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Insights into Substituent Effects of Benzaldehyde Derivatives in a Heterogeneous Organocatalyzed Aldol Reaction

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Organocatalyst immobilization onto solid supports represents a promising method for enabling asymmetric organocatalysis while retaining the advantages of heterogeneous catalysts, including catalyst separation, recycling, and the use of fixed-bed reactors. Understanding how such heterogenized catalytic systems work is fundamental to develop and tailor more efficient ones. Herein, we have elucidated the role of reactant molecular structure on surface interactions and reactivity for asymmetric aldol reactions between benzaldehyde derivatives and hydroxyacetone catalyzed by SBA-15 immobilized *L*-proline.

NMR relaxation time analysis reveals that a stronger interaction between the aldehyde and the catalyst surface reduces catalytic reactivity, which is attributed to reduced access of hydroxyacetone to the *L*-proline surface sites, hence inhibiting the formation of the enamine intermediate between hydroxyacetone and *L*-proline. The results show that surface phenomena in these systems are important considerations for reactant selection, opening up new directions to explore in this area of research.

Introduction

Asymmetric organocatalysis^[1–6] is undoubtedly a pivotal technological platform that is routinely employed by industry.^[7,8] Despite the great advancements and plethora of new reactions and activations discovered, the applications of organocatalysis have sometimes been hampered by its low turnover number (TON), the need for high catalyst loading, and tedious separation processes to isolate the product.^[9,10] Scientists have devised ingenious means to address this low productivity: recycle and reuse, development of highly active catalysts,^[11] or combining different types of catalysts.^[12,13] Another successful approach is represented by immobilization of organocatalysts over solid supports.^[14–19] The immobilization of proline, one of

the privileged organocatalysts, has been frequently investigated.^[20,21] However, unlike homogeneous organocatalysis, the reaction catalyzed by heterogeneous catalysts is heavily influenced by surface interactions between the support and the reaction species. Insights into surface interactions may help in improving and developing more efficient heterogeneous organocatalysts. As such, a technique that can offer a direct means to observe surface interactions in a heterogeneous environment is undoubtedly useful and informative. In recent years, the application of NMR spectroscopy,^[22–24] diffusion^[25–28] and relaxation^[29–32] techniques to heterogeneous catalysts has uncovered novel insights, highlighting the important role that transport, adsorption and surface dynamics of reaction species

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confined within the pore space play in determining catalytic performances.

Surface interactions and surface dynamics of reaction species are also believed to play an important role in the case of organocatalysts immobilized on solid supports. In fact, in many cases, organocatalysts immobilized on porous oxides have much lower catalytic performances when compared to their homogeneous counterpart operating in solution.^[33,34] Interestingly, if polymers are used as support materials, the immobilized organocatalysts tend to perform better than the ones immobilized on silica. In some cases, their activity is comparable to that of their homogeneous counterpart.^[35] Unlike inorganic porous oxides, which tend to have surfaces intrinsically functionalized with hydroxyl groups and potentially other reactive groups such as Lewis and Brønsted acidic sites, polymers are relatively inert. For example, in one of our recent works, we have observed that, by optimizing the choice of the solvent, N-heterocyclic carbene (NHC) organocatalysts immobilized over polystyrene particles show a catalytic activity that is comparable to the catalytic activity measured in homogeneous conditions.^[35]

These observations suggest that the solid support plays a key role and its effect on modulating interactions between organocatalysts, reaction species and solvents may lead to significant changes in reactivity. Investigating these interactions is, therefore, essential to rationalize catalytic behavior.

Whilst most of the efforts in this area have been devoted to the study of solvents, the role of surface interactions of reactant species in organocatalytic reactions occurring over solid surfaces remained largely unexplored. This is particularly the case for the reaction studied in this work, whereby we investigate an aldol condensation between hydroxyacetone and a series of benzaldehyde derivatives, in the presence of *L*-proline supported on SBA-15. In particular, according to a generally accepted reaction mechanism, the formation of an initial complex between the aldehyde partner and the organocatalyst is suggested to affect the catalytic cycle by preventing the formation of the hydroxyacetone/*L*-proline adduct.^[36] Competitive adsorption between reaction partners becomes therefore an important parameter to consider, yet, to the best of our

knowledge, no such data have been reported for this type of catalytic systems.

