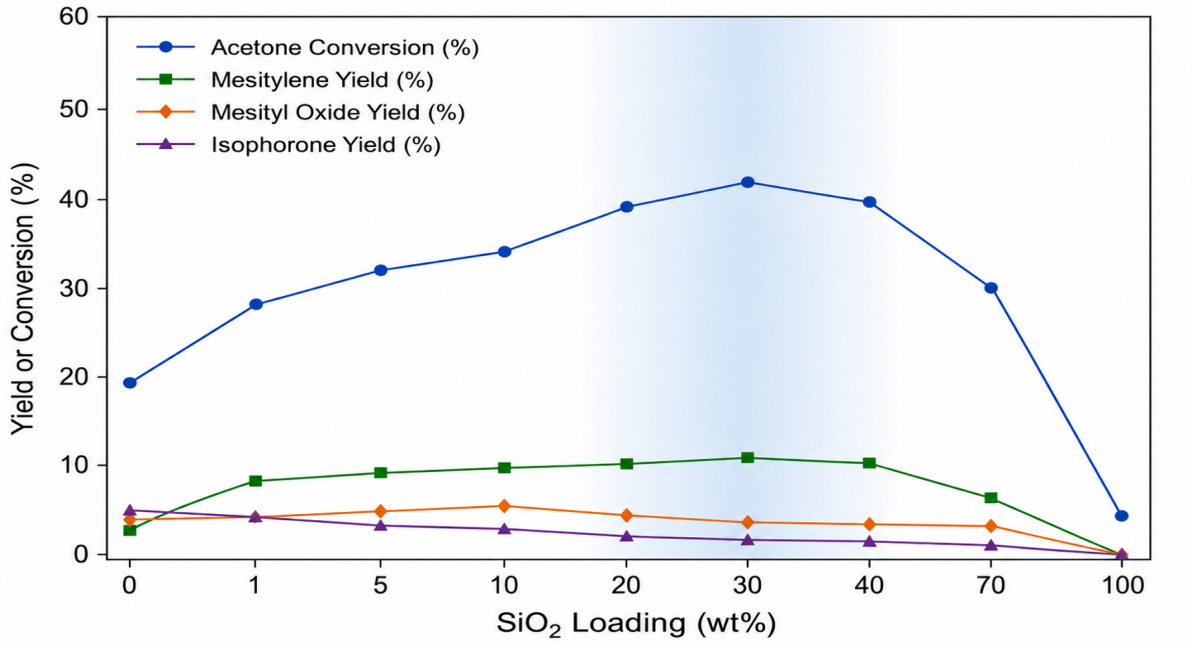


Figure 8: SiO_2 loading and mesitylene formation.

The presence of a higher amount of silica leads to the dilution or weakening of acid sites, which can help to maintain the activity of acetone. Mesitylene activity is highest in samples containing from 20 to 40 wt.% of SiO_2; Siralox 30 falls into this range. This behavior shows that the catalyst must not simply maximize silica content, total acidity, or surface area. It must place the right acid functions in a pore network that remains accessible.

The composition dependence illustrated by Figure 8 clearly shows that silica content is not simply a diluent parameter. Silica incorporation in the alumina catalysts enhances the conversion of acetone and mesitylene yields considerably, whereas excess silica leads to deteriorated catalytic performance. The total amount of acid-sites increases from 0.21 mmol NH_3 g^{-1} for γ-alumina to 0.49 mmol NH_3 g^{-1} upon 1 wt% silica doping; however, further silica addition lowers the number of acid-sites and results in their minimum value of 0.065 mmol NH_3 g^{-1} for Siralox 70. Siralox 30 shows the best performance for mesitylene despite having the smallest total number of acid-sites. Correlation between mesitylene yield and the Brønsted-acid strength descriptor, obtained from CO adsorption experiment, gives $R^2 \approx 0.78$, suggesting that both acid strength and acid identity have more predictive power than NH_3 uptake.

