



# Synthesis of amorphous aluminosilicates by grafting: Tuning the building and final structure of the deposit by selecting the appropriate synthesis conditions



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## ABSTRACT

Despite their wide use in the oil refining process, little is known about the distribution of aluminium and silicon atoms in amorphous aluminosilicates (ASAs). In this paper, we report the synthesis of both Al/SiO<sub>2</sub> and Si/Al<sub>2</sub>O<sub>3</sub> ASAs by grafting aluminium and silicon alkoxides on silica respectively alumina under various conditions. For both supports, we evidence the central roles of the precursor molecule size and reactivity in the grafting yield and the deposit structure. Unless hydrolysis of the alkoxy groups by water and/or thermal decomposition occurs, deposition is saturated at a monolayer of precursor molecules on the support oxide surface. Additional species can be deposited by repeating the grafting process provided that hydroxyl groups of the top layer are recovered after calcination. <sup>27</sup>Al NMR indicates the presence of five-coordinated aluminium species on Al/SiO<sub>2</sub> materials prepared by two successive grafting steps. Transmission electron microscopy (TEM) and time-of-flight secondary ion mass spectrometry (ToF-SIMS) confirm the controlled deposition of species by selecting the appropriate synthesis conditions. Homogeneous and regular deposition is favoured in anhydrous condition and at low temperature, while water addition during synthesis leads to inhomogeneous deposits. In case of Al/SiO<sub>2</sub> grafting in aqueous conditions, alumina nanoparticles form. The accurate knowledge of the surface structure of these ASAs opens the way to a better understanding of the origin of their Brønsted acidity.

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## 1. Introduction

Amorphous aluminosilicates (ASAs) are widely used as catalyst support in the oil refining industry, especially in the conversion of heavy fractions [1]. These mixed oxides provide the moderate acidity required for cracking and isomerization reactions of carbonaceous molecules [2,3]. They thus allow high selectivity towards middle-distillates, for which demand is continuously increasing [4]. Although extensively studied, the structure of ASAs and, more particularly, the nature, localization and number of the sites originating their acidity remain largely debated.

Indeed, the synthesis method of ASAs impacts the degree of intimacy of aluminium and silicon atoms, and their general repartition throughout the particles. Cogelation [5,6] and co-sequenced techniques [7], for example, lead to very complex architectures. Post-treatments such as steaming [8] are known to cause redistribution of species and to induce textural modification (pore diameter, surface area), impacting the nature of active sites. This high level of structural heterogeneity has prevented unequivocal identification of the surface species that are responsible for acidity. On the contrary, zeolites have a well-defined crystalline structure and porosity, and defined Brønsted acid sites consisting of a hydroxyl group bridging an aluminium and a silicon atom.

To rationalize this, ASAs can be synthesized in a more controlled way, e.g. by grafting. Either silicon or aluminium containing species (alkoxides) are deposited on the complementary oxide, to prepare Si/Al<sub>2</sub>O<sub>3</sub> or Al/SiO<sub>2</sub> materials, respectively. By this technique, the mixed-oxide phase is restricted to the surface, which simplifies the interpretation of structural characterization. Moreover, as

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catalytically active sites are located at the surface, activity can directly be related to the surface species arising from the deposition. Eventually, correlations can be established between the surface species and the nature of acid sites, to finally disclose the origin of Brønsted acidity in ASAs. Provided well-chosen synthesis conditions, the synthesis of ASAs by grafting can thus lead to materials representative of the variety of industrial ASAs – but with an enhanced control of the distribution and repartition of silicon and aluminium species.

Aluminium deposition on silica proceeds by anchoring the aluminium species onto the hydroxyl groups of silica [9–17]. Thanks to potentiometric and TGA measurements, Iengo et al. identified that grafted species can be either preferentially monodentately – at low  $\text{Al}(\text{OR})_3$  concentration – or bidentately bound to the surface [18]. This is a first indication of the role played by synthesis parameters on the nature of the grafted deposit. Similarly, the temperature pretreatment, the media in which grafting takes place, and, especially, the water content all impact the support hydroxyl density, leading to different aluminium incorporation into the silica network [16,19]. Yet, generally limited information is available regarding the size and shape of the aluminic deposit and the degree of coverage of the silica surface [10]. Very similar conclusions can be drawn for silicon deposition on alumina, such as the importance of the initial amount of precursor molecules [20,21] and the consumption of hydroxyl groups of the alumina support as observed in IR spectra of the grafted samples [22]. The temperature at which the grafting takes place, as unravelled by the differences between liquid-phase (CLD) and gas-phase (CVD) grafting, affects the building of the deposit and the reactivity of the alumina support anchoring sites [23,24]. Benzotriole ammonia titration, BAT, is based on the specific adsorption and quantification of benzotriole on aluminium sites and allows one to determine the ratio of remaining bare alumina surface [25].