In this work, NMR spin relaxation is used for the first time as a means to investigate competitive adsorption of reaction partners in such catalytic systems. Results on the catalytic performance of different aldehydes are rationalized *via* a critical comparison with NMR relaxation time analysis, and within the context of the accepted reaction mechanism of the reaction, to provide insights between the nature of the aldehyde and catalytic behavior of the supported organocatalyst under investigation.

Results and Discussion

Building on our previous work on the effect of solvents in heterogenized proline mediated aldol reaction,^[33] hydroxyacetone **1** was reacted with electronically diversified benzaldehydes **2a–e** to investigate the role of the acceptor. Proline supported on SBA-15 mesoporous silica **4** was selected as the immobilized organocatalyst for investigation; **4** was prepared according to a previously reported procedure.^[33] All reactions were carried out with *L*-proline (conditions A) and **4** (conditions B) and compared in terms of turn over frequency (TOF).

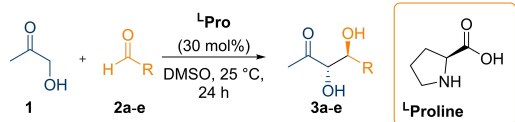
A summary of the results is presented in Table 1. Lower TOFs were always measured when the immobilized organocatalyst **4** (heterogeneous conditions) was used, as opposed to *L*-proline (homogeneous conditions). A similar diastereomeric ratio (dr) is observed in all entries with a relatively small variation. Conversely, enantioselectivity is slightly lower with **4**; this could be attributed to additional non-covalent interactions between silica functional groups and species involved in the stereoselective determining step. We note that the solvent is likely to impact not only the TOF but also the enantioselectivity. However, such effects would be much more complex to unravel purely based on competitive adsorption effects as they would involve other aspects, such as adsorption geometry and changes in transition states. Though other approaches, including computational DFT, could be useful for investigating this behavior, these are out of the scope of this work.

Table 1. Organocatalyzed aldol reaction of **1** with different aldehydes **2a–e**.^[a]

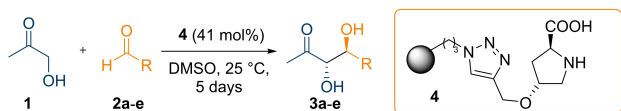
| R | Conditions | TOF [h ⁻¹] × 10 ³ [b] | dr ^[c] | ee [%] ^[d] |
|---|------------|--|-------------------|-----------------------|
| Ph (2a) | A | 60.7 | 74:26 | 88 (42) |
| | B | 11.3 | 79:21 | 78 (29) |
| 2-F-C ₆ H ₄ (2b) | A | 93.3 | 77:23 | 86 (23) |
| | B | 18.9 | 72:28 | 80 (28) |
| 3-Br-C ₆ H ₄ (2c) | A | 104.0 | 76:24 | 68 (41) |
| | B | 15.9 | 73:27 | 73 (54) |
| 4-MeO-C ₆ H ₄ (2d) | A | 60.6 | 73:27 | 88 (48) |
| | B | 10.9 | 71:29 | 76 (31) |
| 4-Me-C ₆ H ₄ (2e) | A | 53.9 | 73:27 | 90 (43) |
| | B | 6.2 | 72:28 | 80 (32) |

[a] Reaction conditions A: hydroxyacetone **1** (2.4 mmol, 24 equiv.), aldehydes **2a–e** (0.1 mmol, 1 equiv.), *L*-proline (30 mol%), DMSO (0.8 mL), 25 °C, 24 h; Reaction conditions B: hydroxyacetone **1** (2.4 mmol, 24 equiv.), aldehydes **2a–e** (0.1 mmol, 1 equiv.), **4** (41 mol%), DMSO (0.8 mL), 25 °C, 5 days. [b] TOF calculated from the averaged rate over the course of the reaction (24 h for the homogeneous catalyst and 120 h for the immobilized catalyst) as mmol-product/(mmol-cat × time in hours). [c] dr determined by ¹H NMR analysis of the crude reaction mixture. [d] ee determined by HPLC on a chiral stationary phase; ee values of minor diastereoisomer are reported in brackets. See ESI for further details.

