



# The role of water in the reusability of aminated silica catalysts for aldol reactions



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## ABSTRACT

The reusability of methylaminopropyl active sites grafted on mesoporous amorphous silica, either with cooperative silanol groups or trimethylsilylated, was assessed in the aldol reaction of acetone with 4-nitrobenzaldehyde. Raman, <sup>13</sup>C NMR, and UV–Vis spectroscopy demonstrated the presence of stable enamines on the spent catalysts. These enamines are produced as a side product from iminium intermediates in the catalytic cycle. Water co-feeding enhances the desorption of the iminium intermediates and, hence, suppresses the formation of these stable enamine species. The reusability of the cooperative catalyst increased to 70% with co-feeding 0.69 wt% water, while an almost complete reusability was achieved for the trimethylsilylated catalyst. Continuous-flow experimentation showed that the cooperative effect of the silanol groups was lost during the first 7 h on-stream, yet activity losses continued, most likely due to silica hydrolysis. Activity losses persisted on the more hydrophobic trimethylsilylated catalyst, but were significantly less pronounced.

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## 1. Introduction

Aldol reactions constitute an important class of reactions to produce new carbon-carbon bonds in a wide range of processes, such as in the production of chalcones in the pharmaceutical industry [1] and 2-ethylhexanol for PVC plasticizers [2]. A potential novel application in the bio-based industry is the production of liquid fuels from lignocellulosic biomass by upgrading smaller furanic molecules, such as 2-furaldehyde (furfural) and 5-(hydroxymethyl) furfural (HMF), to heavier hydrocarbons [3]. At present, commercial scale aldol reactions are catalyzed by a homogeneous, strong base catalyst, such as NaOH, which permits to perform the reaction even at room temperature [4]. However, these catalysts also exhibit several important disadvantages, such as a short lifetime, an environmental risk, equipment corrosion and an energy intensive separation from the reaction products [5,6]. Hence, the pursuit of a reusable, heterogeneous catalyst could lead to a more sustainable

alternative production route. In this sense, either an acidic or a basic heterogeneous catalyst can be employed.

Heterogeneous acid catalysts, such as the widely employed zeolite-type materials, have already been investigated for liquid-phase aldol reactions [7–9]. However, unlike base catalysts, the Brønsted acid function in zeolites promotes undesired side reactions such as isomerization and cyclodehydration [9]. Moreover, the formation of large condensation products inside the micropores causes rapid pore-blocking and subsequent deactivation [10]. Development of zeolites with larger mesopores reduces the catalyst's susceptibility to coking, but also decreases its acid strength [8]. Hence, acidic zeolite-type materials appear not ideal as reusable, sustainable heterogeneous catalysts for liquid-phase aldol reactions.

Candidate heterogeneous base catalysts for liquid-phase aldol reactions comprise mixed oxide materials such as hydrotalcite based catalysts [11–17], ion-exchange resins [18], and cooperative acid-base silica catalysts [19–37]. The mixed oxide and hydrotalcite materials typically suffer from fast deactivation by strong adsorption of reagents and ambient CO<sub>2</sub> during storage. Complete

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regeneration of its basic character is difficult [14,15]. Additionally, side-reactions such as the Cannizzaro reaction, typically occur to a significant extent on such catalysts [38]. Anion-exchange resins are composed of quaternary ammonium ions interacting with free  $\text{OH}^-$  ions, which are the actual active sites. These catalysts are also subject to deactivation, caused by neutralization of the  $\text{OH}^-$  ions and pore-blocking [39,40]. Aminated mesoporous silica materials, either ordered or amorphous, possess large mesopores and have basic amine sites [41]. Despite a typically lower activity, these materials are less prone to pore-blocking by large condensed products.

The idea for using amines in aldol reaction reactions originates from natural aldolase enzymes, which catalyze aldol reactions via an enamine-type mechanism [42]. List et al. [43] employed the amino acid L-proline as a homogeneous catalyst in the aldol reaction of 4-nitrobenzaldehyde with acetone in dimethylsulfoxide (DMSO). They proposed a cooperative effect between the acidic carboxylate and the basic amine: the acid function promotes the nucleophilic attack of the basic amine on this carbonyl group, and assists in proton-transfers [43]. A heterogeneous amine catalyst can be synthesized by functionalizing aminosilanes on silica [19–35,44]. The weakly acidic silanol groups, which are intrinsically present at the silica surface, act as the cooperative partner in the reaction mechanism, equivalent to the cooperative effect of the carboxyl group in L-proline [28,37]. Secondary amines are preferred, since primary amines allow the formation of a stable inhibiting imine species, and tertiary amines do not allow the formation of the crucial enamine intermediate [22,23]. However, care should be taken that the substituent on the secondary amine is not too large, in order to minimize steric hindrance when approaching the nitrogen lone electron pair [24]. It has been shown that a methyl substituted secondary amine with a propane linker on a mesoporous amorphous silica is an efficient catalyst for the aldol reaction when silanol groups are neighboring the amine [25–27]. Previously it was found that, when the amines are grafted randomly on the surface, at least 1.7 of these silanol groups are required per amine function to assure full promotion [29]. Increasing the acid strength of the promoting acid function has been observed to decrease the catalytic activity [30–33]. This can be explained by an unfavorable shift in the equilibrium of the free acid base couple to the neutralized one [30]. Hence, currently the most active aminated mesoporous amorphous silica catalyst for aldol reactions is a secondary amine, with a small substituent such as a methyl group, promoted by an excess of silanol groups.

