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Insights on hydrogen bond assisted solvent selection in certain acid–base heterogeneous catalysis through acceptor and donor numbers†

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The choice of an appropriate solvent in heterogeneous catalysis is not always straightforward but it affects significantly the activity and selectivity in organic reactions. Here we show that the acceptor number (AN) and donor number (DN) make the selection of solvent robust and competitive compared to traditional solvent properties such as dielectric constant, polarity and nature. The conversion rates measured in selected acid or base-catalysed reactions in the liquid phase (alkylation, acylation, esterification, condensation) consistently vary with the AN or DN of the solvents in which they are achieved. The impact of the AN and DN in these reactions was understood by addressing the interactions between the catalyst, solvents, and reactants through spectroscopic (FTIR and UV-vis) techniques and DFT simulations. The association between the AN and DN, and the catalytic performance is shown to proceed *via* the strength of the non-covalent hydrogen bond established between the partners of the reaction. The strength of hydrogen bonds of the solvent with the catalyst influences the acid sites of the catalyst directly and by this means plays a crucial role during the reaction. These findings build strong fundamental scientific information on the solvent effects in heterogeneous catalysis.

1. Introduction

Solvents are used extensively in all the steps of a catalytic process, such as during catalyst synthesis, catalytic testing, and product purification.[1] The role of the solvent is critical during the catalytic reaction as it dictates the reaction rate, conversion, and selectivity to different products.[2,3] However, the solvent effect during catalysis is often overlooked and is discussed cursorily in research papers. One reason for this could be the difficulty in selecting for a given reaction the appropriate solvent from a large variety of these solvents with different physicochemical properties, such as polarity, dielectric constant, solubility, boiling point, and so on. Nevertheless, selecting the best solvent could considerably improve the outcome of the reaction. The influence of solvents in organic synthesis and homogeneous catalysis has been extensively reviewed and is well understood.[2,3] However, very little attention was paid to understand the role of solvents in liquid-phase heterogeneous catalysis, and it remains a herculean task.[4,5] This could be due to the interface between the solid and liquid, making the investigation of boundary interactions complicated.[6]

The literature addresses in detail the influence of solvents in hydrogenation reaction of C–C double/triple bonds,[7] and nitro,[8,9] nitrile[10,11] and carbonyl[12] compounds over a supported metal catalyst.[13–15] However, limited work has been done on the solvent effect in acid–base heterogeneous catalysis.[16–20] There are no easily applicable criteria for selecting a solvent for any acid–base catalysis. Therefore, we tried to correlate the different classical properties of solvents, such as dielectric constant and polarity, boiling point, and nature of solvent, in particular whether they are protic or aprotic, with the observed catalytic activity in several acid–base reactions (see *infra*). None of these properties did directly correlate with the activity and selectivity we measured. Therefore, we came up with other "less classical" properties in the form of numbers proposed by Gutmann *et al.*, *i.e.* the acceptor number (AN) and donor number (DN) of solvents. These numbers are indicators of the Lewis acidic and basic properties of the solvents.[21,22] AN is based on the

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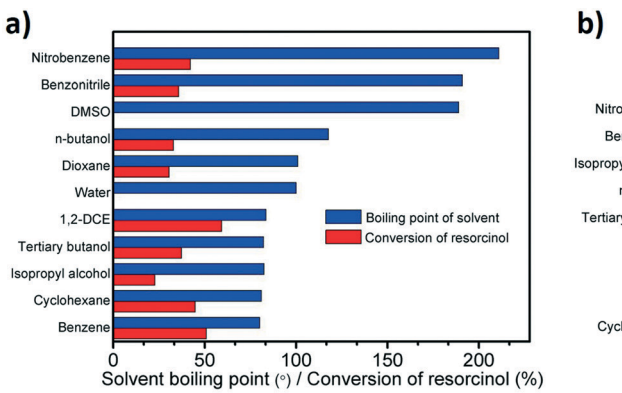
^{31}P-NMR chemical shift of triethyl phosphine oxide in the described solvent, whereas DN originates from the heat of reaction between the described solvent and $SbCl_5$ in CH_2-$ClCH_2Cl$.[3] These numbers have been well documented in organic chemistry, homogeneous catalysis and ionic liquids, but their application in heterogeneous catalysis has only scarcely been evoked.[23–26] Therefore, the current study will use these numbers to establish a new approach for solvent selection in heterogeneous acid–base catalysis.

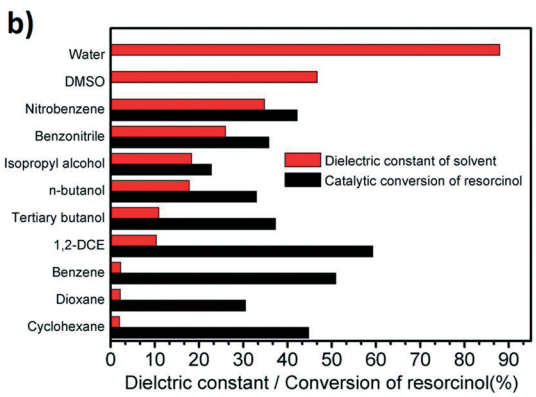
In the current work, well-known solid acid catalysts such as zeolites and sulphated zirconia (SZ) were selected for acid catalysed reactions, such as Friedel–Crafts alkylation of resorcinol, butanol esterification, Prins cyclization, and condensation. Hydrotalcite was employed for the base-catalysed Knoevenagel and Claisen–Schmidt condensation reactions. We looked at the correlation existing between the AN and DN and the catalytic activities measured in these different reactions performed in various solvents (cyclohexane, benzene, 1,2-dichlroroethane, nitrobenzene, acetonitrile, benzonitrile, *N*,*N*-dimethyl formamide, dimethysulfoxide, isopropanol, water, butanol, and triethylamine). The impact of the AN and DN in these reactions was understood by addressing the interactions between the catalyst, solvents, and reactants through spectroscopic (IR and UV-vis) techniques and DFT simulations. A major piece of understanding of our work is the fact that the strength of the hydrogen bonding established between the solvents and catalyst or reactant is intimately linked to the AN and DN of the solvents, which explains how these numbers are themselves related to the activity and selectivity in the explored reactions.

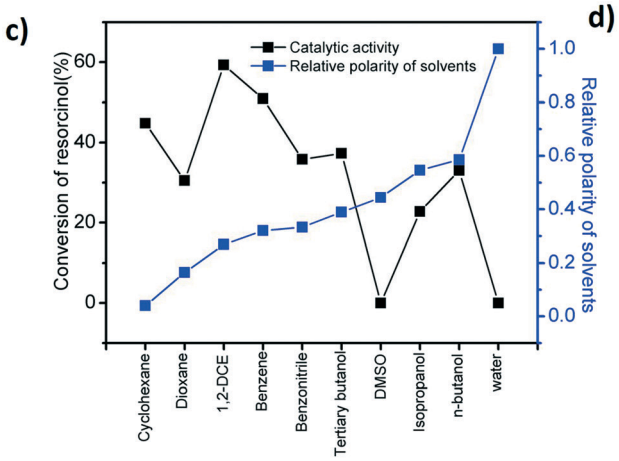
2. Results and discussion

To investigate the role of the solvents in acid catalysed reactions, Friedel–Crafts alkylation of resorcinol with tertiary butyl alcohol (TBA) was performed over HY zeolite (Scheme S1a†). Performing the reaction without solvent, or with the use of TBA in large excess, did not lead to significant modification of catalytic activity (Table S1† entries 1 and 2). The reaction was then carried out in different solvents. Completely distinct catalytic activities were obtained over the employed solvents (Table S1† entries 3–12).

