Brønsted acid sites of zeolitic strength in amorphous silica-alumina†

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The most acidic OH groups in silica-aluminas (zeolites, clays, amorphous silica-aluminas) can be made to react selectively with C_6D_6 to give acidic OD groups; quantification by IR spectroscopy shows that differences in the overall Brønsted acidity of aluminosilicates are dominated by differences in the density of sites of similar acid strength.

The Brønsted acidity of zeolites, clays and amorphous silica-alumina (ASA) makes these aluminosilicates technologically important materials, extensively used as acid catalysts in the oil refining and petrochemical industry.[1–3] Although ASAs are less acidic than zeolites, present-day composite hydrocracking catalysts often contain ASA next to steam stabilized Y zeolite. ASAs are the main acid component in diesel-selective hydro-cracking catalysts. Tetrahedral Al atoms in the silica network are assumed to be the highly active ingredients in alumino-silicates: compensation of the resulting negative charge by a proton gives rise to a Brønsted acid site (BAS). Although widely accepted for zeolites and clays,[1,3,4] this relation between local structure and surface acidity remains strongly debated for ASA.[5–8] If BAS were to have similar strength in these aluminosilicates, their concentration in ASA should be very low to account for its much lower Brønsted acidity.[9] The Al-for-Si substitution model to explain ASA acidity was already proposed very early by Thomas[10] and Tamele.[11] Despite some indications of bridging hydroxyl (OH) groups,[7,12] convincing spectroscopic evidence is still lacking. Instead, various more complex surface models of ASA have been invoked.[5–8,13,14] The higher acidity of silanol groups near Lewis acid Al^{3+} in silica has recently attracted most attention.[5,7,15] In this model, ASA's acidity would stem from many sites of modest acidity. Crépeau et al.[7] have however suggested that such sites are of zeolitic strength. A computational study of Chizallet and Raybaud[15] has pointed to pseudo-bridging silanols as the seat of ASA acidity. The acidity has also been linked to Al^{3+} on the silica surface.[13,14] A generic method to quantify strong acid sites in aluminosilicas, which is desirable to establish quantitative relations between their acid properties and catalytic activity, has not been possible yet.

Herein we provide spectroscopic evidence of the presence of bridging OH groups of zeolitic strength in ASAs. The protons of the most acidic OH groups in aluminosilicates can be made to react selectively with C_6D_6 to give deuteroxyl (OD) groups, which can be observed by IR spectroscopy. The suitability of H/D exchange of strongly acidic protons in zeolites with C_6D_6 has been shown earlier.[16] Combined with IR, sites of varying acid strength such as for instance in stabilized Y zeolites can be distinguished semi-quantitatively. The unprecedented sensitivity of our method allows a first direct spectroscopic glance at acid sites in ASAs. To prepare ASAs in an as controlled a way as possible, we choose a well-defined variant of grafting, viz., homogeneous deposition–precipitation (HDP).[17] The presence of acid OH groups is followed by H/D exchange FTIR. The acid activities of aluminosilicas are correlated with BAS concentrations.

The preparation of an ASA precursor by HDP involved homogeneous basification via urea decomposition of a starting solution of Al^{3+} in the presence of a silica aerogel. ASAs with nominal Al content of 5, 10, 15 and 20 wt% Al_2O_3 were prepared. The grafted Al atoms are presumably not the active sites,[13] as the ASA precursors need to be calcined to bring about the desired acidity. Bifunctional hydroconversion of n-heptane was used as an acid activity test for Pd-loaded ASAs. The Pd loading is chosen such that alkene isomerization is rate limiting. We express the acid activity here as the temperature required to obtain an n-heptane conversion of 40% (T_{40}). Calcination of the ASA precursor with 5 wt% Al_2O_3 at 1073 K affords a more acidic ASA (T_{40} = 618 K) than calcination at 773 K does (T_{40} = 630 K). These acid activities are very similar to those for an industrial ASA prepared by grafting aluminium to in situ prepared silica-gel at a pH of 3 (T_{40} values of 623 and 613 K after calcination at 773 and 1073 K, respectively).

We will first illustrate the usefulness of our method to distinguish and quantify acid sites in ultrastabilized Y zeolite. Deuteration of the non-acidic silanol groups in silica and of the weakly acidic hydroxyl groups in γ-alumina does not occur under the chosen conditions. The validation of our method is discussed in detail in the ESI.† Fig. 1 shows the IR spectra of an ultrastabilized Y zeolite after dehydration and progressive H/D exchange with C_6D_6. The OH region of the spectrum for such a zeolite with a considerable amount of EFAl is very complex.[18] The spectrum contains typical bands of high-frequency (HF) and low-frequency (LF) OH groups vibrating in large and smaller cages, respectively. Clearly, these two bands are composite. Additional sites of enhanced acidity give rise to bands below the main HF and LF bands, because of their perturbation by extraframework Al.[19] Weakly acidic aluminol of extraframework aluminium and non-acidic silanol groups are observed as well. After H/D exchange, the OD region contains mainly bands due to the most acidic groups.

