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DFT+*U* investigation of the catalytic properties of ferruginous clay

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ABSTRACT

The formation of fossil oil within clay minerals i.e., mineral-catalyzed decarboxylation, is a mechanism awaiting a thorough chemical explanation. To contribute to such an explanation, the study presented here investigates this mechanism at the level of first-principles, electronic structure computations, employing density functional theory (DFT plus Hubbard-*U*), planewaves, pseudopotentials, and periodic cells of two types of ferruginous clay minerals, specifically two types of nontronite [$Fe_2(Si,Al)_4O_{10}(OH)_2$]. The formation of the fossil oil is modeled as a decarboxylation pathway, converting the fatty acid propionic acid, C_2H_5COOH to an alkane, C_2H_6 and the intermediate stages along this conversion pathway are represented by five configurations of interlayer species within the clay minerals. In this study, we test both the effect of the presence of iron on the theoretical stages of decarboxylation, together with the effect of two different density functionals: with and without strong correlations of the d-orbital electrons of iron. We have found that inclusion of the d-orbital electron correlations in the guise of a Hubbard parameter results in the introduction of three new intermediate configurations (one of which is potentially a new transition state), alters the location of the occupied Fermi level orbitals, and changes the band gaps of the clay mineral/interlayer species composites, all of which serves to inform the chemical interpretation of mineral-catalyzed decarboxylation.

Keywords: DFT, Hubbard value, oil formation, iron-bearing clay minerals