As can be seen from the above discussion, the above composition trends are supported by spectroscopic characterization of silica-aluminas. Acidity of these materials originates from a heterogeneous collection of sites with involvement of silanol groups, aluminum cations, as well as interfacial Si-O-Al groups [23] unlike a uniform distribution of one kind of sites. Acidity characterization of amorphous silica-alumina confirms that such sites vary in strength and adsorption properties [24]. Atomic-scale NMR work further supports the presence of specific Brønsted acid environments [26]. The network of reactions profits from this heterogeneity only in a certain range of compositions. Excess amounts of alumina favor the condensation and ring trimerization reactions while lacking Brønsted acid sites required for aromatization. On the other hand, excess amount of silica decreases the number of acid sites needed to maintain catalytic turnovers. Intermediate SiO_2 content provides the most favorable balance between Lewis-assisted dimer formation and Brønsted-assisted dehydration, cyclization, and aromatization.

Table 4: Composition-performance interpretation for the silica-alumina series.

Composition region	Dominant catalytic feature	Consequence for acetone aromatization
Alumina-rich surface	Greater Lewis or amphoteric contribution	Initial condensation is favored but mesitylene selectivity remains limited
20-40 wt% SiO_2	Balanced Brønsted-Lewis acid function with open mesoporosity	Mesitylene formation and catalyst stability are optimized
Silica-rich surface	Low total active-site population	Acetone conversion and aromatic yield decrease

A closer examination of the data in Table 4 gives us more valuable information on the design rules of the catalysts. Specifically, the most active catalyst does not have any extreme characteristics – it is an intermediate material and not an end-member in terms of acidity. The significance of the finding is that catalyst development is frequently associated with stronger acids and bigger surfaces. Yet, in acetone aromatization, it is not sufficient. For one, the catalyst has to create mesityl oxide at a reasonably fast rate. At the same time, it must also drive mesityl oxide towards mesitylene formation. On top of that, there must not be a lot of heavy species formed either from mesityl oxide or from mesitylene. Finally, the catalyst has to allow enough open pores for mesityl oxide to leave the porous system. In this sense, Siralox 30 is superior because it exhibits the needed chemical functionality in mesoporous networks.

Network of reactions and selectivity hierarchy

The data obtained suggest a consecutive competitive reaction network. Acetone first forms a dimeric pool consisting of mesityl oxide. Then, it becomes productive for mesitylene formation via additional reaction with acetone, dehydration, cyclization, and aromatization. The formation of isophorone is also part of this process; however, its role is to show that the catalyst can form C_9 structures although it does not proceed with them. Heavy compounds and deposits can be formed only when dimers or mesitylenes are further subjected to severe conditions.

The apparent rates of reactions are as follows: $r_1 = k_1 C_A^2$ (dimer), $r_2 = k_2 C_A C_D$ (productive mesitylene), $r_3 = k_3 C_A^3$ (trimer), $r_4 = k_4 C_A C_D$ (heavy products), and $r_5 = k_5 C_M$ (secondary reactions with mesitylene). These equations do not need to define the microkinetics of the process but show which selectivity hierarchy is desirable. One should look for the catalysts that provide a regime in which r_2 is significant enough to destroy the intermediate pool, while r_4 and r_5 are insignificant enough.

