MCAT

Editor's choice paper

Highly selective hydrogenation of phenol to cyclohexanol over nano silica supported Ni catalysts in aqueous medium

CrossMark

J. He [a,b], X.-H. Lu [a,b,*], Y. Shen [a,b], R. Jing [a,b], R.-F. Nie [a,b], D. Zhou [a,b], Q.-H. Xia [a,b,*]

[a] Hubei Collaborative Innovation Center for Advanced Organic Chemical Materials, Hubei University, Wuhan 430062, PR China
[b] Ministry-of-Education Key Laboratory for the Synthesis and Application of Organic Functional Molecules, Hubei University, Wuhan 430062, PR China

ARTICLE INFO

ABSTRACT

Cyclohexanol is an excellent starting material for fuel production, but direct selective hydrogenation of phenol to cyclohexanol under mild conditions is a challenge. Herein we report a catalyst made of Ni nanoparticles supported on high-surface silica, which is highly active for selective formation of cyclohexanol under 1.0 Mpa pressure of hydrogen in aqueous medium without additives. Conversion of 100 mol% and selectivity up to 100% are achieved within 4 h and 1.0 MPa H_2. Some factors such as the type of the source of silica, the loading of Ni, the reaction temperature and time, the H_2 pressure play important roles in controlling the selective hydrogenation. The generality of the 10%Ni/SiO_2-1 catalyst for this reaction is demonstrated by selective hydrogenation of other hydroxylated aromatic compounds as well.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Hydrogenation of phenol has attracted much attention both in industry and in the synthesis-oriented research laboratory in recent years [1]. The reason for this interest lies in one fact that the hydrogenation of phenol is an industrially important reaction required for the production of caprolactam and adipic acid used to manufacture nylon 6 and nylon 66 [2,3]. Particularly, cyclohexanol could also be used in pharmaceuticals, plasticizers, surfactant, paint, industrial solvent. And it is also an excellent starting material for fuel production [4,5]. For instance, cyclohexane, which can be obtained from cyclohexanol through dehydration and hydrogenation under mild conditions, is one of main components of gasoline. The dimer of cyclohexanol can be used as a precursor for jet fuel. Cyclohexanol can also be converted to cyclohexanone and then with high quality fuel through consecutive aldol condensation and HDO processes [6]. Furthermore, cyclohexanol is also an excellent oxygenate additive in enhanced multi-component diesel fuel used to improve emissions. Industrially, cyclohexanol can be produced either by the oxidation of cyclohexane or via the hydrogenation of phenol. The oxidation of cyclohexane requires high temperatures and high pressures and suffers from low product yields and complicated

recovery/separation steps [7]. In the latter route, the hydrogenation of phenol to cyclohexanol may take place in a 'two-step' process [8–10], which involves hydrogenation of phenol to cyclohexanone followed by hydrogenation to cyclohexanol [1,7,11–13].

Traditionally, phenol hydrogenation can be conducted in gas [14] or liquid phase [15]. The reaction has been carried out in the gas phase, with supported Pd [16], Pt [17,18], Ru [19,20], Rh [21] catalysts as the most efficient systems and different supports for this reaction. However, high temperatures are normally required for this process (300 °C) [8,14,22], and the generation of carbonaceous deposits (coking) in the course of the reaction leads to deactivation of the catalyst. Liquid-phase phenol hydrogenation offers energy savings, because the reaction can be performed at relatively low temperatures [9,13,23,24]. Up to now, many researchers have contributed to this area, and many catalysts have been screened; however, an important drawback of current liquid-phase hydrogenation protocols relates to the use of noble metals. So exploring the substitution of precious metal catalysts with earth-abundant and less toxic cheap metals thus occupies the forefront of contemporary molecular catalysis research. Nowadays hydrogenation of phenol with non-noble metal catalyst is becoming the preferred industrial process for the production of cyclohexanol, more advantageous in terms of capital costs and energy savings than the two-steps process via cyclohexanone.

