



Effects of spatially restricted Ni nanocrystals within ordered mesopores on the production of syngas



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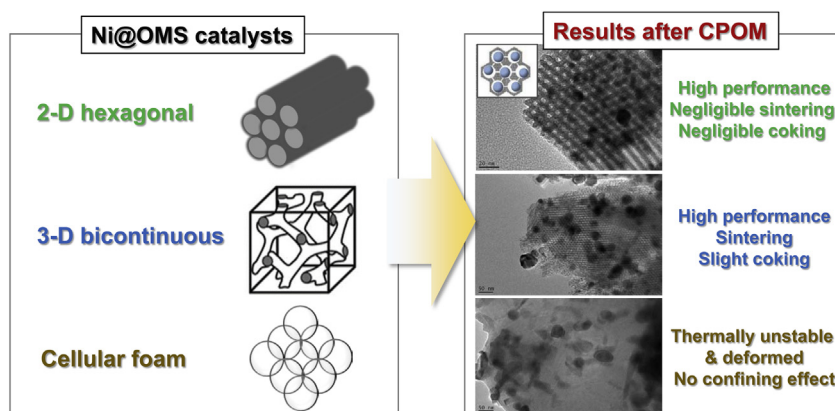
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HIGHLIGHTS

- Effects of ordered mesopores on catalytic performance are investigated.
- 2-D hexagonal mesostructure helps suppress sintering and carbon deposition.
- 3-D bicontinuous mesostructured catalyst shows sintering and slight coking.
- Thin foam-type mesoporous silica is vulnerable to harsh reaction condition.

GRAPHICAL ABSTRACT



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ABSTRACT

Ordered mesoporous silica (OMS) materials such as SBA-15, MSU-H, KIT-6, and MSU-F were utilized as catalyst supports for the catalytic partial oxidation of methane (CPOM) to produce syngas and hydrogen. The 2-D hexagonal ordered mesoporous structure was found to play a crucial role in evenly distributing Ni nanocrystals during the preparation. The OMS supports also helped maintain the position and size of the Ni nanocrystals even after partial oxidation at elevated temperatures. Various characterization techniques were utilized to assess the catalytic performance as well as to investigate the deactivation phenomena. The 2-D hexagonal and 3-D bicontinuous OMS-supported catalysts were found to have great resistance against carbon deposition. In addition, the 2-D hexagonal mesostructured catalysts showed greater resistance against sintering than other OMS-supported and the conventional refractory material-supported catalysts. Under oxygen deficient conditions in terms of stoichiometry, the OMS-supported Ni catalysts were shown to be less deactivated and more resistant against coke formation compared with Ni catalysts with conventional refractory materials.

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1. Introduction

Gas-to-liquids (GTL) technologies such as synthesis gas generation, Fischer-Tropsch synthesis (FTS), and methanol synthesis have been gaining consistent attention as promising alternatives for converting natural gas resources to environmentally benign syn-

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thetic fuels [1,2]. Despite their economic importance, only a few commercial GTL technologies are available for the production of synthesis gas (syngas), which is composed of hydrogen and carbon monoxide as its primary components [3,4]. Among these reforming technologies, autothermal reforming of methane (ATR) and non-catalytic partial oxidation of methane (POM) are prevalent [2]. In ATR, two types of reforming processes such as steam reforming of methane (SRM) and partial oxidation of methane (POM) take place simultaneously. When attempting to control the syngas composition, it is difficult to balance SRM and POM at elevated reaction temperature (around 1000 °C). In the non-catalytic POM at very high temperature (1200–1400 °C), the generated syngas is slightly deficient in hydrogen for Fischer-Tropsch synthesis (FTS); therefore, additional hydrogen is supplied by methods such as reforming of tail gas from the FTS section. The catalytic partial oxidation of methane (CPOM), however, can produce syngas with a H₂/CO ratio close to 2 (the optimum value for FTS and methanol synthesis) without additional chemicals and reactions [4]. This CPOM can be also utilized for the production of hydrogen gas accompanied by water gas shift reaction [5]. In addition, the catalysts for CPOM can significantly reduce the reaction temperature and the emission of greenhouse gases. Furthermore, CPOM is more favorable from an energetic viewpoint because it is slightly exothermic ($\Delta H = -44$ kJ/mol). In contrast, the other representative reforming reactions such as steam reforming of methane (SRM, $\Delta H = +226$ kJ/mol) and carbon dioxide reforming of methane (dry reforming, $\Delta H = +261$ kJ/mol) are highly endothermic, and the reactions require a great deal of energy to be activated. As a consequence of the combustion of fuels for the heating, a lot of CO₂ is also generated. Despite the advantages of CPOM technology, several problems need to be addressed before CPOM can be considered for commercialization. The high temperatures and dry conditions of CPOM can lead to the catalyst deactivation by sintering and carbon deposition. Accordingly, many studies have focused on overcoming these limitations. Modifications are typically made to reduce the crystal size of the Ni catalysts and to stabilize them against sintering because the carbon formation is detrimental to their function [6,7]. Asencios et al. found that solid solutions of NiO/MgO promoted the fine dispersion of Ni upon reduction of the oxide, inhibited the formation of large Ni⁰ clusters, and could reduce coke formation significantly [8]. Furthermore, Xia et al. [9] found that a sol-gel method strengthened the NiO-SiO₂ interactions, decreased the Ni particle size, improved the catalytic performance, and extended the catalytic lifetime of the compounds. Shen et al. [10] also reported that catalytic nanocrystals confined in Ni-Mg-Al oxide mesopores could promote coke resistance during SRM. On the other hand, Takehira et al. argued that the small size of the catalyst nanocrystals was not the only cause of coke resistance. Through CO₂ pulse reactions, they found that mobile oxygen from the supports (such as perovskites) might be also effective for coke resistance [11]. Through catalytic tests with ZrO₂-, CeO₂-, and Ce-ZrO₂-supported Ni catalysts, Dong et al. [12] elucidated that the addition of ceria to zirconia increased the carbon storage capacity and oxygen mobility of the catalyst, which facilitated the removal of the deposited carbon. Carrero et al. [13] reported that the formation of easily removed defective carbon with Mg- and Ca-promoted Cu-Ni/Al₂O₃ catalysts. Recently, ordered mesoporous silica (OMS) materials have been employed for the supports of catalysts due to their high surface area and good thermal stability at elevated temperatures. However, the studies only focused on a limited number of ordered mesoporous materials (OMMs). It was reported that the addition of Cu to Ni/SBA-15 catalysts improved their catalytic performance due to an enhancement of their redox properties, but the structural effects among the different types of OMMs were not investigated [14]. It was also reported that SBA-

