

# Tuning Acid Strength in Amorphous Aluminosilicates with Oxygen Vacancies



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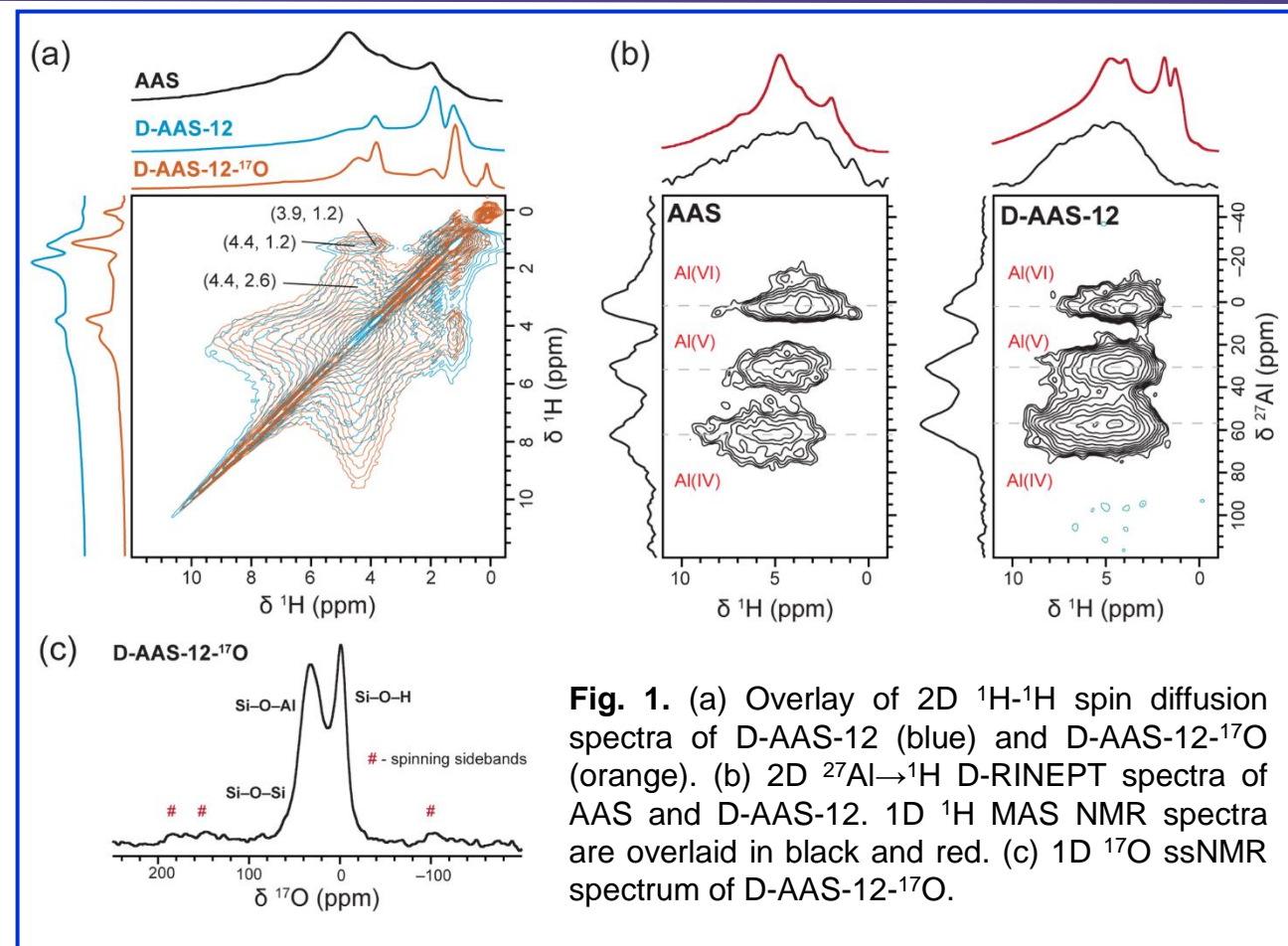
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Finding solid materials with both high porosity and strong acidity is a significant challenge in the design of heterogeneous catalysis. Crystalline zeolites are known for their strong acidity, but their small pores limit access to active sites. Conversely, mesoporous amorphous aluminosilicates have larger pore sizes, but typically have low acidity. In this study, we demonstrate that introducing defects, specifically oxygen vacancies, can enhance the acidity of amorphous acidic aluminosilicates (AAS). This approach improves both the effectiveness and accessibility of their active sites, addressing the challenge of balancing porosity and acidity and paving the way for the design of more efficient catalysts for various chemical reactions.

In this work, we utilized high-field solid-state nuclear magnetic resonance (ssNMR) spectroscopy at the MagLab to investigate structural changes in defective amorphous acidic aluminosilicates (D-AAS), in which oxygen vacancy defects were introduced. <sup>27</sup>Al, <sup>17</sup>O, and <sup>1</sup>H ssNMR spectra were acquired at 18.8 T (800 MHz) due to the significantly enhanced spectral resolution at this high field (**Fig. 1**). The powerful analytical capabilities at the MagLab are demonstrated, with notable shifts in <sup>1</sup>H ssNMR spectra indicating changes in hydrogen bonding and formation of new hydroxyl species, <sup>27</sup>Al ssNMR revealing alterations in aluminum coordination environments upon introducing defects, and <sup>17</sup>O ssNMR showing how water interacts with defect sites, linking structural modifications to acidity changes.

This research shows how manipulating defects in amorphous aluminosilicates can enhance their acidity, opening doors to the creation of new and improved catalysts. These advancements could lead to more efficient industrial processes and help tackle environmental challenges associated with many heterogeneous catalytic techniques.



**Fig. 1.** (a) Overlay of 2D <sup>1</sup>H-<sup>1</sup>H spin diffusion spectra of D-AAS-12 (blue) and D-AAS-12-<sup>17</sup>O (orange). (b) 2D <sup>27</sup>Al-<sup>1</sup>H D-RINEPT spectra of AAS and D-AAS-12. 1D <sup>1</sup>H MAS NMR spectra are overlaid in black and red. (c) 1D <sup>17</sup>O ssNMR spectrum of D-AAS-12-<sup>17</sup>O.

**Facilities and instrumentation used:** NMR User Program: NMR experiments were run at 18.8 T (800 MHz) with 3.2 mm HXY and 1.3 mm HXY probes designed and built at the MagLab.

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