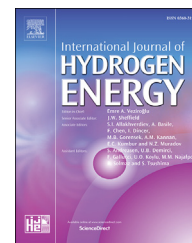


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Effect of impregnation sequence of Mg on performance of mesoporous alumina supported Ni catalyst in dry reforming of methane

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ABSTRACT

In this study, effect of Mg impregnation sequence on the activity of the mesoporous alumina supported Ni catalysts was investigated in dry reforming of methane. Characterization and activity test results showed that Mg incorporation sequence significantly influenced the physicochemical properties and the activity of the catalyst as well as coke deposition during reforming reaction. The synthesized catalysts were characterized by x-ray diffraction, N₂ adsorption, temperature programmed reduction, scanning electron microscopy, CO₂-temperature programmed desorption, inductively coupled plasma optical emission spectrometry, x-ray photoelectron spectroscopy, Fourier-transform infrared spectroscopy (FTIR) and pyridine adsorbed diffuse reflectance FTIR spectroscopy techniques. Mg incorporation altered the reduction profile of the monometallic catalyst and increased the reduction temperature of the nickel particles. XRD diffraction peaks corresponding to γ -Al₂O₃ and α -Al₂O₃, as well as nickel-magnesium spinels and metallic Ni were observed depending on Mg incorporation sequence. The monometallic Ni catalyst showed higher activity than the bimetallic Ni–Mg catalysts. However, coke formation was significantly influenced as a result of synthesis route. Total organic carbon, thermogravimetric analysis and SEM images exhibited that the highest coke formation was obtained over the catalyst which was prepared by sequential impregnation of Mg and then Ni. Almost no coke formation was observed on the spent catalyst, which was synthesized by simultaneously impregnation of Mg and Ni, due to the high interaction between Ni and Mg with the formation of a NiO–MgO solid solution during the high calcination temperature.

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Introduction

Dry reforming of methane is an attractive reaction to utilize waste CO₂, by reacting it with methane to produce industrial syngas (H₂ + CO) [1]. Stoichiometry of dry reforming reaction indicated a H₂ to CO molar ratio of one in the produced syngas. Syngas produced through the dry reforming process can be

used as a fuel in solid oxide fuel cells [2] and as a raw material for the synthesis of valuable chemicals, such as methanol, olefins, gasoline, diesel fuels and dimethylether as well [3,4]. Coke deposition on the surface of the catalyst is one of the major drawback in dry reforming of methane. Coke deposition may cause catalyst deactivation through encapsulating and blocking of active sites of the catalyst or dissolving and diffusing into the structure of the catalyst. Methane cracking

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and Boudouard reactions are the main contributors to the coke deposition during dry reforming of methane reaction [5]. Boudouard reaction is thermodynamically favorable below 650 °C, while methane cracking is expected to gain importance above 550 °C [6,7].



Up to now, dry reforming studies focused on activity, stability and coke resistance of VIII B metals based catalysts [8–13]. Especially in recent years, activity of Rh [14], Ru [15], Pt [16], Pd [17], Ni and Co [18] based catalysts were investigated in dry reforming of methane. Among them, Ni based catalysts attracted major attention of researchers due to its high activity in reforming reactions and lower price compared to noble metals [9,11–13,18]. However, elimination of the deactivation problem of the Ni based catalysts due to coke deposition is required much effort. To minimize the coke deposition problem of the Ni based catalysts, several strategies were examined in dry reforming studies. In these studies, a small amount of noble metals (Ru [10,19], Rh [20], Pt [21]) or promoters (Ca, La [22], Mg [23], Ce [24]) into the structure of the Ni based catalysts was incorporated to enhance the resistance of the Ni based catalysts to coke formation. Among these promoters, Mg has been attracted attention because it changes the physicochemical properties of the alumina supports such as thermal stability with the formation of MgAl_2O_4 spinel and the surface basicity [25,26]. Previous studies showed that the acidity-basicity of the support material has significant effects on the activity of catalyst and coke deposition [27,28]. The surface acidic properties of the alumina support can help the catalyst to exhibit higher activity; however, may prone to carbon deposition. An increase in the strong Lewis basicity of the alumina support by coating with metal oxides, having a strong basicity, would increase the ability of the catalyst to chemisorb CO_2 . The chemisorbed CO_2 molecules may lead to oxidize carbon deposited on the surface of the catalyst [28]. Previous studies showed that Mg incorporation changed the activity of the catalysts in reforming reactions as well as the amount of the coke deposition on the catalysts [19,21,23,29–33]. Alipour et al. investigated effect of MgO incorporation on the activity of the Al_2O_3 supported Ni catalysts and coke formation in dry reforming of methane. During synthesis procedure, the alumina support was prepared by a sol-gel method. Consecutively, Mg and then Ni was impregnated into the structure of the catalyst. Their results exhibited that MgO incorporation enhanced the catalytic activity and decreased the amount of deposited coke [29]. Yasyerli et al. reported that modification of MCM-41 supported Ru–Ni based catalyst by impregnating Mg improved its performance at initial times of dry reforming activity test [19]. Arbag et al. showed that incorporation of Mg into the sol-gel alumina supported Ni catalyst did not change CO_2 conversion but decreased methane conversion due to the elimination of the cracking reactions. In the study, the alumina material was synthesized using two different synthesis procedures namely traditional sol-gel and hydrothermal methods. Mg was impregnated into the sol-gel alumina