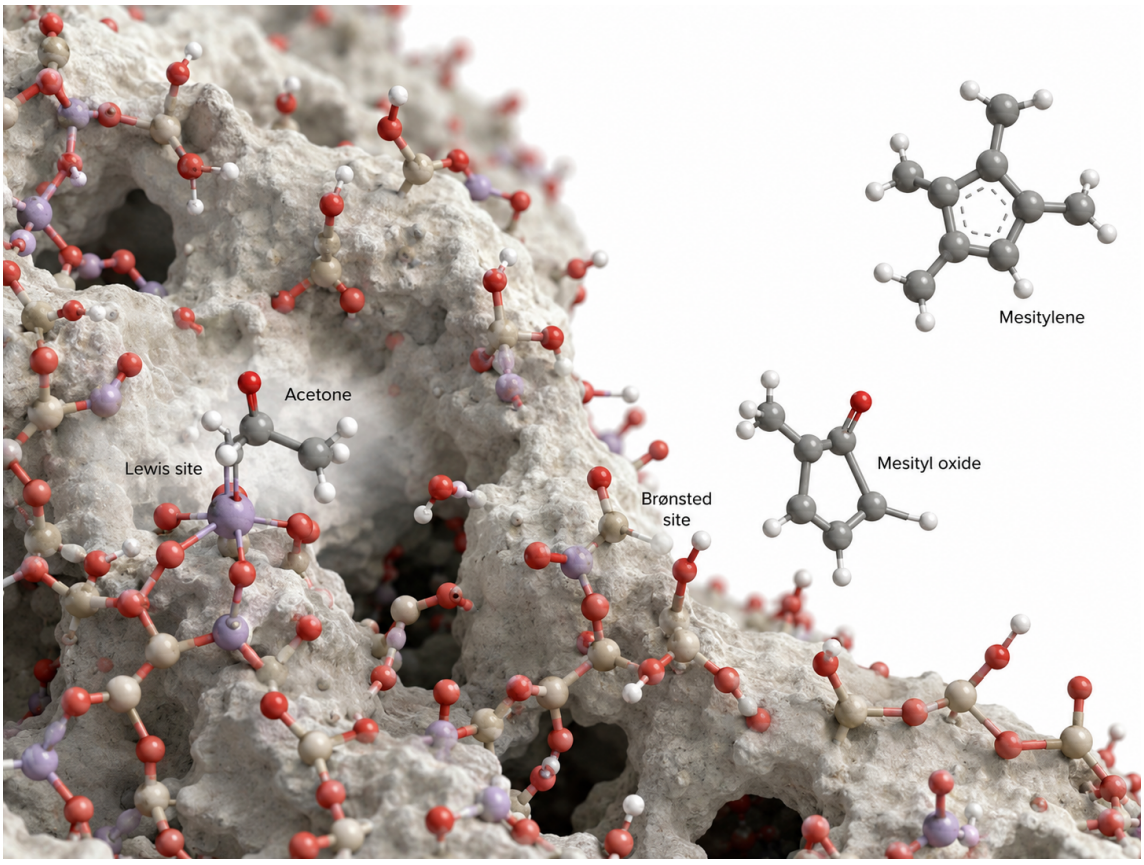


Figure 9: Local acid environments on Siralox 30.

This hierarchy is responsible for the observation that mesitylene selectivity could be decreased despite rising acetone conversion rates. It is also responsible for the effect of rising conversion at the extended residence times and unchanged target yield. Thus, the network analysis suggests that isophorone and heavy compounds should not be considered side-products. Isophorone shows the ability to form C_9 structures. Heavy compounds imply that the same acid functionalities continue to participate in the process even though they were no longer needed for further progress.

The best catalyst is not one that stops all the undesired reactions at the very beginning but that allows the intermediate pool to be directed towards mesitylene formation faster than the latter is converted into heavy and strongly adsorbed substances. Aluminosilicate acetone-condensation studies show that product selectivity depends heavily on the configuration of acid sites and pores [17]. One-pot conversion studies with acid and basic catalysts confirm that mesitylene selectivity depends on directing the competing reaction network rather than maximizing acetone conversion alone [18].

Accordingly, the acid site functionality is clear from the above network. Mesityl oxide formation is supported by Lewis and alumina-associated acid sites. Brønsted acid sites provide dehydration, cyclization, and aromaticity stabilization. Over-strength, long residence time, or limited diffusion may cause condensation of intermediates and products. In this regard, the design constraint arises: the acid functionality must be powerful enough for aromatization but not trapped in a structure prone to excessive condensation. That is why Siralox 30 outperforms other materials not only by acidity but by the combination of all the three features.

Explanation of the surface structure shown in Figure 9 gives molecular level explanation of catalyst performance. The first reaction is acetone activation, which involves coordination of the molecule to the carbonyl group via Lewis acid functionality. Mesityl oxide activation necessitates involvement of Brønsted acid functionality in dehydrogenation and aromatization processes. Desorption and transport of mesitylene are as crucial as acidity, as the final aromatic species need to be transformed to heavier products.

The molecular family in Figure 10 makes the competition among product routes evident. Mesityl oxide is in the central position since it can go toward mesitylene or produce heavier products under too harsh conditions. Isophorone stands for C_9 cyclic routes competing with aromatic routes, whereas the heavy product section makes it necessary to control temperature and time of contact despite further increasing acetone conversion.

