Supporting Information

Kinetic and Mechanistic Examination of Acid-Base Bifunctional Aminosilica Catalysts in the Aldol and Nitroaldol Condensations

Virginia E. Collier, Nathan C. Ellebracht, George I. Lindy, Eric G. Moschetta,* and Christopher W. Jones*

School of Chemical & Biomolecular Engineering, Georgia Institute of Technology, 311 Ferst Drive NW, Atlanta, GA 30332, USA

*Corresponding authors: eric.moschetta@chbe.gatech.edu, cjones@chbe.gatech.edu

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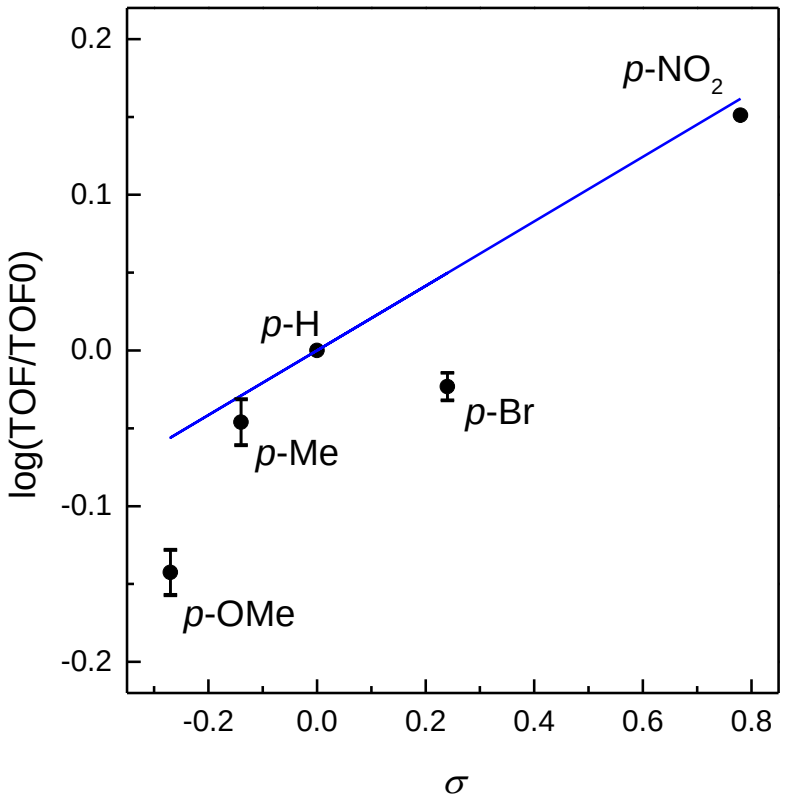


Figure S1. Hammett plot for *para*-substituted benzaldehydes in the nitroaldol condensation with nitromethane at 40 °C using σ values. The TOF values were obtained using the initial rate over the first hour of reaction. The TOF_0 value is the TOF obtained when using the reference benzaldehyde (*p*-H). Compared to Figure 6 in the main text, notice that (i) the linear fit is substantially worse when using σ values and (ii) the traditional σ value for *p*-OMe does not account for the through-resonance effects discussed in the main text, which is why σ^+ values allowed for a better linear fit of the reactivity data.

