



Revisiting carbenium chemistry on amorphous silica-alumina: Unraveling their milder acidity as compared to zeolites



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ARTICLE INFO

Article history:

Received 28 August 2014

Revised 28 January 2015

Accepted 18 February 2015

Available online 16 March 2015

Keywords:

Heterogeneous catalysis

Amorphous silica alumina

Zeolite

Cracking

Carbocation

Alkoxide

DFT

Isobutene

2,4,4-Trimethyl-2-pentene

Confinement effect

ABSTRACT

Amorphous silica-aluminas (ASA) are prominent solids for their acidic properties. They are of first interest in catalysis, in particular for cracking reactions. Their relative acidity as compared to zeolites is a long-lasting general issue, driven by the limited knowledge of the surface structure of ASA, due to their amorphous nature. In the present contribution, thanks to a first principles approach based on our original ASA surface model, and on the study of a model mordenite zeolite (MOR), we propose a rational explanation for this feature. We compare by density functional theory calculations the ability of ASA and MOR to generate carbenium species from isobutene, versus π -complexes and alkoxide species. On ASA, carbenium species can be formed on pseudo-bridging silanols (PBS) only and are much less stable than in MOR. Then, we investigate the cracking pathway of a model alkene, 2,4,4-trimethyl-2-pentene (DIB), by quantifying the stability of relevant intermediates of carbocationic and alkoxide natures. The carbocationic pathway is favored in MOR, whereas on ASA, this pathway is strongly activated. By contrast, the PBS on ASA initiate preferentially a tertiary alkoxide route, or possibly a combined carbocationic/alkoxy route. Finally, the *i*-butene desorption step is also limiting in MOR due to the confinement effect induced by the zeolite pores. As a result, the higher cracking reactivity of zeolites as compared to ASA is mainly attributed to the favored nature of the carbenium route, stabilized by higher electrostatic confinement effect.

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1. Introduction

The concept of Brønsted acidity [1] has been studied for a long time in the context of aqueous solutions, but its application to solid surfaces still remains an issue. One significant example is the case of amorphous silica-alumina (ASA) materials, which are widely used in fine chemistry [2–4], biomass conversion [5,6], and in industrial refining processes [7]. Indeed, the intimate chemical mixing of silica with alumina in ASA materials is empirically known to promote an enhanced surface Brønsted acidity with respect to the reference alumina or silica solids themselves. At the same time, this acidity is milder than the one observed in microporous aluminosilicates such as zeolites [8,9]. This milder acidity is targeted in industrial processes such as hydrocracking (HCK) in order to reach optimal cracking selectivity into middle distillate products [10,11]. However, the origin of this milder acidity as compared to zeolites is still questioned, due to the difficulty

to reach a resolution at the molecular scale of ASA surfaces – amorphous systems – and of the intermediates involved during reactions even by using cutting edge operando techniques. Understanding the acidity of ASA is moreover of prominent interest because they are also suspected to be present as debris in (non-leached) de-aluminated zeolites [12,13]. Interestingly, ASA and ultrastable Y zeolite have been found to exhibit similar hydrocracking patterns in the conversion of the pristane model molecule [14].

Bifunctional catalysts such as used in HCK processes require an optimal control of the balance between the hydrogenation function and the acidic function [7,15–18]. For that purpose, various types of catalytic supports exhibiting a tuneable acidity scale (mesoporous alumina, ASA, or zeolites) are industrially used in combination with a hydrogenating active phase (either a transition metal sulfide or a reduced metal) [7,17]. Indeed, it is crucial to optimize the acidic function of the HCK support: the milder acidity of ASA as compared to zeolites is profitably used to convert petroleum feeds containing also refractory compounds (such as nitrogen organic ones) in a selective way.

Many experimental studies [19–29] have analyzed the nature of possible Brønsted acid sites (BAS) on ASA: zeolite-like Si(OH)–Al

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groups [19–22], silanols in the vicinity of aluminum atoms [23–25], and water molecules adsorbed on aluminum atoms [26,27]. However, at a molecular scale, it remains crucial to understand the precise chemical behavior of the ASA Brønsted acid sites, how they catalyze cracking reactions and the reasons of their milder acidity of ASA as compared to zeolites. In particular, it is proposed that ASA surface would exhibit very few BAS with an acidic character very similar to BAS found in zeolite [21,30]. However, this interpretation remains questionable because it is also well-known that the strength depends on both the local BAS atomic structure and the confinement effect depending on the pores' size surrounding the BAS [31,32].

Using density functional theory (DFT) calculations, some of us recently established a relevant ASA surface model which renders the diversity of surface Brønsted acid sites and highlights the existence of pseudo-bridging silanols (PBS) [33]. In particular, PBS-Al sites consist of silanols whose oxygen atom is close to an aluminum atom and able to be bonded to it upon deprotonation (Fig. 1). The surface model also shows the presence of silicic PBS site (PBS-Si, see Fig. 1), other silanols, for which Si–O–Al bridges coexist (called hereafter Silanol-Al), and water molecules adsorbed on aluminum atoms (III₁ in Fig. 1).

So far, DFT approaches investigated the surface Brønsted acidity by calculating the adsorption of probe molecules [34], in particular 2,6-lutidine [35] and CO [36]. The lutidine protonation was shown to be favored when the conjugated base of the BAS is stabilized. In particular, the PBS-Si site depicted in Fig. 1 and the PBS-Al site called Si(V₁)–OH···Al_{IV} (III₃) are both able to transfer their proton to lutidine, thanks to the formation of a new Si–O and Al–O bond

after deprotonation, respectively. Other PBS-Al sites were not able to do so due to angular constraints [33], while Silanol-Al sites are not deprotonated because the conjugated silanolate cannot be stabilized. The water molecule adsorbed on the III₁ aluminum atom can generate lutidinium, as an Al–OH group is formed. Cascade proton transfer can also occur from this adsorbed water molecule to the neighboring silanol group [35]. The vibrational stretching of CO was found sensitive to the electrostatic field at the surface of aluminosilicates [36]. In the course of a reaction involving a hydrocarbon, both aspects (proton transfer and local electrostatic field) are expected to play a role. In particular, the relation between the structure of the sites, the protonation ability, the electrostatic field, and the reactivity in cracking reactions remains to be understood.