In order to correlate the catalytic activity with different physicochemical properties of the solvents used, the conversion of resorcinol was plotted against the dielectric constant, boiling point, and polarity (Fig. 1a–d). None of these properties was well related with the observed catalytic







d)

Nature of Solvents	Conversion of Resorcinol (%)
Nonpolar	
Cyclohexane	44.8
Benzene	50.9
1,2-Dichloroethane	59.3
Polar -Aprotic	
Nitrobenzene	42.2
Benzonitrile	35.8
Dioxane	30.5
Dimethyl sulfoxide	0
Polar Protic	
Tertiary butanol	37.3
Isopropyl alcohol	22.8
n-butanol	33.0
Water	0.0

Fig. 1 Correlation of solvent's a) boiling point, b) dielectric constant, c) polarity, and d) nature with the resorcinol conversion in the Friedel–Crafts alkylation reaction. (Reaction conditions: resorcinol = 20 mmol, TBA = 40 mmol, solvent = 2 ml, temperature = 80 °C, *o*-xylene = 0.9 ml (internal standard), reaction time = 14 h, catalyst HY zeolite = 0.22 g).

activities. Benzene, cyclohexane, and dioxane, all with a similar dielectric constant ($\varepsilon \sim 2.2$) and boiling point (80 °C), exhibited significantly different resorcinol conversions (Fig. 1a and b). The relative polarity of the solvents plotted against the catalytic activity was also not effective (Fig. 1c). Finally, the attempt to associate resorcinol conversion with the solvent polarity did not reveal a strong interrelationship. The polar aprotic solvents nitrobenzene and dimethyl sulfoxide (DMSO) indeed exhibited 42.2% and 0% conversion, respectively. Similarly, cyclohexane and 1,2-dichloroethane (1,2-DCE) belonging to the group of non-polar solvents exhibited a marked difference in catalytic activity (Fig. 1d).

On the other hand, further investigation of other solvent features, like their AN and DN, provided a better understanding on the impact of the solvent in the reaction. An increase of the AN from cyclohexane to benzene and then to 1,2-DCE (all three having DN = 0) led to an increase of the resorcinol conversion, whereas an increase in the DN from nitrobenzene to DMSO through benzonitrile and 1,4-dioxane (all four having an AN of about 13) decreased the resorcinol conversion (Fig. 2a).

In comparison, polar protic solvents isopropanol, water and *n*-butanol, exhibiting both a high AN and DN, were not effective for the explored acid-catalysed reaction. Except butanol, for polar solvents isopropanol (AN = 33.5) and water (AN = 54.8), an increase of the AN (both having DN ~ 19) induced a decrease of activity from 28 to 0%. It is interesting to note that the catalytic activity decreases as the AN for polar solvents increases, in contrast to nonpolar solvents like cyclohexane and benzene. This could be due to the presence of intermediate basicity (DN) for polar solvents whereas DN = 0 for nonpolar ones.

The above analysis shows the AN and DN as decisive solvent descriptors related to the catalytic activity. To check the general applicability of this concept in heterogeneous

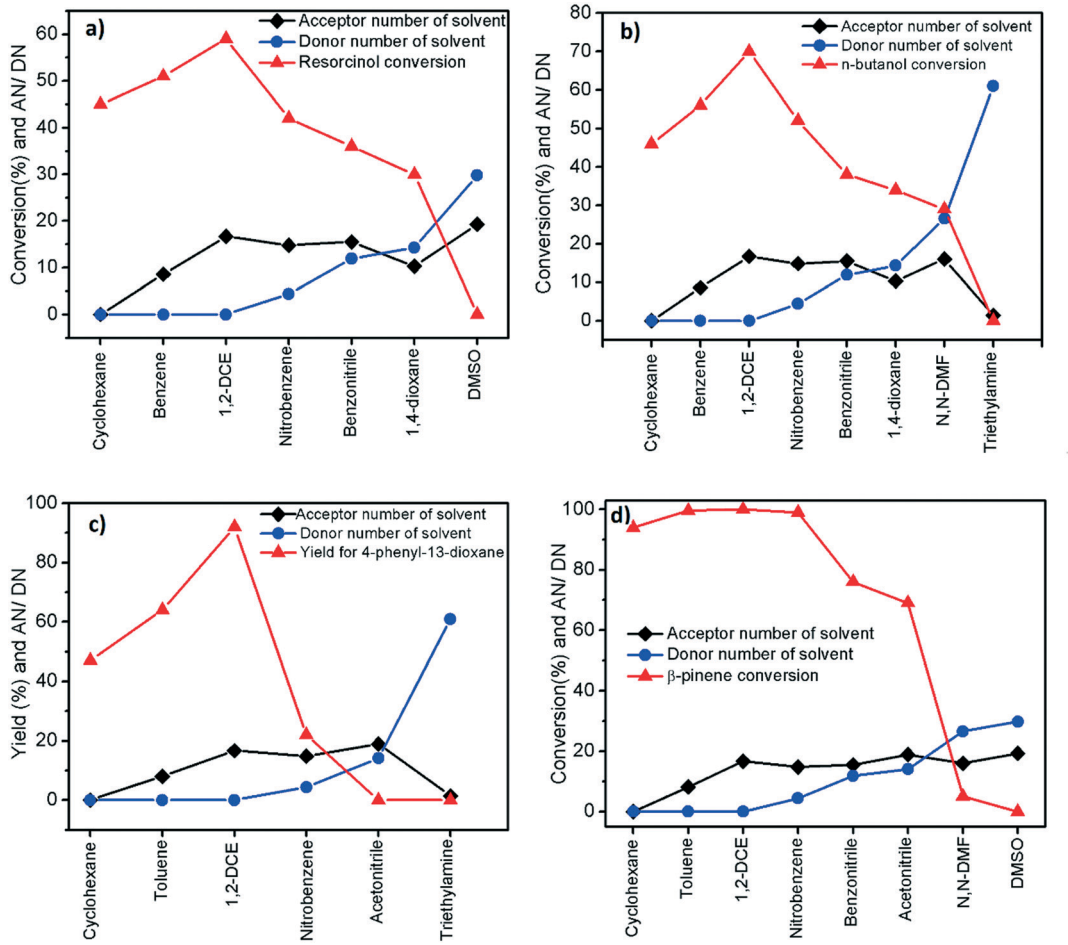


Fig. 2 Plot of catalytic activity *versus* the AN and DN of solvents in the acid catalyzed reaction a) Friedel–Crafts alkylation (reaction conditions: resorcinol = 20 mmol, TBA = 40 mmol, solvent = 2 ml, temperature = 80 °C, catalyst = HY zeolite, *o*-xylene = 0.9 ml (internal standard), reaction time = 14 h, catalyst HY zeolite = 0.22 g); b) esterification (reaction conditions: butanol = 50 mmol: acetic acid = 200 mmol, solvent = 5 ml, temperature = 80 °C, catalyst-H-beta = 0.4 g); c) Prins condensation (reaction conditions: β-pinene = 10 mmol, PF = 20 mmol, solvent = 5 ml, catalyst = Zn–H-beta, catalyst amount = 0.27 g, temperature = 80 °C, reaction time = 10 h); d) Prins cyclization (reaction conditions: styrene = 10 mmol, PF = 30 mmol, catalyst = sulphated zirconia, catalyst amount = 0.14 g, solvent = 5 ml, temperature = 80 °C, reaction time = 7 h). (Solvents such as water, *n*-butanol, *t*-butanol and isopropanol showing almost nil activity in the reactions are not included in the graph for clarity).

acid catalysis, we focused on butanol esterification as another acid catalysed reaction. Butanol esterification with acetic acid was performed in the liquid phase at 80 °C using H-beta zeolite as the catalyst[27] (Scheme S1b†). The selectivity to butyl acetate was in all cases 100%. The plot of butanol conversion with the AN and DN of the different solvents is shown in Fig. 2b. It confirms that an increase of the AN improved the butanol conversion, and contrarily a decreased butanol conversion occurred with an increase of the DN.

