Liquid phase oxidation of p-cresol over cobalt saponite catalysts

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Hydroxybenzaldehydes produced by the oxidation of corresponding phenol derivatives, are important starting materials widely used in the manufacture of fragrance, soaps, preservatives, pharmaceuticals etc. which fall in the domain of fine chemicals. In the production of fine chemicals it is imperative that the reactions are selective. The traditional oxidation methods often involve the use of stoichiometric amounts of inorganic oxidants, such as chromates, which create serious effluent problems which can be overcome by developing catalytic processes for oxidation. From an industrial point of view, oxidation catalysis poses three challenges: a) activation of molecular oxygen, b) avoid over oxidation of the substrate, and c) overcome the lack of functionality in the feedstock. In continuation of our work on developing heterogeneous catalysts for liquid phase oxidations, we present here our results on synthetic saponite containing Co²⁺ in the octahedral layer as a highly efficient catalyst for selective liquid phase oxidation of p-cresol. Saponite clay is an example of trioctahedral smectite in which the charge imbalance due to isomorphic substitutions in the structure layers is compensated by cations placed in interlamellar position. Therefore, Co-saponite obtained can be viewed as a nanocomposite (100nm) of Co phases over aluminosilicate support as a catalyst for oxidation reactions.

Various Co-saponite samples were prepared with 5, 13 and 30% Co content and their BET surface area was found to be in a range of 397-417 m²/g. DRUV-visible of Co-saponite shows bands at about 495, 530, 570 and 645 nm assigned to tetrahedral Co(II) species. Band at 250nm could be due to oxygen-to-metal charge transfer (CT) transition. A broad and intense band at 530 nm suggests the presence of extra-lattice Co(II) in octahedral symmetry. In XPS studies, core level BE of Co2p½ was at 781.9 eV, indicating cobalt coordinated to lattice oxygen and probably associated with silanol groups. The core level BE of Co2p½ is at 797.6 eV along with the satellites for 2p½ and 2p½ observed at 787.4 and 803.3 eV respectively, confirmed that cobalt was mainly present in (II) oxidation state. A broad peak (FWHM=3.4 eV) of Co2p½ in Co-saponite suggests the presence of octahedrally and tetrahedrally coordinated divalent cobalt species. Activity measurement studies of 13% Co-saponite sample gave the highest conversion of 92% of p-cresol at 827 kPa of oxygen pressure with 92% selectivity to p-hydroxybenzaldehyde. Formation of benzoic acid could be significantly minimized while formation of non oxidation products were completely suppressed using our catalyst. Activation energy from the Arrhenius plot was found to be 41.47 kJ/mol. Oxidation experiments with Co-saponite without oxygen along with XPS characterization, support that the liquid phase p-cresol oxidation proceeds probably through Mars-van Krevelen pathway involving the lattice oxygen and the subsequent reoxidation of the vacant sites by molecular oxygen.

References