Homogeneous catalyst (conditions A)



Heterogeneous catalyst (conditions B)



NMR relaxation measurements were performed to characterize surface interactions between benzaldehyde derivatives and the surface of immobilized organocatalyst 4. A typical data set of T_1 and T_2 data is shown in Figure 1, which shows the

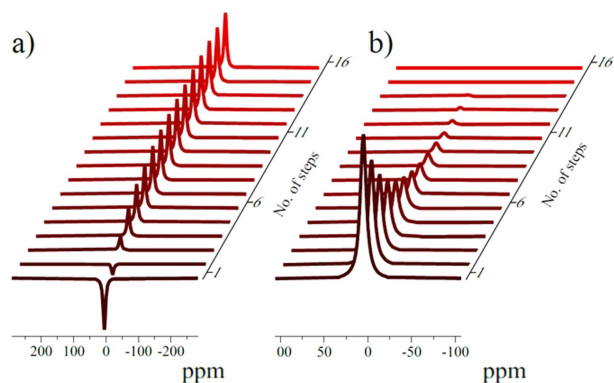


Figure 1. (a) T_1 NMR signal and (b) T_2 NMR signal as a function of time delay steps of 3Br-benzaldehyde 2c adsorbed in the immobilized organocatalyst 4.

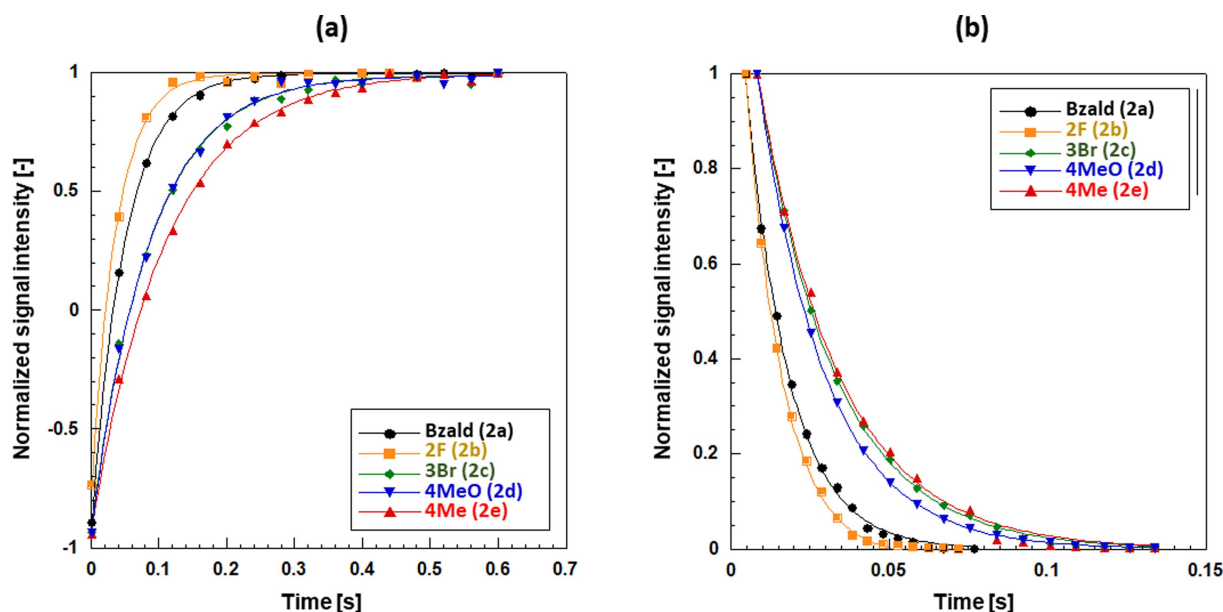


Figure 2. (a) T_1 inversion recovery and (b) T_2 CPMG experimental data for the various benzaldehyde derivatives adsorbed within the SBA-15-immobilized catalyst 4. Solid lines are fitting to (a) Equation (S1) and (b) Equation (S2).

evolution of the NMR spectra for T_1 inversion recovery (Figure 1a) and T_2 Carr-Purcell-Meiboom-Gill (CPMG) (Figure 1b) experiments for 3-Br-benzaldehyde 2c adsorbed within 4.

