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Effect of synthesis route of mesoporous zirconia based Ni catalysts on coke minimization in conversion of biogas to synthesis gas

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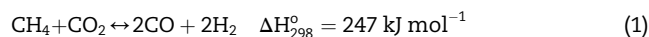
ABSTRACT

Mesoporous zirconia and nickel incorporated zirconia catalysts were prepared following different routes. Synthesis of mesoporous zirconia and Ni incorporated zirconia with very narrow pore size distributions and high surface area was achieved. Ni incorporated mesoporous zirconia materials showed high activity in carbon dioxide reforming of methane, performed at 600 °C. Coke formation during dry reforming was eliminated over the Ni incorporated zirconia catalyst prepared by the one-pot procedure, using Pluronic P123 as the surfactant. It was shown that Ni was very well distributed within this material with cluster sizes smaller than the detection limit of XRD. This catalyst also showed highly stable catalytic performance. However, the catalysts prepared by the impregnation method showed higher activity but much higher coke formation than the catalyst prepared by the one-pot route.

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Introduction

Fast depletion of fossil resources and the related environmental concerns initiated significant research for the production of alternative fuels and petrochemicals from bio-waste. Biogas contains large quantities of two of the most abundant greenhouse gases, namely methane and carbon dioxide. Catalytic reforming of methane with CO₂ (Eq. (1)) is a promising method to convert biogas to synthesis gas [1–4].



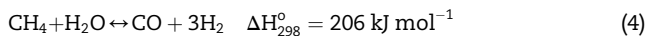
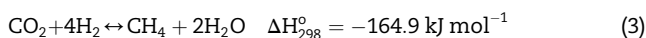
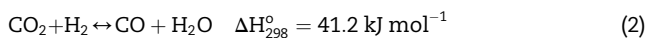
Synthesis gas, containing CO and H₂ may then be converted to valuable chemicals through Fischer–Tropsch synthesis, or may be used to produce methanol and/or dimethyl ether. Product distribution of CO₂ reforming of methane and hence the ratio of CO to H₂ in the product stream, are strongly influenced by the occurrence of number of side reactions, namely reverse water gas shift (RWGS) reaction (Eq. (2)),

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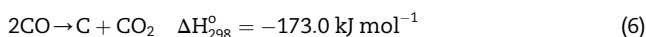
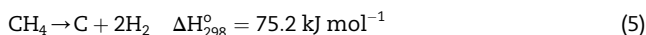
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methanation (Eq. (3)) and steam reforming of methane (Eq. (4)).



Noble metals were reported to show high activity for dry reforming of methane [5–8]. Much cheaper Ni and Co based catalysts were also reported to show good activity for this reaction [9–16]. However, coke formation is the major problem of using Ni based catalysts in dry reforming of methane [14,15]. Coke formation through methane cracking (Eq. (5)) and/or Boudouard reaction (Eq. (6)) may cause catalyst deactivation, as well as clogging of the reactor. Coke formation at lower temperatures is mainly due to Boudouard reaction. However, endothermic decomposition reactions become more significant at higher temperatures.



Coke formation was reported to be decreased by the modification of Ni based catalysts through incorporation of noble metals. As it was shown in our recent studies, performance of MCM-41 incorporated Ni based catalysts could be improved by the addition of Ru or Rh to the catalyst structure [3,11].

Another very important factor effecting coke formation is the type of support material used in the synthesis of Ni based catalytic materials [16,17]. Conventionally, γ -alumina or zeolites [6,18] were used as the catalyst support for this reaction. It was reported in the literature that mesoporous catalyst supports, like MCM-41, were less susceptible to catalyst deactivation due to coke formation than the conventional microporous materials [19]. In a more recent publication of ours, it was reported that mesoporous alumina supported Ni based catalysts showed good catalytic performance and coke formation was significantly decreased by the modification of these catalysts by tungsten [15].

