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Density functional theory study of the zeolite-mediated tautomerization of phenol and catechol

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ABSTRACT

Because the structure of lignin consists mostly of inter-linked phenolic monomers, its conversion into more valuable chemicals may benefit from isomerization processes that alter the electronic structure of the aromatic rings. The tautomerization of phenolic-type compounds changes the hybridization from sp_2 to sp_3 of the carbon atom at the *ortho* position, which disables the aromaticity and facilitates the subsequent hydrogenation process. Here, we have performed a Density Functional Theory study of the tautomerization of phenol and catechol at the external surface of zeolite MFI. The tautomerization starts with the adsorption of the molecule on three-coordinated Lewis acid sites, followed by the dissociation of the phenolic hydroxyl group, with the transfer of the proton to the zeolite framework. The rotation of the deprotonated molecule enables a more favourable orientation for the back-transfer of the proton to the carbon atom at the *ortho* position. The energy barriers of the process are smaller than 55 kJ/mol, suggesting that this transformation is easily accessible under standard reaction conditions.

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1. Introduction

Lignin is one of the most abundant components of biomass, representing 10–35% in mass and 40% in energy [1,2]. However, lignin is a three-dimensional polymer with a high number of C—C and C—O linkages between the phenolic building blocks, which limits its use as a source of more valuable chemicals and fuels [2–4]. Various processes have been reported to depolymerize lignin to smaller and soluble components, which are then chemically transformed depending on their future applications. Relevant examples include the mechano-catalytic depolymerisation of lignocellulose [5], the catalytic fast pyrolysis [6] or the metal-catalysed hydroprocessing of organosolv lignin [7]. Lignin-derived compounds have significant potential to replace fossil fuels as a source of heat and power [2], but first their energy content has to be enhanced by increasing the C:O and H:C ratios [1,8].

The modification of the C:O and H:C ratios is primarily restricted by the aromatic moieties that constitute the lignin: the C—O bond in phenolic species is approximately 84 kJ/mol stronger than the same type of bond in aliphatic compounds [9]. In this regard, mono- and bi-metallic nanoparticles supported on zeolites show promising results towards the hydrodeoxygenation (HDO) of lignin [7,10–13]. These methods effectively increase the C:O and H:C ratios whilst using milder conditions than pyrolytic processes [6,14–16], leading to higher yields and selectivity with practically no solid residues. The role of the zeolite in the HDO treatment is assumed to be related to the removal/addition of aliphatic side chains and the dehydration of aliphatic alcohols, which is carried out by Brønsted and Lewis acid sites. The hydrogenation/hydrogenolysis of the aromatic ring is essentially considered to be due to the metal catalyst, although an enhancement of its function is noted in the presence of the zeolite [13].

In the present work, we have analysed the activation of phenolic monomers on the external Lewis acid sites of zeolite MFI. The proposed transformation is the keto-enol tautomerization shown in Scheme 1, which involves the transfer of the hydroxyl hydrogen of phenol to one of the carbon atoms at the *ortho* position, thereby changing the hybridization of the carbon atom from sp_2 to sp_3. This loss of molecular aromaticity promotes the hydrogenation of the molecule [17,18]. For instance, the initial tautomerization of m-cresol to an unstable cyclo-hexadienone has been reported to be the preferred pathway towards HDO over the Pt/SiO_2 catalyst [19]. Likewise, the tautomerization of phenol is considered a possible intermediate process during the hydroprocessing on Pd/SiO_2, Pd/Al_2O_3, and Pd/ZrO_2 [20]. Similar bifunctional catalysts use zeolite as a support during the HDO of lignin and phenols [10,13],

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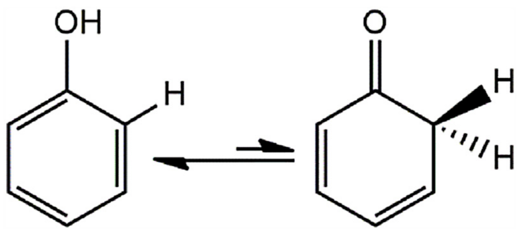
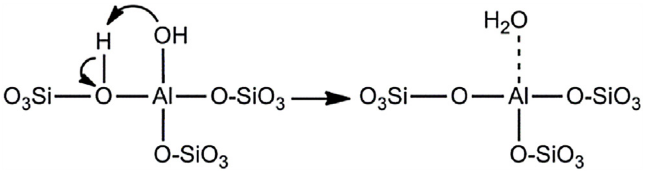


Scheme 1. Representation of the keto-enol tautomerization of phenol.



Scheme 2. Representation of the dehydration of an Al-substituted silanol with the subsequent formation of a three-coordinated Al centre.

which has prompted us to use computational tools to understand the potential role of the zeolite's active sites in the tautomerization process.

