

Modelling of the tautomerization of phenol mediated by zeolite MFI

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Previous theoretical and experimental reports have outlined that tautomerization may be an intermediate step during the hydroprocessing of phenol, using noble metal surfaces or metal clusters supported on different materials [1–3]. The tautomerization of phenol and catechol changes the hybridization of one, out of six carbon atoms forming the aromatic ring, to sp^3 , which disables the aromaticity and facilitates the subsequent hydrogenation process. The structure of lignin consists mostly of inter-linked phenolic monomers, and hence, its conversion into more valuable fuel may benefit from the presence of tautomerization along the hydrogenation process.

We have proposed a Density Functional Theory analysis of the possible tautomerization of phenol and catechol over the external Lewis acid sites of MFI zeolite, under gas phase and low-loading conditions. The transformation is conceived as a three-step process, involving the dissociation of the phenolic hydroxyl group, transferring the proton to the zeolite framework, followed by the rotation of the molecule to a more favourable orientation, and concluding with the back-transfer of the proton to the carbon at ortho position to the keto group. The energy barriers of the entire process are smaller than 55 kJ/mol, assuming a temperature of 473 K, suggesting that this transformation is easily accessible under standard reaction conditions.

[1] L. Nie & D.E. Resasco (2014) *J. Catal.* **317**, 22. [2] G. Li *et al.* (2015) *ACS Catal.* **5**, 2009. [3] P.M. de Souza *et al.* (2015) *ACS Catal.* **5**, 1318.