

Supporting information for

**Insights into Functionality-Specific Adsorption Dynamics and
Stable Reaction Intermediates Using Fast Field Cycling NMR**

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Characterization of ^1H and ^{13}C NMR spectra of acetone adsorbed on γ -alumina.

NMR spectroscopy experiments were performed on a Bruker Ascend 300 MHz spectrometer equipped with Micro 5 probe and a 5 mm $^1\text{H}/^{13}\text{C}$ coil. ^1H spectra were acquired in a single scan and the experiment was repeated over the course of several days to monitor the time dependence of the reaction (Fig. S1). ^1H chemical shifts are referenced to the ^1H resonance of tetramethylsilane.

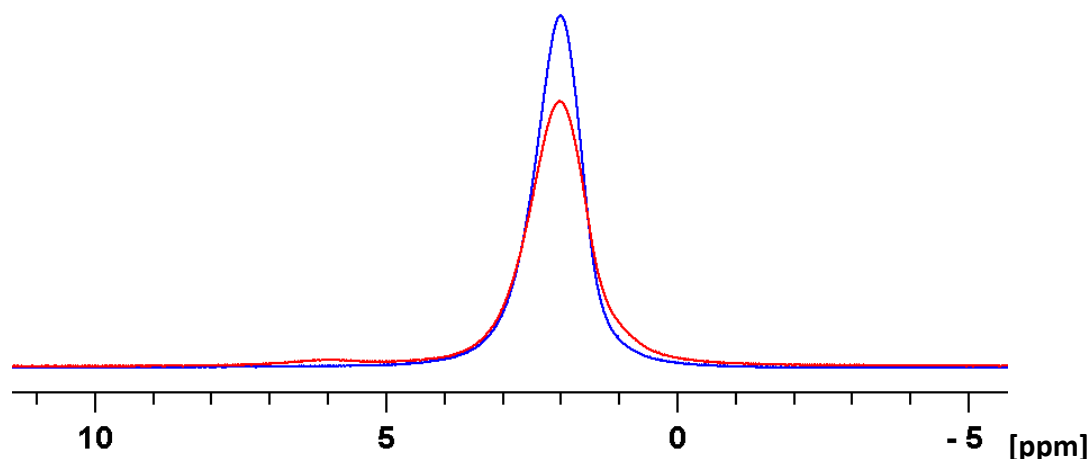


Figure S1: The ^1H spectra of acetone adsorbed on γ -alumina 10 min after preparing the sample (blue) and after 48 h (red).

Significant line broadening is observed due to internal gradient effects within the sample, making full resolution of individual ^1H resonances impossible. It is worth noting, however, that over time the intensity of the starting material peak decreases, and there is a concurrent growth of a side peak at 1 ppm and a second peak at 6 ppm. The latter corresponds to either ^1H spins associated with hydrogen atoms attached to unsaturated carbon environments or water, both of which are expected in the case of an aldol reaction. To confirm that the aldol reaction was occurring, the sample was studied using ^{13}C NMR (Fig. S2). This allowed the clear identification of acetone (A), a β -hydroxy ketone intermediate (C) and the final product mesityl oxide (D), as referred to in the reaction scheme (Fig. 7) in the manuscript. Assignments were performed based on the expected chemical shifts and through comparison with literature data for similar systems.¹ No evidence of the enolate intermediate (B) was observed, however its existence (or an equivalent reaction intermediate) is implied by the formation of the other species. As was evidenced by the change in the ^1H spectra with time, the acetone- γ -alumina system was chemically reactive. The ^{13}C NMR spectroscopy data recorded over the same timescale showed that the concentration of the β -hydroxy ketone intermediate reached steady state in only a few hours, whilst the concentration of mesityl oxide increased with time – suggesting that the β -hydroxy ketone intermediate is formed in a rapid pre-equilibrium.

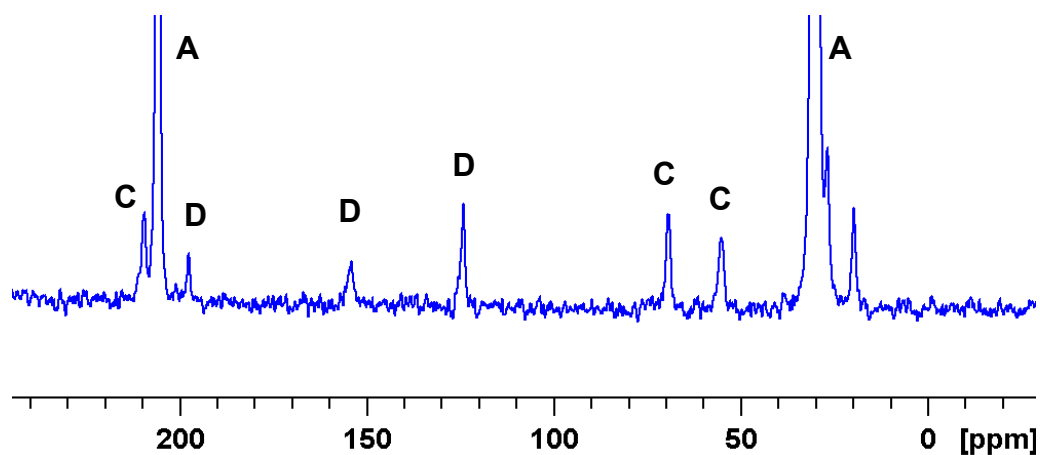


Figure S2: The ^{13}C spectrum of acetone adsorbed on γ -alumina. The spectrum was acquired with 4096 signal averages 18 h after the start of the reaction, allowing the unambiguous assignment of acetone (A), a β -hydroxy ketone intermediate (C), and mesityl oxide (D). ^{13}C chemical shifts are referenced to the ^{13}C resonance of tetramethylsilane.

References

- (1) Singhal, A.; Pai, M. R.; Rao, R.; Pillai, K. T.; Lieberwirth, I.; Tyagi, A. K. Copper (I) Oxide Nanocrystals – One Step Synthesis , Characterization , Formation Mechanism, and Photocatalytic Properties. *Eur. J. Inorg. Chem* **2013**, 2640–2651.