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Methane decomposition over high-loaded Ni-Cu-SiO_2 catalysts

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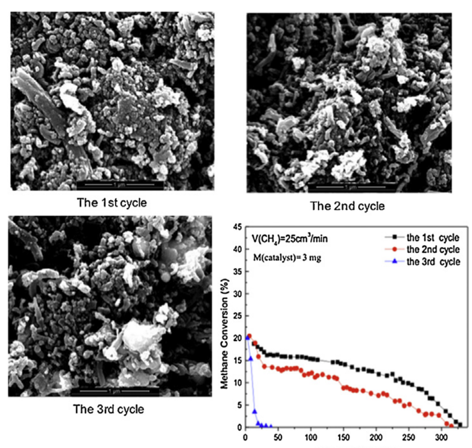
HIGHLIGHTS

- Methane decomposition over Ni-Cu-SiO_2 was studied.
- The deactivated catalysts were regenerated by air.
- Introduction of Cu could enhance the catalytic performance of Ni-SiO_2.
- The increase of the Ni-Cu particle influences the performance of the catalysts.

GRAPHICAL ABSTRACT

Methane decomposition-regeneration with air cycles over 65%Ni-20%Cu-10%SiO_2 catalysts.



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ABSTRACT

The performance of Ni-SiO_2 and Ni-Cu-SiO_2 during repeated catalytic decomposition of methane (CDM) reactions and subsequent regeneration of the deactivated catalysts with air has been studied. The catalytic activity of the 75%Ni-25%SiO_2 catalyst in the second and third CDM was lower than that during the first, while the lifetime of the catalyst did not change significantly. Both the lifetime and the catalytic activity of 65%Ni-10%Cu-25%SiO_2 in the second and third CDM reactions decreased significantly. 55%Ni-20%Cu-25%SiO_2 showed better performance than the other two catalysts, and its activity and lifetime did not change significantly until the third CDM reaction. The hydrogen yields of 55%Ni-20%Cu-25%SiO_2 were 56.8 gH_2/gcat., 42.8 gH_2/gcat., and 2.4 gH_2/gcat. for the first, second, and third CDM reactions, respectively. Spherical carbon structures were observed on the catalysts following all three CDM reactions over 75%Ni-25%SiO_2. However, similar carbon structures were only observed following the second and third CDM over 65%Ni-10%Cu-25%SiO_2, and only following the third cycle with 55%Ni-20%Cu-25%SiO_2. The formation of spherical carbon during the repeated CDM reactions strongly influenced the performance of the catalysts.

1. Introduction

In the field of fusion energy, carbon fiber composites consider to be employed as plasma facing components in the design

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of the International Thermonuclear Experimental Reactor (ITER), and deuterated and tritiated methane may be a considerable constituent of the impurity gas stream [1–6]. The catalytic decomposition of methane (CDM) reaction is a safe and simple method for recovering deuterium and tritium from deuterated and tritiated methane, and an optional catalyst bed for the CDM is currently included in the design of the tokamak exhaust processing (TEP) system in the ITER [7]. The gas exhaust from the D-T fusion reaction in the ITER, which contains Q_2, Q_2O, CQ_4, He, CO, CO_2, Q = H, D, and T, enters the TEP system first. A catalyst bed that contains Ni-based catalysts is included in the 2nd stage of the TEP system, and the function of this catalyst bed is to decompose the deuterated and tritiated methane to recover deuterium and tritium [8].

Much research on the CDM has been reported [9–17]. The catalysts traditionally used in the CDM consist of 3d transition metals (Ni, Fe, Co) supported on different metal oxides (e.g., Al_2O_3 or SiO_2). For CDM reactions, Ni-based catalysts exhibit better performance than Fe-based and Co-based catalysts between 500 °C and 700 °C. Therefore, Ni-based catalysts for the CDM have drawn much attention [18–23]. However, one disadvantage of Ni-based catalysts is that they are deactivated at temperatures above 600 °C [24]. There is a consensus in the literature that catalyst performance in the CDM is highly dependent on the crystallite size of the catalyst particles, where larger particle sizes cause the catalyst to be deactivated more rapidly [25]. Therefore, support materials, such as SiO_2, Al_2O_3, and CeO_2, have been introduced to control particle size and

dispersion, which is possible through physical or chemical interactions between the support and the active metallic particle. Takenaka et al. [26] studied the effect of different supports on the performance of Ni catalysts, and they reported that SiO_2, TiO_2, and graphite are effective supports for Ni in the CDM.

Although much research on the CDM has been undertaken by many researchers, the regeneration of these catalysts after deactivation has been rarely investigated. In view of this, this study concerns the catalytic performance of high loaded Ni-SiO_2 and Ni-Cu-SiO_2 catalysts during repeated CDM reactions, and the subsequent regeneration of the deactivated catalysts with air. The carbon structures formed over the catalysts during the repeated CDM reaction is also studied.