Figure 2 shows the experimental data obtained from T_1 inversion recovery (Figure 2a) and T_2 CPMG (Figure 2b) measurements for the various benzaldehyde derivatives adsorbed within the catalyst pore space. The data set is obtained by integrating the area under each NMR peak (*cf* Figure 1) as a function of the time delay associated with each acquisition step. The T_1 data were fitted using Equation (S1) and the T_2 data were fitted using Equation (S2) (see ESI). The agreement between the experimental data and fitting are excellent in all cases.

The obtained values of the T_1 and T_2 time constants are reported in Table 2, together with the values of the T_1/T_2 ratio. As expected for liquids adsorbed inside the porous catalysts, the T_1/T_2 ratio for all cases is greater than 1. This ratio is a robust indicator to characterize surface interactions of liquids adsorbed over surfaces, including organic liquids adsorbed over silica, metal oxides and supported metal nanoparticles.^[37] This has been confirmed by experimentally (temperature-programmed desorption) and computationally (Density-Functional Theory).^[38]

Taking benzaldehyde 2a as a reference, the results in Table 2 suggest that halogen-substituted benzaldehyde species, such as 2-F-benzaldehyde 2b and 3-Br-benzaldehyde 2c have a lower T_1/T_2 , i.e., a lower affinity with the solid surface of the heterogenized catalysts, whereas 4-MeO-benzaldehyde 2d and 4-Me-benzaldehyde 2e have higher T_1/T_2 values, hence higher affinity. This may suggest that the electronic properties of the substituents are likely to affect the adsorption properties of the benzaldehyde derivatives, and that electron-donating groups (such as in 2d and 2e) tend to increase substrate/surface affinity.

Table 2. Values of T_1 and T_2 NMR relaxation time constants and their ratio T_1/T_2 for different benzaldehyde derivatives adsorbed in the solid organocatalyst **4**.

| Reactant | T_1 [ms] | T_2 [ms] | T_1/T_2 [-] |
|-----------|------------|------------|---------------|
| 2a | 51 ± 1 | 13.4 ± 0.3 | 3.81 ± 0.09 |
| 2b | 36 ± 1 | 11.0 ± 0.2 | 3.27 ± 0.08 |
| 2c | 87 ± 2 | 24.5 ± 0.5 | 3.55 ± 0.09 |
| 2d | 85 ± 2 | 21.3 ± 0.4 | 3.99 ± 0.10 |
| 2e | 111 ± 2 | 25.5 ± 0.5 | 4.35 ± 0.10 |

For further insights, it is interesting to correlate catalyst activity and adsorption properties as probed by the NMR T_1/T_2 ratio. Figure 3 shows a plot of the TOF of the heterogeneously catalyzed reaction against the T_1/T_2 ratio. The plot shows that the higher the affinity of the benzaldehyde derivatives **2a–e** with the catalyst surface (i.e., higher T_1/T_2), the lower the TOF recorded for the reaction. To rationalize this correlation, the reaction mechanism, including possible side reactions need to be taken into account. Kinetics and computational studies, that were performed to elucidate both the additive effect of water and the rate-determining step of the reaction, are of paramount importance in this regard.^[39] Experimental evidences suggest that interactions between proline and aldehyde could be detrimental for the reaction. In fact, according to Blackmond *et al.*,^[36] the kinetics of the reaction is driven by the addition of the enamine adduct to the aldehyde and small amount of water was reported to be beneficial for the reaction by hydrolyzing the iminium, generated by condensation of aldehyde with proline.

