Communication

Chemoselective hydrogenation of phenol to cyclohexanol using heterogenized cobalt oxide catalysts

Zhongzhe Wei[a], Yi Li[b], Jing Wang[b], Haoran Li[b], Yong Wang[b,*]

[a] Institute of Industrial Catalysis, College of Chemical Engineering, State Key Laboratory Breeding Base of Green-Chemical Synthesis Technology, Zhejiang University of Technology, Hangzhou 310014, China
[b] Advanced Materials and Catalysis Group, ZJU-NHU United R&D Center, Department of Chemistry, Zhejiang University, Hangzhou 310028, China

ABSTRACT

Cyclohexanol is an important intermediate in the synthesis of Nylon-6 and plasticizers. In this work, cobalt oxide nanoparticles (NPs) supported on porous carbon (CoO_x@CN) were fabricated by one-pot method and the hybrids could efficiently and selectively hydrogenate phenol to cyclohexanol with a high yield of 98%. The high catalytic performance of CoO_x@CN was associate with the high surface area ($340\,m^2/g$) and uniformly dispersed NPs. Furthurmore, by detailed analysing the relationship between catalytic activity and catalysts composition, it clearly indicated that the Co_3O_4 in CoO_x@CN played an important role for the adsorption and activation of phenol and the in situ gernerated Co was responsible for hydrogen adsorption and dissociation. These findings provide a fundamental insight into the real active sites in hydrogenation of phenol using Co-based catalysts.

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Cyclohexanol is an important intermediate for the synthesis of Nylon-6 and as well as the component of KA oil using in petroleum industrial chemistry [1,2]. In addition, the catalytic transformation of phenols to stable hydrocarbons is of great significance in the upgrading of bio-oil [3]. At present, several catalytic systems have been successfully applied into the transformation, such as the selective oxidation of cyclohexane [4,5], direct hydration of cyclohexene [6] and the hydrogenation of phenol [7,8]. For selective oxidation of cyclohexane and direct hydration of cyclo-hexene, more or less drawbacks existed, such as complicated steps, explosion risk, low conversion and selectivity [9]. Among these processes, the hydrogenation of phenol was considered to be the most efficient and promising strategy considering the high atom utilization and the green process. What is more, phenol is readily available from naturally lignins, which is one of the most abundant available feedstocks [10]. The wide sources of raw materials guarantee the reaction take place smoothly and provide the possibility for industrial applications.

Up to now, a series of studies have been reported for the hydrogenation of phenols. Particularly, heterogeneous catalysts have received an astonishing amount of attention due to their easy recovery and good reusability. The active metals play an important role in the selective hydrogenation reactions. Specifically, the adsorption and dissociation of hydrogen and the adsorption behavior of substrate on active metals are directly related to the catalytic activity and selectivity [11]. The present catalysts used in the catalytic hydrogenation of phenols are mainly precious metals, especially Pd [12–22], Pt [23,24], Rh [25,26] and Ru [27–29]. Although the precious metals catalysts showed good catalytic activity and selectivity to cyclohexanone or cyclohexanol, the risk in supply and volatile price of noble metals inhibited to accomplish industrializaiton. To circumvent the problems, development of catalysts based on earth-abundant metals, such as Fe, Co, and Ni, was regarded as an impressive strategy considering their distinct electronic structures [30] and low cost. Very recently, important progress made in the fabrication of earth-abundant metal catalysts using in chemoselective hydrogenation reactions [31–36], oxida-tion reactions [37–39] and electrocatalytic reactions [40–42]. However, the hydrogenation of phenol using non-noble metal catalysts is rare reported [7,43] and should be emphasized. It is worth mentioning that base metals are easy to be oxidized and cause irreversible deactivation of the catalysts under liquid-phase conditions. Therefore, it is necessary to develop a convenient strategy for the synthesis of stable, high activity and selectivity non-noble metal catalysts.

Porous carbon materials are fascinating materials that have attracted widespread attention due to the high surface area, rich pore sturcture, high stability and so on. They provide access to a

* Corresponding author.
  E-mail address: chemwy@zju.edu.cn (Y. Wang).

wide range of applications, especially act as good supports for heterogeneous catalysts [44,45]. The introduction of porous carbon can stable the nanoparticles (NPs) and enhance the interaction between the supports and NPs, thus benefiting the catalytic process. Herein, we effectively combine porous carbon and cobalt oxides by direct pyrolysis of D-glucosamine hydrochloride (GAH), melamine and $CoCl_2 \cdot 6H_2O$. The obtained hybrids (CoO_x@CN) show high activity and selectivity in the hydrogenation of phenol to cyclohexanol. Almost full conversion (98%) of phenol with excellent selectivity (>99%) toward cyclohexanol were obtained under optimized reaction conditions. Detailed analysis of the relationship between catalytic performance and catalyst component indicates that the synergistic effect occurs during the raction. In particular, the original Co_3O_4 in CoO_x@CN is benificial for the adsorption and activation of phenol and the *in situ* gernerated Co is responsible for hydrogen adsorption and dissociation, which greatly improve the catalytic activity. The successful integration of porous carbon and earth-abundant metals in the new hybrid paves the way for design of more intriguing materials in heterogeneous catalysis.

