



Effects of amine structure and base strength on acid–base cooperative aldol condensation



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ABSTRACT

Aminated silica materials are known to efficiently catalyse aldol condensations, especially when silanol groups are neighbouring the amine function. The effect of the amine structure and base strength has been analysed experimentally and by kinetic modelling using commercially available precursors to graft primary, secondary and tertiary amines on the silica surface. While primary amines are arranged in a clustered manner on the catalyst surface, secondary amines are arranged randomly which results in a higher percentage of promoted amines in the low silanol-to-amine ratio range. An enamine compound formed by the reaction between the amine active site and acetone has been identified as the key intermediate to explain the experimental observations. In the case of a primary amine this enamine intermediate can form an inhibiting imine with which it is in equilibrium. As a secondary amine has only one hydrogen atom bonded to the nitrogen atom, the inhibiting imine cannot be formed, resulting in a comparatively higher concentration of reactive enamines on the catalyst surface. In case of a tertiary amine the formation of the reactive intermediate is impossible due to the absence of any hydrogen atom bonded to the nitrogen atom. The activation entropies of all reaction steps occurring on the amine sites, as obtained by regression, could be correlated to the deprotonation entropies of the amine sites. As the deprotonation enthalpy does not account for steric effects, no such correlation could be found between the activation energies of these reaction steps and the deprotonation enthalpies of the amine sites.

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1. Introduction

There are some inherent disadvantages to homogeneous catalysis such as (i) the necessity of energy intensive separation steps, (ii) a short catalyst life time and (iii) the low reusability, (iv) important waste streams and (v) intensive equipment corrosion [1,2]. Heterogeneous catalysis may help to overcome many of these disadvantages. Therefore, it is important to develop new and optimize existing heterogeneous catalysts that can, potentially, replace homogeneous ones. Since about a decade, so-called high-throughput technologies have emerged in order to speed up catalyst development and optimization. However, the discovery rate may be further enhanced by exploiting more rational feedback obtained by means of kinetic modelling in the catalyst design cycle [3–5].

Aldol condensations are important reactions, typically employed in the pharmaceutical industry and fine chemicals production, to create new C–C bonds and, hence, heavier and more complex molecules [6–9]. A bright future has also already been forecasted for aldol condensation reactions in the transition from a fossil resources based towards a more sustainable society, e.g., in the valorization of glycerol, which is a byproduct in the production of biodiesel, or the conversion of furan compounds such as 2-furaldehyde (furfural) and 5-(hydroxymethyl)furfural (HMF), which are obtained by dehydration of sugars, into hydrocarbon fuels [10–15]. At present aldol condensations are industrially mostly catalysed by strong, homogeneous base catalysts such as KOH, Ca(OH)₂, NaOH or Na₂CO₃. Recent research focuses on hydrotalcite catalysts and other layered double hydroxides [16–21] or functionalized silica materials [22–35] as possible alternatives. Silica materials on which amine containing silanes are grafted by means of a stirring or a reflux procedure have been found to perform well [24–32]. Moreover, many authors agree that the incorporation of weak acid sites, such as silanol groups, next to the

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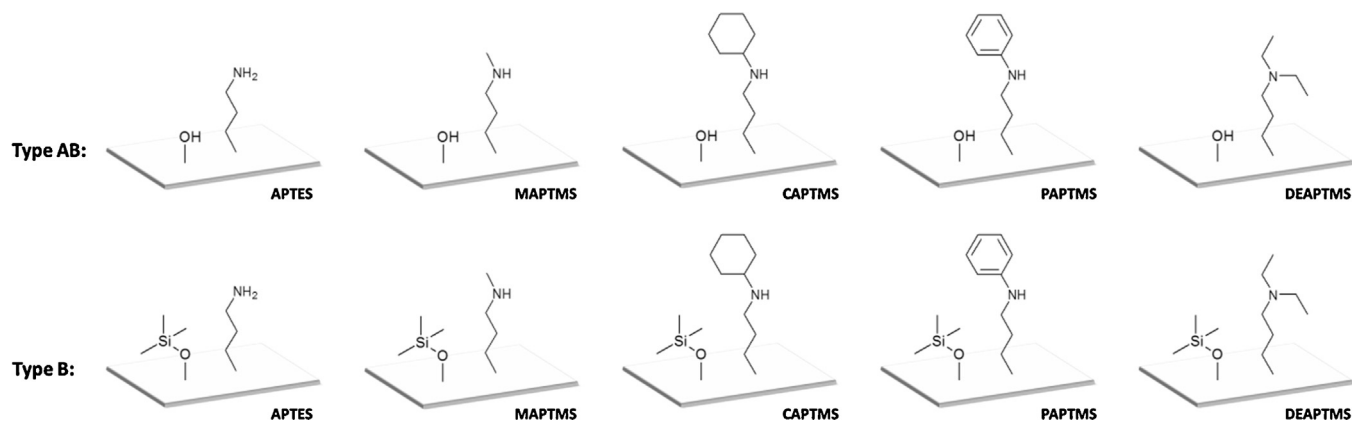


Fig. 1. Representation of the catalyst surfaces.

base amine sites has an enhancing effect on the catalytic activity of these amines in aldol condensations and other important C–C coupling reactions [22–30,33–38]. Recently it has been demonstrated that an increasing acid strength of the promoting site leads to a decreasing activity which could be explained by a pronounced shift in the equilibrium from the free acid and free base towards the resulting neutralized ion pair [25,26,32].