The dependence of reaction rate on the aldehyde's electronic properties is well-known and has been investigated via Hammett plot experiments by Benaglia *et al.*^[40] From proline catalyzed aldol reaction between cyclohexanone and benzaldehyde derivatives, they observed a positive correlation between

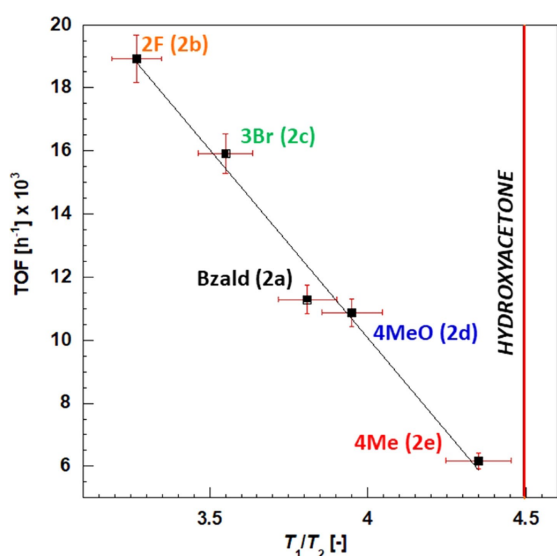


Figure 3. TOF vs T_1/T_2 for benzaldehyde derivatives **2a–e** adsorbed within **4**. The vertical red line indicates the T_1/T_2 for hydroxyacetone **1**.

the rate of reaction and electrophilicity (Hammett electrophilic constants) of benzaldehyde, i.e. electron-poor benzaldehyde derivatives with withdrawing substituents exhibit an increased reactivity. The undesired formation of the iminium adduct, by condensation of benzaldehydes with proline, has been demonstrated by Blackmond^[36] and Pihko,^[41] with the addition of small amounts of water suppressing this undesirable process. It is reasonable to assume that a high affinity between the aldehyde and the surface of the solid matrix can facilitate the interaction with the proline moiety anchored over the surface, leading to a deactivation of the active site through the formation of a proline-aldehyde iminium adduct, which in turn inhibits the formation of the hydroxyacetone-proline adduct and leads to a decrease in reactivity.

Indeed, a lower TOF is measured for T_1/T_2 of **2a–e** closer to T_1/T_2 of hydroxyacetone **1** (vertical red line), and this can be correlated to higher substrate inhibition resulting in a decreased catalyst activity (Figure 3). Whilst previous studies using NMR relaxation in heterogeneous catalysis^[42,43] and heterogenized organocatalysis^[33,35] have focused exclusively on solvent/substrate interactions, by performing a systematic screening of solvents using the same reaction system, here we show that competitive adsorption between substrates bearing substituents with different electronic properties is also a critical parameter for consideration.

It is important to clarify that adsorption effects on solid surfaces are not the only effects to consider when explaining reactivity in such systems. Stereo-electronic effects also play an important role in reactivity, as indicated by Linear Free Energy Relationship^[40] experiments, such as Hammett plots, that provided a quantitative relationship between reactivity and structure, reported for proline-catalyzed aldol reactions. Electrophiles bearing electron-withdrawing group tend to exhibit higher reactivity. However, from Table 1 it is possible to observe some deviation from the expected behavior based on Hammett parameters. For example, 3-Br substituted benzaldehyde **2c** shows higher reactivity than 2-F analogue **2b** in homogeneous conditions whereas the trend is inverted in the heterogeneous ones. Furthermore, the reactivity observed for 4-MeO- and 4-Me-benzaldehyde derivatives (**2d** and **2e**, respectively) in homogeneous conditions is comparable, whereas the TOF, in heterogeneous conditions is almost halved for **2d** when compared to **2e**. These results show that the electrophilicity of the acceptor (i.e. the aldehyde) influenced by the substituent does not fully explain the reactivity trend in heterogeneous conditions; reversible deactivation, due to electrophile adsorption, plays an important role, in line with previous observations reported in the literature, whereby the aldehyde acceptor-proline interaction is the main cause of the decreased reactivity.^[39,41] Whilst these effects might be challenging to explore and decouple, it is possible to make some qualitative considerations by normalizing the TOF of the heterogeneous reaction over the one of the homogeneous reaction. When such a normalized ratio is considered against T_1/T_2 (see ESI, Figure S1), it is possible to observe that a qualitative trend still exists, which suggests that, indeed, adsorption effects of benzaldehyde substrates are an

important factor to consider in the reaction system investigated in this work.