Apart from these two reactions, we also identified an analogous trend in Prins reactions.[28–30] The Prins cyclization of styrene with paraformaldehyde to produce 4-phenyl-1,3-dioxane was executed in the liquid phase over a SZ catalyst at 80 °C (ref. 28) (Scheme S1c†). The yield for the product (4-phenyl-1,3-dioxane) in solvents with different ANs and DNs is given in Fig. 2c. Prins cyclization followed the same trend as observed for the alkylation and esterification reactions, namely a high AN solvent with a low DN resulted in a high yield of 4-phenyl-1,3-dioxane. Another reaction that shows the same impacts of the AN and DN is the Prins condensation of β-pinene with paraformaldehyde (PF) to nopol over Zn-exchanged beta-zeolite[29] (Scheme S1d†). Our extensive past work on this reaction has revealed that only weak Brønsted or Lewis acid sites facilitate the condensation, whereas the presence of strong Brønsted acid sites on the catalyst leads to the isomerization of β-pinene to mainly camphene, limonene and α-pinene.[29,30] The results of the Prins condensation reaction are plotted against the AN and DN of the different solvents used (Fig. 2d). As the AN increased (keeping DN = 0) from cyclohexane to 1,2-DCE, the conversion improved from 94 to 100% (Fig. 2d), whereas the selectivity for nopol decreased from 16 to 8.2% (Fig. S1†). Increasing the DN (for solvents having similar ANs) from 1,2-DCE to benzonitrile, the conversion dropped from 100 to 76.4%, but the selectivity to nopol increased substantially from 8.2 to 89%. It is worth noting that both the conversion and selectivity of the reaction depend on the AN and DN of the solvent used. The polar solvents isopropanol (AN = 33.5) and water (AN = 54.8), both having DN ∼ 19, showed no activity in both Prins reactions. Since the conversion rates were measured after completion of the reaction, in order to test their kinetic reliability, initial rates of conversion in all the acid catalysed reactions were measured and they followed same trend for the AN and DN solvents as noticed after completion of the reaction (Fig. S2†).

It is fascinating to see the excellent trend that the catalytic activity develops with the AN and DN of solvents in acid catalysed reactions. This drove our curiosity to look at base catalysed reactions, *a priori* expecting to observe the opposite trend, *i.e.* solvents with a high DN lead to higher catalytic activity when compared to solvents with a high AN. To verify this hypothesis, Knoevenagel and Claisen–Schmidt condensations were performed over hydrotalcite as the basic catalyst.[31,32] The Knoevenagel condensation was carried out between benzaldehyde and ethyl cyanoacetate in the liquid phase at 80 °C and an inert atmosphere (Scheme S2a†). The selectivity for the product ethyl cyanocinnamate was always 100%. The conversion measured for the reaction in the different solvents is given in Fig. 3a. As the AN increased from cyclohexane to 1,2-dichloroethane the benzaldehyde conversion decreased from 53% to 38.5%, and a further increase of the DN from nitrobenzene to dimethyl sulfoxide increased the catalytic activity. These results completely confirm our hypothesis evoked above of the reverse trend in the base catalysed reactions. However, for polar solvents with similar DNs (∼19) an increase of the AN from *t*-butanol (AN = 37.1) to isopropanol (AN = 33.5), *n*-butanol (AN = 36.8), and water (AN = 59.7) led to a comparable benzaldehyde conversion of ∼55%.

In order to further validate the impact of solvents in base-catalysed reactions, Claisen–Schmidt condensation of acetophenone with benzaldehyde was carried out over a hydrotalcite catalyst at 140 °C (Scheme S2b†). Since the reaction was performed at high temperature, the exploration of the impact of the DN was limited to solvents with high boiling point only. The selectivity for the product chalcone was always 100%. The evolution of acetophenone conversion with reaction time using different solvents is shown in Fig. 3b. The catalytic activity clearly increases as the DN of the solvent increases from bromobenzene (DN = 3) to nitrobenzene (DN = 4.4), benzonitrile (DN = 11.9) and finally DMSO (DN = 29.8). These two-base catalysed Knoevenagel and Claisen–Schmidt reactions consistently illustrate the reverse trend for the impact of the AN and DN compared to what was observed in acid catalysed systems. Precisely, our observations reveal solvents with high DNs and low ANs as being excellent in base-catalysed reactions. More generally, they support the idea that the intrinsic acidity (AN) and basicity (DN) of the solvents influence the catalytic activity in acid and base reactions.

To understand the mechanism of the impact of the solvents in relation to their AN and DN in acid–base catalysis, it is appropriate to study the mode and strength of the interaction between the solvents on the one hand, and the catalyst and/or reactants on the other hand. Therefore in the following, the influence of the AN and DN in the explored reactions will be addressed *via* theoretical DFT calculations establishing links *via* the experimental data reported above. We assume three possible reasons for the trend observed in these reactions: 1) solvent–reactant interaction, 2) solvent–catalyst interaction and 3) solvent–reaction intermediate ion interaction.

2.1. Solvent–reactant interaction

The solvent may interact or react with a starting reactant, activating it towards the reaction or deactivating it. Non-covalent interactions, such as hydrogen bonds, between solvents and substrates, also strongly affect the reaction beyond the simple solvation.[2] Therefore, solvent–reactant interactions for the Friedel–Crafts alkylation reaction were initially studied. The resorcinol and TBA interactions with

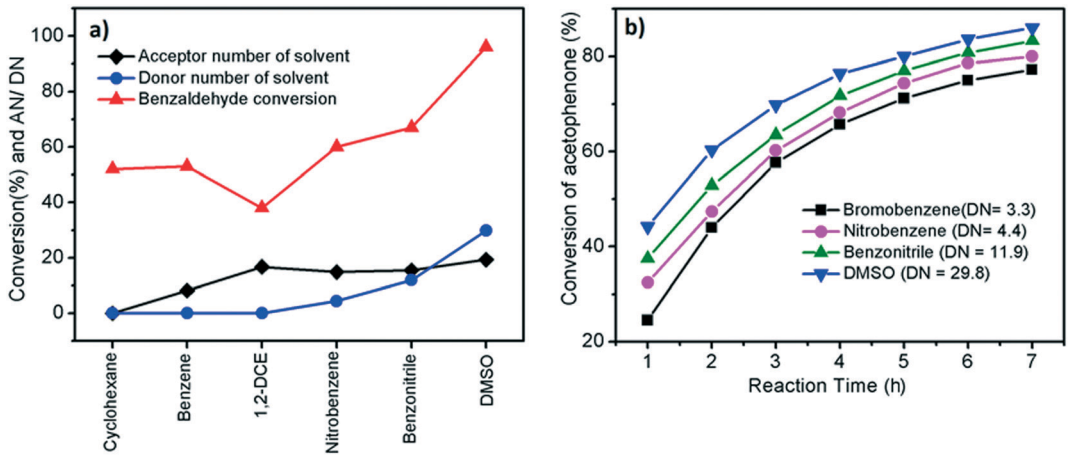


Fig. 3 Graph of catalytic activity *versus* the AN and DN of solvents in base catalysed reactions a) Knoevenagel condensation (reaction conditions: benzaldehyde 10 mmol, ethyl cyanoacetate = 12 mmol, catalyst hydrotalcite = 50 mg, solvent = 3 ml, *N*,*N*-DMF = 0.2 ml (internal standard), temperature = 80 °C, reaction time = 3 h, for DMSO reaction time = 1 h) and b) Claisen–Schmidt condensation (reaction conditions: acetophenone = 10 mmol, benzaldehyde = 15 mmol, solvent = 3 ml, *N*,*N*-DMF = 0.2 ml (internal standard), temperature = 140 °C, catalyst hydrotalcite = 0.2 g, reaction time =7 h).

solvents were measured *via* IR and UV-vis spectroscopic techniques.