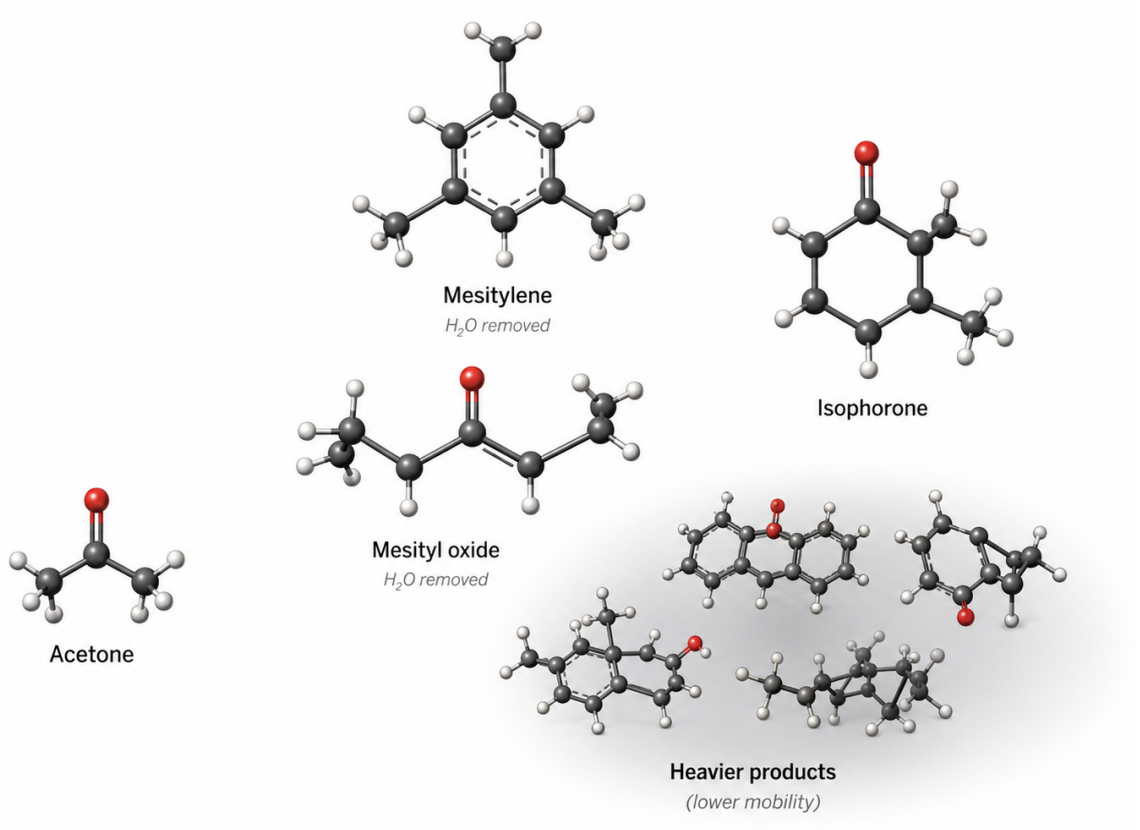


Figure 10: Acetone-derived product family.

Recycle of acetone and mesityl oxide in continuous mode

The absence of solvent in the system offers separation feasibility without the need to recover any added solvent. Differences in volatility of acetone, mesityl oxide, mesitylene, isophorone, and heavy products enable the separation scheme where acetone gets recycled back to the reactor, mesityl oxide serves as an intermediate recycle stream, mesitylene is distilled off as