For zeolite catalysts, it is quite widely admitted that olefin cracking proceeds via carbenium ions (formed on protonic sites of the material) [37] well-known in organic chemistry [38–40]. After formation, and possible isomerization, these species are considered to undergo β-scission (Fig. 2) [16,18,41–44].

However, isolating carbocations within or on the surface of aluminosilicates remains a challenging task due to their supposed short lifetime [45,46]. Highly resonant species mainly could be observed in zeolites [45,47,48], even if indirect evidence was provided by ¹³C NMR for the transient formation of short-live carbenium ions in the case of long-chain or branched olefins [49–51]. Alternative proposals to carbenium β-scission can thus be recorded. Sie [52] proposes a pathway invoking hydride shifts and highly non-classical cyclopropane-like intermediates, by analogy with what is known about isomerization reactions [53]. Up to date, no confirmation of this kind of pathway could ever be given [16]. Moreover, alkoxides (Fig. 3) were characterized in zeolites thanks to ¹³C NMR [51,54,55] and FTIR [56,57] and were calculated as stable species by earlier quantum chemical calculations [58–64], which led some authors to refute the existence of carbenium ions as cracking intermediates in zeolites, even for tertiary carbenium. The intermediate or transition state nature of carbenium in zeolites as calculated by quantum chemistry, however, appears to be strongly dependant on the alkene considered [65], but also on the level of theory (DFT, with or without dispersion corrections, versus post-Hartree-Fock methods for example) [66,67], on the kind of model – small clusters versus periodic cells – and on the local geometry of the active site [65,68–75]. Indeed, taking into account the electrostatics induced by the porosity leads to a stabilization of charged species, whereas the stability of the neutral species remains almost unchanged. Temperature effects are also shown to affect the alkoxide existence probability over that of carbenium, according to DFT calculations [76–78].

In the case of ASA, the formation of carbenium ions thanks to surface proton transfers was also invoked for a long time [15,79,80] even if alkoxides are mainly observed by FTIR [56]. Generally, the catalytic activity of ASA in acid-catalyzed reactions is lower than that of zeolites [18,81]. This could be either due to intrinsically weaker sites [82], or to a lower amount of the same kind of sites (bridging Si–(OH)–Al groups) than in zeolites [21,30]. There is, however, a lack of detailed data both on the stability of carbenium species on these solids, and on their implication in the conversion of hydrocarbons, in particular cracking of alkenes.

In the present work, we propose to determine the energetics of carbocation/alkoxide formation followed by C–C β-scission for BAS located on ASA surface and in a reference zeolite (mordenite, MOR), thanks to periodic DFT + D calculations. As indicated above, we suspect that confinement effects may play a key role, so it is mandatory to include dispersion corrections. We chose a model molecule, 2,4,4-trimethyl-2-pentene (DIB, 8 carbon atoms), as its branched character is expected to render the formation of

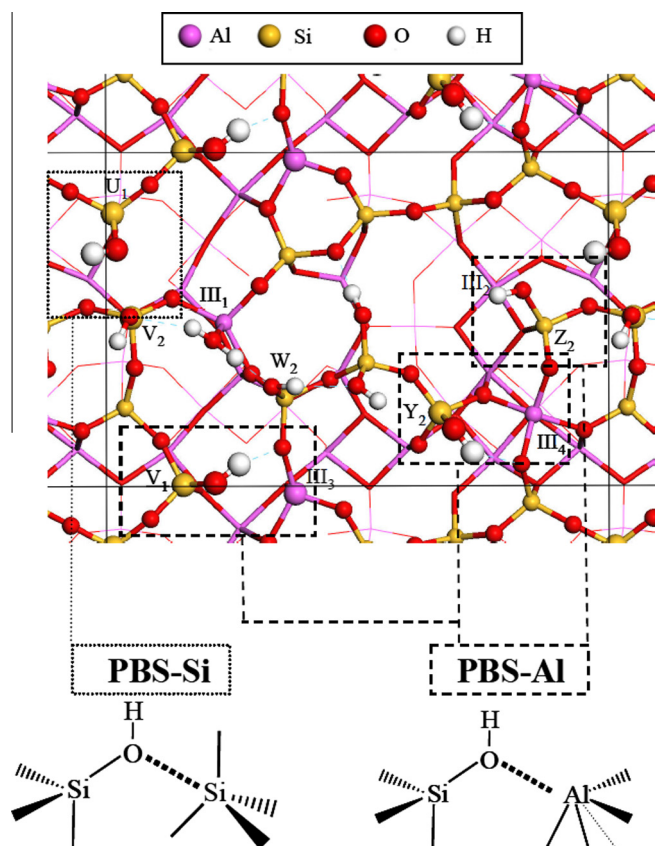


Fig. 1. ASA surface model for $\theta_{\text{OH}} = 5.4 \text{ nm}^{-2}$, as established in Refs. [37,38]. Some pseudo-bridging silanols (PBS) are shown, in particular silicic PBS (PBS-Si, Si(V₁)–OH···Si(V₂)), and aluminic PBS (PBS-Al, Si(V₁)–OH···Al_{IV} (III₃)) are able to protonate lutidine, others are not.

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