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Simple fabrication of nano-sized NiO_2 powder and its application to oxidation reactions

Hongbing Ji[a,*], Tingting Wang[a], Meiying Zhang[b], Yuanbin She[c], Lefu Wang[a]

[a]School of Chemical and Energy Engineering, South China University of Technology, Guangzhou 510640, PR China
[b]Analytical and Testing Center, South China University of Technology, Guangzhou 510640, PR China
[c]Institute of Green Chemistry, Beijing University of Technology, Beijing 100022, PR China

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Abstract

A novel, facile, and environmentally-friendly process for fabrication of NiO_2 was developed and used as both a stoichiometric oxidant and an effective catalyst for benzyl alcohol oxidation. That simultaneous stoichiometric and catalytic reactions might exist in many reactions is proposed.

Keywords: NiO_2; Stoichiometric oxidant; Catalyst; Benzyl alcohol oxidation

1. Introduction

Using solid materials as catalysts is of great interest and importance in organic synthesis [1]. The obvious advantages are as follows: firstly and most important, improved separation and handling process, and secondly, the potential of creating active sites with improved catalytic performance. Employing precious metals such as ruthenium as active components, two types of solid catalysts based on the unique characteristics of inorganic matrices, i.e. $Ru/CeO_2/CoO(OH)$ [2,3] and mixed oxide Ru–Mn–Fe–Cu–O [4–6] have been successfully applied into various alcohols oxidation by our research group. Besides, recently published reports could be found about other solid catalysts using Ru-modified [7–9] or Pd-modified [10] materials for alcohol oxidation.

In our endeavor to use these precious metal-modified catalysts in practical applications, the expensive cost of the precious metals is not acceptable in the industry. Although these catalysts were reported to be recoverable, the complete recovery of these precious catalysts is seldom attained since very fine particles in these catalysts make them impossible to recover completely using cost-effective, simple filtration. From this point of view, employing non-precious metals as active components might be the possible path for practical applications. Some non-precious metals, such as Ni-modified [11], V-modified [12] and Cu-modified [13] inorganic matrices were successfully applied to the oxidation of alcohols using molecular oxygen as an oxidant.

In this present paper, a non-precious metal oxide, i.e. NiO_2, was simply fabricated without using NaClO as an oxidant, making this preparation process rather novel, environmentally-friendly and different from the original preparation method [14,15]. It is well-known that NaClO is necessary for the preparation of NiO_2, which is a strong oxidant towards organic oxidation [15]. However, in the present research this NiO_2 does not need NaClO and the as-prepared NiO_2 is available both as a stoichiometric oxidant and as an effective catalyst for benzyl alcohol oxidation. These double properties also give us the idea that the phenomenon of simultaneous stoichiometric and catalytic reactions might exist in many reactions.

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* Corresponding author. Tel.: +86 20 87114136; fax: +86 20 87114136.
E-mail address: cehbji@scut.edu.cn (H. Ji).

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2. Experimental

2.1. Novel method for preparing nano-sized NiO_2

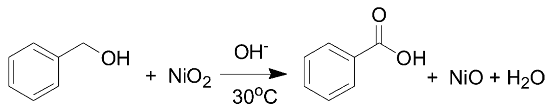
A wet chemical method was used to prepare NiO_2. A typical example is as follows: a three-neck round bottle flask equipped with a thermometer and mechanical stirrer was charged with 120 mL of de-ionized water, 5.60 g of Na_2CO_3 and 7.40 g of NaOH pellets. A second solution containing 18.00 g of $Ni(NO_3)_2{\cdot}6H_2O$ and 60 mL of water was prepared and added at the rate of 1 mL/min to the first solution while stirring with 1400 rpm. The resultant mixture was heated for 18 h at 65 °C. The dark slurry was filtrated, washed with deioned water, dried at 110 °C for 12 h, and calcined at 400 °C for 3.5 h, yielding 2.92 g of black powder.