At first, the interactions between resorcinol and the solvents were addressed. When resorcinol was dissolved in different organic solvents, the absorption band of resorcinol broadened with the increase of the solvent's DN (Fig. 4a). In 1,2-DCE which has a high AN, resorcinol had its absorption band at 282 nm, and a further increase of the DN from acetonitrile to DMSO indeed broadened it from 284 to 288 nm. These observations confirm the establishment of significant hydrogen bonding between resorcinol and these solvents. Such broadening for resorcinol in basic NaOH

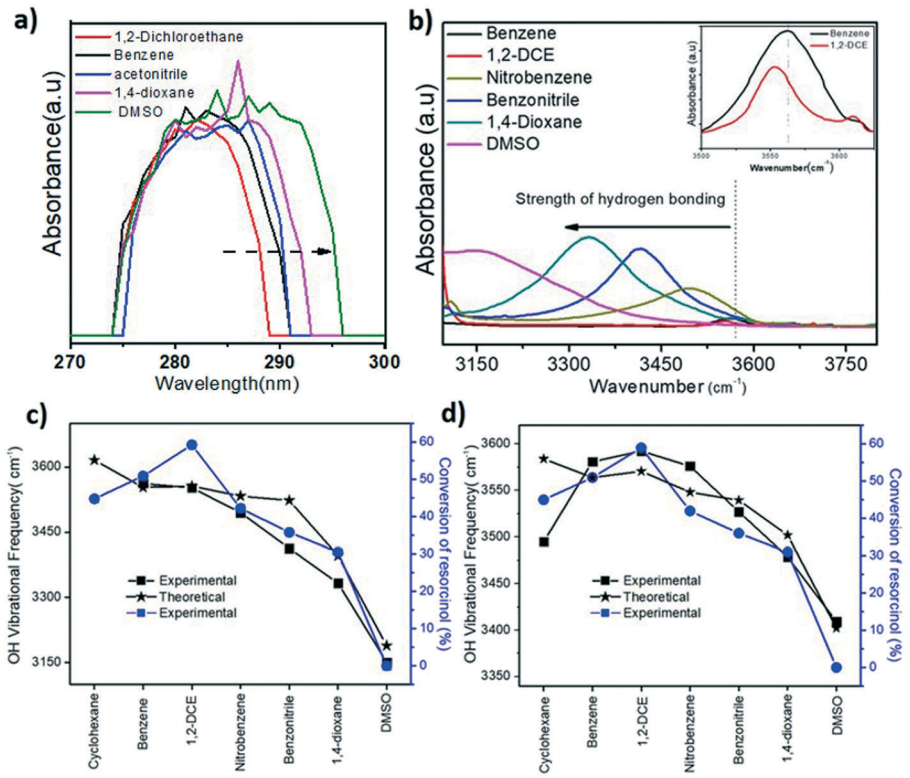


Fig. 4 a) UV spectra of resorcinol dissolved in different solvents (resorcinol = 20 mg, solvent = 10 ml.), b) FTIR spectra of resorcinol in different solvents. (100 mg of resorcinol, solvent = 5 ml), c) plot of the (–OH) vibrational frequency of resorcinol with the catalytic activity, and d) plot of the –OH vibrational frequency of *tert*-butanol against the catalytic activity.

solution due to the formation of phenolate ions was already reported.[33] This indicates that a high DN solvent with a basic nature is the cause of the broadening. The UV spectrum of resorcinol could not be measured in solvents like nitrobenzene, benzonitrile, and cyclohexane due to the interference of the solvent peak and insolubility reasons.

In order to get a clear perspective of these solvent effects, FT-IR spectra of resorcinol in all the used solvents were additionally collected (Fig. 4b). Resorcinol exhibits a broad –OH vibration peak at 3600 cm^{-1} due to intermolecular hydrogen bonding.[34] A red shift of this –OH peak occurred after interaction with the solvent, and it increased with the DN from 1,2-DCE (DN = 0) to DMSO (DN = 29). This increasing red shift with an increase of the DN reflects a growing strength of hydrogen bonding of the solvent with resorcinol. To further support this, –OH bond vibrations of resorcinol due to the interactions with solvents were calculated theoretically. The hydrogen bond distance and interaction energy between the respective solvents and resorcinol were calculated (Table S2†). The interaction energy of resorcinol increases with an increase of the AN and DN from cyclohexane to DMSO. The positive interaction energy (+1.25 kcal) demonstrates the insolubility of resorcinol in cyclohexane, as observed experimentally. Furthermore, a plot of the –OH vibrational frequency of resorcinol with the catalytic activity provided an appealing hint towards the role of hydrogen bonding in the reaction (Fig. 4c). The hydrogen bonding is optimum for 1,2-DCE in order to solubilize resorcinol completely through weak hydrogen bonding with Cl. As a counterpart, high DN solvents through their O or N atom establish strong hydrogen bonding with resorcinol and make it less prone to undergo the reaction.[35] Similarly, low AN solvents like cyclohexane and benzene with no hydrogen bonding make resorcinol less soluble in the reaction medium, hence a lower activity for these systems.

Nevertheless, the other reactant TBA is also an alcohol and could form a hydrogen bond with solvent molecules. The –OH vibrational peak for pure TBA is very broad (3600 to 3100 cm^{-1}) and is mainly assigned to its dimeric and polymeric forms.[34,36] The addition of solvent to TBA gave rise to a new peak at a higher wavenumber between 3400 and 3550 cm^{-1}. The resolved FT-IR peak of TBA in the different solvents is shown in Fig. S3.† This additional peak is due to the association of TBA with solvent molecules and the shift of the main peak (observed at lower wavenumbers of 3200–3400 cm^{-1}) is due to TBA–TBA–solvent (dimer/polymeric) interactions.[34,36] The positions of the –OH vibration peak of TBA in both configurations were plotted against the catalytic activity (Fig. S4†). Out of the two types of interactions, the –OH vibrational frequency of TBA in TBA–solvent (dimer) well correlated with the observed catalytic activity. This is similar to what was seen with resorcinol. Initial solvation energy calculated for resorcinol and TBA in different solvents did not correlate well with the catalytic activity trend. But, experimental and theoretical studies support that solvation of the reactant (polymeric interaction) is not a crucial factor but in contrast the dimer formation between the reactant and solvent is significant in controlling the activity (Fig. 4d). Furthermore, this was supported by the theoretically calculated –OH vibration frequencies between TBA and the respective solvents. The trend of TBA–solvent interaction energy and the bond length was analogous to that found for the resorcinol–solvent interaction (Table S2†). The resorcinol–solvent and TBA–solvent interactions confirm that hydrogen bonding between them is the actual cause for the impact of the nature of the solvent on the catalytic activity. Out of these two types of interactions, we then logically wanted to decipher which one (between resorcinol and solvent interaction or TBA and solvent interaction) would mostly have an impact on the catalytic activity. To address this point, we performed a Friedel–Crafts reaction using methyl tertiary butyl ether (MTBE) as an alkylating agent instead of TBA. MTBE was chosen as it cannot form any hydrogen bond with solvent molecules due to the absence of the –OH group in its molecular structure.[37] Since the reaction requires a low temperature of 60 °C, SZ was employed as the catalyst. The tendency of the catalytic activity with the AN and DN was still the same for MTBE as for TBA (Fig. S5†). This undoubtedly demonstrates that the resorcinol–solvent interaction exerts a stronger effect on the catalytic activity than the TBA–solvent one. The lower interaction energy of solvents with TBA than with resorcinol also supports the above view (Table S2†). Similar kinds of possible intermolecular hydrogen bonds exist between *n*-butanol and solvents in the esterification reaction (Fig. S6†). The –OH vibrational frequency shift due to hydrogen bonding with solvents was again well related to the catalytic activity (Fig. S7†).