Especially, the supported nickel catalysts have been widely applied in industrially important chemical processes, such as hydrogenation [25–28], dehydrogenation [29], methanation, reforming, hydrocracking and so on. To obtain the supported nickel

catalysts with high activity, some approaches and techniques have been developed, in which aqueous chelated metal complexes and organic nickel precursors are supported by a wet impregnation and directly reduced with hydrogen without calcination in air [30].

As part of our continuing interest in the development of supported metal Ni NPs on SiO_2 for hydrogenation of dinitronaphthalene [30], herein we report the synthesis of nickel supported on high-surface silica (Ni/SiO_2) and its exceptional performance for the selective hydrogenation of phenol to cyclohexanol in the liquid phase at low temperature and H_2 pressure. The 10%Ni/SiO_2-1 catalyst exhibits superior conversion of phenol (100 mol%) and high selectivity of cyclohexanol (100%) at 1.0 MPa H_2, and remains highly active even after eight reuse cycles. Furthermore, the catalyst can also catalyze selective hydrogenation of a variety of phenol derivatives under mild conditions.

2. Experimental

2.1. Materials

Nickel (II) nitrate hexahydrate (Ni$(NO_3)_2$·6H_2O 98%), Cobalt (II) nitrate hexahydrate (Co$(NO_3)_2$·6H_2O 98%), Copper (II) chloride dehydrate (CuCl$_2$·2H_2O 98%), Tin (II) chloride dehydrate (SnCl$_2$·2H_2O 98%), Ruthenium (III) chloride trihydrate (RuCl$_3$·3H_2O Ru 45%), Coconut Shell Charcoal (CSC) (98%) were purchased from Shanghai Aladdin Chemical Co. Aerosil-200 was obtained from Degussa Co., and CT-150 (98.5%), CT-200 (99%), CT-380 (99.9%) silica from Shan Dong Shou Guang Chemical Co. Gel silica was obtained from Tian Jin Long Hua Chemical Co. (China). Ludox AS-40 colloidal silica was purchased from Sigma Aldrich Co. The main reagents used in the hydrogenation were phenol (AR), tetrahydrofuran (THF) (99.0%), which was purchased from Shanghai Aladdin Chemical Co.

2.2. Preparation of catalysts

Silica-supported nickel, with various Ni loadings, were prepared by incipient-wetness impregnation with different silica sources like aerosil-200 silica (SiO_2-1), CT-150 silica (SiO_2-2), CT-200 silica (SiO_2-3), CT-380 silica (SiO_2-4), Gel silica (SiO_2-5) and AS-40 colloidal silica (SiO_2-6). These catalysts were prepared via the following procedure. Typically, 1.082 g of Ni$(NO_3)_2$·6H_2O was dissolved in 80 mL of deionized water, followed by the addition of 2.0 g silica. Then, the resulting mixture was heated to 90 °C in a microwave reactor with magnetic stirring. Then water was completely evaporated off by rotary evaporator, and the recovered solid was dried overnight at 100 °C. Separated precipitate was then converted to nickel oxide/SiO_2 by calcination at 400 °C for 3 h in air. The resulting powder was transferred into a crucible, heated to 400 °C at a rate of 5 °C min^{-1} under a flow of hydrogen and kept for 3 h in a tube furnace. The catalysts were denoted as x wt% Ni/SiO_2-m, where x represents the loading of Ni in wt% and m stands for different silica. Other metal catalysts were also prepared through the same method of incipient-wetness impregnation, which was designated as 10%Co/SiO_2-1, 10%Cu/SiO_2-1, 10%Sn/SiO_2-1 and 2.2%Ru/SiO_2-1.