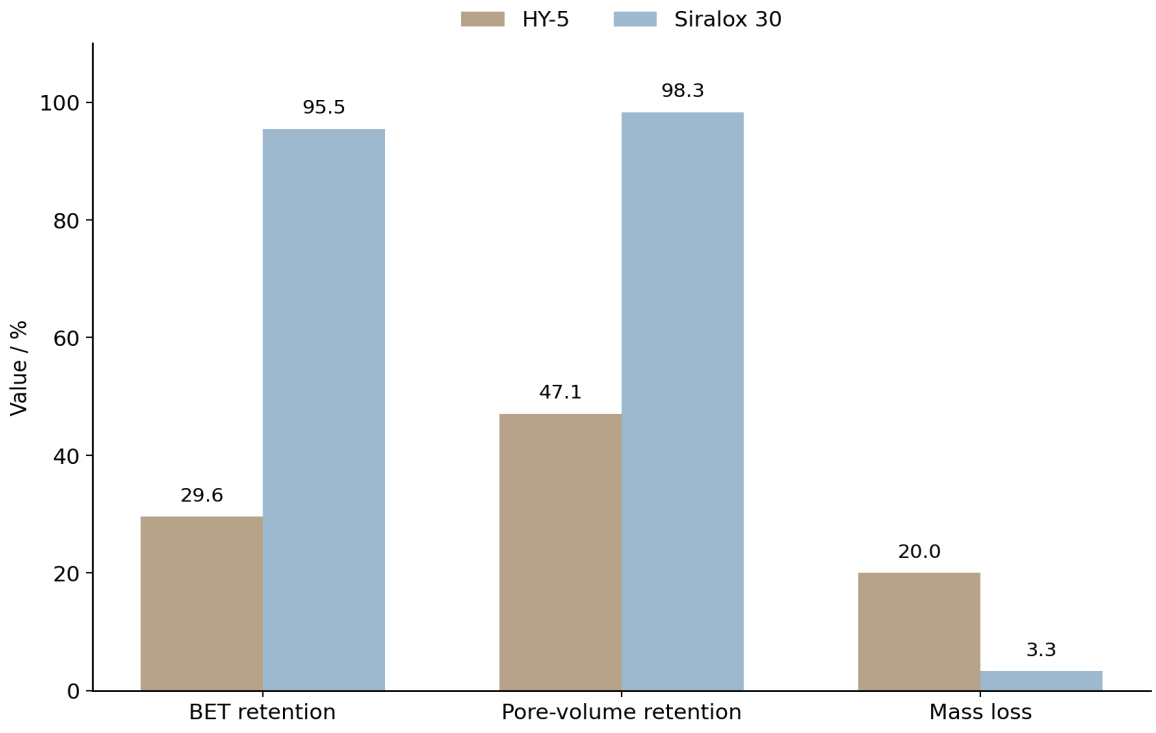
the desired aromatic stream, and heavy products get removed from the system. The separation strategy can be understood through the product family analysis. Acetone recycling maximizes carbon efficiency without the need for extremely high single-pass conversion. Mesityl oxide recycling plays an essential role because mesityl oxide itself does not belong to waste products; rather, it belongs to mesitylene precursor pool.

The recycle logic alters the criteria according to which the yield of mesitylene should be assessed. Yield of 10.1% seems relatively low when viewed merely as the single-pass batch conversion result, but it acquires a different dimension in the continuous case, where unreacted acetone and mesityl oxide can be recycled back to the reactor. What counts is now not how high the conversion can be pushed per pass, but rather the robustness of the selective window and the capacity to maintain carbon atoms within recyclable/recoverable streams. It follows that a catalyst with relatively high stability of pore access that allows obtaining a stable distribution of intermediates can be advantageous compared to an aggressive catalyst that provides higher one-pass conversion, accelerating, however, the generation of heavy products. In catalytic processing, it is well known that a balance between conversion, selectivity, separation effort, and catalyst longevity determines the best operating point in terms of productivity rather than a maximum of a single parameter.

The process approach relieves pressure on deactivation management too. An attempt to push single-pass conversion up through temperature increase or contact time leads to the accumulation of condensable heavy products. In a continuous process with recycle, it is possible to maintain conversion at an appropriate level within the selectivity window, allowing acetone and mesityl oxide to enter the reactor anew. The prolonged stability of performance demonstrated by Siralox 30 for over 50 hours suggests that this is possible as far as catalysts are concerned, if separation of mesitylene and heavy products is efficient enough. In this way, an important process consideration is the integration of catalyst and separation technologies. While catalysts generating high conversion rates and unstable pore accessibility would impose significant downstream burden, those producing moderate conversion with stable selectivity and recyclable intermediates can be highly valuable for continuous renewable aromatic production.

Retained accessibility in durable ketone-to-aromatic catalysis

From the results obtained, it appears that the underlying principle of catalysis based on retained pore accessibility is applicable. HY-5 catalyst has a large surface area and abundant acidic sites in the fresh state, but its microporous structure can be blocked by bulky condensable products. Siralox 30 catalyst is characterized by a lower initial surface area and relatively moderate acidity, but retains mesopore access even under conditions of long-term reaction. The performance difference is therefore not a contradiction of acid catalysis; only accessible acid sites participate in sustained turnover. Fresh acidity can initiate conversion, but retained accessibility controls durability.