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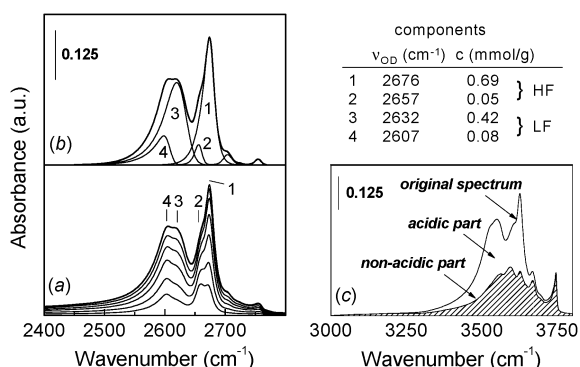
Fig. 1 H/D exchange FTIR of an ultrastabilized Y zeolite (SAR = 8.1): (a) OD region after progressive exchange at 303 K with increasing time (10 s, 30 s, 300 s, 600 s, 1200 s, 1800 s) and at 323 K (1800 s), (b) deconvolution of the spectrum after H/D exchange at 323 K with the components' concentration (top right) and (c) OH region before and after H/D exchange at 323 K. The spectrum after H/D exchange at 303 K for 1800 s is very similar to the one after H/D exchange at 323 K for 1800 s.

Fig. 2 H/D exchange FTIR of an ASA prepared by HDP (5 wt% Al_2O_3, calcined at 1073 K): (a) OD region after progressive exchange at 303 K with increasing time (10 s, 30 s, 300 s, 600 s, 1200 s, 1800 s) and at 323 K (1800 s), (b) OD region after progressive exchange at 323 K, 353 K, 373 K, 423 K and 523 K and (c) deconvolution of the spectrum after H/D exchange at 323 K with the concentrations of the various components (top right).

Four types of bridging OH groups can be distinguished. The evolution of these components evidences the higher acidity of the perturbed OH groups. What is not evident from the original spectrum, but clearly so from the spectrum in the OH region after H/D exchange is the presence of additional weakly acidic sites. These sites are part of an extraframework silica-alumina phase due to the ultrastabilization process[20] and they exhibit modest acidity.[21] Quantification of strong BAS is more easy from the spectra in the OD region after extensive exchange at 323 K than from the parent spectra. We will show that the acid activities of a larger set of zeolites correlate with the concentration of BAS determined by H/D exchange FTIR.

The OH region of the dehydrated ASA calcined at 1073 K contains only an intense silanol band at 3745 cm^{-1} with a strong tail towards lower wavenumbers (see ESI†). Fig. 2 shows spectra after progressive H/D exchange of an ASA with a nominal Al_2O_3 content of 5 wt%. A weak band around 2683 cm^{-1} appears next to a stronger one around 2757 cm^{-1} due to deuterated silanols. With increasing H/D exchange, a broad band below these features appears towards lower frequency. After exchange at the reference conditions for acidity determination, the spectrum contains two weak bands at 2632 and 2683 cm^{-1}. Their position and their exchange under these conditions make them candidates for strong BAS. H/D exchange at higher temperature results in an increase of the intensity of the broad band to such an extent that the bands at 2632 and 2683 cm^{-1} are not observed anymore. This trend provides a reasonable explanation for the absence of bridging OH stretching bands in the IR spectrum of ASA: they are hidden below a broad band which resembles that of the weakly acidic silica-alumina phase in the ultrastabilized zeolite. The exchange of weakly acidic sites of this phase and silanols is still very minor, as the decrease of the silanol band at 3745 cm^{-1} is less than 1% of its original intensity (ESI†). From the absence of H/D exchange after Na$^+$ exchange of the ASA (ESI†), we infer that the appearance of deuterated silanols is a secondary process, likely due to surface H/D exchange of the most acidic surface hydroxyl groups with nearby silanols.
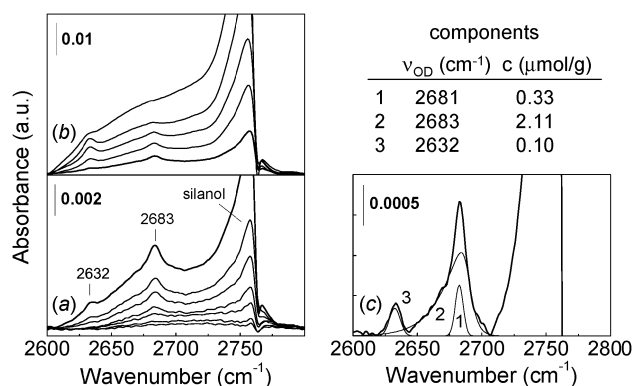
The surface silanol density of ASAs is much higher than that of zeolites. Thus, the high selectivity and sensitivity of H/D exchange FTIR is crucial to observe the suspected BAS. The band at 2632 cm^{-1} becomes more intense upon H/D exchange at elevated temperatures. This suggests that this band represents sites of lower acidity. However, the contribution of these sites to the total concentration of BAS is very small. The spectrum was fitted by several bands after removal of the background. The band around 2683 cm^{-1} consists of two components of which one tails strongly towards lower frequencies. The total concentration of these sites is 2.6 μmol g^{-1}, which is two orders of magnitude lower than for Y zeolite. ASA calcined at 773 K contains only 1.6 μmol g^{-1} of such sites in accord with its lower acid activity.