These findings enlightens that the reactants containing –OH groups are the cause for the impact of the solvents on their reactivity. However, the Prins reaction of olefin (styrene, β-pinene) with paraformaldehyde (PF) does not involve any –OH group, even though the catalytic activity was also well correlated with the AN and DN of the explored solvents. Careful investigation of the PF structure reveals that it consists in a long chain of formaldehyde (8 to 100 units) with a hydroxyl group at each end. During the reaction, self-decomposition of PF at 80 °C begins and leads to smaller PF chains, making the system present more free –OH groups (Fig. S8†). High DN solvents may thus also stabilize the –OH groups of these small or long PF chains through hydrogen bonding. As a result, in high DN solvents *in situ* formation of formaldehyde is hindered, and low activity is observed. Conversely, a high AN solvent like 1,2-DCE could weakly interact with these –OH groups of PF and facilitates further decomposition of PF chains to produce more formaldehyde. Hence, a higher activity was observed in high AN solvents. This explanation is supported by solubility tests. Indeed, 100 mg of PF was added to 5 ml of each solvent (1,2-DCE and DMSO) and heated to 80 °C for 10 min. In 1,2-DCE, the solution became more cloudy, indicating the absence of stabilization of the formed intermediate small or long PF

chains (Fig. S9†). Meanwhile in the case of DMSO, a clear solution was observed indicating that the *in situ* formed smaller PF chains are well stabilized (*i.e.* solubilized) in DMSO through its association with –OH ending the PF chains. Hence, generation of formaldehyde is a more difficult event in high DN solvents (DMSO) than in high AN solvents (1,2-DCE), explaining therefore the higher activity in high AN solvents compared to that in high DN ones.

The existence of a trend between the catalytic activity observed and the AN/DN of the solvents in the case of base catalysis suggests that such an interaction of solvents with reactants is also involved in the corresponding systems. But, in both Knoevenagel and Claisen–Schmidt reactions, the reactant has no –OH group to form a hydrogen bond with high DN solvents. Actually both these base-catalysed reactions primarily proceed through the abstraction of an acidic proton from ethyl cyanoacetate (ECA) and acetophenone over the basic catalyst (Scheme S3†).[38,39] High DN solvents like DMSO could accelerate the abstraction of these acidic protons. In other words, basic solvents like DMSO and benzonitrile interact with the acidic protons through their highly electronegative O or N atoms, as a result, the reaction accelerating. This kind of interaction is not possible with high AN solvents, hence the lower activity. In order to validate this explanation, the interaction energy between ECA and the solvent, the Mulliken charge on the acidic proton and the bond distance between the acidic proton and nearest atoms of the solvent were calculated theoretically (Table S3†).[40] The charge on the acidic proton increases with the increase of the DN from 1,2-DCE to DMSO (Fig. 5a). Benzene, cyclohexane, and polar solvents like *n*-butanol, water, isopropanol, and tertiary butanol showed a very similar charge on the acidic proton and exhibited similar catalytic activity. Still it is unclear from Table S3† why the use of 1,2-DCE having higher interaction energy and higher charge on the acidic proton compared to what happens in benzene and cyclohexane led to a lower catalytic activity. To investigate this, structural interactions between the solvent and ECA was carefully analysed (Fig. 5c). In the case of 1,2-DCE, there exists another hydrogen bonding between the carbonyl oxygen of ECA and $-CH_2$ protons of the solvent with a bond distance of 2.31 Å. This is stronger compared to the interaction of –Cl with the acidic proton of ECA. This decreased electron density on the carbonyl of ECA could inhibit the formation of the carbanion. Moreover, the bond distance between the acidic proton (of ECA) and Cl (of 1,2-DCE) is longer (2.92 Å) compared to the sp^2–C interaction of benzene (2.89 Å). These two facts could be the cause of the lower catalytic activity in 1,2-DCE compared to the situation in benzene and cyclohexane. A similar kind of increase of the positive charge on the acidic proton of acetophenone with the increase of the DN of the solvent was observed (Fig. 5b).

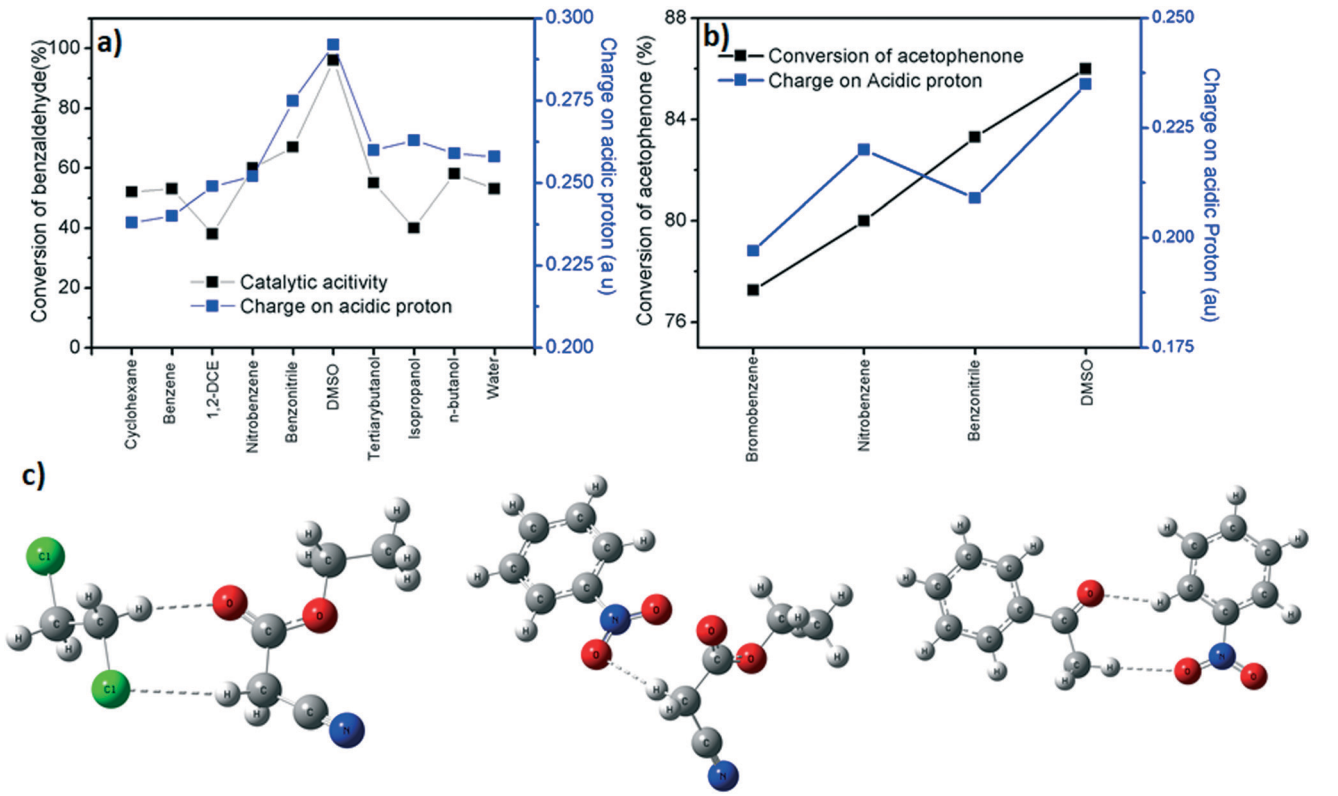


Fig. 5 Plot of the charge on the acidic proton of a) ethyl cyanoacetate and b) acetophenone in different solvents with the catalytic activity. c) The possible hydrogen bonding interaction between the solvent (1,2-dichloroethane and nitrobenzene) and the reactant (ethylcyanoacetate and acetophenone) molecules.

Again, nitrobenzene was an exceptional case with two kinds of different interactions (Fig. 5c). This finding strongly suggests that using high DN solvents will help in making the loosely bound protons even more acidic and as a result, their abstraction over basic catalysts will be easier and eventually improve the conversion rate of the reaction.

2.2. Solvent–catalyst interaction

A solvent may also interact or coordinate with the catalyst and by this means activate or deactivate the catalyst.[2] Besides, it can also influence the selectivity of the reaction and influence the catalyst stability. In the above discussion, it is established that high DN solvents make hydrogen bond with the reactants having –OH groups or with their acidic protons. Hence, it sounds much plausible that the acidic proton of zeolites could also form a hydrogen bond with high DN solvents, and that these interactions could lead to the alteration of the active catalytic sites.

