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Catalyst-free reduction of nitrobenzene to aniline using lignocellulosic biomass

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PURPOSE OF THE ABSTRACT
Aromatic amines are widely considered as promising platform chemicals for the production of dyes, antioxidants, pharmaceuticals and agricultural chemicals.1 Generally, the catalytic hydrogenation processes of aromatic nitro compounds were conducted with transition metals, such as platinum, nickel, or palladium.2 However using metal catalysts could pose some concerns such as high cost, recycling from the system, as well as some environmental concerns. And some organic solvents were also employed during these processes, which required high-energy consumption for the recovery of aromatic amines. On the other hand, H2 usually serves as the hydrogen resource, which will also cause security risks.3 In this context, our group has developed a green and safe method for the reduction of aromatic nitro compounds to aromatic amines catalyzed by carbonaceous bio-based materials in subcritical water without added metal and H2.4

In the present work, new "home-made" carbon materials made from sawdust as vegetable waste were produced under microwave irradiation as an alternative technique for the production of aniline as a basic intermediate in industrial chemistry. Two general methods are used for the preparation of our heterogeneous material. The first is physical activation with carbonization of the raw material and then activation using carbon dioxide. The second is chemical activation with carbonization and then activation step occur simultaneously with the addition of a desiccant (H3PO4, ZnCl2...). Nitrobenzene in the presence of our ?home-made? material in water at 310°C for 6 hours furnished the aniline in 70% yield.

Another new process based on non-heat-treated sawdust and impregnated with KOH has also been developed. For this process H2 is generated from decomposition of lignocellulosic biomass,5 in subcritical conditions thanks to the hydrothermal liquefaction. Hydrothermal liquefaction is thermochemical process that produces bio-oil from lignocellulosic biomass. During this process, biomass macromolecules are first hydrolyzed and degraded into smaller molecules.6 The hot alkaline degradation of macromolecules can lead to generate dihydrogen, which will serve to reduce nitroaromatic compounds.7 Using optimized conditions (nitrobenzene, wood, KOH, MeOH, 240°C, 6 h), the aniline was obtained in 93% yield.

FIGURES

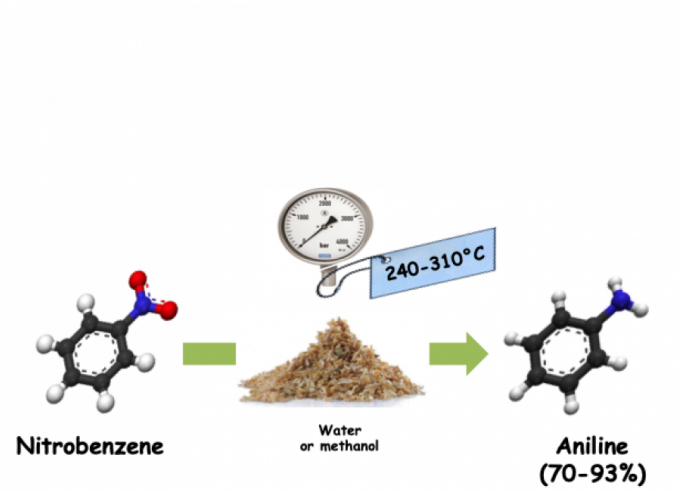

FIGURE 1

Catalyst-free reduction of nitrobenzene to aniline in the presence of sawdust.

Catalyst-free reduction of nitrobenzene to aniline in the presence of sawdust.

FIGURE 2

KEYWORDS

heterogeneous catalyst | microwave | catalyst-free reduction | water

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