The hybrids (CoO_x@CN) were prepared in one step through pyrolysis of GAH, melamine and $CoCl_2 \cdot 6H_2O$ at 800 °C. For comparasion, $CoCl_2$/AC and $CoCl_2$/commercial-CNTs were synthesized under the identical conditions, and the resultants were named CoO_x@AC and CoO_x@CNT, respectively. To access the microstructures of CoO_x@CN, a series of characterizations, such as transmission electron microscopy (TEM), N_2 adsorption/desorption isotherms, X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) were conducted. As shown in Fig. S1a (Supporting information), the N_2 adsorption/desorption isotherm resembled type IV with a hysteresis loop, indicating the existence of mesopores. The calculated specific surface area (SSA) was 344 m^2/g and the mean pore size was 10 nm. Such large SSA and wide pore diameter were beneficial to expose more active sites and mass transfer. In the XRD pattern of CoO_x@CN (Fig. S1b in Supporting information), the diffraction peak at 26° was ascribed to the (002) reflection of the graphitic-type lattice. The diffraction peaks at 19°, 31.2°, 36.8°, 44.8°, 55.7°, 59.4°, 65.2° could be assigned to the (111), (220), (311), (400), (422), (511), (440) planes of Co_3O_4 nanocrystal (PDF 42-1467). Besides, a weak reflection at 61.5° was the characteristic (220) plane of CoO. Therefore, Co_3O_4 is the main phase in CoO_x@CN. TEM images further revealed the microstructure of CoO_x@CN. In Fig. S1c in Supporting information, the carbon support consisted of multi-walled carbon nanotubes and graphite layers. The CoO_x NPs dispersed uniformly on the carbon support with a mean size of 13.8 nm by counting >300 metal NPs. The ICP-AES test demonstrated that the content of cobalt was 27 wt%.

To evaluate the catalytic performance of CoO_x@CN, we select the hydrogenation of the benchmark substrate phenol as a model reaction. The reaction conditions were optimized through variation of the solvent, temperature, and hydrogen pressure. First, we assessed the effects of solvent on the reaction. Among the tested solvents listed in Table S1 (Supporting information), water gave the best result, furnishing a satisfying yield (98%) toward cyclohexanol, which was economically viable because raw bio-oil contains 10–13 wt% water. Ethanol and *i*-propanol also performed moderate catalytic activity and perfect selectivity. In contrast, completely no conversion was obtained in THF, dimethyl sulfoxide and dioxane. It seems that the reaction rate is not correlated with solvent polarity or solubility of H_2. It should be noted that CoO_x@CN performed much better activity in protic solvent, while CoO_x@CN had no activity in nonprotic solvents at all. This phenomenon was consistent with the conclusion reported by Lercher [46]. Protic solvents can provide proton and form hydrogen bond with phenol, which can lower the activation energy of the reaction and promote the hydrogenation process [47,48].

Additionally, the temperature and hydrogen pressure affected the performance of catalysts enormously. As shown in Table S2 (Supporting information), the catalytic system is sensitive to temperature and hydrogen pressure, especially the conversion of phenol. At 120 °C and 3 MPa H_2, the conversion of phenol was 43% and the selectivity was perfect. Elevating the temperature to 135 °C with constant pressure, the conversion increased to 62%. Pleasingly, furthur raising the reaction temperature to 150 °C afforded an excellent conversion, furnishing cyclohexanol in 98% yield. At 150 °C, decreasing the hydrogen pressure from 3 MPa to 2.5 MPa, the conversion of phenol declined markedly to 35% yet excellent selectivity. Further reducing the hydrogen pressure to 2 MPa led to the worst conversion, obtaining only 17% yield of the target product. For follow-up studies, we conducted the reaction at 150 °C and 3 MPa, as these conditions represented the best performance of CoO_x@CN.

As the cobalt-based hybrids were prepared under high temperature, different pyrolysis temperature can affect the structure and composition of the catalyst, thus influencing its catalytic activity. We then investigated the performance of the catalysts pyrolysis from 700 °C to 1000 °C under optimized reaction conditions (150 °C, 3 MPa H_2). Evolution of conversion with reaction time by a series of catalysts were conducted and the results were compiled in Fig. 1. We found that the catalysts pyrolyzed at different temperature behaved differently. On increasing the pyrolysis temperature from 700 °C to 1000 °C, the activity of the resulting catalyst increased firstly and then decreased. The catalytic activity of CoO_x@CN-700 °C was relatively weak, affording only 12% yield of cyclohexanol. While the material pyrolyzed at 800 °C exhibited the highest catalytic activity, producing cyclohexanol in 98% yield.

In order to study the reasons for the difference in catalytic activity, a series of characterizations were performed. As the valence state of active metal is closely related to the catalytic activity, the species of cobalt should be discussed. To this end, we used XPS and XRD to access the cobalt composition in different catalysts (Fig. S2 in Supporting information). The XPS results showed that the valence state of Co in different catalysts was almost the same. The peaks located at 780 eV and 795.6 eV in the spectrum were corresponding to the Co_3O_4 phase, and the characteristic peak of the metallic Co was not found. Therefore, Co_3O_4 was the main phase in the tested catalysts, which was also verified by the XRD results (Fig. S2d). The similar cobalt species in the catalysts pyrolyzed at different temperature is not possible to explain the reason of the difference in the activity.

As we know, the SSA and pore structure can affect mass transfer during the reaction. Next, we applied N_2 adsorption/desorption to analysis the textural properties of different catalysts. As displayed

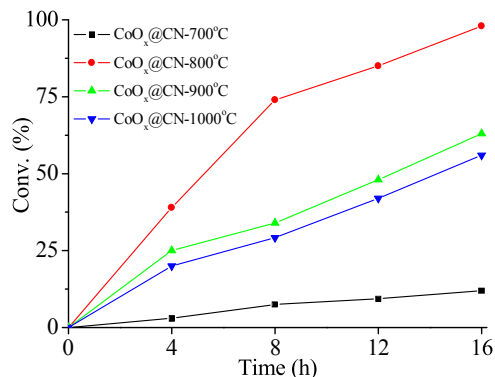**Fig. 1.** Evolution of conversion with reaction time by CoO_x@CN under different pyrolysis temperature.