In order to assess the strength of these interactions in Friedel–Crafts alkylation, the preferential adsorption of different solvents on the zeolitic catalyst in the presence of TBA was measured. Details are given in the experimental section 1.4 (ESI†). Except for DMSO, the catalyst treated with any other solvents shows in TGA analysis a weight loss similar to that of the fresh catalyst (Fig. S10a†). Precisely they all exhibited single weight loss at 120 °C due to the physically adsorbed water. The catalyst subjected to DMSO displayed two desorption peaks: one at 120 °C and another at 250 °C due to desorption of water and of DMSO, respectively. The adsorption of DMSO on the catalyst is supported by the presence of S–O and C–H peaks in its FT-IR spectrum (Fig. S10b†), and indicates that high DN solvents can chemically adsorb on the acidic zeolite catalyst. Hence, in DMSO the activity was found to be null for all the acid catalysed reactions. However, solvents with an intermediate DN such as benzonitrile or dioxane did not chemically adsorb on the catalyst, but still could physically interact with acid sites and interfere with the adsorption of the reactants. It is challenging to study these boundary interactions between the liquid solvent and a solid acid catalyst. Hence, we tried to estimate theoretically the adsorption energy of each solvent on the zeolite acid sites using a zeolite 4T model (Table S4†).[41] The adsorption energy of each solvent on the acidic zeolite was then plotted against the resorcinol conversion in Friedel–Crafts alkylation (Fig. 6a).

Except cyclohexane, a more negative adsorption energy of the solvent (*i.e.* a more stabilizing adsorption) decreased the catalytic activity. DMSO, with a markedly negative adsorption energy of −77.6 kJ mol^{-1}, efficiently chemically adsorbed on the acidic zeolites as supported by the FTIR and TGA analysis. 1,2-DCE with a least negative adsorption energy

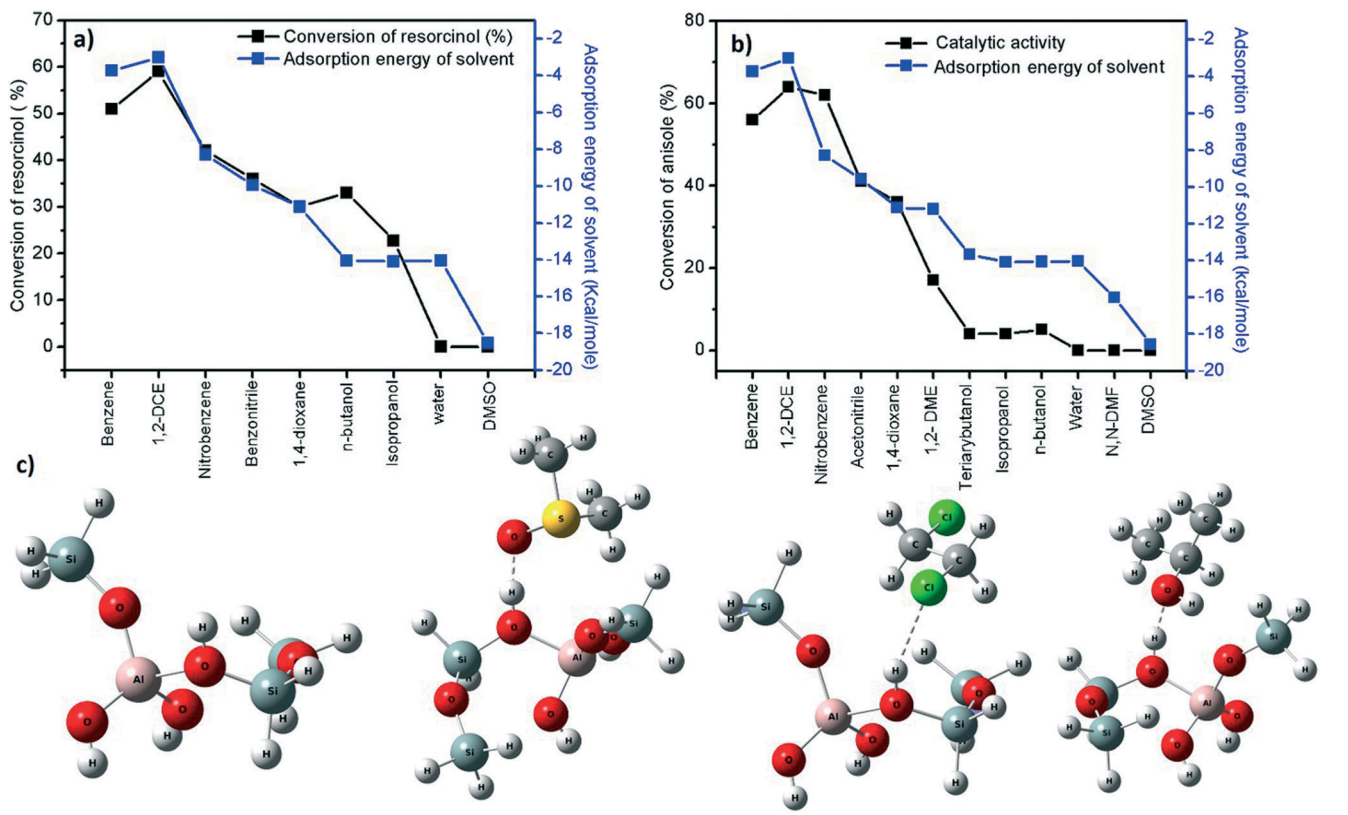


Fig. 6 Plot of catalytic activity against the adsorption energy of the solvent on a zeolite 4T model in the a) Friedel–Crafts alkylation reaction, b) acylation of anisole reaction, and c) schematic representation of the 4T zeolite model along with adsorption of 1,2-dichloroethane, isopropanol and DMSO.

makes all the acidic sites available for the reactant and improves the catalytic activity. The adsorption energy increase with the increase of the DN from nitrobenzene to DMSO reveals that there is a possible physical interface between the solvent and the catalyst. The addition of the catalyst to the solvent brings this weak physical interaction, but at the instant the catalyst is removed from the solvent, these interactions vanish due to their weak strength, and hence the extent of the physical adsorption increases with the DN of the solvents. Hence, this physical interaction between the catalyst and the solvent will hinder the contact time between the zeolite and the reactant, as a result the lower activity observed. All the polar solvents showed similar markedly negative adsorption energy on the zeolite, hence the lower activity in these solvents.

To further support and prove experimentally that catalyst–solvent associations play a vital role, a reaction of interest was chosen with the criterion that reactants are unable to make any hydrogen bond with the solvents. For this purpose, acylation of anisole with acetic anhydride was performed at 80 °C in the liquid phase using an H-BEA catalyst. Within this system the hydrogen bonding between the solvent and the reactants is impossible and only the catalyst–solvent interactions may affect the catalytic activity. The impact of the AN and DN of the explored solvents still followed the same trend, as observed in the previous acid-catalysed reactions (Fig. S11†). Polar solvents indeed showed almost no catalytic activity. The plot of anisole conversion against the adsorption energy of the solvents on the 4T-zeolite model is shown in Fig. 6b. To further take account of interaction of porous zeolite structure with the solvent, adsorption energies of different solvents over the BEA structure were calculated (see Computational details in the ESI†). The plot of adsorption energy of solvents *vs.* the conversion of anisole determined over zeolite BEA and zeolite 4T models were analogous in trend (Fig. 7a). Compared to the zeolite 4T model higher adsorption energies obtained (~20 kcal mol^{-1}) over the BEA zeolite structure are ascribed to dispersion interactions of solvents with the zeolite walls. The exceptionally low adsorption energy of water obtained over BEA zeolite was due to the smaller size of water molecules leading to unsaturated adsorption sites. The adsorption studies of solvents over BEA zeolite suggest that there are four main groups of solvents as seen from Fig. 7b–g: 1) molecules with very weak interactions (benzene, cyclohexane, 1,2-DCE), 2) molecules with weak hydrogen bonds (nitrobenzene, acetonitrile, 1,2-DME, dioxane), 3) strong hydrogen bonded molecules (water, IPA, butanol) and finally 4) very strong hydrogen bonded molecules (trimethylamine, *N*,*N*-DMF, DMSO), where acidic protons of the zeolite are transferred to molecules.