Conclusions

Asymmetric aldol reactions between benzaldehyde derivatives **2a–e** and hydroxyacetone **1** catalyzed by *L*-proline immobilized over SBA-15 silica **4** have been studied by combining catalytic reaction screening in homogeneous (*L*-proline) and heterogeneous (immobilized *L*-proline) conditions with NMR relaxation studies. NMR studies were instrumental in characterizing the strength of surface interactions between the various benzaldehyde derivatives and the catalyst surface. The results show that adsorption effects are an important consideration that can affect reactivity within the heterogenized proline catalyst **4**. In particular, spectroscopic measurements of NMR relaxation times, T_1 and T_2 allowed the characterization of the affinity between the catalyst surface and aldehyde derivatives; the results indicate that aldehydes with higher affinity for the catalyst surface tend to limit the catalyst activity, leading to lower TOFs. This may be attributed to the inhibition caused by the presence of off-cycle species due to the formation of the iminium ion intermediate between benzaldehyde derivatives and *L*-proline.

It is worth noting that the current study has been carried out on proline immobilized SBA-15 and an extrapolation to other supports^[19] is hardly reliable given the differences in surface properties of different supports. However, this work proves that surface phenomena in immobilized organocatalysts are important considerations for the selection of substrates, hence rationalizing these effects can help in the optimization of reactions.

Experimental Section

Organocatalyzed reactions: To a mixture of *L*-proline (30 mol%, 3.5 mg) or **4** (41 mol%, 78 mg), hydroxyacetone **1** (2.4 eq., 2.4 mmol, 165 μ L) and DMSO (800 μ L) aldehyde **2a–e** (1 eq., 0.1 mmol) was added. After the reaction mixture was stirred at room temperature for 24 hours (with *L*-proline) or 5 days (with **4**). The reaction was quenched with 5 mL of NH_4Cl 0.5 M. The aqueous mixture was extracted with DCM (4 \times 5 mL) and the combined organic layers were washed with brine and dried over MgSO_4 and concentrated under vacuum after filtration. The crude reaction was dissolved in 1 mL of a solution of internal standard (durene) in CDCl_3 (stock solution containing 0.5 eq. of durene with respect to the aldehyde). The products have not been purified. NMR yield was determined by $^1\text{H-NMR}$ of the crude reaction mixture using durene as internal standard (NMR D1 parameter was set to 10 seconds). **NMR experiments:** Samples for NMR experiments were prepared by soaking the catalyst particles in the liquid reagent under investigation for 24 hours. The catalyst particles were then gently dried on a pre-soaked filter paper in order to remove any excess liquid on the outer surface of the particles and then transferred to 5 mm NMR tubes. The sample was finally placed into the magnet and left for approximately 20 minutes to thermally equilibrate before the start of the measurements. All measurements were carried out at atmospheric pressure and $26^\circ\text{C} \pm 0.5^\circ\text{C}$. NMR relaxation measurements were performed in a Magritek SpinSolve benchtop NMR

spectrometer operating at a ^1H frequency of 43 MHz. T_1 relaxation measurements were performed using an inversion recovery pulse sequence, acquiring 16 experimental points for each experiment with time delay values between 1 ms and 1000 ms, 16–64 scans and a repetition time of 1000 ms. T_2 relaxation measurements were performed with the CPMG (Carr Purcell Meiboom Gill) pulse sequence, with an echo time of 120 μ s, using 16 steps with a number of echoes per step varying in the range 40–70, 64–128 scans and a repetition time of 1000 ms.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

All data supporting this study are provided in full in the 'Results and Discussion' section of this paper as well as in the associated supporting information.

Keywords: heterogeneous catalysis · NMR relaxation · organocatalysis · proline

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