Solid-state magic-angle spinning (MAS) NMR of  $^{27}\text{Al}$  and  $^{29}\text{Si}$  nuclei is an efficient tool to investigate the deposit structure of, respectively,  $\text{Al}/\text{SiO}_2$  and  $\text{Si}/\text{Al}_2\text{O}_3$  materials. Hensen et al., for example, ascribed four-, five- and six-coordinated aluminium atoms as detected by  $^{27}\text{Al}$  NMR to certain positions within the aluminium containing deposit [5]. While six-coordinated aluminium atoms belong to a pure aluminium oxide phase, four-coordinated and five-coordinated species would be located, respectively, in a mixed silica–alumina phase and at the interface between this mixed phase and the pure aluminic domains. Conversely, Goldbourt et al. considered the alumina deposit to display the same ratio of tetrahedral to octahedral aluminium atoms of 1/3 as in transition aluminas. If a higher ratio is found, the excess  $\text{Al}(\text{IV})$  atoms are supposedly inserted into the silica matrix, in a similar way as in zeolites [26]. Due to the rareness of the  $^{29}\text{Si}$  isotope,  $^{29}\text{Si}$  NMR spectra of  $\text{Si}/\text{Al}_2\text{O}_3$  often display low signal-to-noise ratios which render interpretation difficult. CP (cross-polarization) NMR allows enhancement of the signal by polarization of the nuclei by neighbouring protons. Sato et al. noticed that the loading of alumina with silicon atoms at 240 °C, using CVD, progressively leads to the accumulation of up to three layers of silica, by successive completion of silica monolayers [27]. Such assertions are based on the characteristic NMR chemical shifts of the  $\text{Si}/\text{Al}_2\text{O}_3$  materials, ranging between –70 (isolated  $\text{SiO}_4$  species) and –110 ppm ( $\text{SiO}_4$  in siliceous environment). There is a clear impact of the grafting temperature, but opinions differ regarding the formation process of the deposit. Precursor molecules can be randomly grafted onto the alumina surface or previously deposited species, rather than first forming a uniform monolayer [28].

This paper aims at describing the parameters governing the deposition of alumina, respectively silica species on silica and alumina to obtain aluminosilicates as reference materials for ASAs. To cover a wide range of elemental composition, both  $\text{Al}/\text{SiO}_2$  and  $\text{Si}/$

$\text{Al}_2\text{O}_3$  grafting techniques have been used. To modify the deposit structure, water has been added to the reaction mixture, to embody different hydrolysis/condensation states of the precursors and the temperature has been varied; CLD/CVD techniques have been employed to assess the role of the grafting technique. Comprehension of the phenomena occurring on the surface during grafting allows one to understand the processes giving rise to a given deposit structure. Control of the process enables to finely tune the structure and properties of the materials, ultimately leading to unique acidic behaviour. This is a simplified and consistent way to obtain a set of samples depicting the variety of industrial aluminosilicates resulting from very different, but less controlled synthesis paths.

## 2. Experimental

Main characteristics of the materials and their synthesis conditions are detailed in Table 1.  $\text{Si}/\text{Al}_2\text{O}_3$  samples were synthesized either in liquid media (CLD) or in gas phase (CVD). Gamma-alumina (236  $\text{m}^2/\text{g}$ , entry 1 in Table 1) – resulting from calcination of boehmite Pural SB3 (Sasol) at 540 °C – and silicon – obtained from tetraethyl-orthosilicate (TEOS,  $\text{Si}(\text{OCH}_2\text{CH}_3)_4$ , Aldrich) were used as support and precursor, respectively. Anhydrous CLD on alumina consisted of vacuum pretreating the alumina at 40 °C (10<sup>–2</sup> mbar) for 4 h to eliminate physisorbed water from the surface (referred to as “normal”  $\text{Si}/\text{Al}_2\text{O}_3$  pretreatment further in the document). Then the appropriate amount of precursor, TEOS, was added under inert atmosphere (argon) together with dry toluene (<5 ppm water) so that the solvent volume (mL):alumina weight (g) ratio was 10. The mixture was stirred under reflux (110 °C) for 5 h. The solvent, the excess precursor molecules which did not react, and the organic molecules stemming from alkoxide decomposition, were eliminated by filtration and washing with dry toluene. Washing was repeated three times to ensure that no non-grafted TEOS molecules were remaining. The obtained impregnated gel was dried under a flow of argon, then the remaining solvent was eliminated by pumping under vacuum. The powder was kept in open air overnight, which allowed hydrolysis of the alkoxy groups grafted on the surface. The material was then dried at 100 °C during 24 h and finally calcined in a muffle furnace at 550 °C for 4 h under air (entry 2 in Table 1). Repetition of the grafting (once: entry 3, and twice: entry 4) following the same procedure was done on part of the resulting material.

In aqueous CLD a controlled amount of water was added after the pretreatment step and mixed for 1 h. Thus, the water to precursor molar ratio was precisely known: 4 and 12 for  $\text{Si}/\text{Al}_2\text{O}_3$  (entries 5 and 6); 1 and 3 for  $\text{Al}/\text{SiO}_2$  (entries 22 and 23, vide infra).

CVD samples were prepared following a method close to that previously described by Katada et al. [29]. Nitrogen or air (4 L h<sup>–1</sup>  $g_{\text{support}}^{-1}$ ) was passed through a saturator containing TEOS and maintained at 70 °C. All lines downstream of the TEOS saturator were insulated and heated to avoid deposition of TEOS. The Si-containing flow then reached a quartz reactor containing the  $\gamma$ -alumina support heated between 200 and 400 °C, i.e. above the TEOS boiling point (166–169 °C). Prior to grafting, the alumina support was pretreated under an argon flow at 250 °C to eliminate physisorbed water. Similar to the CLD procedure, samples were finally exposed to air moisture overnight and calcined at 550 °C for 4 h under air flow. The amount of precursor during grafting depended on the vapour pressure of TEOS – at the saturator temperature, the flow rate of the carrier argon and the length of grafting. CVD samples correspond to entries 7–13 in Table 1.

The preparation of  $\text{Al}/\text{SiO}_2$  samples in liquid media followed the same procedure as for  $\text{Si}/\text{Al}_2\text{O}_3$  in case of both anhydrous (entries 15–21) and aqueous (entries 22 and 23) grafting, but using silica ground into powder (silica gel beads from Grace, 552  $\text{m}^2/\text{g}$ , entry 14) and aluminium isopropoxide ( $\text{Al}(\text{O}^i\text{Pr})_3$ ) as support and

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