Arabian Journal of Chemistry (2018) xxx, xxx–xxx

King Saud University

Arabian Journal of Chemistry

www.ksu.edu.sa
www.sciencedirect.com

ORIGINAL ARTICLE

Hierarchical nanocrystalline NiO with coral-like structure derived from nickel galactarate dihydrate: An active mesoporous catalyst for methyl ethyl ketone production

Samih A. Halawy *, **Mohamed A. Mohamed, Adel Abdelkader**

Chemistry Department, Faculty of Science at Qena, South Valley University, Qena 83523, Egypt

Received 24 October 2017; accepted 24 March 2018

KEYWORDS

2-Butanol;
Characterizations;
Catalysis;
Nickel galactarate;
Nanocrystalline;
Methyl ethyl ketone

Abstract Nanocrystalline NiO with a coral-like structure (38 nm) has been prepared *via* thermal decomposition of a new precursor, nickel galactarate ($NiC_6H_8O_8{\cdot}2H_2O$), at 500 °C for 3 h in air. Thermal decomposition of that precursor was studied by TG and DSC techniques. The resultant NiO was physicochemically characterized by XRD, FTIR, SEM, surface area, porosity and CO_2-TPD. NiO was found to exhibit a remarkable activity towards the synthesis of MEK from 2-butanol between 200 and 325 °C. In addition, it has shown a great tendency to ease regeneration of the used catalyst after 192 h in stream by simple refreshing method.

1. Introduction

Design of hierarchical nanocrystalline metal oxides with special structure is of crucial interest, due to their diverse applicability in a range of areas. Nanocrystalline NiO, as a transition metal oxide, is considered as a promising material for its potential applications in topics, such as: waste-water treatment (Zheng et al., 2017; Zhao et al., 2015), photocatalysis (Fazlali et al., 2015), catalysis (Bonomo et al., 2017; Younas et al., 2016; Ye et al., 2016; Gajengi et al., 2015), gas sensors (Li, 2017; Khalaf et al., 2017), as anode material for Li-ion batteries (Li et al., 2017; Mollamahale et al., 2017) and as antibacterial and anti-inflammatory material in biomedicine (Ezhilarasi et al., 2016; Shanaj and John, 2016). Numerous experimental methods have been applied for the preparation of NiO, with different morphologies, from various precursors including: NiO nanowires (Li, 2017), nanoflakes (Suresh et al., 2017), nanorods and nanocubes (Bai et al., 2013), flowerlike porous hollow nanostructures (Feng et al., 2016), ultrathin nanosheets (Yao et al., 2015) and hollow microspheres (Li et al., 2017). Previously we have reported the thermal decomposition of another nickel carboxylate salt, in different atmospheres, such as nickel oxalate dihydrate (Mohamed et al., 2005). A major interest of our research group, at the moment, is directed towards exploring the morphology, structure and catalytic activity of metal oxides that are prepared from new and trace-

* Corresponding author.
E-mail address: Samih.halawy11@gmail.com (S.A. Halawy).
Peer review under responsibility of King Saud University.

Production and hosting by Elsevier

https://doi.org/10.1016/j.arabjc.2018.03.023
1878-5352

Please cite this article in press as: Halawy, S.A. et al., Hierarchical nanocrystalline NiO with coral-like structure derived from nickel galactarate dihydrate: An active mesoporous catalyst for methyl ethyl ketone production. Arabian Journal of Chemistry (2018), https://doi.org/10.1016/j.arabjc.2018.03.023

less precursors like metal galactarates. We have recently reported the preparation of nanocrystalline MgO using magnesium galactarate hemihydrate $MgC_6H_8O_8{\cdot}0.5H_2O$, with high surface area and strong basic properties (El-Nahas et al., 2017).

Methyl ethyl ketone (MEK) is used as a multi-purpose solvent, in surface coatings, removal of paints and varnish, printing inks, and as an extraction medium for oils, fats, resins and waxes (A.M.T.H., 2014). Also, MEK has potential applications as a fuel substitute (Thion et al., 2017; Hoppe et al., 2016) and as a catalyst for polyester resins hardening (Al-Sunbul et al., 2016).

The main objective of this study is to provide an easy method to prepare hierarchically nanocrystalline NiO, with a characteristic morphology, in a short time using a novel and non-toxic precursor nickel galactarate dihydrate, $NiC_6H_8O_8{\cdot}2H_2O$. Also, the obtained NiO was physicochemically characterized and was tested for the catalytic activity for the synthesis of MEK from 2-butanol.

2. Material and methods

2.1. Preparation of the precursor

The home-made crystalline nickel galactarate was prepared as the recently published method (El-Nahas et al., 2017). Briefly, a calculated amount of galactaric acid ($C_6H_{10}O_8$, Merck) was dissolved in 100 mL of deionized water at 70 °C. Nickel basic carbonate hydrate powder [$NiCO_3{\cdot}2Ni(OH)_2{\cdot}xH_2O$] was slowly added with continuous stirring, until there was no further CO_2 released, indicating the complete reaction between the two reactants. This results in the formation of a pale green precipitate of Ni-Galactarate, which was then washed several times with deionized water, and was then dried in an oven at 100 °C overnight. Then the resultant solid was calcined at 500 °C in static air for 3 h in a muffle furnace.