Siralox 30 preserves accessible texture while HY-5 shows high deposit-associated loss.

Figure 11: Retained accessibility controls durability.

The retention information in Figure 11 provides a concise representation of the spent catalyst data through three numbers. The BET area of Siralox 30 is retained at around 95%, and the pore volume is retained at about 98%. However, in HY-5, these numbers are retained at 30% and 47%, respectively. This inverse relationship regarding the mass lost is another indication that the difference in performance has nothing to do with the initial catalytic activity.

Table 5: Catalyst-design implications for acetone aromatization.

Design variable	Required function in the reaction network
Brønsted acid strength	Promotes dehydration, cyclization, and aromatic formation from the dimer pool
Lewis acid contribution	Assists initial acetone condensation to mesityl oxide and related C_6 species
Mesopore accessibility	Allows mesitylene, isophorone, and oligomeric products to leave before further condensation
Moderate acid-site density	Limits the rate of deposit-forming secondary reactions
Recycle-compatible selectivity	Supports moderate single-pass conversion with acetone and mesityl oxide return

The design implications stated in Table 5 outline the features required for efficient, stable acetone aromatization reactions. Hierarchical silica-alumina catalyst structures, designed mesoporous solids with control of internal tortuosity, and intentionally structured catalyst systems with tunable Brønsted-Lewis distributions would have to be assessed on the extent of retained surface acidity in steady-state conditions rather than merely on NH_3 uptakes or fresh surface areas. Maximizing mesitylene production without compromising access to active catalytic sites would imply promoting mesityl oxide aromatization preferentially to the dimeric route to heavier products.

Conclusions

Solvent-free stable acetone aromatization reactions rely upon maintaining the acid-surface availability under operational conditions, rather than simply on fresh acidity or surface area. While HY-5 starts with higher fresh surface area and acid-site content than Siralox 30, its micropore surface area decreases significantly as it becomes heavily loaded with deposits after acetone conversion, reaching a total mass accumulation of 20 wt%. Siralox 30 exhibits lower surface area but also lower acidity and retains essentially 100% of mesoporous surface and pores, showing only a mass loss of 3.3%. Therefore, acetone aromatization reaction selectivity depends upon acid-site accessibility.

The optimum operating condition in the reactor is not necessarily the one of highest acetone conversion rate. The conditions of 260 °C, 75 bar pressure, and $W/F = 12.5$ g_{cat}h mol^{-1} provide for 10.1% mesitylene yield and no signs of instability even after more than 50 hours on stream. An increase in temperature or excessive contact time raises the consumption of acetone, resulting in greater production of heavy or even undetectable products. Mesityl oxide should undergo fast transformation to mesitylene and never be left on the acid site long enough to participate in forming heavy compounds. Hence, mesitylene formation should occur faster from the dimeric pool than heavy product formation from dimeric and mesitylene intermediates.

It was shown from the silica-loading series that the optimal silica-alumina catalyst composition lies in between the extremes. With no silica added, the mesitylene yield is low, while a higher proportion of silica leads to catalyst inactivity. The mesitylene peak in the range of 20 to 40 wt% of SiO_2 corresponds to the largest mesitylene yield. Maximum mesitylene selectivity was found with 30 wt% of SiO_2. This composition provides the optimal combination of Lewis-accelerated condensation, Brønsted-mediated dehydration and aromatization, and mesopore-based product transport. The stable conversion of 2-butanone at high yields for more than 40 hours further confirms the importance of mesoporosity in the formation of larger ketonic products.

In a practical acetone-to-mesitylene industrial process, the catalyst operation should take place in the selective window rather than at maximum severity. Acetone can be easily recycled into the reactor, mesityl oxide is an easily recoverable intermediate product for reuse, and mesitylene should be separated from the product stream immediately after reaction completion to prevent heavy product formation. It is thus clear that an ideal acetone-to-mesitylene process should include a system based on durable and acid-active catalyst that would produce mesitylene selectively. A good example of such a system is the series with the best selectivity, Siralox 30.

Conflict of interest

The author declares no conflict of interest.

