Applied Catalysis B: Environmental 132–133 (2013) 469–478

Contents lists available at SciVerse ScienceDirect

Applied Catalysis B: Environmental

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

Decomposition of methane over unsupported porous nickel and alloy catalyst

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ARTICLE INFO

Article history:
Received 5 September 2012
Received in revised form
12 December 2012
Accepted 14 December 2012
Available online 21 December 2012

Key words:
Nickel catalyst
Nickel-copper catalyst
Unsupported catalyst
Methane decomposition
Hydrogen production
Carbon nano-fibre

ABSTRACT

Unsupported NiO and NiO-CuO nano-particles were prepared by a facile method and these nano-particles showed promising catalytic activity towards methane decomposition. The decomposition of fibrous nickel (or mixed) oxalate precursors led to the formation of porous oxide aggregates with small primary oxide particles of 8–20 nm. Similar to supported catalysts, nickel–copper alloy particles showed steady catalytic activities even at high reaction temperatures (>700 °C). Unlike the supported catalysts, it was necessary to introduce methane to the reactor at lower temperatures to avoid catalyst particles sintering into bigger ones during the reaction. The initial carbon nano-fibres (CNFs) acted as living supports to take the catalyst particles away and prevent them from sintering with adjacent particles. The textural properties of the CNFs were characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD) and N_2 adsorption. The textural and micro-structural properties depended on the composition of the catalyst and the reaction temperature.

1. Introduction

Presently, concerns over environmental effects of energy use, in the form of global warming, ozone layer depletion and acid rains, have led to intense research on the exploration of clean energy. Hydrogen is widely considered to be one of the most promising, alternative energy carriers and clean fuels. Hence, much research has focused on the development of efficient, low cost and environmental friendly methods for hydrogen production [1]. Among the many hydrogen production reactions, the catalytic decomposition of methane (CDM) over catalysts has generated much interest [2]. The methane decomposition reaction,

$$CH_4 \rightarrow C + 2H_2, \Delta H_{298}{}^{\circ} = 75.6\,\text{kJ/mol} \quad (1)$$

is a moderately endothermic reaction which is thermodynamically favoured at higher temperature. CDM is a green route to produce hydrogen with carbon nanotubes (CNTs) or carbon nanofibres (CNFs) as the only side product. This will eliminate the need for CO_x separation and sequestration processes altogether. It was found that transition 3d-metals (Fe, Co, Ni) show considerable catalytic activity towards dissociation of hydrocarbon [2]. On one hand, their non-filled 3d-orbitals can accept electrons from hydrocarbon molecules which facilitate the dissociation. On the other hand, the overlap of non-filled 3d-orbitals with carbon orbital will not only favour the hydrocarbon dissociation process but will also play an important role in the initial stage of the CNTs or CNFs growth [3].

In general, for CDM reactions, Ni-based catalysts are more active than Co-based and Fe-based catalysts in the temperature range 500–700 °C [4,5]. Therefore, supported metallic nickel catalysts for CDM has attracted much attention [2,6–19]. There is a consensus in the literature that the catalyst performance in CDM is highly dependent on the crystallite size of the catalyst particles. Larger crystallite or particle size would render the catalyst to be deactivated rapidly. Normally, support materials such as Al_2O_3, SiO_2, MgO are used to control the catalyst particle size and dispersion by physical interactions (porous support) or chemical interaction (charge transfer effect) [3]. Martínez-Arias and co-workers [20] studied the support effect of Ni-Cu/CeO_2 catalyst for its catalytic activity towards methane oxidation and decomposition as well as its reduction activity. Their results showed that Gd-doped support would promote the formation of Ni-Cu alloy with greater homogeneous composition, higher CH_4 oxidation and similar methane decomposition activities when compared with using CeO_2 as support.