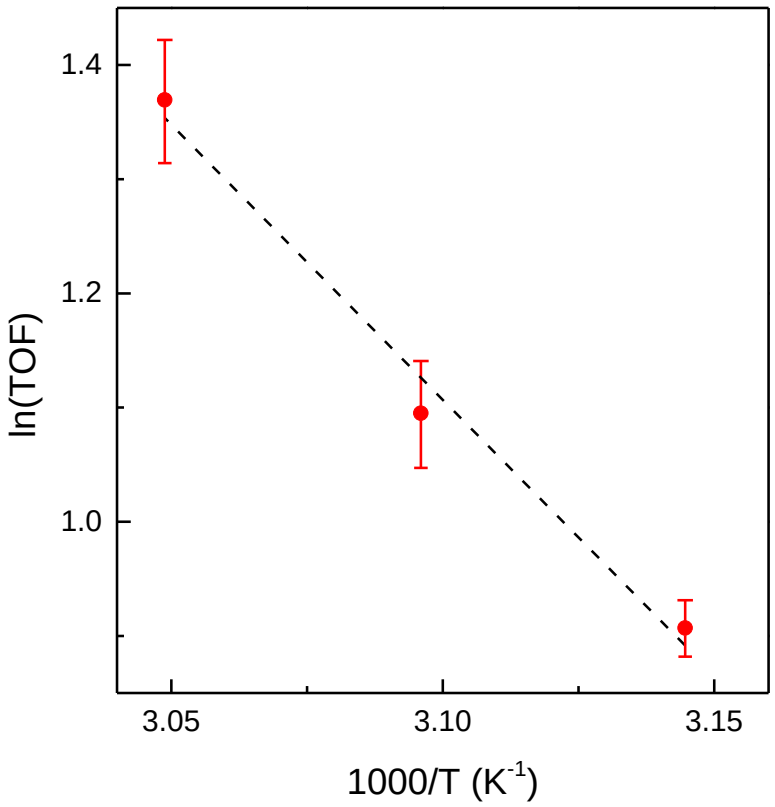


Figure S2. Arrhenius plot for the aldol condensation of 4-nitrobenzaldehyde with acetone from 45-55 °C using catalyst MCM-C4-0.57-A with available silanols.

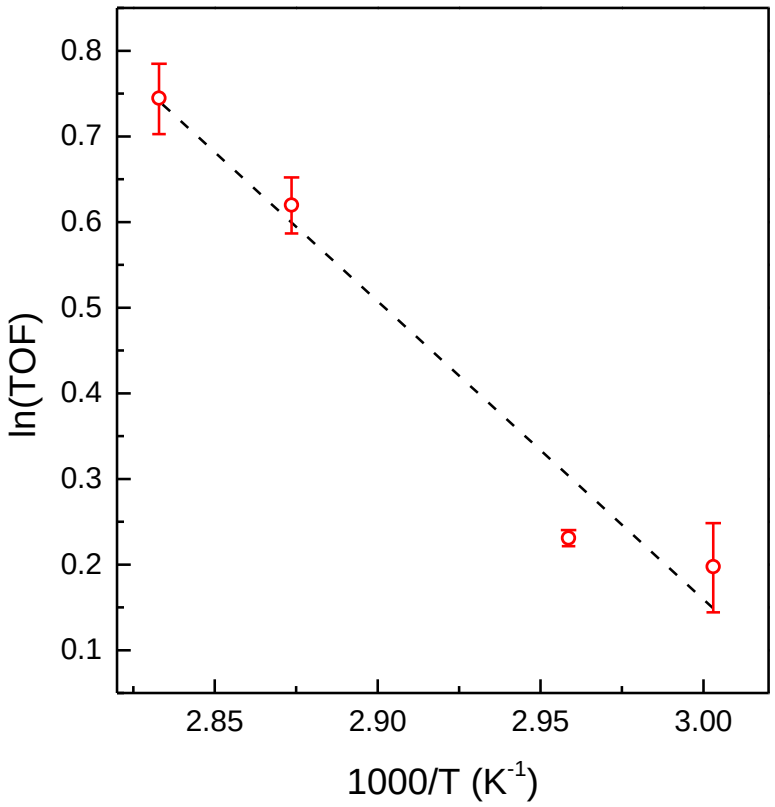


Figure S3. Arrhenius plot for the aldol condensation of 4-nitrobenzaldehyde with acetone from 60-80 °C using catalyst MCM-C4-0.57-A-HMDS with trimethylsilyl-capped silanols.