In this work, a kinetic model is developed for the acid–base cooperative catalysed aldol condensation reaction. The focus is on the effect of the structure and base strength of the amine functional groups on the aldol condensation kinetics. A catalyst library comprising both base and acid–base catalysts was synthesized by functionalization of a commercial, mesoporous silica, Silicagel 60, with different commercially available primary, secondary and tertiary amine containing silanes. The effect of the reaction conditions as well as the structure and base strength of the active site on the catalyst activity is investigated by means of both an experimental kinetic study and kinetic modelling.

2. Procedures

2.1. Preparation of catalysts

2.1.1. Grafting of amines on Silicagel 60

Different catalysts were prepared using five commercially available amine containing silanes, (3-aminopropyl)triethoxysilane (98%, APTES, ABCR), N-methylaminopropyltrimethoxysilane (MAPTMS, ABCR), N-cyclohexylaminopropyltrimethoxysilane (CAPTMS, ABCR), N-phenylaminopropyltrimethoxysilane (95% PAPTMS, ABCR) and (N,N-diethyl-3-aminopropyl)trimethoxysilane (DEAPTMS, ABCR). These aminosilanes were grafted on a mesoporous silica, Silicagel 60 (Grade 7734, Sigma–Aldrich). First, the silica is calcined at 700 °C for 6 h with a heating rate of 2 °C/min. After the calcination the material is slowly cooled to a temperature of about 150 °C. 5 g of pretreated material is diluted in 30 ml of toluene (Extra Dry, Acros) while still hot to avoid rehydration of the samples. The aminosilane is subsequently added. The added volume of the amine precursor is varied between several batches in order to silylate the silica with different amounts of amine groups. The molar ratio of added precursor to free silanols is varied in the range of 0.1–5. The necessary volume of precursor is calculated assuming the number of free silanols is equal to 1.1 OH/nm² [39]. However, caution is required as the silica, even after a treatment at 700 °C can still readsorb water, and variations up to 25% are possible when comparing different kinds of silica [40,41]. Therefore, it is very important to individually characterize each catalyst batch. After adding the precursor, the mixture is refluxed under an argon

atmosphere at 110 °C for 24 h. The solid is recovered by filtration and is, subsequently, diluted in chloroform (>99.8%, Roth) and stirred for 3 h in order to remove all the remaining toluene and precursor from the pores. After drying in vacuo at room temperature for 24 h the cooperative acid–base catalysts (samples AB) were ready for kinetic testing.

2.1.2. Endcapping of the silanol groups in samples AB with 1,1,1,3,3,3-hexamethyldisilazane

About half of each sample of the cooperative acid–base catalysts (samples AB) was subsequently treated with 1,1,1,3,3,3-hexamethyldisilazane (98%, HMDS, ABCR) in order to prepare the base catalysts (samples B). 2.5 g of the dried cooperative catalyst is added to a flask and completely covered with 30 ml of HMDS. The mixture is vigorously stirred at room temperature for 3 h and subsequently, the mixture is filtered and thoroughly washed with chloroform for 3 h using the same method as during the grafting of the amine containing silanes. Finally, the solids are dried in vacuo at room temperature for 24 h. HMDS quantitatively reacts with the surface silanols of silicagel if the silica is calcined at a temperature above 400 °C [42,43]. Hence, this HMDS treatment endcaps all remaining silanols on the surface by replacing it with a trimethylsilyl function. The synthesis procedure finally led to 10 different catalysts as represented in Fig. 1.

2.2. Catalyst characterization

Nitrogen adsorption–desorption measurements are carried out at 77 K using a Belsorp Mini II gas analyser. Samples are degassed at 120 °C for 17 h prior to measurement. The specific surface area and pore volume are determined using the Brunauer–Emmett–Teller (BET) method. The average pore size of the silica is obtained using the Barrett–Joyner–Halenda (BJH) method.

The concentrations of amine and silanol groups are determined using elemental (CHNS) analysis. These experiments are performed on a Thermo Flash 2000 elemental analyser using V₂O₅ as catalyst. Sample cups are tightened and the analysis waiting time is kept as short as possible to avoid, or at least minimize, readsorption of water, impacting on the weight and elemental composition of the samples.

The presence of amine groups after grafting and silanol removal through HMDS treatment is demonstrated by means of Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectroscopy. These measurements are performed on a Nicolet 6700 of Thermo Scientific with a nitrogen cooled MCT-A detector. The DRIFT spectra are obtained using a Graseby Specac diffuse reactant cell, operating in vacuo at 140 °C.

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