It had been reported that unsupported pure nickel was inactive for the CDM process as these large polycrystalline particles (500–1000 nm) showed no catalytic activity [21,22]. Few studies have focused on the catalytic activity of unsupported catalyst for the CDM although bulk catalyst may offer some advantages

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http://dx.doi.org/10.1016/j.apcatb.2012.12.014

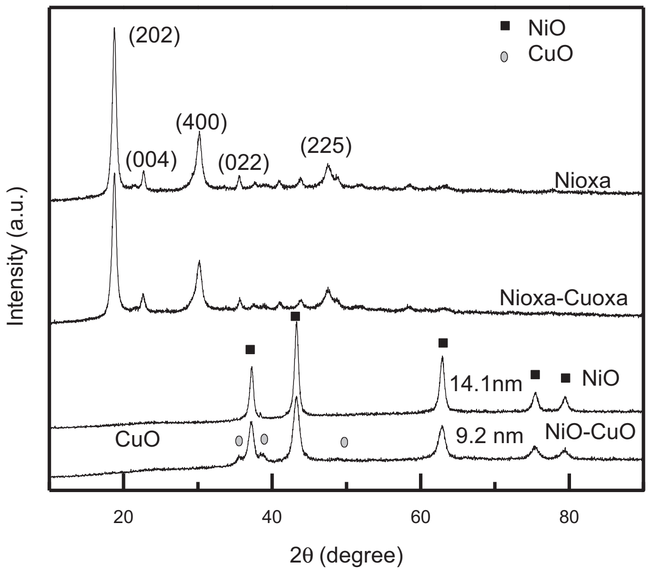

Fig. 1. XRD patterns of the samples Nioxa, Nioxa-Cuoxa, NiO and NiO-CuO. (The crystal sizes of the metal oxides were calculated from the most intense peak at around 43°).

over supported catalyst. Unsupported catalyst, for instance, may prevent the formation of traceable CO via the reaction of the carbonaceous residues with the oxygen in the support, like SiO_2 and Al_2O_3 [6,8,23]. Moreover, the bulk nickel catalyst could provide easy recovery of the catalyst and a convenient way for the purification of the CNFs by leaching the bulk metal catalyst with a mild acid solution [24] or simply using a magnetic field [25].

The magnetic property of Ni nanostructures has been extensively examined in terms of size and shape but its catalytic property is less understood. This is probably due to the insufficient thermal stability of these nickel nanomaterials under the reaction conditions [26]. In the present work, the application of mesoporous metal oxide (NiO or NiO-CuO) as catalyst for methane decomposition is reported. The thermal decomposition of nickel oxalate or mixed metal oxalate would result in their respective mesoporous oxides with nano-sized primary particles (8–20 nm) which could further be reduced into active Ni and Ni-Cu alloy catalysts for the thermal decomposition of methane. These Ni and Ni-Cu alloy particles were used as unsupported CDM catalysts in which the textural and micro-structural properties were also studied.

2. Experimental

2.1. Catalyst preparation

Metal oxide nano-particles were synthesized by the decomposition of metal oxalate [27]. In a typical procedure for preparing nickel oxide or nickel oxide-cupric oxide, 2.6 g Ni $(NO_3)_2{\cdot}6H_2O$ or 2.6 g $Ni(NO_3)_2{\cdot}6H_2O$ and 0.72 g $Cu(NO_3)_2{\cdot}3H_2O$ (with 3:1 Ni/Cu atomic ratio) was dissolved into 30 ml of pure ethanol. A stoichiometric amount of oxalic acid, dissolved in 30 ml pure ethanol, was titrated to the above solution using a burette under magnetic stirring for 30 min. The light blue suspension was transferred into a 100 ml capacity Telfon-lined stainless steel autoclave and kept at 120 °C for 12 h. After cooling to room temperature, a bluish solid precipitate was obtained by filtration and then thoroughly washed with distilled water. The resulting precipitate was dried at 80 °C under vacuum. The dried samples would be denoted as Nioxa and Nioxa-Cuoxa. Then, they were calcined in a quartz tube reactor at 500 °C for 2 h under oxygen flow to obtain the final products: NiO and NiO-CuO.