15 could be applied to a tri-reforming reaction; however, the coke formation was barely discussed [15].

In this study, we utilized several types of ordered mesoporous materials (OMMs) such as 2-D hexagonal, 3-D network, and thin foam-type mesoporous silica materials as catalyst supports. The OMM-supported catalysts as well as the original OMMs were characterized by several analytical methods. The catalytic performances of the OMM-supported catalysts were compared with each other, as well as with the performances of the conventional refractory material-supported catalysts. The effects of the spatially restricted Ni nanocrystals within the ordered mesopores on sintering were elucidated. In addition, the carbon deposition was assessed after the test under O₂-deficient reaction condition. Even in commercialized process using modern equipment, it is often very hard to maintain the exact amount of flowrate due to various unexpected and unknown disturbances and sometimes control failures. Through this experiment, we want to especially show the effects of the O₂-deficient condition on the performance and resistance against coke formation.

2. Experimental

2.1. Catalyst preparation

Catalysts were prepared by incipient wetness impregnation (IWI). Before impregnation, each support was dried at 500 °C for 5 h followed by cooling down to room temperature, and vacuum drying for additional 30 min. The preparation methods and procedures for the supports are provided in the [Supplementary data](#) file. An appropriate amount of aqueous solution containing the Ni (NO₃)₂·6H₂O precursor (Samchun Pure Chemical, Co., 98%) was impregnated on each support. If needed, the IWI and vacuum drying method mentioned above were conducted several times to keep the surface of the impregnated supports dry and facilitate the multi-step impregnation. The impregnated supports were dried at 110 °C for 12 h. Calcination was conducted stepwise; first, each dried catalyst was heated at a rate of 2 °C/min to 400 °C and calcined at 400 °C for 3 h under flowing air. The catalysts were then heated at a rate of 2 °C/min up to 800 °C and calcined at 800 °C for 5 h under flowing air. The resulting catalysts were denoted as Ni@SBA-15, Ni@KIT-6, Ni@MSU-H, Ni@MSU-F, Ni/γ-Al₂O₃, Ni/α-Al₂O₃, Ni/Q-10, and Ni/Dav-645. Ni@SBA-15 implies that most of the Ni nanocrystal species are located inside the ordered mesopores of SBA-15. 15 wt% Ni was incorporated in each catalyst.

2.2. Catalyst characterization

The surface areas, pore sizes, and pore volumes of the supports and catalyst particles were estimated from nitrogen desorption isotherms obtained at -196 °C using a constant-volume adsorption apparatus (Micromeritics, ASAP-2400).

The powder XRD patterns of the fresh and spent catalysts were obtained on a Rigaku diffractometer using Cu-K α radiation. The XRD patterns were used to identify the crystalline phases of the Ni, NiO, and NiAl₂O₄ species and to measure the particle sizes of the crystalline products. The NiO and Ni particle sizes were calculated from the most intense diffraction peaks at $2\theta = 43.3^\circ$ and 44.5° , respectively, using Scherrer's equation [16]. Small angle X-ray scattering (SAXS) was performed using a Rigaku Multiplex instrument with Cu K α radiation ($\lambda = 1.5406$ Å) at 40 kV and 40 mA.

Temperature-programmed reduction (TPR) experiments were performed to determine the reducibility of the oxidized Ni species. Prior to the TPR experiments, the fresh catalysts were preheated

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