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 hydropyrolysis 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 sp3, 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.