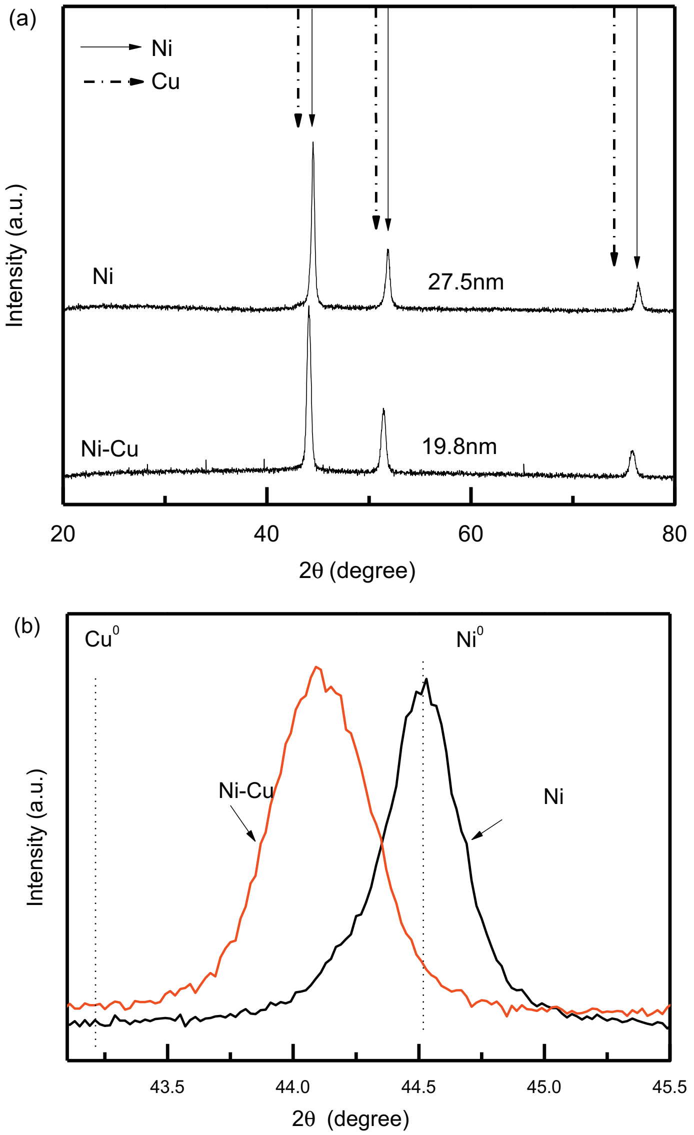

Fig. 2. XRD patterns of the Ni and Ni-Cu samples after reduction in H_2. The crystal sizes were calculated from the most intense peak of metallic Ni or Ni-Cu alloy. The bottom graph (b) shows the expanded region corresponding to the most intense peaks of the Ni and Ni-Cu alloy along with the positions expected for the pure metals.

2.2. Characterization

In order to characterize the freshly prepared reactive nickel catalyst, a passivation treatment was conducted to avoid self-ignition of the nickel catalyst. After the nickel oxide particles were reduced in the quartz tube reactor, it was subsequently cooled down to ambient temperature in a nitrogen atmosphere. Then, a slightly oxidizing O_2–N_2 mixture stream consisting of 0.5% O_2 was allowed to flow through the prepared metallic nickel particles for 1 h at room temperature before the sample was removed from the reactor.

Powder X-ray diffraction (XRD) patterns were measured by an X-ray diffractometer (Philips, PW1830) using CuKα ($\lambda = 1.5406$ Å) radiation at 40 kV and 30 mA and operated on a continuous scan mode. The X-ray diffraction patterns were recorded in the scan range of $2\theta = 10$–$90°$ at a scan rate of 1°/min. Scherrer equation, employing the most intense diffraction peak in each case, was used to determine the crystal size, whereby the particle shape factor was taken as 0.9.

Nitrogen adsorption–desorption isotherms of the catalysts were determined at 77 K on a volumetric adsorption analyzer