Catalysis Today 263 (2016) 128–135

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

One-step hydrothermal synthesis of honeycomb 3D graphene-like Co_9S_8 and its catalytic characteristics for $NaHCO_3$ reduction by H_2S

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ARTICLE INFO

Article history:
Received 4 July 2015
Received in revised form 20 August 2015
Accepted 16 September 2015
Available online 7 November 2015

Keywords:
Cobalt
Hydrothermal synthesis
Honeycomb structure
Co_9S_8 catalyst
CO_2 reduction

ABSTRACT

Honeycomb 3D graphene-like Co_9S_8 nanocrystallines were successfully synthesized using cobalt and $Na_2S{\cdot}9H_2O$ as starting materials without a template via a simple hydrothermal route. The composition, structure, morphology, and catalytic activity of the as-prepared Co_9S_8 were characterized by investigation of XRD, SEM, EDS, XPS, GC–MS and HPLC. It was found that an appropriate concentration of inexpensive $NaHCO_3$ play a critical role for the formation of honeycomb Co_9S_8 nanocrystallines. On the other hand, Co_9S_8 acted as a catalyst in the hydrothermal reaction, producing formic acid reduced from $NaHCO_3$ as high as 3680 mg/L. It indicates that the present study not only proposes a simple way of honeycomb Co_9S_8 synthesis, but also provides a potential approach to CO_2 reduction.

1. Introduction

Transition metal sulfides are a set of important minerals known for their complicated structure along with outstanding electronic and magnetic properties [1,2]. In addition, the transition metal sulfides are cheap and abundant, many of which are found in nature in the form of minerals such as pyrite (FeS_2), heazlewoodite (Ni_3S_2), chalcocite (Cu_2S), and so on. Recent researches have also found that the deposits around fluids in hydrothermal vents mainly consist of transition metal sulfides such as pyrite (FeS_2), Ni–S, Co–S and Fe–Ni–S [3–5]. The transition metal sulfides around the deep-sea hydrothermal vents have played a catalyst role in prebiotic synthesis of organic carbon [6,7]. Hence, transition metal sulfides has attracted more and more attentions and are widely used in different areas due to their multi-forms of various valence state as well as their special crystal structures. Among them, cobalt forms a variety of binary sulfides, such as CoS, CoS_2, Co_2S_3, Co_3S_4, and Co_9S_8, similar to the other transition metals. Among these cobalt sulfides, Co_9S_8 has been used as an important catalyst for hydrogenation and hydrodesulfurization in the industrial field due to the complicated structure, good properties and important applications [8–12]. It is also reported that Co_9S_8 plays a high catalytic activity for the oxygen reduction reaction (ORR) in acidic solution [13,14]. In addition, as an important magnetic material, Co_9S_8 has important application in magnetic devices and in lithium ion battery as a promising anode material [15–17]. Due to the important applications of Co_9S_8 in multiple fields, many methods have been developed for the synthesis of Co_9S_8 material. For example, preparation of polycrystalline Co_9S_8 under hydrothermal conditions at 160 °C for 8 h via two-step route [18]; by the decomposition of precursor cobalt–thiourea complex at 400 °C [19]; by a hydrothermal-reduction method at 120 °C [20]. To enhance the performance of Co_9S_8, compositing with graphene, reduced graphene oxide or graphene-like carbon is also considered to be a viable way, in which graphene-like structure as a soft support for the deposition of active nanoparticles and a second current collector for electron transfer at the nanoscale [21–23].

Since the discovery of graphene, it has been widely used in composites with different materials to improve their performances. Especially, 3D structures equip the graphene materials with high specific surface areas, strong mechanical strengths and fast mass and electron transport kinetics. Thus, the attractive 3D graphene materials are widely used in flexible electronics, supercapacitors, catalysis, hydrogen storage, sensors and environmental remediation [24,25]. The potential applications of graphene or other materials with 3D micro-/nano-graphene-like

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http://dx.doi.org/10.1016/j.cattod.2015.09.035
0920-5861/

architectures have attracted substantially more attention, and a variety of methods including template guided growth, self-assembly, organic sol–gel reaction and light scribe patterning technology have been developed for fabricating 3D graphene architectures [26–32]. It is revealed that the 3D graphene architectures are able to improve functions resulting from their unique nano-sized and porous structures. For other materials, the special 3D graphene-like structures also result in excellent properties. Therefore, numerous efforts have been made to design new materials with 3D graphene-honeycomb architectures to optimize their performances [33]. Although Co_9S_8 nanoparticles [34], hollow Co_9S_8 nanospheres [35–37], hierarchical hollow Co_9S_8 microspheres [38,39] and Co_9S_8 nanotubes [18] have been fabricated and investigated recently, to the best of our knowledge, few study on the synthesis of honeycomb 3D graphene-like Co_9S_8 powders based on template-free hydrothermal route has ever been reported.

In this work, honeycomb 3D graphene-like Co_9S_8 nanocrystallines have been synthesized by a simple hydrothermal route using Co and H_2S. The concentration of $NaHCO_3$ was found to have a significant influence on the morphology of the product, and an appropriate concentration of $NaHCO_3$ is essential for the formation of honeycomb 3D graphene-like structure. Moreover, the prepared Co_9S_8 is found as a catalyst in the process of CO_2 reduction.

2. Experimental

All reagents were commercially available from Sino-pharm Chemical Reagent Co. Ltd with analytical grade and were used without further purification. $Na_2S{\cdot}9H_2O$, as source of H_2S, was used for experimental convenience.

