



Deactivation and kinetic studies of unsupported Ni and Ni–Co–Cu alloy catalysts used for hydrogen production by methane decomposition



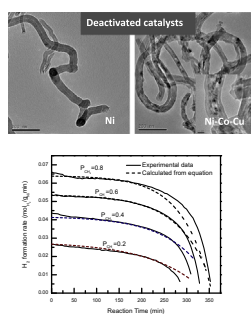
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HIGHLIGHTS

- Hydrogen production by the thermal decomposition of methane was studied.
- Metallic Ni and Ni–Co–Cu nano-particles were prepared as catalysts for the process.
- A series of kinetic experiments were conducted using these two types of catalysts.
- Empirical and phenomenological models were used to simulate the deactivation process.
- Different deactivation mechanisms of Ni catalysts and Ni–Co–Cu catalyst were compared.

GRAPHICAL ABSTRACT



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ABSTRACT

Metallic nickel nano-particles and Ni–Co–Cu alloy particles were prepared primarily as catalysts for the thermal decomposition of methane to produce hydrogen. A series of kinetic experiments were conducted using these two types of catalysts. The effects of methane partial pressure and reaction temperature on the maximal hydrogen formation rate were studied. The reaction order and activation energy were estimated. Based on the TEM micrographs and the deactivation process of catalyst, the widely used empirical model (general power law equation) and a phenomenological model (exponential decay model) were used to simulate the experimental results of Ni catalysts.

By quantifying the relationship between the kinetic parameters and the reaction conditions (methane partial pressure and reaction temperature), the transient hydrogen formation rate over the reaction time was derived and validated by comparing with the experimental data. A detailed catalytic deactivation study of Ni and Ni–Co–Cu catalysts was also carried out. Different deactivation mechanisms of pure Ni catalyst and Ni–Co–Cu alloy catalysts were compared and discussed.

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1. Introduction

In this century, intense efforts have been made to establish an environmentally sustainable carbon energy system due to the climate changes associated with the release of greenhouse gases. Hydrogen is an environmentally friendly energy vector which can be converted to electricity efficiently via fuel cells with zero emissions of greenhouse gases or hazardous species such as volatile

organic compounds [1]. Presently, there is an increasing interest in using fuel cells as a mean to generate electricity [2,3] and it is believed that in the near future, mass production of hydrogen will be possible on a large commercial scale. However, the current viable method of hydrogen production such as steam reforming of methane or partial oxidation of methane will generate large quantities of CO₂ and CO. This necessitates the removal of greenhouse gases which are known for contributing to global warming. Moreover, CO concentrations must be reduced to a few parts per million (ppm) to prevent poisoning of the electrocatalysts used in fuel cells [4–7].

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Among the many hydrogen production reactions [8–11] the direct catalytic decomposition of methane (CDM) in the presence of a catalyst has attracted widespread attention [12]. The major driving factor for the research activities in CDM is the highly desirable products – CO_x-free hydrogen and carbon nanotubes (CNTs) or carbon nanofibers (CNFs) instead of gaseous CO_x. This reaction will eliminate the need for CO_x separation and sequestration processes altogether. The catalytic decomposition of hydrocarbon first attracted the public attention back in the late 19th century. It was reported in a patent published in 1889 that carbon filaments were obtained in a metallic crucible while heating carbon-containing gases [13]. The pioneering work during the 1950s discovered that carbon filament could grow by the interaction of a series of carbon containing gases (e.g. hydrocarbons, CO) with metals [14]. The most active metals consist of iron, cobalt and nickel. The detailed studies in this area in the period 1950–1970s focused on suppressing the undesirable formation of carbon deposits on the surface of industrial catalysts or metallic steam cracker tubes [15]. In the last 20 years, with the development of advanced characterization techniques, the unique structure of the carbon materials triggered an outburst of research interest. The growth mechanism of carbon nanomaterials (CNM) including carbon nanotubes (CNTs), carbon nanofibers (CNFs) on transition metal catalysts, had been explored extensively [14,16–19]. CDM is a special case which focused on the production of hydrogen with CNM as by-products. The idea of “simultaneous production of hydrogen and nanocarbon from methane decomposition” has aroused great interest and a great cumulative effort is underway to investigate this process [12,20–29]. However, several major challenges, such as reaction and deactivation mechanisms, optimization of the process and reactor, still remain unresolved [12]. Different kinetic models in the literature had been proposed to describe the CNT growth process from methane decomposition [30–34]. In general, the deduced rate equations can be roughly classified into two categories: detailed mechanism rate equations and mathematically fitted deactivation rate equations.

