



Highly selective hydrogenation of phenol to cyclohexanol over MOF-derived non-noble Co-Ni@NC catalysts



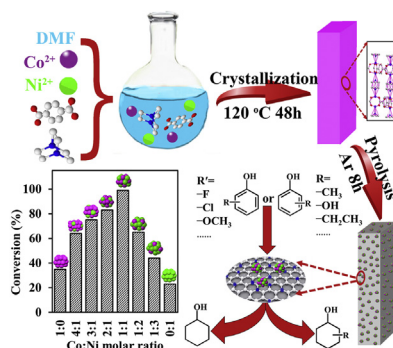
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HIGHLIGHTS

- Non-noble bimetallic catalysts for the hydrogenation of phenol.
- Bimetallic Ni-Co alloyed NPs encapsulated in N-doped carbon matrix.
- Much higher activity than its monometallic counterparts.
- Completely catalyze the hydrogenation of phenol to >99.9% cyclohexanol.
- Reaction mechanism for the hydrogenation of phenol are revealed.

GRAPHICAL ABSTRACT



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ABSTRACT

The selective hydrogenation of phenol is an attractive routine to produce cyclohexanol that is an important basic chemical raw in chemical industry, but the design of cost-efficient and highly selective catalysts remains a great challenge. Herein, we report the first example of non-noble bimetallic nanocatalysts for the selective hydrogenation of phenol with cyclohexanol as the sole product. These catalysts consisting of bimetallic Ni-Co alloy nanoparticles (NPs) encapsulated in N-doped carbon matrix were simply synthesized by using our previously developed MOF-templated strategy (Long et al., 2016). The sum of characterization results revealed that the Co and Ni elements were successfully alloyed in every individual NPs that were confined by N-doped carbon layers. Detailed catalytic test results suggested that both the pyrolysis temperature and the composition of these alloy NPs played the key roles in guiding their catalytic performance in the selective hydrogenation of phenol. It has been shown that Co-Ni@NC system was much more effective for hydrogenation of phenol than Cu@NC, Co-Cu@NC and Ni-Cu@NC systems. The optimal 1Co-1Ni@NC could completely catalyze the hydrogenation of phenol to >99.9% cyclohexanol with a TOF of 0.21 h⁻¹, which was approximately 2.8- and 4.3-fold higher than that of the Co@NC and Ni@NC respectively, underscoring a strong positive synergistic effect between Ni and Co for this reaction. The mechanism study revealed the cyclohexanol was formed directly by the one-step hydrogenation of phenol in our catalyst system. This one-step pathway could avoid the formation of other hydrogenated intermediate product thereby leading to >99.9% selectivity of cyclohexanol. Furthermore, this catalyst also showed good recyclability, magnetically reusability and general applicability for a wide range of phenol substrates, which together with the superior activity and selectivity make it a good potential for the industrial applications.

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1. Introduction

The catalytic hydrogenation of phenol is an important commercial reaction required for the synthesis of KA oil (a mixture of cyclohexanone and cyclohexanol), which play pivotal roles as feedstocks in petroleum industrial chemistry (Claus et al., 2000; Ungnade and McLaren, 1944). On the other hand, phenol is also one of the most common organic pollutions, and phenolic waste are inevitably produced from a variety of industrial sources associated with oil refineries, petrochemical units, polymeric resin manufacturing, and plastic units (Kumar et al., 2005; Prince et al., 2015). Because of its toxic, carcinogenic, mutagenic and teratogenic properties, phenol has been classified as a priority pollutant in the USEPA list with limitation of discharge below 0.5 mg/L imposed by present legislation (Santos et al., 2006; Yang et al., 2015). Therefore, catalytic hydrogenation of phenol is significant from both a commercial standpoint as a synthesis route to value-added chemicals and the destruction of a pollutant, and thereby has been extensively studied in recent years (Nelson et al., 2015; Yoon et al., 2014; Zhu et al., 2014). So far the hydrogenation of phenol in the gas and liquid phase has been developed for a range of supported noble metal catalysts with the Pd-based systems as the most promising catalysts for this reaction (Li et al., 2013; Liu et al., 2009; Neri et al., 1994; Wang et al., 2011). However, their applications on an industrial scale are severely restricted by the limited reserves and high price of noble metals. On the other hand, almost all of these reported catalysts place the emphasis firmly on achieving high cyclohexanone selectivities (Li et al., 2013; Liu et al., 2009; Neri et al., 1994; Wang et al., 2011). In contrast, the selective hydrogenation of phenol to cyclohexanol, which is another important hydrogenated product of phenol, has received far less attention. Actually, apart from its much lower toxicity than phenol and cyclohexanone, cyclohexanol is also widely used in industrial processes as important intermediates for the production of adipic acid, caprolactam and nylon, and as key feed stocks for preparing surfactants, plasticizers, detergents and emulsion stabilizers (Long et al., 2015; Misono and Inui, 1999). In addition, it can also be utilized as an excellent oxygenate additive in enhanced multi-component diesel fuel (Herrerros et al., 2014).