Zirconia is another attractive support material for Ni based catalysts. There are few studies for catalytic performances of zirconia modified catalysts in the recent literature [20–26]. Zirconia (ZrO_2) presents three crystalline phases, which are monoclinic, tetragonal and cubic. It has excellent properties, such as high mechanical strength, high thermal stability, high fracture toughness and hardness. ZrO_2 is very stable at high temperatures and is quite suitable to be used as a catalyst support for endothermic catalytic reactions, which are generally performed at high temperatures and require catalysts with high thermal stability [27,28].

In the present study, mesoporous zirconia supported Ni based catalysts were synthesized following different routes using different templates, and catalytic performances of these materials were tested in dry reforming of methane. Ni based catalysts were prepared by both impregnation and one-pot procedures and the best catalyst synthesis route for coke elimination was illustrated.

Experimental

Synthesis of catalysts

Synthesis of mesoporous zirconia by different routes

Zirconia can be synthesized by various methods, such as precipitation, hydrothermal synthesis, surfactant-assisted, co-precipitation and sol-gel [29–32]. Considering the diffusion resistance minimization advantages of mesoporous materials, zirconia catalyst supports were synthesized in the present study using different templates in order to obtain ordered mesoporous pore structures [33]. These mesoporous zirconia materials were synthesized following three different procedures. In the first two procedures, zirconia supports were synthesized using two different surfactants as the templates, namely, cetyl-trimethyl-ammonium bromide CTMABr (denoted as $\text{ZrO}_2\text{-C}$) and Pluronic P123 (denoted as $\text{ZrO}_2\text{-P}$). In the third procedure, mesoporous zirconia was prepared following an ammonia solution route. This material was denoted as ZrO_2 .

For the synthesis of $\text{ZrO}_2\text{-C}$, a hydrothermal route similar to the procedure described in a recent publication of ours, for the synthesis of MCM-41, was used [34]. In this procedure, cetyl-trimethyl-ammonium-bromide (CTMABr, $\text{C}_{16}\text{H}_{33}(\text{CH}_3)_3\text{NBr}$, Merck) was used as the surfactant. CTMABr was first dissolved in deionized water by continuous stirring at 40 °C. Zirconium (IV)-oxynitrate-hydrate ($\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$, Aldrich) was then added to this solution. This is a basic synthesis route and in order to have a solution pH of 11.5, NaOH was added drop-wise to the solution during mixing. Hydrothermal synthesis of mesoporous zirconia was then achieved in a Teflon lined stainless steel autoclave at 60 °C for four days. The product was then filtered, washed with deionized water, dried and calcined at 600 °C in a tubular furnace in a flow of dry air.

In the case of synthesis of $\text{ZrO}_2\text{-P}$, the procedure described by Rezai et al. [20] was used. In this method, Pluronic P123 ($(\text{EO})_{20}(\text{PO})_{70}(\text{EO})_{20}$, Sigma-Aldrich) was used as the surfactant and 28–30% aqueous ammonia solution (Merck) was used as the precipitation agent. A solution containing zirconium (IV)-oxynitrate-hydrate ($\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$, Aldrich) in deionized water was prepared and then P123 was added (P123: ZrO_2 molar ratio = 0.03), by continuous stirring. A precipitate was obtained by drop-wise addition of ammonia. The slurry was then refluxed at 88 °C for 24 h with continuous stirring. The resultant mixture was then filtered, washed with deionized water and calcined at 600 °C in a flow of dry air.

For the synthesis of zirconia by the hydrothermal ammonia route (ZrO_2), the procedure described by Djinović et al. for the ceria/zirconia support was modified and used [21]. In this procedure, zirconium (IV)-oxynitrate-hydrate ($\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$, Aldrich) was dissolved in deionized water. This solution was added into the 30% aqueous ammonia solution (Merck) by continuous stirring. The final mixture was placed into a Teflon lined stainless steel autoclave and aged at 120 °C for 6 h. The final product was filtered, washed with deionized water and ethanol and then calcined.

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