Kinetic analysis is an important aspect in any catalysis process. Kinetic studies are chemical steps performed in order to find a model that describes the rate of reaction and defines the chemical process. In other words, kinetic analysis means correlating kinetic models to the experimental data. Studies have been conducted on the deactivation kinetic models to measure the deactivation rate [31–33]. The normalized activity factor a is introduced and defined by the expression:

$$a = \frac{\text{on-stream reaction rate at any time}}{\text{reaction rate with fresh catalyst}} = \frac{r}{r_{\max}} \quad (1)$$

where r is the reaction rate at any time t and r_{\max} is the initial reaction rate. The decrease in normalized activity can generally be related to catalyst deactivation. The following equation is considered as a general form for the determination of activity factor,

$$\frac{da}{dt} = r_d a^d \quad (2)$$

where d is called the order of deactivation and r_d is a function of the reaction temperature, methane and hydrogen partial pressures.

Demicheli et al. [31] studied the catalyst performance with time during the reaction. After processing and plotting the data, it was found that it was a first order deactivation ($d = 1$) for catalyst Ni/CaO–Al₂O₃ and the deactivation rate increased with the reaction temperature and was proportional to $P_{\text{CH}_4}/P_{\text{H}_2}$. The following expression for activity factor was obtained,

$$a = \exp \left[-\frac{k_d P_{\text{CH}_4} (t - t^*)}{P_{\text{H}_2}} \right] \quad (3)$$

where k_d is the deactivation rate constant (h⁻¹), t^* is the time at which the deactivation process begins ($a = 1$ at $t = t^*$), and P_{CH_4} and P_{H_2} are the partial pressures of methane and hydrogen respectively.

Borghei et al. [34] used the general form of activity factor a and calculated it from Eq. (2) with d as an unknown parameter. Different d values were attempted to achieve the best fit for the data. A value of $d = 2.11$ was found to be the optimum value using the F-test method and hence the deactivation of the catalyst was determined to be a second order reaction. It was shown that methane and hydrogen composition had a parabolic effect in the form of $(P_{\text{CH}_4}/P_{\text{H}_2})^2$, on the reaction of the catalyst and a higher temperature caused a faster deactivation of the catalysts (deactivation energy $E_d = 178$ kJ/mol).

Phenomenological approaches [32,35] were also used to quantitatively describe the process of the catalyst deactivation due to its complexity. A parabolic relationship was observed between a and c/c_{\max} which could be approximately formulated into a parabolic dependence relationship:

$$a = 1 - \left(\frac{c}{c_{\max}} \right)^2 \quad (4)$$

$$\frac{dc}{dt} = r_{\max} \quad (5)$$

where c is the specific weight of carbon deposited on the catalyst (g/g_{cat}), c_{\max} is the total specific weight of carbon deposited on the catalyst after the complete deactivation of the catalyst (g/g_{cat}). The analytic solution of Eqs. (4) and (5) is

$$a = \frac{1}{\cosh^2 \left(\left(\frac{r_{\max}}{c_{\max}} \right) t \right)} \quad (6)$$

$$c_{\max} = \sqrt{\frac{2}{k_d r_{\max}}} \quad (7)$$

where k_d is a temperature-dependent coefficient as determined from the experimental data of maximal carbon content versus reaction temperature. The discrepancy between the calculated and experimental data was no more than 10% [32].

In a CDM process, carbon deposits will form on the surfaces of the catalysts continuously until complete deactivation. The deactivation process varies under different reaction conditions. It could be a long or a very short period. In a CDM process, the released carbon should be removed and transferred to the precipitating sites for CNT/CNF growth as well as for keeping the catalytic active surfaces clean. Under steady state, the rate of methane dissociation, carbon diffusion and CNF growth should be almost at the same quantity [12]. If the diffusion rate cannot keep up with decomposition rate, the carbon will accumulate at the catalytic active face and prevent methane dissociation. The most common observation in the deactivated catalyst is catalyst particles at the tips of CNFs which are covered with carbon layers on the active surfaces for methane activation [36–38]. Takenaka et al. [39,40] proposed that the changes in the Ni catalyst structure led to the catalyst deactivation. They found nickel carbide species (not Ni₃C) gradually formed after a long reaction time which was subsequently followed by a complete deactivation. The collision between carbon fibers or coating of carbon on the metal surface was suggested as the reason behind the formation of nickel carbide. Space limitation is also proposed as a reason for deactivation since the formed filaments could interfere with each other, inhibiting the CNF growth [41]. Avdeeva et al. [42] reported a similar conclusion that the Ni particle at the tip of a filament would stop moving when the porous CNF granules achieved near close-packed structure which would lead to nickel encapsulation by carbon. For the Ni–Cu catalyst, atomic erosion of the catalyst was postulated to be the deactivation reason [42]. Another deactivation mechanism suggested was that the catalyst particles would be fragmented and drawn

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