2.3. Characterization of catalyst

Powder X-ray diffraction (XRD) was performed on a Bruker D8A25 diffractometer with using the Ni filtered Cu K$_\alpha$ radiation (λ = 1.54184 Å) operating at 40 kV and 40 mA with scan the range of 5–80° 2θ. The surface area and pore volume and pore radius of samples were used to determine from the N_2 adsorption–desorption properties of the samples. The specific surface area was determined from isotherms using the BET equation at the relative pressure between 0.05 and 0.25. The Barrett–Joyner–Halenda (BJH) method

was used to measure the pore volume. Prior to the measurements, the samples were degassed at 300 °C under vacuum of 10^{-2} Mbar for 10 h. The morphologies and sizes of all samples were obtained by field-emission scanning electron microscope (SEM) (JEOLJSM-6510A). Ni particles morphology was obtained by Tecnai G20 transmission electron microscope operated at an accelerating voltage of 200 kV. The temperature-programmed reduction (TPR) with H_2 was performed on a TP-5076 automatic gas sorption analyzer, the catalyst was carried out with N_2 flow of 50 mL/min (10 vol% H_2), from room temperature to 600 °C at a heating rate of 10 °C/min. The content and chemical states of Ni were performed by X-ray photoelectron spectroscopy (XPS) with Perkin-Elmer PHI ESCA system. The dispersion of Ni metal species on the support was determined by equilibrium hydrogen chemisorption at room temperature in Quantachrome iQ-MP. Prior to H_2 chemisorption analysis, the samples were evacuated at 200 °C for 1 h, then exposed to static H_2 at 300 °C for 2 h and finally placed under dynamic vacuum at 300 °C for 3 h [31,32].

2.4. Catalytic activity tests

Catalytic tests were conducted in a 100 mL stainless steel autoclave with a magnetic agitator. 100 mg heterogeneous Ni catalyst, 0.5 g phenol, and 9.5 g water were introduced into the autoclave, which was then vacuumed and purged three times with H_2 before it was finally pressurized with 1.0 MPa of H_2 gas. Subsequently, the reaction mixture was stirred at a given temperature. After being cooled down to room temperature (RT), excess H_2 was carefully released, and the mixture was filtered through centrifugation to separate the catalyst. The resultant product mixtures were analyzed by gas chromatograph to determine the conversion of products. The results were calculated using the follow equations:

$$\text{Conversion Phenol} = \left(1 - \frac{\text{mol of Phenol after reaction}}{\text{mol of Phenol intial}}\right) \times 100\%$$

Selectivity of Cyclohexanol

$$= \frac{\text{mol of Cyclohexanol}}{\text{mol of the amounts of products}} \times 100\% s$$

3. Results and discussion

3.1. Catalyst characterization

The Nitrogen adsorption and desorption isotherms and pore distribution of 10%Ni/SiO_2 are shown in Fig. 1. The N_2 adsorption isotherms of the catalysts show the presence of a hysteresis loop, associated with capillary condensation, which indicates the formation of the mesoporous structure [33]. The result was attributed to mesoporous materials with cylindrical pores and a narrow pore size distribution. The surface area, pore volume and average pore radius of samples are given in Table 1. It is clear that all of the materials different in the specific pore size that decreases in the follow order: 10%Ni/SiO_2-1 > 10%Ni/SiO_2-2 > 10%Ni/SiO_2-4 > 10%Ni/SiO_2-3 > 10%Ni/SiO_2-6 > 10%Ni/SiO_2-5. The pore radius of Aerosil-200 is almost 2.7 times higher than that of Gel silica.

The XRD patterns of different SiO_2 supports and the supported Ni catalysts are shown in Fig. 2. It is found that typical broad characteristic peak at around 2θ = 22° is assigned to the [002] plane reflection of amorphous SiO_2. For all of the prepared 10%Ni/SiO_2 catalyst, a group of diffraction peaks at 44.5°, 51.8° and 76.4° are observed, which corresponding respectively to the [111], [200] and [220] diffraction of the Ni (PDF# 04-0850). In addition, the peak at 37.4° is assigned to the [111] diffraction of NiO (PDF# 02-0406). The result can be attributed to the fact that a small part of NiO species