Abstract

Geopolymers have found prominence recently as suitable candidates for heterogeneous catalysis, which is prefered in industries because of the properties like easier separation, neutralisation and reusability. They have semi-crystalline or amorphous structure analogous to zeolites. Geopolymers consists of three dimensional networks of SiO_4 an AlO_4 connected by oxygens. They have a wide variety of applications owing to the properties like high mechanical strength and high thermal resistance. The catalytic properties of geopolymes are primarily derived through the network forming ability at ambient temperature, Si:Al ratio and the presence of extra framework cations in the network. Several experimental studies have demonstrated the catalytic applications of geopolymers. We have carried out computational investigation on geopolymers under density functional theory framework.

Geopolymers are amorphous in nature and thus, periodic models cannot be built for them for computational analysis. We developed molecular models of geopolymers with different Si:Al ratios (1:1, 1:2, 2:1) and K^+, Ca^{2+} as the extra-framework cations. Geopolymers with Si:Al=2:1 and Ca^{2+} as the extra framework cations were found to be the most stable ones.

Geopolymers can be used as catalyst support and catalysts as well. In the series of designing heterogeneous catalysts we developed catalytic model of copper oxide with geopolymeric support. The developed catalyst model was implemented to test the experimentally reported oxidation of benzaldehyde to benzoic acid. Though copper oxide is a well developed catalyst for oxidation reactions, geopolymers imparted heterogeneity to the process and improved the catalytic properties. The reaction mechanism was developed for oxidation of benzaldehyde. The developed free energy landscape hence revealed the significant improvement of the reaction kinetics with the use of catalytic support.

The catalytic attributes of geopolymers have been studied well with experiments for transesterification for the production of biodiesel. Considering the importance of biodiesel we intended to explore the mechanistic aspects of transesterification with computations. However, the size of the associated reactants and products pose serious issues in the direct implementation of DFT to understand geopolymer-catalysed biodiesel synthesis in its native form. The study of the catalytic properties of geopolymers for esterification is expected to act as a proxy for transesterification as well since the literature suggests the similarities between the molecular phenomena of both the reactions. Thus, we have put efforts in unravelling the mechanistic details of esterification of butanoic acid with ethanol. Two possible reaction pathways and the associated reaction mechanisms were developed. The barriers for both the pathways were comparable with barriers of 42 kcal/mol and 40 kcal/mol. The factors influencing the reaction mechanism were discussed.

Keywords: Geopolymers; heterogeneous catalysis; computational models; structure; stability; density functional theory.