



Synthesis-property-performance relationships of amorphous silica-alumina catalysts for the production of methylenedianiline and higher homologues



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ABSTRACT

Although amorphous silica-alumina catalysts (ASA) are a promising candidate for the replacement of HCl in the production of methylenedianiline (MDA) and higher homologues, their industrial implementation has been hampered by the lack of systematic studies targeting their design. The complexity of both, the materials as well as the reaction, necessitates the development of synthesis-structure-performance relationships to indicate if, and how, the stringent specifications in terms of activity, selectivity, and stability can be met. Herein, we investigate a large set of ASA obtained by coprecipitation, deposition-precipitation, grafting, and from commercial sources. A detailed analysis of their porosity, composition, Al speciation, acidity, and morphology reveals that every synthesis method leads to a unique combination of material properties. Through high-throughput batch experiments we investigate the importance of each of these parameters for the catalytic performance. The properties that determine the activity relate to the specific surface area, which should be as large as possible while featuring tetrahedrally-coordinated aluminum atoms in the silica matrix. In contrast, the selectivity is determined by the employed reaction conditions, namely the reaction temperature and the aniline content of the feed. Continuous tests under industrial conditions reveal that ASA deactivate *via* fouling during the initial restructuring of aminal. Pore-mouth blockage by fouling was minimized and optimal lifetimes ensured by employing mesopore networks consisting primarily of pyramidal or cylindrical pores. Based on these insights, we demonstrate that ASA can outperform hierarchical zeolites in terms of activity, while approaching industrially attractive oligomer contents and keeping the concentration of byproducts low at a high catalyst lifetime, advertising their potential for large-scale implementation.

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1. Introduction

Methylenedianiline (MDA) is the most common isocyanate precursor used for the production of polyurethanes [1,2]. Industrially, it is obtained by the reaction of aniline and formaldehyde using a homogeneous acid catalyst, typically HCl, yielding a complex mixture comprising the 2-ring MDA isomers (4,4'-MDA, 2,4'-MDA, and 2,2'-MDA), higher MDA homologues with ≥ 3 benzene rings (oligomers), and undesired disproportionation byproducts such as N-formyl-MDA and N-methyl-MDA *via* a series of catalytic rearrangements (Fig. 1) [3,4]. Separation of the homogeneous catalyst is in conducted by quenching the reaction mixture with expensive soda

lye, preventing catalyst reutilization and resulting in large quantities of chloramine-contaminated brine waste. Additionally, the highly reactive and corrosive nature of HCl imposes a large capital investment for commercial units due the required construction materials and the need for accurate temperature control [4].

Accordingly, substantial efforts have been devoted to identify suitable heterogeneous catalysts capable of meeting the stringent selectivity specifications of the established product: (i) a high ratio (>4) of the 4,4'-isomer to the less desired 2,4' isomer (herein referred to as 'isomer ratio'), (ii) a substantial (>25 wt.%) oligomer fraction, and (iii) a low byproduct content (<5000 ppm of N-methyl-MDA or N-formyl-MDA), which all lead to a polyurethane product with a high degree of cross-linking. Among the numerous solid acids investigated, including sulfonated ion-exchange resins [5–7], clays [8], amorphous and mesostructured silica-aluminas

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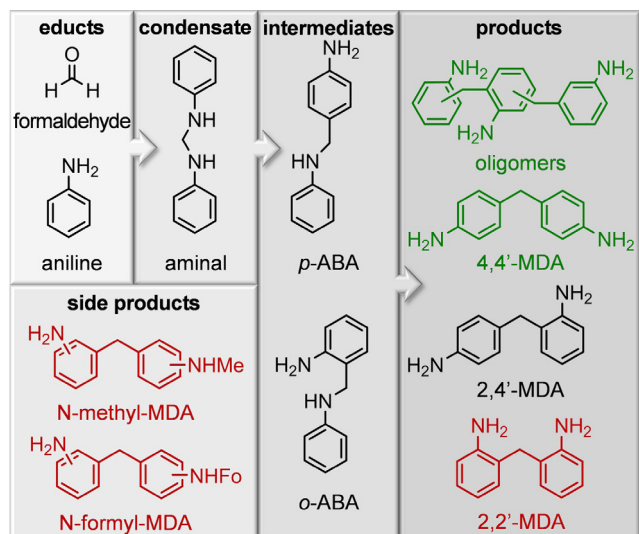


Fig. 1. Synthesis of MDA mixtures from aniline and formaldehyde. Desired products in green and undesired products in red.

[9–15], and delaminated zeolites [15–18], ultra-stable Y zeolites (FAU framework) stood out as their unique shape selectivity leads to high isomer ratios (>6.5) [19–21]. However, the bulky nature of the involved reactants and products imposes mass transfer limitations, translating into meager activity, a low selectivity to oligomers, and short lifetime. These problems could be alleviated via controlled demetallation of the zeolite crystals, thereby introducing an interconnected network of mesopores that lead to improved activity, oligomer selectivity, and stability, while the high isomer ratio was retained [21]. Nevertheless, the frequent regeneration through calcination, necessitated by the entrapment of oligomeric MDA in the micropore network [14], makes the process less appealing for large-scale application in continuous operation.