Not only the activity, but also the catalyst stability is an important factor to take into account when assessing the commercial potential of a catalyst [45]. This means that a catalyst should exhibit the same level of activity throughout its lifetime. However, due to the nature of a batch reactor, deactivation cannot be observed separately from the normal time-evolution in the course of a single experiment. Hence, recycling of the spent catalyst in a subsequent experiment should be performed. Opposed to a batch-type reactor, a continuous-flow reactor can be used to observe catalyst deactivation directly by measuring the catalytic activity with time-on-stream. This allows for more detailed insights into the specific deactivation behavior and corresponding mechanism. For aldol reactions using homogeneous L-proline, Zovota et al. [46] identified off-cycle species such as oxazolidinones and oxapyrrolizidines, using H-NMR, when insufficient water is present. We have also recently reported that an ethylene-bridged ordered periodic mesoporous organosilica material, functionalized with cysteine, exhibits a lower turnover frequency (TOF) in a recycle experiment [35]. Shylesh et al. [23] have performed gas-phase self-aldol reaction of butanal in a continuous-flow reactor on a cooperative acid-base mesoporous amorphous silica catalyst, but reported no information about catalyst deactivation with time-on-stream. Clearly

no detailed information about the deactivation behavior of aminated silica materials has been reported yet for aldol reactions.

In the present work, our aim is to systematically investigate the phenomena potentially involved in catalyst deactivation in heterogeneous amine catalyzed aldol reactions. Consecutive experiments in a batch-type reactor have been performed as well as time-on-stream experiments in a continuous-flow reactor. Using a variety of characterization techniques combined with mechanistic insights, conditions have been identified whereby the recyclability of the aminated mesoporous amorphous silica catalysts for the aldol reaction approaches 100%.

## 2. Experimental procedures

### 2.1. Synthesis of the cooperative acid-base catalyst and the monofunctional base catalyst

The procedure for grafting secondary amine functional groups on mesoporous amorphous silica, and the endcapping of the silanol groups with trimethylsilyl groups, was reported more elaborately before [24] and is briefly summarized here. Silica gel 60 (grade 7734, Sigma-Aldrich) was used as a catalyst support material. For experiments in the batch reactor, a pellet size range between 63  $\mu\text{m}$  and 210  $\mu\text{m}$  was employed. For the continuous-flow reactor, the pellet size was increased to a range between 250  $\mu\text{m}$  and 500  $\mu\text{m}$  to avoid a significant pressure drop over the catalyst bed. The support material was first heated at a rate of 2  $^\circ\text{C}/\text{min}$  and calcined in air at 700  $^\circ\text{C}$  for 6 h. After calcination, the material was maintained at a temperature of 150  $^\circ\text{C}$  to avoid adsorption of moisture. Next, 5 g of the hot support material was suspended in 30 mL of toluene (Sigma-Aldrich, anhydrous, 99.8%). The amine precursor, N-methylaminopropyltrimethoxysilane (MAPTMS, ABCR), was subsequently added with a molar ratio of precursor to free silanol groups of 0.25. The necessary volume of precursor is calculated assuming that, because of the employed calcination procedure, the number of free silanol groups is equal to 1.1  $\text{OH}/\text{nm}^2$  [21]. To ensure full promotion of each randomly grafted amine site by the silanol groups, at least 1.7 silanol groups are required per amine site [29]. Hence, in this work a ratio of 4 free silanol groups for each methylaminopropyl function was employed. After adding the precursor, the mixture was refluxed for 24 h at 110  $^\circ\text{C}$  under an argon atmosphere. The obtained catalyst was then filtered and subsequently stirred in 250 mL chloroform (>99.8%, <50 ppm  $\text{H}_2\text{O}$ , Carl Roth) for 4 h. After vacuum drying for 24 h at room temperature, the cooperative acid–base catalyst was ready to be used in catalytic experiments. A desiccator was used for storage of the catalysts in order to avoid modifications due to the presence of atmospheric water vapor.

To obtain the monofunctional base catalyst, the silanol groups of the cooperative material were endcapped with trimethylsilyl groups [29,47]. For this, 5 g of the dried cooperative acid-base catalyst was completely covered with 100 mL of 1,1,1,3,3,3-hexamethyltrisilazane (99%, HMDS, ABCR). The mixture was then stirred at room temperature for 4 h, subsequently filtered, and stirred in 250 mL chloroform (>99.8%, <50 ppm  $\text{H}_2\text{O}$ , Roth) for 4 h. After vacuum drying for 24 h at room temperature, the monofunctional base catalyst was ready to be used in catalytic experiments. This catalyst was also stored in a desiccator.

### 2.2. Characterization of the fresh and spent catalysts

Nitrogen adsorption-desorption measurements were carried out at  $-196\text{ }^\circ\text{C}$ , using a Micromeritics Tristar II surface area and porosity analyzer. The specific surface area and pore volume were determined using the Brunauer–Emmett–Teller (BET) method. The

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