Previous reports have underlined the synergy arising at the metal-support interface for hydrogenation processes, derived from the combined action of support and nanoparticles; this cooperation rules the pathway and selectivity of the reaction during the hydroprocessing [20,21]. Metal nanoparticles should be found at the external surface of the zeolite because their sizes are larger than 2 nm [10,13], which is bigger than the pore dimension of zeolite frameworks. As such, the external active sites of zeolites will be relevant in the synergistic effect of the metal-support interface. Accordingly, we have focused our attention in this study on the adsorption and reaction of representative molecules, phenol and catechol, on the external surface of the zeolite MFI, modelled here as a periodic slab. This model is not far from reality; MFI nanosheets have been successfully synthetized as thin as a single unit cell along the [010] direction, whilst extending two-dimensionally over its (010) plane [22]. We have chosen the three-coordinated aluminium centre within the zeolite framework as the active site to adsorb the molecules. This site presents Lewis acidity owing to the under-coordination of the aluminium atom, as shown in Scheme 2, which has been shown by computer simulations to be thermodynamically and kinetically favoured [23,24].

The first part of the result section is dedicated to the determination of the most stable aluminium-substituted silanol to adsorb the molecules. In the second part, we have presented a detailed mechanistic analysis of the adsorption and reaction of phenol, including the energy barriers along the pathway, to achieve its isomerization. We have examined the catechol adsorption in the final section, and analysed the consequences of the second hydroxyl group in the tautomerization process.

2. Computational methods

We have performed all calculations within the framework of the Density Functional Theory, using the plane wave code *Vienna Ab-initio Simulation Package* (VASP) [25–28]. We used the generalized gradient approximation (GGA), as derived by Perdew, Burke and Ernzerhof (PBE) [29], in combination with Grimme's correction for the dispersion forces to account for the exchange-correlation energy at short- and long-range. In a previous report, we have shown that the inclusion of Grimme's atomic pairwise dispersion correction (PBE-D2) [30] decreases the error of the computed volume of the MFI unit cell, and also gives a better prediction of the bulk modulus [24]. In the present work, we have considered a more recent approach to the dispersion interactions, which incorporates geometry information into the *ab-initio* parametrization of the dispersion coefficients (PBE-D3) [31,32]. The PBE-D3 method closely agreed with PBE-D2, but the best outcome was achieved considering the Becke-Johnson damping (PBE-D3_BJ) protocol, reducing the volume error of the unit cell to only 0.5% (see Table 1). This result prompted us to choose the PBE-D3_BJ approach to perform all calculations.

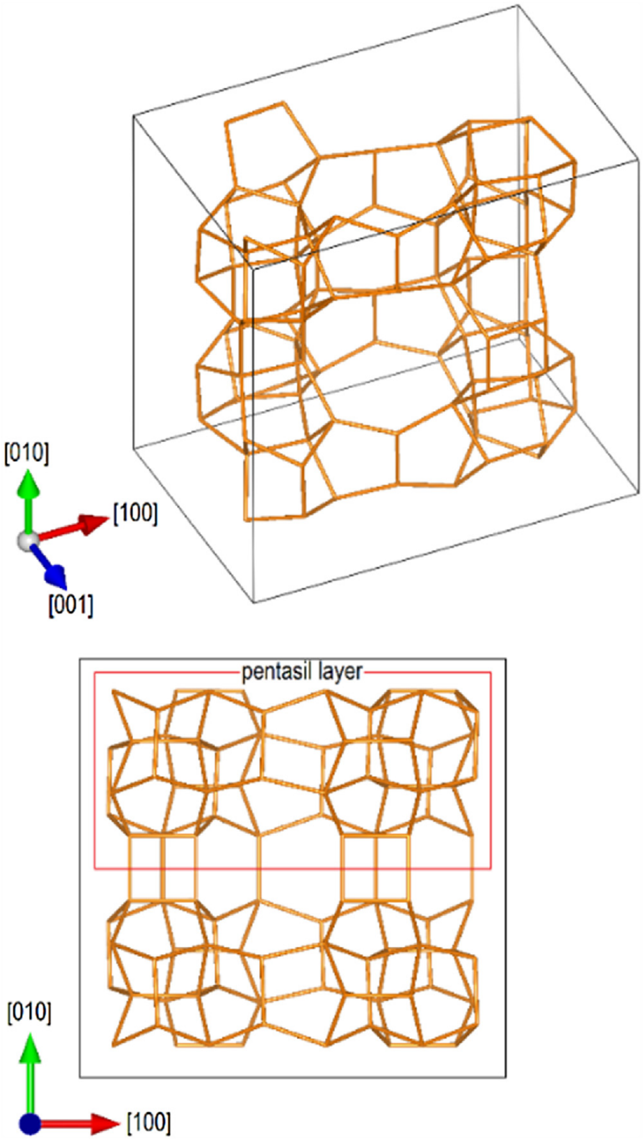


Fig. 1. Top and lateral views of the optimized unit cell of the zeolite MFI. One of the two pentasil layers is highlighted within red lines. The O atoms are deleted for an enhanced view. Vicinal Si atoms are linked by orange sticks. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

We have optimized the orthorhombic unit cell of the MFI framework, available from the Structure Database of the International Zeolite Association (IZA) [35]. A representation of the optimized MFI framework is shown in Fig. 1. A set of fixed-volume calculations were performed, allowing the relaxation of the lattice shape and atomic positions. Thereafter, the correlation of the optimized lattice energy versus the cell volume was fitted to the Birch-Murnaghan equation of state [34]. This methodology eliminates the problems related to the Pulay stress [36] whilst giving the equilibrium volume and the bulk modulus as adjustable parameters (see Table 1).

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