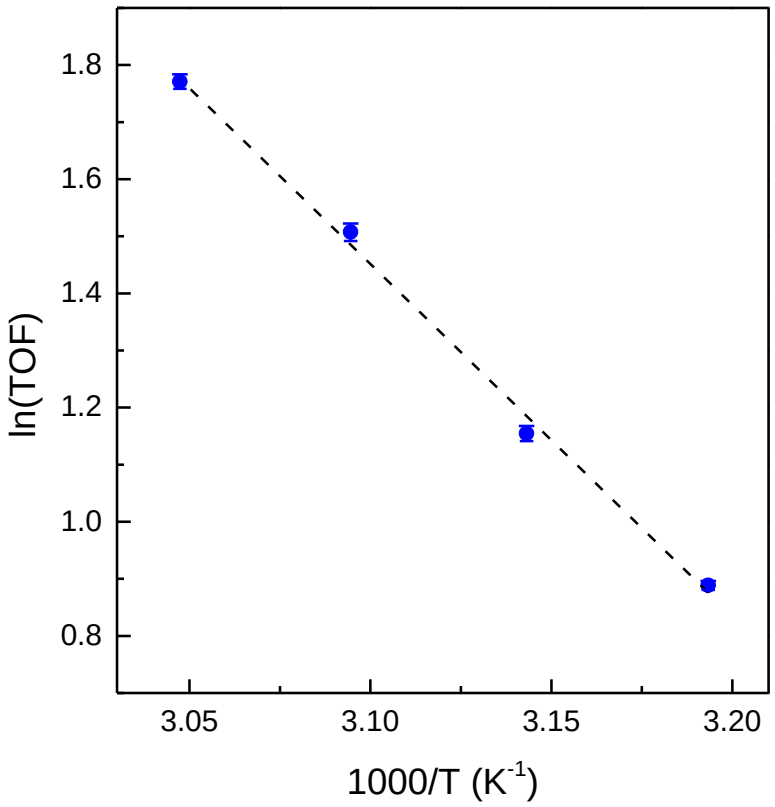


Figure S4. Arrhenius plot for the nitroaldol condensation of 4-nitrobenzaldehyde with nitromethane from 40-55 °C using catalyst MCM-C4-0.57-A with available silanols.

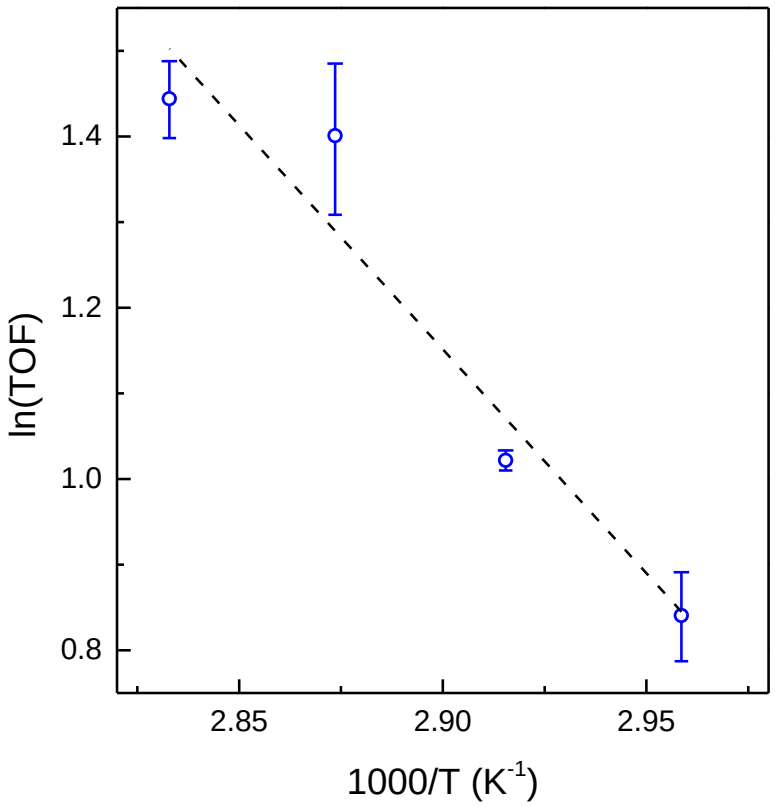


Figure S5. Arrhenius plot for the nitroaldol condensation of 4-nitrobenzaldehyde with nitromethane from 65-80 °C using catalyst MCM-C4-0.57-A-HMDS with trimethylsilyl-capped silanols.