2.2. Characterization methods

Numerous bulk and surface investigation methods have been used in order to characterize both the precursor and the final oxide (NiO).

2.2.1. Bulk characterization

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed at a heating rate of 3 °C/min in a stream of dry nitrogen flowing at 40 mL/min, using a 50H Shimadzu thermal analyzer (Japan). The thermal analyzer is equipped with a data acquisition and handling system (TA-50WSI). Highly sintered α–Al_2O_3 was used as the reference material in DSC measurements, while temperature and enthalpy readings were calibrated versus the melting point, i.e. 156.3 °C (Lide, 2004) and the heat of fusion, ΔH_f = 28.24 J/g (Lide, 2004) of Specpure Indium metal (a Johnson Matthey product), respectively. Elemental analysis was carried out using Perkin Elmer 2400 Series II CHNS/O analyzer.

Samples of the Ni-Galactarate precursor and NiO were analyzed by X-ray powder diffraction (XRD) method using a Brucker AXS-D8 Advance diffractometer (Germany), equipped with a copper anode generating Ni-filtered CuK_α radiation (λ = 1.5406 Å), in the 2θ range between 10°-80°, supported with interfaces of DIFFRAC^{plus} SEARCH and DIFFRAC^{plus} EVA to facilitate an automatic search and match of the crystalline phases for identification purposes with ICDD data base.

The FTIR spectra were recorded using a Magna-FTIR 500 (USA), between 4000 and 400 cm^{-1}, operating a Nicolet Omnic software and adopting the KBr disk technique.

The Scanning Electron Microscopic study, SEM, of NiO sample was carried out using a FEI Quanta environmental SEM Oxford Ex-ACT using XT microscope Control software.

2.2.2. Surface characterization

The surface textural properties of NiO sample that has been calcined at 500 °C (*viz*. specific surface area, pore volume and mean pore radius) were determined from nitrogen adsorption-desorption isotherms recorded at liquid nitrogen temperature, −196 °C, using an automatic Micromeritics ASAP 2010 (USA), equipped with an online data acquisition and handling system operating BET and BJH analytical software for the adsorption-desorption data, assuming a cylindrical pore model (Sing et al., 1985). The measured sample was degassed at 200 °C and 10^{-5} Torr for 2 h before measurement (1 Torr = 133.3 Pa).

The surface basicity/basic sites strength distribution over NiO sample was investigated by temperature-programmed desorption of CO_2 (CO_2-TPD). NiO sample (≅100 mg) was initially heated at 450 °C for 1 h in air, then was immediately transferred into a Pyrex-glass chamber fitted with inlet/outlet allowing for a CO_2-stream (100 mL/min) to pass at room temperature. After 48 h, ≅20 mg of the CO_2-covered sample were subjected to DSC analysis using 40 mL/min as N_2-flow with 20 °C/min heating rate.

2.3. Catalytic activity measurements

Catalytic activity and selectivity of NiO for the conversion of 2-butanol (2BA) to 2-butanone, methyl ethyl ketone (MEK), in the temperature range of 200–325 °C were investigated. For each test, 0.2 g of catalyst was preheated at 400 °C inside a continuous-flow fixed bed reactor for 1 h in N_2-flow before measurements, then the temperature was lowered gradually to 200 °C. Two values of gas hourly space velocity (GHSV) i.e. 12,000 and 24,000 mL g_{cat}^{-1} h^{-1} were used. The carrier gas (N_2) was passed through a bubbler containing liquid 2BA (Fluka, ≥99%) held at 0 °C. The temperature in the experiment was varied stepwise from 200 to 325 °C. The alcohol vapours in N_2-feed flow were adjusted using mass flow controller Shimadzu FC-40. The reactor effluent was analyzed by a (Shimadzu GC-14) gas chromatograph, equipped with a data processor model Shimadzu Chromatopac C-R4AD. Automatic sampling was continuously performed using a heated gas sampling cock, type HGS-2 at 140 °C, using (FID) flame ionization detector and a stainless steel column (PEG 20 M 20% on Chrmosorb W, 60/80 mesh, 3 m × 3 mm) at 80 °C. The retention time of 2BA and the expected products has been calibrated, in separate experiments, using pure samples.

Please cite this article in press as: Halawy, S.A. et al., Hierarchical nanocrystalline NiO with coral-like structure derived from nickel galactarate dihydrate: An active mesoporous catalyst for methyl ethyl ketone production. Arabian Journal of Chemistry (2018), https://doi.org/10.1016/j.arabjc.2018.03.023