2.2. Preparing β-NiOOH

β-NiOOH was synthesized according to the literature [16]. A solution containing 1.98 g of $NiSO_4{\cdot}6H_2O$ and 15 mL of de-ionized water was added dropwise into 480 mL of NaOH with pH value 12.5 and kept at 25 °C for 24 h while stirring. The obtained slurry was firstly filtered, then dried for 16 h at 100 °C, and aged for 4 h in 9 M KOH at 90 °C. Then, after another filtration to neutrality and after being dried for 24 h at 120 °C; 0.44 g of pale green $Ni(OH)_2$ was obtained. This solid $Ni(OH)_2$ was added into 30 mL of 1 M NaOH solution, followed by the addition of 1.88 g $K_2S_2O_8$, with stirring for 24 h; 0.32 g dark β-NiOOH was obtained after filtration and dried at 100 °C for 2 h.

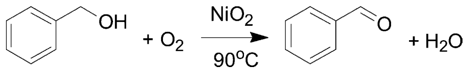
2.3. Stoichiometric oxidation of benzyl alcohol using NiO_2 as an oxidant

To a solution of 1 mmol of benzyl alcohol and 0.10 g of NaOH in 5 mL of deioned water, 0.30 g of as-prepared NiO_2 was added while stirring on a magnetic stirrer, and the heterogeneous solution was allowed to react at 30 °C for 3 h in Ar atmosphere. Benzyl alcohol was purified before use. The solid material was filtered off and GC analysis of the acidified filtrate showed the yield with naphthalene as an internal standard. In the presence of NaOH, NiO_2 presents strong oxidative performance as an oxidizing agent. The stoichiometric oxidation is expressed as follows:



2.4. Catalytic oxidation of benzyl alcohol using as-prepared NiO_2 as a catalyst

To a solution of 1 mmol of benzyl alcohol in 5 mL of toluene, 0.30 g of as-prepared NiO_2 was added while stirring on a magnetic stirrer, and the heterogeneous solution was allowed to react at 90 °C for 6 h in the molecular oxygen atmosphere. Benzyl alcohol was purified before use. The solid catalyst was recycled by filtration. GC analysis of the filtrate showed the yield. Naphthalene was used as an internal standard. The catalytic oxidation is expressed as follows:



2.5. Recovery and reuse of as-prepared NiO_2

The spent as-prepared NiO_2 was firstly washed with acetone to remove the adhering of organic compounds; followed by washing with 10% of aqueous Na_2CO_3 and de-ionized water. After drying at 110 °C, the obtained recyclable catalyst was subjected to the oxidation of benzyl alcohol under the identical conditions.

2.6. Characterization

Chemical composition was determined with a Z-5000 type atomic absorption spectrometer (AAS) manufactured by Hitachi Co. (Japan), with the detection limit for Ni element less than 0.2 ppm and with analytical error less than 5%.

Thermogravimetry (TG) and differential thermal analysis (DTA) curves were measured with STA449C Jupiter analysers (NETZSCH Gerätebau GmbH). The samples were heated under inert nitrogen atmosphere at a rate of 10 °C/min.

Temperature-programmed reduction (TPR) with H_2 was performed in fixed-bed flow reactor. The sample was pretreated in 100% O_2 flow at 120 °C for 0.5 h, and then it was cooled down to 50 °C and exposed to nitrogen flow in order to purge the line. The TPR profile of each sample was recorded from 50 to 850 °C under a flow of 5.0% H_2/Ar. The flow rate of 5.0% H_2/Ar was 60 mL/min, and the catalyst weight was 50 mg. The heating rate was 10 °C/min. The consumption of H_2 was monitored continuously with a TCD gas chromatograph-equipped molecular sieve 5A in order to remove H_2O from the effluent gas.

Powder XRD data were collected on a XD-3A difractometer (nickel-filtered Cu Kα X-radiation, $\lambda = 0.15418$ nm) with a curved graphite monochromator, an automatic divergence slit (irradiated length 20.00 mm), a progressive receiving slit (slit height 0.05 mm) and a flat plate sample holder, in a Bragg–Brentano para-focusing optics configuration. Intensity data were collected at a rate of 0.02° per step in the range $10^\circ \leq 2\theta \leq 70^\circ$ with a scan time of 0.3 s step^{-1}. The diffractograms were compared with the JCPDS for identification purposes.

High-resolution transmission electron microscopy (HRTEM) analysis was carried out using a Philips CM300 FEGTEM microscope operated at an accelerating voltage of 200 kV with the resolution of 0.2 nm. The specimens were prepared by ultrasonic dispersion in