Transmission electron microscopy (TEM) was performed on an FEI Tecnai G2 F30 electron microscope with a field emission gun and acceleration voltage set at 300 kV. Images were recorded with a Gatan US4000 CCD camera. A representative TEM image of the MCM-41 used in this study is shown in Figure S6 below.

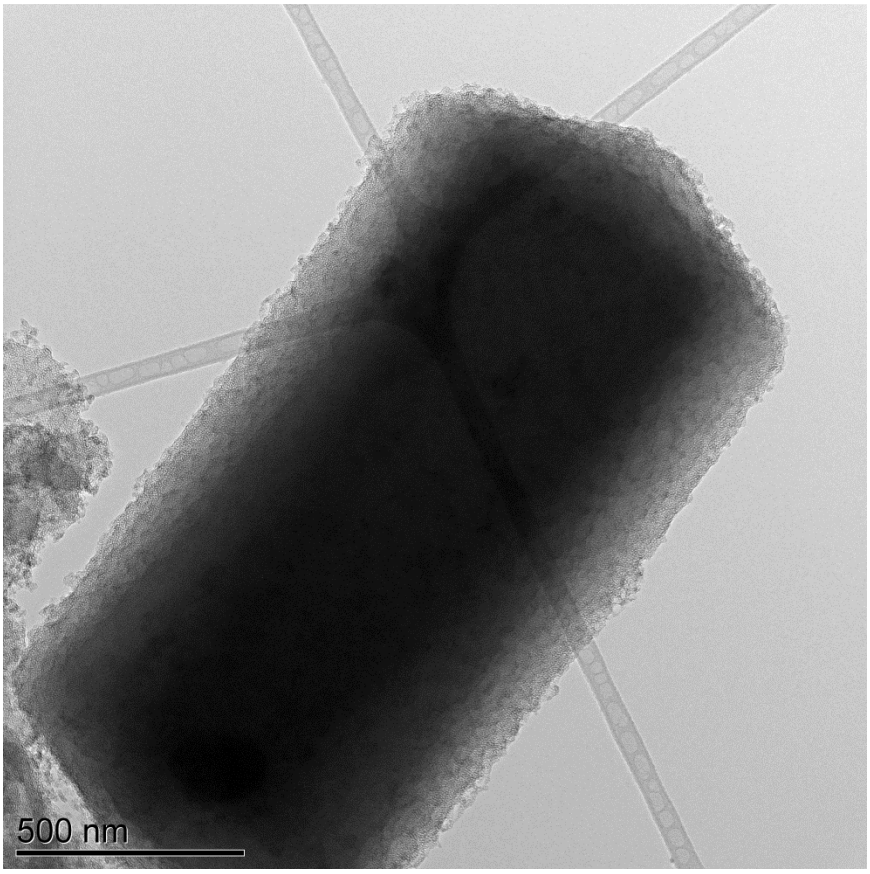
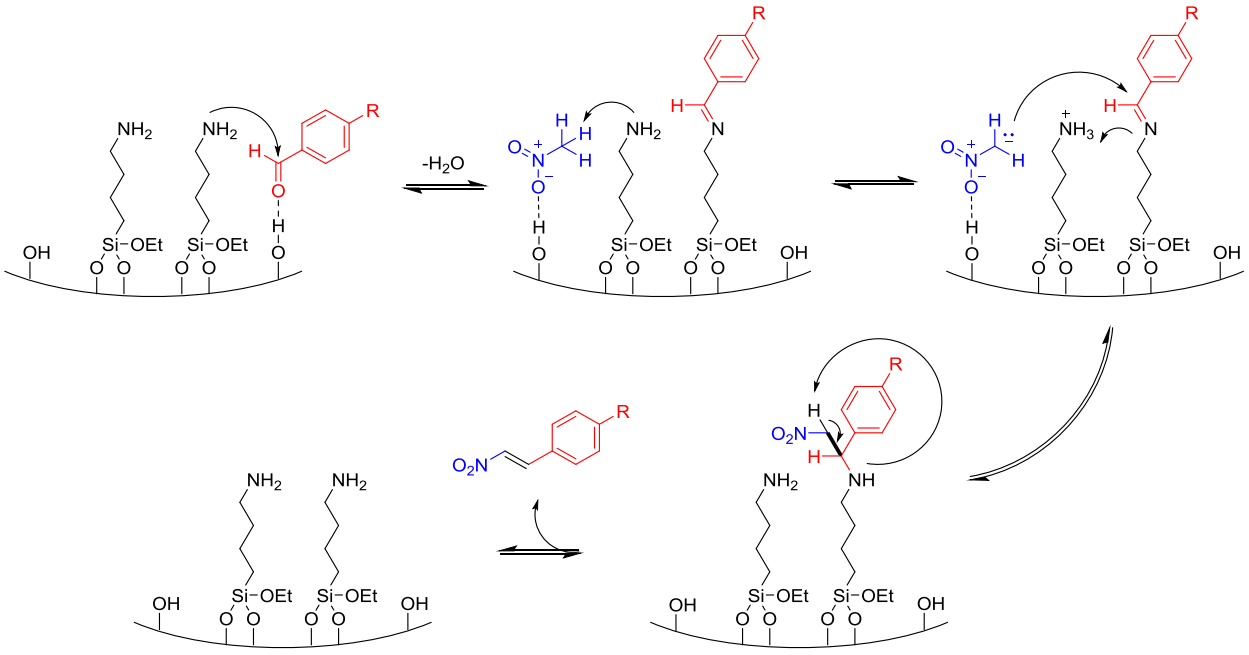


