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Amorphous Aluminophosphates: An Insight to the Changes in Structural Properties and Catalytic Activity by the Incorporation of Transition Metals

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Abstract : Aluminophosphates, both amorphous and crystalline materials find applications as adsorbents, ceramics, and pigments and as catalysts/catalyst supports in organic fine chemical synthesis. Most of the applications are varied depending on the type of metal incorporated, particle size, surface area, porosity and morphology of aluminophosphate. The porous and surface properties of these materials are normally fine-tuned by adopting various preparation methodologies. Numerous crystalline microporous and mesoporous aluminophosphates and metal-aluminophosphates have been reported in literature, in which the synthesis has been carried out by using structure directing organic molecules/surfactants. In present work, amorphous aluminophosphate (AlP) and metal-aluminophosphates MAlP (M = Cu, Zn, Cr, Fe, Ce and Zr) and their mixed forms M-1M2AlP are prepared under a typical precipitation condition, i.e. at low temperature in order to keep the Von-Weirmann relative super saturation of the precipitating medium and obtain small size precipitate particles. These materials are prepared without using any surfactants. All materials are thoroughly characterised for surface and bulk properties by N2 adsorption-desorption technique, XRD, FT-IR, TG and SEM. The materials are also analysed for the amount and the strength of their surface acid sites, by NH3-TPD and CO2-TPD techniques respectively. All the materials prepared in the work are investigated for their catalytic activity in following applications in the synthesis of industrially important Jasminaldehyde via, aldol condensation of n-heptanal and benzaldehyde, in the synthesis of biologically important chalcones by Claisen-shmidth condensation of benzaldehyde and substituted chalcones. The effect of the amount of the catalysts, duration of the reaction, temperature of the reaction, molar ratio of the reactants has been studied. The porosity of pure aluminophosphate is found to be changed significantly by the incorporation of transition metals during preparation of aluminophosphate. The pore size increased from microporous to mesoporous and finally to macroporous by following order of metals Cu = Zn < Cr < Ce < Fe = Zr. The change in surface area and porosity of double metal-aluminophosphates depended on the concentration of both the metals. The acidity of aluminophosphate is either increased or decreased which depended on the type and valence of metals loaded. A good number of basic sites are created in metal-aluminophosphates irrespective of the metals used. A maximum catalytic activity for synthesis of both jasminaldehyde and chalcone is obtained by FeAlP as catalysts; these materials are characterized by decreased strength and concentration of acidic sites with optimum level basic sites.

Keywords : amorphous metal-aluminophosphates, surface properties, acidic-basic properties, Aldol, Claisen-Shmidth condensation, jasminaldehyde, chalcone
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