References

[1] Rahimpour, M. R., Jafari, M., & Iranshahi, D. (2013). Progress in catalytic naphtha reforming process: A review. Applied energy, 109, 79-93.
[2] Corma, A., Iborra, S., & Velty, A. (2007). Chemical routes for the transformation of biomass into chemicals. Chemical reviews, 107(6), 2411-2502.
[3] Chheda, J. N., Huber, G. W., & Dumesic, J. A. (2007). Liquid-phase catalytic processing of biomass-derived oxygenated hydrocarbons to fuels and chemicals. Angewandte Chemie International Edition, 46(38), 7164-7183.
[4] Climent, M. J., Corma, A., & Iborra, S. (2014). Conversion of biomass platform molecules into fuel additives and liquid hydrocarbon fuels. Green Chemistry, 16(2), 516-547.
[5] Sherwood, J. (2020). The significance of biomass in a circular economy. Bioresource technology, 300, 122755.
[6] Carlson, T. R., Tompsett, G. A., Conner, W. C., & Huber, G. W. (2009). Aromatic production from catalytic fast pyrolysis of biomass-derived feedstocks. Topics in Catalysis, 52(3), 241-252.
[7] Cheng, Y. T., & Huber, G. W. (2012). Production of targeted aromatics by using Diels–Alder classes of reactions with furans and olefins over ZSM-5. Green Chemistry, 14(11), 3114-3125.
[8] Maneffa, A., Priecel, P., & Lopez-Sanchez, J. A. (2016). Biomass-derived renewable aromatics: selective routes and outlook for p-xylene commercialisation. ChemSusChem, 9(19), 2736-2748.
[9] Benson, T. J., Daggolu, P. R., Hernandez, R. A., Liu, S., & White, M. G. (2013). Catalytic deoxygenation chemistry: Upgrading of liquids derived from biomass processing. In Advances in Catalysis (Vol. 56, pp. 187-353). Academic Press.
[10] Liew, F. E., Nogle, R., Abdalla, T., Rasor, B. J., Canter, C., Jensen, R. O., ... & Köpke, M. (2022). Carbon-negative production of acetone and isopropanol by gas fermentation at industrial pilot scale. Nature biotechnology, 40(3), 335-344.
[11] Sacia, E. R., Balakrishnan, M., Deaner, M. H., Goulas, K. A., Toste, F. D., & Bell, A. T. (2015). Highly selective condensation of biomass-derived methyl ketones as a source of aviation fuel. ChemSusChem, 8(10), 1726-1736.
[12] Reif, P., Rosenthal, H., & Rose, M. (2020). Biomass-derived aromatics by solid acid-catalyzed aldol condensation of alkyl methyl ketones. Advanced Sustainable Systems, 4(10), 1900150.
[13] Herrmann, S., & Iglesia, E. (2018). Selective conversion of acetone to isobutene and acetic acid on aluminosilicates: Kinetic coupling between acid-catalyzed and radical-mediated pathways. Journal of Catalysis, 360, 66-80.
[14] Sardon, H., Irusta, L., & Fernández-Berridi, M. J. (2009). Synthesis of isophorone diisocyanate (IPDI) based waterborne polyurethanes: Comparison between zirconium and tin catalysts in the polymerization process. Progress in organic coatings, 66(3), 291-295.
[15] Paulis, M., Martın, M., Soria, D. B., Dıaz, A., Odriozola, J. A., & Montes, M. (1999). Preparation and characterization of niobium oxide for the catalytic aldol condensation of acetone. Applied Catalysis A: General, 180(1-2), 411-420.
[16] Bej, S. K., & Thompson, L. T. (2004). Acetone condensation over molybdenum nitride and carbide catalysts. Applied Catalysis A: General, 264(2), 141-150.
[17] Herrmann, S., & Iglesia, E. (2017). Elementary steps in acetone condensation reactions catalyzed by aluminosilicates with diverse void structures. Journal of Catalysis, 346, 134-153.
[18] Faba, L., Gancedo, J., Quesada, J., Diaz, E., & Ordonez, S. (2021). One-pot conversion of acetone into mesitylene over combinations of acid and basic catalysts. Acs catalysis, 11(18), 11650-11662.
[19] Guisnet, M., Costa, L., & Ribeiro, F. R. (2009). Prevention of zeolite deactivation by coking. Journal of Molecular Catalysis A: Chemical, 305(1-2), 69-83.
