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Research Paper

Co-N-doped carbon nanotubes supported on diatomite for highly efficient catalysis oxidative carbonylation of amines with CO and air

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ABSTRACT

Cobalt-nitrogen-doped carbon nanotubes stably supported on diatomite were obtained by employing $Co(OAc)_2$/phenanthroline. The resulting material was found to be excellent catalysts for the carbonylation of a variety of amines with CO other than phosgene. Both high activity and selectivity were achieved in this carbonylation process, and it allows air as a cheap oxidizing agent. Moreover the catalyst could be recycled for several times with relatively higher activity compared to homogeneous catalyst palladium acetate.

1. Introduction

Ureas are important carbonyl derivatives in agricultural chemicals, pharmaceutical intermediates and resin precursors[1–3]. The classical synthetic route for ureas are based on the use of phosgene and its derivatives, which are poisonous[4], and therefore cause environmental problems. In recent years alternative routes have been developed by employing carbonyl derivatives, CO or CO_2 [5–7]. Particularly, the method using CO, amines and oxide as the raw materials is very attractive from the atom economic point and the only by-product is water. Several homogeneous catalysts have been proposed for this reaction showing high yields to the desired urea products [8–10]. However, homogeneous catalytic systems have the common drawback of difficult separation of catalyst and product, leading to limited industrial applications. To overcome these problems, variety of heterogeneous catalysts for has been reported [8,11–13]. However, most of these catalysts have employed noble metal like Pd and Au [2,4–6]. Herein, we developed a new heterogeneous catalyst of high activity and selectivity for carbonylation of amines through pyrolysis of cobalt acetate and 1,10-phenanthroline with diatomite. In the past, the metal/N doped graphene (M/NGr) catalyst has been mainly supported on carbon or graphene, the preparation process of which are usually energy consumble. While the supporter diatomite is cheap and environment-friendly, and our system can be easily recovered and recycled for several times. In addition, unlike the traditional metal/N doped carbon material, the morphology of the resultant carbon were found to be nanotubes attached on surface of diatomite.

Recently, the incorporation of dopants into the matrix of the parent support has become an attractive area in material sciences. More specifically, N-doped carbon materials generated major interest. So far, these Cobalt oxide/NGr has been applied in the selective hydrogenation of nitroarenes, imines, and the selective oxidation of alcohols to esters [14–22]. As far as we know, this is the first time for this kind of catalysis used in carbonylation of amines.

2. Experimental

2.1. Catalyst preparation

In a similar procedure to prepare the Co/N-doped graphene, dispersible and uniform nanotubes were obtained by using cobalt acetate as metal agent and 1,10-phenanthroline as nitrogen-rich ligand. Cobalt (II) acetate (1 g, 2.5 mmol) and 1, 10-phenanthroline (990 mg, 5.5 mmol) were stirred in ethanol (90 mL) for 3 h at room temperature. Then, diatomite powder (5 g) was added and the whole mixture was kept stirring at room temperature for 6 h. Ethanol was removed by vacuum. The obtained pink solid sample was dried at 80 °C for 24 h, after that it was grinded to a fine powder in an agate mortar. Then, the grinded powder was transferred into a corundum crucible and placed in the oven. The oven was heated to 800 °C at the rate of 10 °C per minute, and held at certain temperature (600, 800 and 1000 °C) for 2 h under flow of nitrogen gas. The oven was allowed to cool to room temperature naturally in a nitrogen atmosphere. The resultant black material was grinded again so as to obtain a fine powder (Scheme 1).

For comparison, the identical procedure was applied to the preparation of Ni-based or metal free N doped carbon catalyst using the same starting materials except the nickel acetate. For Co/diatomite the detailed procedure could be seen in the supporting information.

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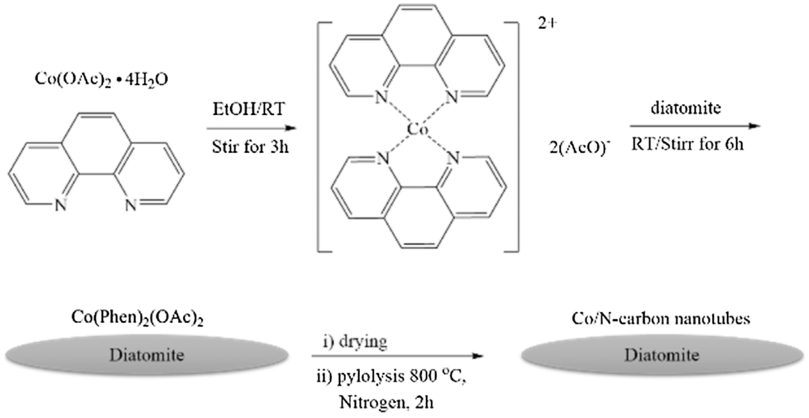

Scheme 1. Preparation of Co/N-CN @ Diatomite.