In contrast, Salzinger et al. established that the deactivation rates of amorphous silica-aluminas (ASA) can be 10 times slower compared to dealuminated USY zeolites [14]. However, this advantage has to be weighed against the loss of the shape selective properties and a ca. 30% lower activity, as expressed by the rate of 2-ring MDA formation. Furthermore, although the first reports of ASA date back ca. 50 years [9,10], the properties governing their catalytic performance remain poorly understood. The best activities so far were claimed for mesoporous silica-aluminas with a specific surface area above 500 m² g⁻¹ and a Si/Al ratio in the range of 5–250 [22]. In a recent patent application, Weiner et al. [23] suggested a descriptor based on the ratio of strong to weak Lewis acidity (as quantified by infrared spectroscopy of adsorbed pyridine) that correlates with the activity of the materials. However, both works limit themselves to one preparative approach for ASA, and the influence of critical parameters such as porosity and Brønsted acidity were disregarded [24].

The amorphous nature of ASA has translated into the development of a wealth of synthesis pathways, including coprecipitation [28,29], sol-gel synthesis [30–32], the grafting [33–35] or deposition-precipitation [36,37] of alumina-precursors on a silica support, and *vice versa*. Summarized in a conceptual way, the acidity of ASA originates from intermixed, oxygen-bridged Si and Al atoms on the material surface [25–27]. As these fundamentally different approaches yield ASA with unique morphology, porosity, composition, Al speciation and distribution, and thus ultimately acidity, it is evident that a conclusive assessment of the industrial potential of ASA can only be made if their catalytic activity, selec-

tivity, and also stability can be rationalized based on all these properties.

To enable such a conclusion, we herein examine a wide range of ASA, obtained commercially as well as self-prepared following various preparative approaches. The materials are characterized in depth, and subsequently evaluated in high-throughput batch experiments, as well as continuous stability tests under industrial conditions, as detailed in Fig. 2. Based on these results, we develop structure-property-performance relationships and give a clear assessment of the advantages of ASA compared to benchmark catalysts such as mesoporous or delaminated zeolites.

2. Experimental methods

2.1. Catalyst preparation

2.1.1. Coprecipitation

Two aqueous solutions (100 cm³ each) of sodium water glass (26.5% SiO₂) and sodium aluminate were mixed and dispersed with an IKA Ultra-Turrax T25 disperser (9500 rpm), aged until gelation (ca. 1–10 min), and redispersed. The concentration of the precursors was adapted according to the desired product composition while maintaining a constant oxide loading (50 g L⁻¹). The gel (30 cm³ min⁻¹) and 0.5 M HNO₃ (ca. 20–30 cm³ min⁻¹) were simultaneously pumped into a beaker charged with H₂O (50 cm³) and equipped with the disperser (9500 rpm). The acid flowrate was adapted to ensure a pH between 9.7 and 9.9. Subsequently, the solids were filtered off, ion-exchanged three times with 0.5 M NH₄NO₃ (0.5 L, 8 h), dispersed in water (250 cm³) and pumped (3 cm³ min⁻¹) into a Büchi Mini Spray Dryer B-290 equipped with a two-fluid nozzle of 1.4 mm diameter together with an air flow of 0.5 m³ h⁻¹. The inlet temperature was set at 493 K, the aspiration rate at 35 m³ h⁻¹, and the outlet temperature at 383 K. The dried particles were separated by using a cyclone and calcined (550 °C, 5 h) with a heating rate of 2.5 °C min⁻¹. The samples are referred to as **CP-x**, where x represents the nominal Si/Al ratio.

2.1.2. Deposition-precipitation

A 250 cm³ flask was charged with water (150 cm³), SiO₂ (5 g, Silicagel, Sigma-Aldrich), urea (7.2 g), and the desired amount of AlNO₃·9H₂O, and stirred (500 rpm) at 90 °C for 6 h. The solids were filtered off, washed three times with water (50 cm³), dried (65 °C, 12 h), and calcined (550 °C, 5 h) with a heating rate of 2.5 °C min⁻¹. The samples are referred to as **DP-x**, where x represents the nominal Si/Al ratio.

2.1.3. Al-grafting

SiO₂ (5 g, silicagel, Sigma-Aldrich, ‘-h’, or silica nanoparticles 10–20 nm 99.5%, Sigma-Aldrich, ‘-l’) was evacuated overnight at 60 °C in a round bottom flask. The flask was charged with isopropanol (50 cm³) and the desired amount of aluminum isopropoxide and refluxed for 5 h. The solids were filtered off, washed three times with isopropanol (50 cm³), dried (65 °C, 12 h), and calcined (550 °C, 5 h) with a heating rate of 2.5 °C min⁻¹. The samples are referred to as **GAl-x-y**, where x represents the nominal Si/Al ratio and y the SiO₂ precursor used.

2.1.4. Commercial samples

Silica-alumina catalysts were obtained from Sasol (Siral[®] 1–40). According to the manufacturer’s specifications [38], they were prepared by doping a boehmite-phase Al₂O₃ with 1–40 wt.% of SiO₂. The samples are referred to as **SA-x**, where x represents the nominal Si/Al ratio.

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