supported Ni (16% wt.) catalyst and its activity test was performed at 600 °C [30]. However, Sengupta et al. reported that modifying alumina with MgO decreased the activity of the Ni–Co catalyst [26]. There are several studies investigated effects of promoters and preparation procedures on dry reforming of methane for SiO_2 , SiC and alumina supported catalysts. Zhu et al. reported impregnating Mg prior to Ni is more beneficial to improve the activity and stability of Mg-promoted Ni/ SiO_2 catalysts in dry reforming of methane [31]. García-Vargas et al. investigated the effect of the order of Ni and Mg impregnation on the catalytic activity and the stability of the β -SiC supported catalysts for the tri-reforming (steam reforming, dry reforming and partial oxidation) of methane. Activity results showed that only Ni impregnated catalyst had the worst catalytic behaviours; however, co-impregnated Ni–Mg catalyst had best catalyst due to its high catalytic activity and stability and low coke generation [32]. Cheng et al. reported that the effects of promoter loading sequences on the activity of the alumina supported Ni catalysts in dry reforming of methane are dramatically sensitive to the methods of the catalyst preparation [33]. However, further analysis is required to define the structural changes of the catalysts after promoter loadings, as well as coke deposition of the spent catalysts. The synthesis procedure of the mesoporous alumina used in the present study is quite different from the traditional sol-gel method. The mesoporous alumina synthesized in the present study has relatively lower surface acidity and intensity of crystalline structure than the alumina synthesized using the traditional sol-gel method. As mentioned before, the surface acidity of the support has a great importance in preventing coke formation in the dry reforming of methane. Furthermore, Mg incorporation sequence during preparation of catalyst may effect the surface acidity-basicity of the catalysts as well as their performance in dry reforming and coke resistance. Considering all these observations, a comprehensive study is required regard on Mg incorporation sequence. Thus, in this study, the effects of Mg incorporation sequence on the structure of the mesoporous alumina supported Ni catalyst, its performance in dry reforming of methane, as well as coke deposition were investigated.

Experimental

Catalyst preparation

In the present study, the mesoporous alumina (MA) was synthesized as the catalyst support, following a hydrothermal route, which has been discussed elsewhere [30]. For this purpose, the surfactant, Pluronic P123 ($(\text{EO})_{20}(\text{PO})_7(\text{EO})_{20}$, Sigma-Aldrich), was dissolved in ethanol with continuous stirring at room temperature. In order to adjust the acidity of the solution, nitric acid (HNO_3 , Merck) were added to the solution under stirring. Then, aluminum isopropoxide ($\text{Al}(\text{OPri})_3$, Merck) were added to this solution while continuous stirring for 5 h. Subsequently, the solution was placed in an oven at 60 °C for 48 h to evaporate the ethanol. Calcination procedure of the solid product was performed in a tubular furnace. The solid product was heated from room temperature to 800 °C at a heating rate of 1 °C/min under the flow of the dry air and kept

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