2.1. Synthesis of honeycomb 3D graphene-like Co_9S_8 nanocrystallines

The experiments were conducted in a SUS316 lined reactor with an internal volume of 42 mL. In a typical procedure, 6 mmol Co, certain amount of $NaHCO_3$ and $Na_2S{\cdot}9H_2O$ were added into the SUS316 lined reactor first, and then the liner was filled with distilled water up to 60% of the total volume. After that, the reactor was sealed and put into an induced heating furnace and heated to a desired temperature at 300 °C for 3 h with an increasing rate of 15 °C/min. The induced heating furnace was swayed at the rate of 20 times/min during the reaction. The water filling was defined as the volumetric ratio of the water put into the reactor to the inner volume of the reactor in the experiments. The reaction time was defined as the time started when the temperature reached to the desired temperature. After a desired reaction time, the reactor was removed from the furnace and cooled by electric fan. Black precipitates were collected by filtration, and washed by deionized water and anhydrous ethanol for several times, respectively. Finally, the as-prepared powders were dried at 60 °C for 8 h. The liquid samples were also collected for the test.

2.2. Characterization of Co_9S_8 nanocrystallines

X-Ray powder diffraction (XRD) patterns were obtained on a Shimadzu XRD-6100 (Shimadzu) diffractometer equipped with graphite monochromatized Cu Kα radiation (λ = 0.154056 nm). The XRD patterns were obtained with a scanning rate of 4°/min at an acceleration voltage of 40 kV and emission current of 30 mA. The X-ray photoelectron spectra (XPS) were collected on an ESCALAB 250Xi (Thermo Electron Corporation) instrument. The binding energies in XPS analysis were corrected by referencing C1s to 284.80 eV. BET spectra were performed on ASAP 2020 (MICROMERITICS INSTRUMENT CORP). The surface area was calculated using the Brunauer–Emmett–Teller (BET) equation. Pore size distributions were calculated by the Barrett–Joyner–Halenda (BJH) method. The morphology and structure of Co_9S_8 nanocrystallines were monitored by using Quanta 200 scanning electron microscope (FE-SEM, FEI, USA).

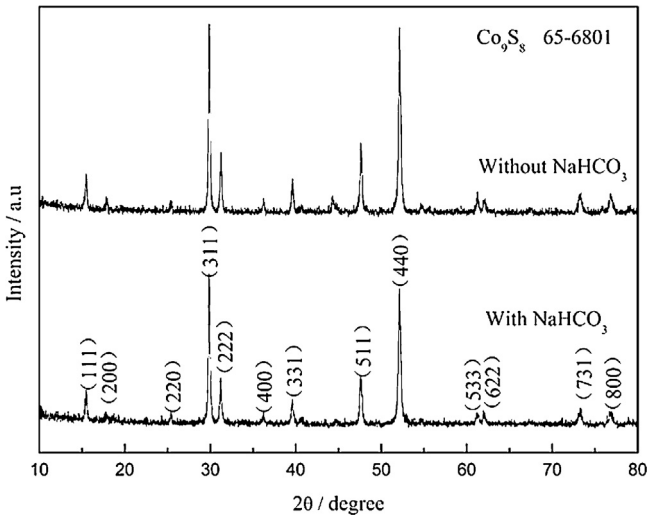

Fig. 1. XRD patterns of the Co_9S_8 samples prepared with or without $NaHCO_3$.

2.3. Liquid product analysis

After being filtered through a 0.22-μm-filter film, liquid samples were analyzed by GC–MS (gas chromatography–mass spectroscopy, Agilent Technologies 7890) analyzer and HPLC (high-performance liquid chromatography, Agilent Technologies 1260 Infinity). GC–MS was analyzed with Agilent Technologies 5975C inert MSD with Tripe-Axis Detector (with 7890A GC system). HPLC was equipped with a Shodex RSpak KC-811 packing column (300 mm × 8 mm i.d.) and a tunable UV detector (absorbance detector adjusted to 210 nm), and the flow rate of the eluent (2 mmol/L $HClO_4$ aq.) is 1.0 mL/min.

3. Results and discussion

The phase composition and purity of the as-prepared samples were examined by XRD. Fig. 1 shows the typical XRD patterns of the sample obtained by reacting of Co and $Na_2S{\cdot}9H_2O$ solution with or without $NaHCO_3$ addition. According to the standard JCPDS cards, all the diffraction peaks can be readily indexed to face-centered cubic structure Co_9S_8 crystallites (PDF No. 65-6801). The lattice constant calculated from this pattern is $a = b = c = 0.9927$ nm, which is consistent with the reported values [18]. There are almost no differences in Co_9S_8 phase when the sample prepared with $NaHCO_3$ or not. The strong and sharp diffraction peaks in the XRD patterns indicate that the obtained Co_9S_8 are well crystallized. In addition, no other phases were observed, indicating that the as-synthesized sample is pure Co_9S_8.

The morphology of the as-prepared Co_9S_8 samples was examined by FE-SEM. The SEM images in Fig. 2a shows that 3D hierarchical honeycomb-like structure is composed of abundant nanoplates. From the higher magnification SEM images (Fig. 2b), it can be found that the honeycomb-like structure consists of 30 nm thick nanoplates with pores of about 500 nm diameter. More details can be given in Fig. 2c and d, i.e., the edge of the nanoplates roll up due to the high surface tension and the surface of the nanoplates are rough. Fig. 2d shows that the plate consisted of a mass of Co_9S_8 nanocrystallites.