Figure S6. TEM of the unfunctionalized MCM-41 silica used as the catalyst support in all experiments.



Scheme S1. Alternative nitroaldol condensation mechanism involving the formation of an imine (a secondary aldimine) directly from nucleophilic attack of the aldehyde.[1–3] Notice that the condensation product, the nitrostyrene, is formed directly in this mechanism. In the mechanisms discussed in the main text, the nitroalcohol product is formed, but in the presence of acids and bases, dehydration of the nitroalcohol is facile, which could explain why only the nitrostyrene products were observed in NMR spectra of the crude mixtures of each benzaldehyde derivative after 1 h of reaction time at 40 °C.

Table S1. Turnover frequencies (TOFs) for the Arrhenius analysis of the aldol condensation. Values were obtained for catalysts with accessible silanols (MCM-C4-0.57-A) and inaccessible silanols (MCM-C4-0.57-A-HMDS) at different temperatures.

Material	Temperature (°C)	TOF (h^{-1})
MCM-C4-0.57-A	45	2.5 ± 0.1
	50	3.0 ± 0.1
	55	3.9 ± 0.2
MCM-C4-0.57-A-HMDS	60	1.2 ± 0.1
	65	1.3 ± 0.1
	75	1.9 ± 0.1
	85	2.1 ± 0.1

Table S2. Turnover frequencies (TOFs) for the Arrhenius analysis of the nitroaldol condensation. Values were obtained for catalysts with accessible silanols (MCM-C4-0.57-A) and inaccessible silanols (MCM-C4-0.57-A-HMDS) at different temperatures.

Material	Temperature (°C)	TOF (h^{-1})
MCM-C4-0.57-A	40	2.4 ± 0.1
	45	3.2 ± 0.1
	50	4.5 ± 0.1
	55	5.9 ± 0.1
MCM-C4-0.57-A-HMDS	65	2.3 ± 0.1
	70	2.8 ± 0.1
	75	4.1 ± 0.4
	80	4.2 ± 0.2

References

(1) Demicheli, G.; Maggi, R.; Mazzacani, A.; Righi, P.; Organica, C.; Mangini, A. *Tetrahedron Lett.* **2001**, *42*, 2401–2403.

(2) Bass, J. D.; Solovyov, A.; Pascall, A. J.; Katz, A. *J. Am. Chem. Soc.* **2006**, *128*, 3737–3747.

(3) Sharma, K. K.; Biradar, A. V; Asefa, T. *ChemCatChem* **2010**, *2*, 61–66.