[20] Kubelková, L., Čjka, J., Nováková, J., Boszácek, V., Jirka, I., & Jíaru, P. (1989). Acetone conversion and deactivation of zeolites. In Studies in Surface Science and Catalysis (Vol. 49, pp. 1203-1212). Elsevier.
[21] Quesada, J., Faba, L., Díaz, E., & Ordóñez, S. (2020). Effect of catalyst morphology and hydrogen co-feeding on the acid-catalysed transformation of acetone into mesitylene. Catalysis Science & Technology, 10(5), 1356-1367.
[22] Li, Y., Wang, H., Dong, M., Li, J., Qin, Z., Wang, J., & Fan, W. (2015). Effect of zeolite pore structure on the diffusion and catalytic behaviors in the transalkylation of toluene with 1, 2, 4-trimethylbenzene. RSC advances, 5(81), 66301-66310.
[23] Crépeau, G., Montouillout, V., Vimont, A., Mariey, L., Cseri, T., & Maugé, F. (2006). Nature, structure and strength of the acidic sites of amorphous silica alumina: an IR and NMR study. The Journal of Physical Chemistry B, 110(31), 15172-15185.
[24] Hensen, E. J., Poduval, D. G., Degirmenci, V., Ligthart, D. J. M., Chen, W., Maugé, F., ... & Veen, J. R. V. (2012). Acidity characterization of amorphous silica–alumina. The Journal of Physical Chemistry C, 116(40), 21416-21429.
[25] Mardkhe, M. K., Keyvanloo, K., Bartholomew, C. H., Hecker, W. C., Alam, T. M., & Woodfield, B. F. (2014). Acid site properties of thermally stable, silica-doped alumina as a function of silica/alumina ratio and calcination temperature. Applied Catalysis A: General, 482, 16-23.
[26] Perras, F. A., Wang, Z., Kobayashi, T., Baiker, A., Huang, J., & Pruski, M. (2019). Shedding light on the atomic-scale structure of amorphous silica–alumina and its Brønsted acid sites. Physical Chemistry Chemical Physics, 21(35), 19529-19537.
[27] Gervasini, A., Bellussi, G., Fenyvesi, J., & Auroux, A. (1995). Microcalorimetric and catalytic studies of the acidic character of modified metal oxide surfaces. 1. Doping ions on alumina, magnesia, and silica. The Journal of Physical Chemistry, 99(14), 5117-5125.
[28] Daniell, W., Schubert, U., Glöckler, R., Meyer, A., Noweck, K., & Knözinger, H. (2000). Enhanced surface acidity in mixed alumina–silicas: a low-temperature FTIR study. Applied Catalysis A: General, 196(2), 247-260.
[29] Wang, Z., Jiang, Y., Lafon, O., Trébosc, J., Duk Kim, K., Stampfl, C., ... & Huang, J. (2016). Brønsted acid sites based on penta-coordinated aluminum species. Nature communications, 7(1), 13820.
[30] Nassreddine, S., Casu, S., Zotin, J. L., Geantet, C., & Piccolo, L. (2011). Thiotolerant Ir/SiO 2–Al 2 O 3 bifunctional catalysts: effect of support acidity on tetralin hydroconversion. Catalysis Science & Technology, 1(3), 408-412.
[31] Takaya, H., Todo, N., Hosoya, T., Minegishi, T., Yoneoka, M., & Oshio, H. (1971). Cleaning Effects of the Reactant in the Liquid-phase Isomerization of m-Xylene over a Silica-Alumina Catalyst under Pressure. Bulletin of the Chemical Society of Japan, 44(9), 2296-2301.
[32] Scanlon, J. T., & Willis, D. E. (1985). Calculation of flame ionization detector relative response factors using the effective carbon number concept. Journal of Chromatographic Science, 23(8), 333-340.
[33] Ambrose, D., Sprake, C. H. S., & Townsend, R. (1974). Thermodynamic properties of organic oxygen compounds XXXIII. The vapour pressure of acetone. The Journal of Chemical Thermodynamics, 6(7), 693-700.
[34] Lónyi, F., & Valyon, J. (2001). On the interpretation of the NH3-TPD patterns of H-ZSM-5 and H-mordenite. Microporous and Mesoporous materials, 47(2-3), 293-301.
[35] Panov, A. G., & Fripiat, J. J. (1998). Acetone condensation reaction on acid catalysts. Journal of Catalysis, 178(1), 188-197.