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Direct use of as-synthesized multi-walled carbon nanotubes for carbon dioxide reforming of methane for producing synthesis gas



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ABSTRACT

In this study, laboratory prepared multi-walled carbon nanotubes (MWCNTs) over Co–Mo/MgO catalysts were used as novel nanocomposite catalysts for carbon dioxide reforming of methane (CRM). The influence of acid treatment process on the catalyst performance was thoroughly investigated. It was determined that Co–Mo/MgO present in the as-synthesized MWCNTs was responsible for high catalytic activity of the reforming reaction. The performance of the nanocomposite catalysts was compared with the conventional Co–Mo/MgO catalysts prepared by sol–gel method, revealing that MWCNTs played a supporting role in preventing catalyst deactivation. The nanocomposite catalysts gave CH₄ and CO₂ conversions of 97% and 98% respectively, for the CRM reactions performed at 850 °C with a GHSV of 120 L/h g_{cat} and a CH₄/CO₂ ratio of 1 under atmospheric pressure. Stability tests, carbon deposition and characteristics of the nanocomposite catalyst shows that CH₄ decomposition and carbon gasification by CO₂ were the two important side-reactions.

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1. Introduction

Carbon dioxide reforming of methane (CRM) is an important process that simultaneously utilizes two greenhouse gases, i.e., methane (CH₄) and carbon dioxide (CO₂), to produce hydrogen (H₂) and carbon monoxide (CO), which is known as syngas (Eq. (1)):

$$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2 \quad \Delta H_{298K^\circ} = 247.3 \text{ kJ/mol}$$
(1)

The production of syngas with a H_2/CO ratio suitable for the formation of oxygenated derivatives and higher hydrocarbons in Fischer–Tropsch synthesis has stimulated great interest recently [1–3]. The produced H_2 and CO can be used separately in other reactions, such as in hydrogen fuel cells [4] and disproportionation reactions for carbon nanotube (CNT) production [5]. The development of a catalyst that resists deactivation is crucial for industrial CRM applications.

Many studies have reported on the CRM reaction over various types of catalysts, including noble metals such as rhodium (Rh) and ruthenium (Ru) [6], and non-noble metals such as nickel (Ni) and cobalt (Co) [7]. Noble metal catalysts have high catalytic

performance with minimal or no carbon deposition in the CRM reaction, and the drawbacks is their limited availability and high cost. Easily available non-noble metal catalysts can provide increased catalytic activity, but they also promote carbon deposition. It is found that the rate of carbon deposition is generally higher for Ni-based catalysts than that of Co-based catalysts. Studies performed on catalysts developed for CRM reactions have indicated that that catalyst deactivation is influenced by carbon deposition and metal sintering [8–11]. Catalyst sintering is a result of exothermic reactions and/or local overheating [8]. Carbon deposition (Eq. (2)) and CO disproportionation reactions (Eqs. (3) and (4)). Additionally, carbon deposition is accelerated by the aggregation of metal particles, which is resulted from the sintering effect [9]:

$$CH_4 \leftrightarrow C + 2H_2 \quad \Delta H_{298K^\circ} = 86.3 \text{ kJ/mol}$$
 (2)

$$2\text{CO} \leftrightarrow \text{C} + \text{CO}_2 \quad \Delta \text{H}_{298\text{K}^\circ} = -159.9 \text{ kJ/mol} \tag{3}$$

$$CO + H_2 \leftrightarrow H_2O + C \quad \Delta H_{298K^{\circ}} = -131.1 \text{ kJ/mol}$$
(4)

Several research studies reported that the characteristics of catalyst support play an important role on the catalytic behavior and carbon deposition in the CRM [10]. Metal oxide supports (MgO, ZrO₂ and SiO₂) have been used to reduce carbon deposition and



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decrease catalyst sintering [3,11,12]. This reduction is attributed to the increased mobility of oxide lattice oxygen molecules when they are intimately mixed with nanoparticle catalysts [12]. The interaction between metal and support was also found to strongly influence the catalytic activity [13]. The addition of a promoter, such as an alkaline or alkaline earth metal [14,15], has been reported to reduce carbon deposition through oxidizing the deposited carbon to form CO. Moreover, the promoter can catalyze CO₂ gasification of the carbon formed during the reaction (reverse of Eq. (3)) [14,15]. The preparation technique used to decrease the size of catalyst particles plays a major role in reducing carbon deposition on the catalysts. It is found that the addition of magnesia (MgO) stabilizes the catalytic activity for non-noble catalysts [11]. It has also been reported that MgO could inhibit coke deposition via adsorbed CO₂ species on the catalyst surface and react with the deposited carbon through the reverse Boudouard reaction [11].

Recently, the development of carbon-based catalytic supports has become of interest for use in the CRM reactions [16-21] as they possess several advantages. They are low cost, have a large surface area, can be modified to achieve desired pore size distributions and surface functionalities and the active metals can be easily recovered from the spent catalysts by burning off the carbon support [10]. Single-walled carbon nanotubes (SWCNTs) have been reported as a suitable substrate to anchor Ni/Co nanoparticles without carbon deposition in the CRM reaction [22]. The properties of carbon nanotubes (CNTs), such as high porosity, high mechanical strength, high thermal conductivity, low specific weight and chemical inertness, make them an attractive catalyst support for highly exothermic and endothermic reactions in which temperature control is important [23]. The as-synthesized CNTs usually contain metal catalyst impurities as a result of complete removal of the metal impurities is extremely challenging [24]. The direct use of as-synthesized MWCNTs as a catalyst is an ideal case because it does not require additional post-treatments.