Currently, the selective oxidation of cyclohexane is the most popular and studied synthetic route for the commercial production of cyclohexanol (Fang et al., 2015; Liu et al., 2011). However, this route often suffers from several shortcomings such as high cost, explosion risk, low conversion and easy generation of a large number of by-products (Chen et al., 2014; Zhou et al., 2005). Another important strategy is the hydrogenation of benzene to cyclohexene with subsequent hydration, which avoids the formation of significant amount of by-products, but the activity is not high in most cases (Yao et al., 2006). So the selective hydrogenation of phenol, a method still being used to a small extent, seems to be an attractive alternative pathway to produce cyclohexanol, where a high-performance catalyst plays an essential role in industrial applications. Therefore, the design of cost-effective and reusable catalysts with superior performance (both the conversion and selectivity are above 99%) is clearly a desired goal for this important reaction.

Recent studies in heterogeneous catalysis have suggested that non-noble metals of 3d metals (especially Fe (Phua et al., 2009; Olcese et al., 2012), Co (Mochizuki et al., 2014) and Ni (Long et al., 2015; Shin and Keane, 2000; Xiang et al., 2008)) could work as promising catalysts for a number of hydrogenation reactions. Unfortunately, many of these low-cost catalytic systems often suffer from poor catalytic performance or rigorous reaction conditions (Georganas, 2012; Long et al., 2016). It has been demonstrated that the addition of a second metal to a parent metal offers numerous opportunities for tuning electronic states of the catalysts and com-

binning the properties associated with two distinct metals (Long et al., 2016; Shen et al., 2015; Wang and Li, 2011). Indeed, enhancements in catalytic performances of alloyed catalysts based on the synergy between two metals have been reported for many important reactions such as hydrogenation (Nakagawa et al., 2014a,b; Studt et al., 2008), oxidation (Kesavan et al., 2011; Long et al., 2013; Sugano et al., 2013), dehydrogenation (Huang et al., 2015; Zhang et al., 2013), biomass upgrading (Alonso et al., 2012; Besson et al., 2014), and so on. These advances combined with our own researches inspire us to explore non-noble alloy NPs as highly active catalysts for the selective hydrogenation of phenol to cyclohexanol.

Herein, we have successfully synthesized a series of Co-Ni alloy NPs embedded in N-doped carbon by our previously reported MOF-templated strategy (Long et al., 2016) for the highly selective hydrogenation of phenol to cyclohexanol. Although previous studies on the use of MOFs as sacrificial templates for catalytic applications are not scarce (Wezendonk et al., 2016; Bai et al., 2016; Wang and Li, 2016), our developed catalyst system presents the first example of MOF-derived non-noble bimetallic catalysts for the selective hydrogenation of phenol to cyclohexanol. It was demonstrated that the optimum 1Co-1Ni@NC-600 could completely catalyze the hydrogenation of phenol to >99.9% cyclohexanol with a much higher activity than its monometallic counterparts. The effect of composition and pyrolysis temperature, and the recyclability and general applicability of 1Co-1Ni@NC-600 have been studied in detail, with the aim to develop a promising catalyst for the highly efficient synthesis of cyclohexanol from phenol.

2. Experimental section

2.1. General information

Cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99%, Aladdin Industrial Corporation), nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 98%, Gouzhou Chemical Reagent Factory), cupric nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 99%, Aladdin Industrial Corporation), 1,4-benzenedicarboxylic acid ($\text{C}_6\text{H}_4\text{O}_4$, 99%, Energy Chemical), triethylenediamine ($\text{C}_6\text{H}_{12}\text{N}_2$, 98%, Aladdin Industrial Corporation), N,N'-dimethylformamide ($\text{C}_3\text{H}_7\text{NO}$, 99%, Guangdong Guanghua Sci-Tech Co., Ltd). All of the chemicals used in this study were analytical grade, and all starting materials and solvents were obtained from commercial sources and used without further purification.

2.2. Synthesis of $x\text{M}-y\text{M}'@NC-z$

All of MOF-templated catalysts were prepared according to our previously reported procedure with some modifications (Long et al., 2016). Typically, a mixture of $\text{M}/\text{M}'(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (The total molar amount of M and M' are fixed to be 9 mmol), H_2bdc (1,4-benzenedicarboxylic acid, 7.2 mmol) and DABCO (triethylenediamine, 5.8 mmol) were dissolved in 120 mL DMF under ultrasound. After stirring for 8 h at room temperature, the above solution was then added to a 250 mL teflon-capped glass flask and heated in an oil bath at 120 °C for 40 h. The produced powders were collected by filtration, washed with DMF thoroughly and then dried at 100 °C for 24 h.

The as-synthesized $x\text{M}-y\text{M}'$ -MOFs were heated at a heating rate of 1 °C/min from room temperature to 200 °C under argon atmosphere and kept at this temperature for 2 h to remove the solvent. Then the temperature was increased to the target and maintained for 8 h. After cooling down to room temperature, the as-prepared black powers were collected and denoted as $x\text{M}-y\text{M}'@NC-z$, where x and y represent the molar ratio of M/M' , and z represents the calcination temperature.

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