2. Experimental

2.1. Catalyst preparation

In this work, 75%Ni-25%SiO_2, 65%Ni-10%Cu-25%SiO_2, and 55%Ni-20%Cu-25%SiO_2 catalysts (where the percentages in the nomenclature represent mass fraction) were prepared by a heterophase sol-gel technique [27]. Catalysts were prepared by mixing the active precursor (NiO or a mixture of NiO and CuO), in a certain amount of an alcohol solution of tetraethoxisilane (TEOS), which acted as a precursor of the structural promoter. The alcohol solution of TEOS was prepared as described by Wang [21] in detail. The turbid liquids, which contained active precursors and alcosol, were dried in flowing air at room temperature and calcined at 650 °C for 3 h. In addition, the mixtures of NiO and CuO were prepared by a simple and convenient process. First, the mixtures of $Ni(NO_3)_2$ and $Cu(NO_3)_2$ were obtained by evaporation of the mixed solution of $Ni(NO_3)_2$ and $Cu(NO_3)_2$. Then, the mixture of NiO and CuO was formed by calcining the mixture of $Ni(NO_3)_2$ and $Cu(NO_3)_2$ at 450 °C.

2.2. Catalyst performance tests

Tests of the catalytic activity and lifetime of the catalysts during the CDM reaction were carried out in a fixed-bed quartz reactor (10 mm i.d.) under atmospheric pressure. Prior to the reaction, the catalysts were reduced with hydrogen at 650 °C for 1 h. Highly purified methane (99.99%) was passed through the reactor for the CDM reaction to take place. Regeneration of the deactivated 75%Ni-25%SiO_2, 65%Ni-10%Cu-25%SiO_2, and 55%Ni-20%Cu-25%SiO_2 catalysts was performed through the gasification of the deposited carbon with 20 cm^3/min of air at 600 °C until the formation of CO_2 no longer occurred. Then, the catalysts were reduced with hydrogen at 650 °C for 1 h, and the catalytic performance in the CDM by the regenerated catalysts was retested. For each catalyst, the CDM reaction and subsequent regeneration were repeated twice. The gaseous reaction products were monitored by on-line gas chromatography (GC) using a TDX-01 column and a thermal conductivity detector (TCD) for H_2, CH_4, and CO_2 analysis.

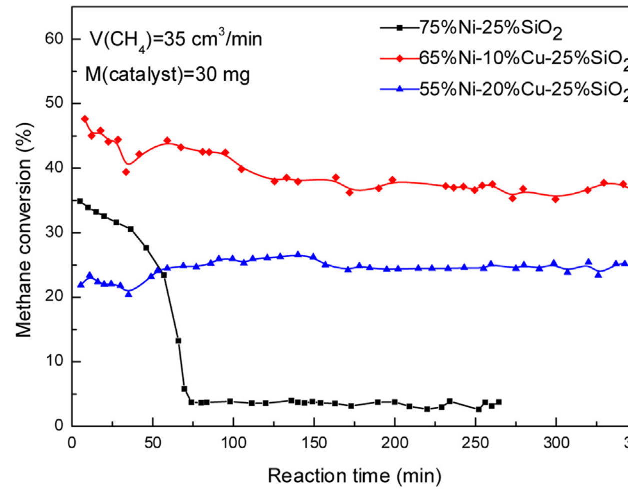

Fig. 1. Kinetic curves of methane decomposition over Ni-SiO_2 and Ni-Cu-SiO_2 catalysts at 650 °C.

2.3. Catalyst characterization

XRD patterns were recorded using a Bruker D8 Advance diffractometer (Cu Ka radiation at 40 kV and 40 mA). Micrographs of the catalysts and the carbon structures were recorded with an FEI Inspect F scanning electron microscope (SEM). The detailed morphological appearances of the carbon structures were observed using a Tecnai G2 F20 S-Twin transmission electron microscope (TEM) operated at 200 kV. For TEM analysis, samples were prepared by drying a drop of an alcohol suspension of the catalyst particles on a cobalt grid. Surface area (BET) and pore volume (PV) were determined from nitrogen adsorption/desorption isotherms, using a JW-BK200C (JWGB SCI&TECH) gas adsorption device. Before analysis, all samples were out-gassed at 100 °C under vacuum (4 h).

3. Results and discussion

3.1. Effect of Cu on Ni-based catalysts during the CDM reaction

Fig. 1 shows the kinetic curves for the CDM reaction over Ni-SiO_2 and Ni-Cu-SiO_2 catalysts at 650 °C. Only hydrogen is obtained as a gaseous product over all the catalysts. The lifetime of the Ni-SiO_2 catalyst without Cu is very short at 650 °C. After 70 min, the methane conversion of 75%Ni-25%SiO_2 decreases to ca. 5% and remains at this value. The introduction of 10% Cu significantly improves the lifetime of the Ni-SiO_2 catalyst, and the methane conversion over 65%Ni-10%Cu-25%SiO_2 is constant at 40% during the reaction. However, when the Cu content is increased to 20%, the methane conversion decreases to ca. 20%. Therefore, the introduc-