In the present work, the as-synthesized multi-walled carbon nanotubes (MWCNTs) containing catalyst particles were investigated in CRM reactions. This is the first observation of catalytic behavior for this nanocomposite catalyst for CRM reactions. The influence of residual Co–Mo/MgO and CNTs on the catalyst performance was thoroughly studied and quantified by determining the conversion of CO₂ and CH₄ and the production of H₂ and CO over long reaction hours. The reaction mechanism was then proposed. This research was conducted to provide insight into the potential of MWCNT-based nanocomposite catalysts for CRM reactions.

2. Experimental

2.1. Catalyst preparation

Bimetallic Co-Mo/MgO catalysts were prepared using sol-gel technique. The synthesis gel was prepared by mixing 10 mol% $Co(NO_3)_2$ · $6H_2O$ (Merck, Malaysia), 20 mol% (NH₄)₆Mo₇O₂₄· $4H_2O$ (Fisher, Malaysia) and 70 mol% Mg((NO_3)_2· $6H_2O$ (Acros, Malaysia) with citric acid and stirring at 90 °C for 1 h. The gel was baked at 120 °C overnight and calcined at 700 °C in air for 2 h. The final

product was denoted as catalyst for CNT production. The MWCNTs were synthesized by catalytic chemical vapor deposition (CCVD) of CH₄ over a Co–Mo/MgO catalyst in a continuous rotary reactor at 800 °C that was supplied with a feed gas containing a CH₄/N₂ volumetric ratio of unity. Hereafter in the manuscript, the assynthesized MWCNTs containing catalyst particles are denoted as Co–Mo–MgO/MWCNTs (CMMW) nanocomposite. The synthesized CMMW nanocomposite was treated with acid under different durations as listed in Table 1.

2.2. Catalyst characterization

The morphology of the nanocomposite catalysts was characterized using high resolution transmission electron microscope (HR-TEM; TECNAI G2 20 S-TWIN, FEI) and field emission-scanning electron microscopy (FE-SEM; Supra-35VP) coupled with energy dispersive X-ray spectroscopy (EDX). X-ray diffraction (XRD) patterns were obtained from a Philips XRD at a scanning rate of 0.015°/s. In a typical experiment, 30 mg of catalyst was placed in a U-shape quartz tube, degassed with a 50 cm³/min stream of N_2 at 150 °C for 1 h to remove traces of water and then cooled to ambient temperature. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) was performed with a SDT Q600 TA instrument. The temperature was increased from room temperature to 850 °C with a ramping rate of 10 °C/min under a 100 cm³/ min flow of purified air to determine the amount of metal particles and the oxidation temperature of the carbon-based material. To determine the ability of the MWCNTs to react with CO₂, the developed catalysts were tested in TGA under a stream of CO₂. First, the temperature was increased from room temperature to 800 °C with a ramping rate of 10 °C/min under a 100 cm³/min flow of N₂. Then, CO₂ was introduced to the system by further increasing the temperature to 1000 °C. The quality of the MWCNTs-based catalyst was determined by Raman spectroscopy (Renishaw, inVia Raman microscope). The surface area of the catalyst was determined by measuring N₂ adsorption/desorption isotherms at -196 °C with a Micrometrics ASAP 2020 instrument and then applying the Brunauer-Emmett-Teller (BET) equation to calculate the total amount of N₂ adsorbed.

2.3. Catalyst activity

The reforming experiments were conducted in a vertical stainless steel reactor (ID 12 mm, length 700 mm) with a preheating zone of 400 mm, which was electrically heated in a furnace under atmospheric pressure. A type-K thermocouple was used to monitor the reaction temperature. In the reactor, 50 mg of the prepared catalyst was sandwiched between quartz wool. The flow rates of the reactant feed gas, which consisted of CH₄ (99.99%, Air Product Co.), CO₂ (99.99%, Air Product Co.) and N₂ (99.99%, Air Product Co.), were controlled by three mass flow controllers (MKS, PR 4000). The gas produced from the reactor was cooled in an icewater cooler and analyzed with an online gas chromatograph (GC, Agilent 6890N) using TCD with Ar as the carrier gas. The GC was equipped with both a molecular sieve column for the

Table 1

The metal catalyst impurities (%) of as-synthesized and acid-treated Co-Mo-MgO/MWCNTs nanocomposite obtained by TGA.

ID	Catalyst	Acid treatment	Treatment time (h)	Metal impurity (%)
СММ	Co-Mo/MgO	-	-	-
CMMW	Co-Mo-MgO/MWCNTs	_	-	32.16
CMMW-1 h	CMMW	HNO ₃ (5 M)	1	4.750
CMMW-3 h	CMMW	HNO ₃ (5 M)	3	1.870
CMMW-6 h	CMMW	HNO ₃ (5 M)	6	0.720
CMMW-20 h	CMMW	H_2SO_4/HNO_3 (1:3)	20	0.001

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