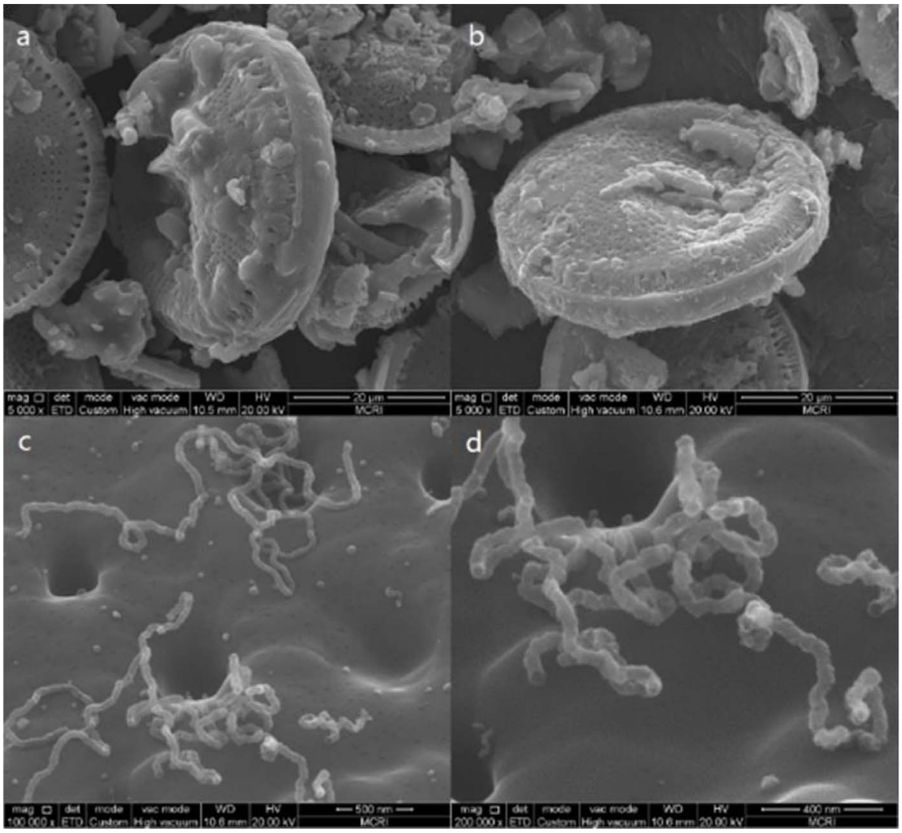

Fig. 1. (a) SEM image of diatomite before loading the catalyst (b) SEM image of Co/N-CN @ Diatomite showing finely distributed carbon nanotubes on the surface of diatomite (c, d) SEM image of carbon nanotube.

2.2. Catalytic activity tests

The standard reaction was carried out in a Teflon-lined stainless-steel reactor 35 mL in capacity with a magnetic stirrer.107 mg of benzylamine (1 mmol), 20 mg of catalyst and 2 mL of 1, 4-dioxane was first added, after that the reactor was charged with 1.5 MPa CO and 0.1 MPa air. The mixture was stirred for 8 h at desired temperature. Then, the reaction mixture was cooled to room temperature and centrifugated to get rid of catalyst. The resultant mixture was then analysed by GC and GC–MS. All GC-yields are averages from at least 3 runs, the starting materials as well as products were calibrated from the commercially available materials. Then the solvent was removed, and the residue was purified by recrystallization from the appropriate solvent to give the corresponding urea.

2.3. Catalyst recycling experiments

For the catalyst recycling experiments, reactions were carried on a 1 mmol benzylamine in the presence of 20 mg of the catalyst. All reactions were conducted in a 35 mL high-pressure reactor according to procedures described above. The catalyst was easily separated from the reaction mixture by centrifugation at 9000 RPM for 15 min, and washed with ethanol for 3 times. Before being resubmitted to the reaction condition, the collected catalysts were dried under a high vacuum for 3 h.

3. Results and discussion

In order to investigate the structure of the catalyst, several characterization were taken out. The scanning electron microscopy (SEM) image showed that the active part of the catalyst was mainly in the form of nanotubes with the mean exterior diameter of about 50 nm and length of several micrometers. As it's shown in Fig. 1(b–c), the carbon nanotubes were uniformly distributed on surface of diatomite. Catalyst GN-Co-600, GN-Co-1000, GN-800 and GN-Ni-800 have also been prepared with the same procedure, however, no carbon nanotubes was