To confirm that these sites are indeed of similar strength to those in zeolites and clays, we determined their concentration in a set of ASAs containing more aluminium after calcination at 773 K and 1073 K and their catalytic activities in hydroconversion of n-heptane. The proportionality between catalytic activity and BAS density in Fig. 3 implies that sites of similar strength are present in these aluminosilicates. We expect a correlation between the acidity required for hydroconversion and the H/D exchange of C_6D_6, since the Wheland-ion-like transition state for aromatic H/D exchange[22] and the transition states for key elementary reactions involving zeolite alkoxides, like isomerization and β-scission, are all fairly ionic and hence expected to display a similar dependence on the strength of the acid.[23] The higher the calcination temperature of the ASA precursor, the higher the acidity. These results show that only a very small fraction of aluminium in ASAs (∼1 out of 400) contributes to the Brønsted acidity. There is little systematic variation in acidity with Al content, as can be expected when the monolayer coverage of silanol group is 5 wt% Al_2O_3. Only an ASA prepared at 1 wt% Al_2O_3 had a substantially lower acid activity (T_{40} = 659 K).

Fig. 4 provides another sort of evidence for the strong Brønsted acidity of the OD groups around 2683 cm^{-1}. The OH frequency shift upon perturbation by CO is a well-known method to probe acidity.[21] IR spectra after CO
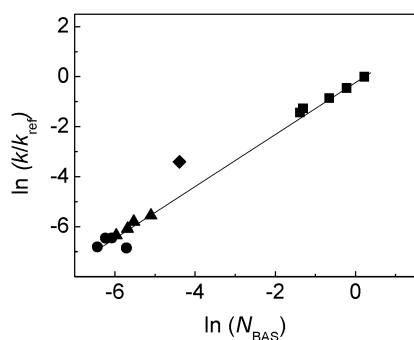
Fig. 3 Comparison of catalytic activity in the hydroconversion of *n*-heptane and the concentration of BAS (mmol g^{-1}) determined by H/D exchange FTIR for (■) ultrastabilized Y zeolites with varying SAR, a Mg saponite clay (◆), and HDP ASAs calcined at 773 K (●) and 1073 K (▲). The reference catalyst is an ultrastabilized Y zeolite with SAR = 8.1.
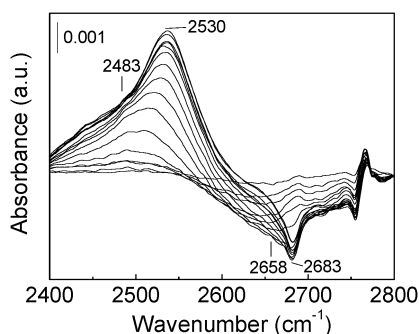

Fig. 4 IR spectra upon CO adsorption at 80 K on the HDP ASA containing 5 wt% Al$_2$O$_3$ calcined at 1073 K after progressive H/D exchange at 323 K for 1800 s.

adsorption on an H/D exchanged ASA point to an asymmetric strong perturbation of the band around 2683 cm^{-1}. First, the low-frequency tail of this band gives rise to a band around 2483 cm^{-1} with $\Delta\nu_{OD} = 175$ cm^{-1} ($\Delta\nu_{OH} = 272$ cm^{-1}). The perturbed band shifts with increasing CO coverage as does the negative feature at higher frequency. These shifts point to the presence of sites of varying acidity. Finally, the band around 2683 cm^{-1} becomes perturbed and shifts to 2530 cm^{-1} ($\Delta\nu_{OH} = 238$ cm^{-1}). These shifts place the intrinsic acidity of these BAS in ASAs close to that of the bridging OHs in zeolites.[21]

Based on propane cracking experiments, Xu *et al.*[8] have earlier concluded that ASAs contain Brønsted acid sites of zeolitic strength. Here we provide the first time spectroscopic evidence for this conjecture. Their density in ASAs is 2–3 orders of magnitude lower than in zeolites. The spectroscopic signature of these sites is in support of the Al-for-Si substitution model. Another indication is that ASA's acidity increases with

the calcination temperature to be understood in terms of more extensive diffusion of Al into the silica network.[24] The acidic hydroxyl groups can be observed by IR spectroscopy after their selective H/D exchange under carefully chosen conditions. The differences in the overall Brønsted acidity of aluminosilicates are dominated by differences in the concentrations of these sites. Thus, the development of strong Brønsted acidity does not require a crystalline framework. This work has two further implications. First, as strong Brønsted acidity can develop over an open surface, it may be safely assumed that the external surface of zeolite crystals can also contain strong acid sites.[25,26] Second, the notion that the acidity of ASAs is limited by the very small number of Si^{4+} → Al^{3+} substitutions provides a clear direction for research to improve the acidity of ASAs.

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