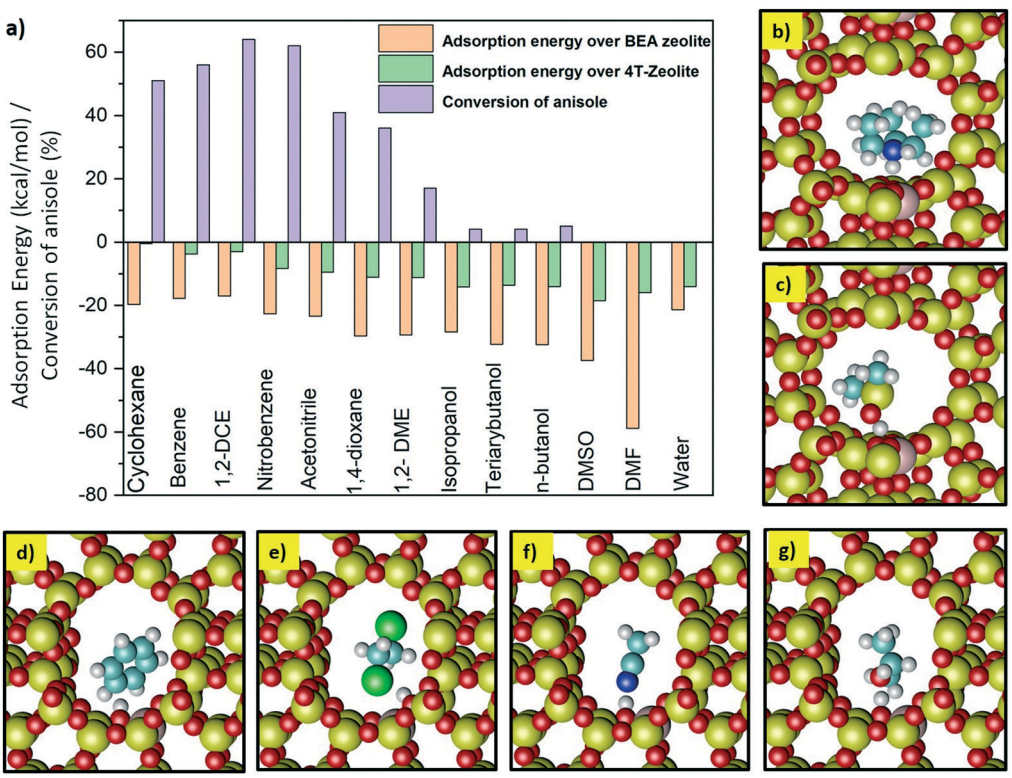


Fig. 7 a) Plot of catalytic activity against the adsorption energy of solvents over zeolite BEA and the 4T zeolite model in acylation of the anisole reaction. Adsorption of different solvents inside the zeolite BEA structure, b) trimethylamine, c) DMSO (proton transfer to solvent molecules from the Brønsted acid sites of the zeolite due to very strong interaction); d) benzene and e) 1,2-DCE (very weak interaction of solvents with acid sites can be observed); f) acetonitrile and g) isopropanol (weak to strong hydrogen bonding of solvents with Brønsted acid sites of zeolite BEA was observed). Atom representation: Si – yellow; O – red; Al – pink; C – sky blue; H– white; Cl – green, N – dark blue; S – pale green.

1,2-DCE, benzene and cyclohexane having DN = 0 interact weakly with the Brønsted acid sites of the zeolite through Cl and C (sp^2/sp^3) with weak hydrogen bonds (Cl/C···H–O-zeolite) of 2.17, 2.14 and 2.22 Å in length, respectively. Nitrobenzene, acetonitrile, dioxane, and 1,2-DME with increasing DN interact strongly with the protons of the zeolite through their O atom (O···H–O-zeolite) having hydrogen bond lengths of "1.85, 1.53, 1.41, and 1.35" Å, respectively. Polar solvents such as *n*-butanol, IPA, *t*-butanol and water with average ANs and DNs exhibited hydrogen bond lengths of 1.3–1.4 Å, leading to stronger interaction with acid sites. Beyond this limit of hydrogen bond (1.3 Å), solvent molecules strongly bound to the zeolite and block the adsorption of reactants. Therefore high DN solvents *N*,*N*-DMF, DMSO and trimethylamine completely extracted the acidic proton from the Brønsted site through their strong hydrogen bonds (N···H and O···H ~1.1 Å).

We similarly calculated the adsorption energies of the reactants over zeolite BEA involved in the acylation reaction. The adsorption energies of anisole and acetic anhydride were −32.8 and −36.8 kcal mol^{-1}, respectively. Anisole and acetic anhydride with high adsorption energy compared to solvents [such as benzene (−17.79 kcal mol^{-1}), cyclohexane (−19.68 kcal mol^{-1}), 1,2-DCE (−17.06 kcal mol^{-1}) nitrobenzene (−22.71 kcal mol^{-1}), acetonitrile (−23.4 kcal mol^{-1}), dioxane (−29.63 kcal mol^{-1}) 1,2-DME (−29.40 kcal mol^{-1}), and *t*-butanol (−32.3 kcal mol^{-1})] can readily adsorb and undergo reaction, hence catalytic activity was observed in these solvents. However, conversion of anisole was not identical in these solvents suggesting that interaction between the solvent and acid sites of zeolites plays a significant role that determines the catalytic activity difference. A higher number of solvent molecules compared to reactant molecules in the reaction mixture undoubtedly spend considerable time at the acid sites due to the hydrogen–bond interactions. DMSO (−37.43 kcal mol^{-1}) and *N*,*N*-DMF (−56.9 kcal mol^{-1}) adsorb strongly compared to reactants on acid sites with no catalytic activity. These interactions of the solvent molecules with themselves and with the zeolite pore walls are much weaker than with the active sites and one might assume that the time spent by solvent molecules at the active sites determined by adsorption energy of the solvent can be well associated with catalytic activity.

This allows concluding that the solvent influences the acid sites of the catalyst directly and by this means plays a crucial role during the reaction. As the AN increases from benzene to 1,2-DCE, the adsorption becomes weaker and as the DN increases from nitrobenzene to DMSO the adsorption reinforces. Hence, the way the adsorption energies vary with the AN and DN of the solvents is crucial in predicting the catalytic activity in a given heterogeneous catalytic system.

Another illustration of the importance of the solvent–catalyst interaction on the catalytic activity is the Prins condensation of β-pinene.[29] The earlier study on solvent–PF interaction indicates that the low conversion of β-pinene in high DN solvents is due to the stabilization of PF by these solvents, and the resulting low reactivity of PF. In such circumstances, the free β-pinene in the reaction mixture would have *a priori* had the possibility to easily isomerize over the acidic sites of the zeolite. However, no such isomerization of β-pinene was observed and a high selectivity for nopol was still observed. A possibility to explain this absence of reactivity of β-pinene is the existence of interactions between these high DN solvents with the acidic sites of the catalyst. More precisely high DN solvents like benzonitrile and nitrobenzene have presumably strongly coordinated with the strong Brønsted acid sites of the zeolite, which has decreased their reactivity, and avoided the isomerization of β-pinene.[29] Therefore, irrespective of the nature of the reactants, the different high DNs of solvents affected most of the acid sites of the catalysts. This last example further shows that proper selection of solvent in the acid–base catalysed reactions is crucial to improve the activity, but it is additionally shown here that certain optimization of the selectivity for the desired products (favouring certain reactions *vs.* preventing some others) is possible *via* this approach. The AN and DN of solvents may certainly help us to achieve such proper selection in a very convenient manner.

