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# Syngas production from CO<sub>2</sub> reforming of methane over Ni supported on hierarchical silicalite-1 fabricated by microwave-assisted hydrothermal synthesis

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## ABSTRACT

The conversion of carbon dioxide and methane to syngas is one of the most environmentally benign routes for methane reforming, where the two major greenhouse gases are converted to hydrogen or syngas (H<sub>2</sub> and CO). Hierarchical silicalite-1 was prepared in one-step by the microwave-assisted hydrothermal synthesis (MAHyS) approach. Ni particles with loadings of 5, 10, 15 and 20 wt.% were impregnated on the silicalite-1, as well as modified silicalite-1. The mesopore volume of the 20 wt.% Ni on S-1 catalyst increased from 0.0712 cm<sup>3</sup>/g to 0.1159 cm<sup>3</sup>/g by ion-exchanging silicalite-1 with Ce, prior to impregnation. The structural integrity of the modified catalysts was maintained as shown by characterization with XRD, FESEM, N<sub>2</sub>-physisorption, XPS and FTIR. Reducibility studies by H<sub>2</sub>-TPR showed that the addition of a second metal enhanced Ni reducibility. The 20 wt.% Ni on silicalite-1 was found to be more active than 10 and 15 wt.% on silicalite-1. Upon modification before impregnation of the 20 wt.% Ni, it was observed that Ce-ion-exchanged silicalite-1 supported Ni catalyst was the most active catalyst during 12 h time-on-stream (TOS). Raman spectroscopy and TGA-DSC revealed that the carbon deposits on the surfaces of the spent catalysts were predominantly crystalline.

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## Introduction

Global warming has become a great concern to humanity due to its debilitating effects on the environment. The main causes being greenhouse gas emissions, which occur at alarming rates, resulting mainly from continuously increasing human activities such as industrialization and unhealthy farming practices. In the recent past, some research work [1,2] have

been carried out to find better ways to reduce or eliminate these harmful gases. Two of the major greenhouse gases are carbon dioxide and methane. Numerous efforts have been dedicated to find better techniques to convert CO<sub>2</sub> and methane to hydrogen and/or syngas, both of which are very useful products. The obvious benefit of this process is putting to use these greenhouse gases that would otherwise be harmful to the environment.

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A large proportion of the world's energy requirement is currently derived from fossil fuels [3], and these sources are not only in limited supply but also release greenhouse gases when combusted. As a consequence of the vertiginous nature of the global economy, many countries have developed acute insatiability for energy. This urge, coupled with the desire to ameliorate global warming has fueled the search for alternative and clean energy sources [4,5]. Syngas, ( $H_2$  and  $CO$ ), serves the purpose of a source of clean energy and synthetic chemicals. In syngas production from methane, the steam reforming of methane technique [6,7] has been used extensively in the industry. Despite its popularity, it does have some drawbacks. This necessitate the need to investigate alternative routes for syngas production from methane. One of the several methods of obtaining syngas from methane is the dry methane reforming technique. It is an environmentally friendly route since it uses  $CO_2$  as the feed in the reaction process [8].

$CO_2$  reforming of  $CH_4$  does not come without challenges. This is an energy intensive reaction (highly endothermic) and the catalysts deactivate quickly on-stream, because of carbon formation and deposition. Catalysts based on noble metals have been found to possess high activities and stabilities in this reaction [9]. But these cannot be deployed on a commercial scale due to the high costs and scarcity of these metals. Ni-based catalysts on the other hand are less expensive but deactivate quickly on stream. Dry ( $CO_2$ ) reforming of methane (DRM) can be catalyzed by some transition metals other than Ni. The difficulties associated with DRM necessitate the need to search for catalysts capable of accelerating the reaction while maintaining stability under the reaction conditions.

Despite the prime importance of the metal function in DRM catalysts, a well-prepared support if utilized tends to improve upon the stability of metal-based catalysts in  $CO_2$  reforming of methane. It has been shown that supports provide the advantage of being able to control the size of Ni particles [10]. Highly dispersed Ni particles on hierarchical porous materials is a recipe to control carbon formation and sintering of the nickel particles [11]. In the work of Mousavi et al. [2] the addition of Ce catalyst support was found to minimize the formation of carbon. They also observed that the catalyst with better performance had small Ni crystalline sizes. The synthesis of metal catalysts on support materials enhances the formation of smaller crystalline sizes, which in the case of dry reforming, suppresses carbon formation. Sun et al. [12] obtained  $CH_4$  and  $CO_2$  conversions as high as 94% and 98% respectively over Co supported on carbon nanotubes. The catalysts also demonstrated remarkable stability. The high activity and stability of the catalysts were attributed to the desirable textural properties of the support material.

