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A simple and efficient zeolite catalyst for toluene oxidation in aqueous media

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ABSTRACT

In this work, it was found that alkali-treated zeolites could efficiently catalyze oxidation of toluene with H_2O_2 in aqueous media. No heavy metals or their oxides were employed in the synthesis of catalyst and no additives were used in this catalytic system. Through optimizing the experimental conditions, alkali-treated HZSM-5 exhibited good catalytic activity for toluene oxidation in only 5 h at a low temperature (below 100 °C): 32.0% conversion of toluene with selective formation of 25.0% benzaldehyde, 20.8% benzyl alcohol and 27.5% benzoic acid. Moreover, the results of reusability studies indicated that alkali-treated HZSM-5 was a durable and green catalyst for toluene oxidation in aqueous media. The changes in acidities and textural features of the zeolites induced by alkali-treatment were characterized by ammonia temperature programmed desorption (NH_3-TPD) and X-ray powder diffraction (XRD), respectively. The results indicated the reactivity for toluene oxidation could be related to the amount of species ≡Al• and ≡AlOH in this system. A probable redox mechanism for toluene oxidation catalyzed by alkali-treated zeolites in aqueous media was proposed in this work.

1. Introduction

Using water as the desirable solvent in organic reactions has received a great deal of attentions and shows significant environmental advantages [1–3]. In organic synthesis, it has been found out that a variety of reactions [4–8], including Claisen rearrangement, Michael addition, Mannich and Diels–Alder reaction, could be accelerated in aqueous media. However, some reactions proceed slowly when pure water is employed as the sole medium due to the hydrophobicity of organic molecules. In order to facilitate these reactions, modification of the hydrophobic reagents and employment of organic cosolvents, phase-transfer catalysts, or surfactants in the reaction processes had been widely investigated [9–13]. In recent years, the research focusing on the development of efficient heterogeneous catalysts for the organic reactions in aqueous media has aroused great interests. Various polymer-supported catalysts [14–16] with rare earth metals as active sites have been successfully produced and have exhibited highly catalytic activity in water for C—C bond formation reactions. Meanwhile, some inorganic materials [17–19] (e.g. amorphous SiO_2) that possess good hydrothermal and mechanical stabilities are also considered as excellent supports to develop heterogeneous catalyst. Kim et al. [19] prepared a Lewis acid solid via immobilization of Lanthanum sulfonate on SBA-15 and used it to catalyze the Diels–Alder and allylation reactions of carbonyl compounds with aqueous media. Besides its advantages in C–C bond formation reactions, water is also a promising medium for the selective oxidation of carbonyl compounds [20].

The catalytic oxidation of toluene has been investigated with great efforts during the past decades. The primary products in selective oxidation of toluene are important organic intermediates, including benzaldehyde, benzyl alcohol and benzyl acid. In deep oxidation of toluene, the formation of carbonaceous deposits (coke) [21] that are mainly composed of aromatic hydrocarbons and oxygenated aromatic compounds, leads to the deactivation of the catalysts in the fix-bed system. The formation and then the removal of coke resulted in a great increase of costs for the industrial production. What's more, in the traditional process of using toluene oxidation to produce benzaldehyde and benzyl alcohol, the employment of inorganic oxidants (e.g. $KMnO_4$ or CrO_3) inevitably generates toxic waste and hazardous byproducts, which are harmful to the environment [22]. By now, great efforts [23–28] have been made to develop new efficient catalytic systems in liquid-phase using non-toxic oxidant (O_2 or air) from the environmental viewpoint. In these catalytic systems, heavy metals or their oxides were widely used as active component in the synthesis of catalysts and additives were also employed to improve the reactivity of toluene oxidation in some cases. Recently, a major breakthrough in this field had been made. Single metal or bimetallic catalyst was hired in O_2 or air oxidation of toluene with or without solvent, especially Hutchings et al. [29] reported that they could selectively oxidize toluene to give benzyl benzoate by using Au–Pd alloy nanoparticles with a very high selectivity.

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