Similarly, we also studied the adsorption of solvents over basic catalysts, precisely over hydrotalcite model. TGA measurements performed after these different solvents were adsorbed on the hydrotalcite showed patterns similar to the bare hydrotalcite, indicating that no solvent had been chemically adsorbed on the catalyst (Fig. S12†). Theoretically calculated adsorption energies of the explored solvents over hydrotalcite catalyst could not be correlated well with the catalytic activity, indicating no role of solvent–catalyst interaction in the base catalysis. The measure cause for this trend are the solvent–reactant interactions *i.e.* weakening of acidic proton of the reactant.

2.3. Solvent–reaction intermediate ion interaction

Aside from the solvent–catalyst and solvent–reactant interactions discussed in previous two sections, there could be another origin of the impact of the nature of the solvent used on the performance of acid–base catalysed reactions, namely the stabilization of carbocation or carbanion intermediates involved in the corresponding acid–base catalytic mechanisms, respectively.[26] The common characteristic in most of the acid catalysed reactions is that their mechanism involves carbocation formation.[42] Similarly, base catalysed reactions proceed through carbanion formation. The careful investigation of the acid catalysed reactions studied in the current work reveals that the carbocation mechanism is influenced by the nature of the solvent used to achieve them. In resorcinol alkylation, tertiary butanol activates the acid sites of the zeolite catalyst to form a tertiary butyl carbocation (Scheme S3†). Similarly, acetic acid in esterification and formaldehyde in the Prins reactions have their C═O groups activated to respective carbocations

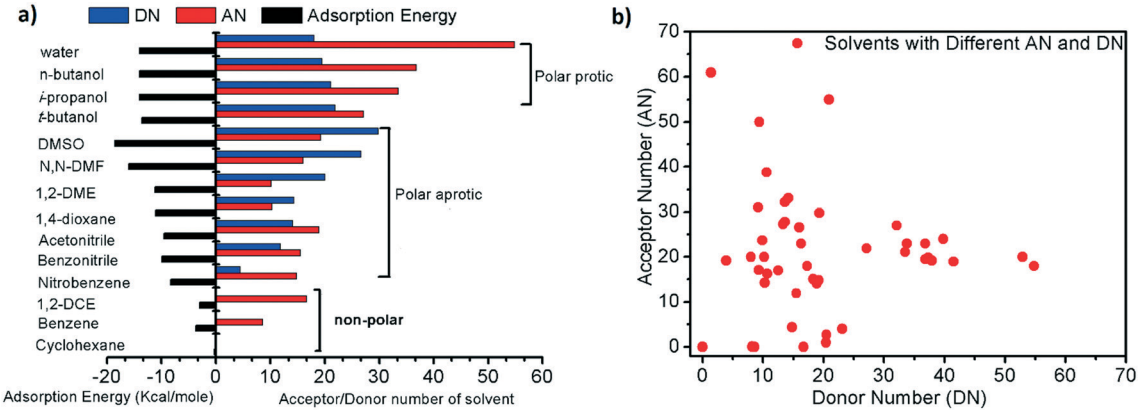


Fig. 8 a) Plot of adsorption energy against the acceptor and donor number of solvents over acidic zeolite catalyst. b) Collection of solvents with varying AN and DN.

by the acid sites of the catalyst (Scheme S3†). These intermediate carbocations might be stabilized by high DN (*i.e.* electron rich) solvents, namely have their reactivity decreased, with as a result the lower conversions observed in such solvents. Likewise, in Knoevenagel and Claisen–Schmidt reactions, high DN solvents are not able to stabilize the carbanion intermediates due to their similar charges, as a result the higher conversion observed than those obtained in high AN (positively charged) solvents. These claims are relatively easy to make, and would indeed be gained from *in situ* spectroscopic studies. This could however be tough work because the solvent might influence the catalytic reaction in several combined different ways, like interacting with the reactant and the catalyst as evoked before; hence, these interactions should be disentangled for proper evaluation of the solvent–intermediate interaction.

2.4. Practical recapitulation

In summary, the solvents with a high AN and very low DN are non-polar compounds and as the AN of the solvent increases for example from cyclohexene to 1,2-DCE, their adsorption strength over zeolite decreases, with little (if any) alteration of the catalytic proton acidity, which results in a catalytic activity increase. The solvents with a high DN are polar aprotic solvents. When their DN increases for example from nitrobenzene to DMSO, their adsorption strength on an acid catalyst increases, which makes the catalytic activity decrease (Fig. 8a). Polar protic solvents with a high AN and intermediate DN are not suitable for acid catalysis, and the catalytic activity decreases as the AN of the solvent increases, for example from isopropanol to water.

In the case of base catalysis, use of high DN polar aprotic solvents such as DMSO results in a higher catalytic activity. As a counterpart high AN solvents and polar aprotic solvents like IPA and water induce intermediate catalytic activity, as they are less favourable for the abstraction of the acidic proton from the reactants. While in acid catalysed systems the adsorption energy of the solvent plays a crucial role in the enhancement of catalytic activity, in base catalysed reactions it is indeed the abstraction of the acidic proton from the reactant that counts more.

There are already a bunch of solvents (~60) assigned with different ANs (acidity) and DNs (basicity), and application of these numbers would eventually stop often-practiced random selection of solvents from huge lists and their extensive time-consuming work ups in catalytic processes (Fig. 8b). This would build strong fundamental based scientific information on the solvent effects in heterogeneous catalysis as seen in organic and homogeneous catalysis. The classification of these solvents will simplify the selection of an appropriate solvent for a given catalyst for a given reaction. The AN and DN of solvents would also help the selection of an appropriate internal standard for a reaction, for example use of acetonitrile or nitrobenzene as an internal standard in the acid catalysed reaction can underestimate the competitiveness of the catalyst in the reaction. Similarly, one can play with this acid-basicity of solvents and improve the product selectivity as observed in the case of the Prins condensation. Based on the strength of acidity and basicity of catalysts, selecting an appropriate solvent in the reaction would become an easier task. Future studies are required in order to further understand the properties of solvents in other acid–base catalysed reactions, with much more *in situ* characterization. This approach is ideally applicable for the other acid–base and complex reaction schemes, and advances in this direction can be accelerated by analysing the solvent effects with the reactant and catalyst using *in situ* experimental and computational methodologies, thereby elucidating the fundamental bases for predicting the solvent effect and rational solvent design for liquid phase acid–base catalytic processes.

3. Conclusions

Our meticulous investigation on the AN and DN of solvents brings new hope as it provides ease of efficiently selecting an appropriate solvent in acid–base catalysis. The AN and DN

make solvent selection robust and competitive compared to the use of traditional properties such as dielectric constant, polarity and nature. Theoretical insights (DFT) and solid experiments (TGA, IR, UV-vis, solubility) demonstrating non-covalent bonding of solvents with reactants and catalysts are indeed altered by the AN and DN in alkylation, condensation, cyclization, esterification, acylation reactions and this builds strong fundamental based scientific information on the solvent effects in heterogeneous catalysis. Solvents with a high AN and low DN such as 1,2-DCE and benzene are excellent in acid catalysis due to their weak hydrogen bond with reactants and acid sites. Solvents with a high DN like DMSO and *N*,*N*-DMF strongly hydrogen bond with the acid sites of the catalyst and hinder the catalysis. A high DN and low AN are ideal for base catalysed reactions due to their ability to abstract the acidic proton from the reactants as seen from the calculated charge on acidic protons of ethyl cyanoacetate and acetophenone. The adsorption energy of the solvent in acid catalysed systems plays a crucial role in the enhancement of catalytic activity, while in base catalysed reactions it is indeed the abstraction of the acidic proton from the reactant that counts more. Considerable advances in this direction can be accelerated by analysing the solvent effects with the reactant and catalyst using *in situ* experimental and computational methodologies.

Conflicts of interest

There are no conflicts to declare.

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