In recent times, zeolites have attracted much interest as supports for DRM catalysts due to their uniform microporosity, high thermal stability and the ability to maintain high metal dispersion during the reaction [13,14]. Zeolites also offer good affinity for  $CO_2$ , specific micropore structure and high surface area [15] all of which are desired properties for DRM catalyst support [16]. It was observed in some studies that the nature of the zeolitic material has a significant effect on the catalytic activity and stability when different zeolites were used as metal supports in dry methane reforming [17].

Beside the application of zeolites in DRM, a number of different types of materials have been explored as supports. These include  $La_2O_3$ ,  $MgO$ ,  $SiO_2$ ,  $CeO_2$ ,  $Al_2O_3$ ,  $TiO_2$  and perovskites [1,18,19]. Amongst the few materials that can be applied as catalysts supports in DRM,  $Al_2O_3$  is found to be relatively unstable at high temperatures due to thermal deterioration whereas zeolites are more stable at such high temperatures [20]. The catalytic performance of some zeolites supports have been evaluated in  $CO_2$  reforming of methane [13,17,21,22].

Hierarchical zeolites have been demonstrated to have improved catalytic performance over conventional zeolites in many environmental and hydrocarbon conversion processes. As a result, much work have been devoted to synthesizing microporous zeolites with some mesopores. Some strategies that have been applied to obtain mesoporous zeolites include the use of different templates, well-ordered mesoporous carbon, as well as desilication and recrystallization [23]. However, some of these templates are expensive. The other preparation strategies are also troublesome. These challenges can still be overcome in most cases.

In this work, we report on the fabrication of well-defined silicalite-1 crystals with significant mesoporosity by the microwave-assisted hydrothermal synthesis [MAHyS]. The MFI silicalite-1 crystal were prepared using the relatively cheap tetrapropylammonium bromide (TPABr) as template. The MFI type silicalite-1 zeolite, a pure silica analog of ZSM-5, was used support for Ni-based catalysts in  $CO_2$  reforming of methane. Silicalite-1 (S-1) is a well-known weak-acidic zeolite due to the absence of the alumina component in its framework. The diffusion of  $H_2$ ,  $CO$ ,  $CO_2$  and  $CH_4$  through the pore of MFI zeolites (ca. 0.56 nm) is considerably faster [24]. This serves as an advantage in protecting the nickel particles from deposition of carbonaceous material.

## Experimental

### Synthesis of catalysts

To prepare a batch of the mesoporous silicalite-1 crystals, 3.41 g of tetrapropylammonium bromide (TPABr; 98%; Sigma-Aldrich) and 0.8 g of sodium hydroxide (98% purity; Sigma-Aldrich) were completely dissolved in deionized water. 23.55 g of Ludox HS-40 colloidal silica (40 wt.% in water; Sigma-Aldrich) was then added to the resulting solution and the gel was stirred for 3 h at room temperature. In total, 42.25 g of deionized water was used. The uniform gel was transferred into a PTFE lined autoclave and treated under microwave irradiation at 180 °C for 6 h. The obtained crystals were retrieved, washed several times with deionized water and allowed to dry at room temperature in static air overnight and then dried for 12 h in air at 110 °C. Nickel was then deposited on the surface of the parent silicalite-1 by incipient wet-impregnation with different weight fractions ranging from 5 to 20 wt.%, using aqueous solutions of  $Ni(NO_3)_2 \cdot 6H_2O$  (98.5% purity; Sigma-Aldrich). The samples were calcined in air at 500 °C for 5 h to decompose the template. To prepare the ion-exchanged samples, 1 M of aqueous solutions of each of  $Ce(NO_3)_3 \cdot 6H_2O$  (99% purity; Sigma-Aldrich),  $Zn(NO_3)_2 \cdot 6H_2O$  (98% purity; Sigma-Aldrich) and  $Y(NO_3)_3 \cdot 6H_2O$  (99.8% purity;

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