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Influence of the oxygen pretreatment on the CO_2 reforming of methane on Ni/β-SiC catalyst

Dinh Lam Nguyen [a,b,*], Pascaline Leroi [b], Marc Jacques Ledoux [b], Cuong Pham-Huu [b]

[a] *Da-Nang University of Technology, University of Da-Nang, 54 Nguyen Luong Bang, Da-Nang, Viet Nam*
[b] *Laboratoire des Matériaux, Surfaces et Procédés pour la Catalyse CNRS, Université Louis Pasteur,*
European Laboratory for Catalysis and Surface Science (ELCASS), 25 rue Becquerel, 67087 Strasbourg Cedex 02, France

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ABSTRACT

The influence of the O_2 pretreatment on the CO_2 reforming of methane to synthesis gas has been investigated with Ni catalysts supported on β-SiC extrudate. The structure and properties of the catalysts were characterised by SEM, TEM and XRD techniques. The pretreatment of the catalyst by a mixture of CO_2 and O_2 significantly improves the catalytic activity for the CO_2 reforming. On the Ni 5 wt.% supported on β-SiC catalyst, the CH_4 conversion has reached 90% with the O_2 pretreatment instead of 80% by direct activation under CO_2/CH_4 mixture. The oxygen pretreatment seems to stabilize the metallic nickel phase instead of $NiSi_2$.

1. Introduction

Synthesis gas, a mixture of H_2 and CO, is an important feedstock for several chemical processes operated in the production of methanol and synthetic fuels through a Fischer-Tropsch synthesis [1]. Synthesis gas is produced via an endothermic steam reforming of methane ($CH_4 + H_2O \rightarrow CO + 3H_2$, $\Delta H = +225.4$ kJ mol^{-1}), catalytic or direct partial oxidation of methane ($CH_4 + (1/2)O_2 \rightarrow CO + 2H_2$, $\Delta H = -38$ kJ mol^{-1}) and CO_2 reforming of methane ($CH_4 + CO_2 \rightarrow 2CO + 2H_2$, $\Delta H = +247$ kJ mol^{-1}). The main disadvantage of these processes is the high coke formation [2–5], essentially in the nanofilament form, which may cause severe deactivation of the catalyst by pore or active site blocking and sometimes, physical disintegration of the catalyst body causing a high pressure drop along the catalyst bed and even, in some cases, inducing damage to the reactor itself [6–7]. Previous results obtained in the catalytic partial oxidation of methane have shown that due to the hot spot and carbon nanofilaments formation the alumina-based catalyst in an extrudate form was broken into powder which induces a significant pressure drop across the catalytic bed [8,9]. In the catalytic partial oxidation with the high exothermicity of the reaction, the hot spots formation also induces temperature runaway that could be detrimental for the process security and selectivity, especially when the supports are insulator, i.e. alumina and silica. In the case of endothermic reactions, steam and CO_2 reforming, the temperature drop within the catalyst bed could also modify the activity of the catalyst. According to these drawbacks, it is of interest to find new support having the same advantages as those of alumina or silica-based supports above mentioned but having a high thermal conductivity and mechanical strength in order to reduce the problems of hot spot and also to maintain the catalyst body integrity.

Silicon carbide (SiC) exhibits a high thermal conductivity, a high resistance towards oxidation, a high mechanical strength, and chemical inertness, all of which make it a good candidate for use as catalyst support in several endothermic and exothermic reactions such as dehydrogenation [10], selective partial oxidation [11–12], and Fischer-Tropsch synthesis [13]. The gas-solid reaction allows the preparation of SiC with medium surface area, i.e. 10–40 m^2 g^{-1}, and controlled macroscopic shape, i.e. grains, extrudates or foam, for it subsequence use as catalyst support [14,10,15,16]. In addition, due to its chemical inertness the recovery of the active phase is extremely easy, i.e. acidic or basic washing, which reduce the cost investment of the process for the final spent catalyst disposal and the fully re-use of the support. The high thermal conductivity of the SiC support could also allow the reduction of the temperature loss during the reaction taken into account the high endothermicity of the reaction.

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* Corresponding author at: Da-Nang University of Technology, Faculty of Chemistry, 54 Nguyen Luong Bang, Da-Nang, Vietnam. Tel.: +84 511 3842 743; fax: +84 511 3842 771.
E-mail address: nguyendl@ud.edu.vn (D.L. Nguyen).

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The aim of the present article is to report catalytic behavior in the combined catalytic reforming of CH_4 by a mixture of CO_2 and O_2 on a nickel-based catalyst supported on a medium surface area β-SiC material. The influence of the oxygen pretreatment on the CO_2 reforming activity will be discussed on the basis of the physical characterisation and catalytic results.

2. Experimental

β-SiC in an extrudate form was synthesized according to the gas-solid reaction between SiO vapor and solid carbon [14,10,15]. The carburization was preceded through a pseudo-morphism mechanism which allows the complete retention of the pristine morphology of the carbon after carburization. After synthesis the support was annealed in air at 700 °C for 2 h in order to remove the residual carbon material. Nickel phase (5 wt.%) was deposited onto the SiC support via incipient wetness impregnation. After impregnation the catalyst was dried at room temperature for 6 h and oven-dried at 110 °C for 2 h. The calcinations were carried out at 350 °C for 2 h in order to decompose the nickel salt precursor into its corresponding nickel oxide. The NiO was further reduced in flowing H_2 at 400 °C for 2 h.

The CO_2/O_2 and CO_2 reforming of methane were carried out in a fixed-bed tubular quartz reactor (1200 mm length, 6 mm inner diameter) at atmospheric pressure, 900 °C and a contact time of 0.9 s (STD). The reactor was purged with argon flow (100 ml min^{-1}) at room temperature for 30 min before admitting the reactant mixture.

The reaction products were analyzed by means of a gas chromatography (GC) technique on a Varian 3800 GC equipped. This device was equipped with a 10 ways valve that permit to inject simultaneously the reaction flux in a Carbobond megabore column coupled to a thermal conductivity detector (TCD) permitting the separation and the detection of H_2 thus, CO, CO_2, CH_4 and possibly of traces of water non-trapped and a DB-1 column related to a flame ionization detector (FID) allowing the detection of CH_4 and other hydrocarbons of C_1 to C_6.

The powder X-ray diffraction (XRD) was carried out using a Siemens D-5000 diffractometer working with a Cu Kα non-monochromatic radiation. The diffraction lines were compared with those of the JCPDS data bank (Joint Committee Powder Diffraction Standard). The microstructure of the catalyst was observed by means of the transmission electron microscopy (TEM) on a Topcon 002B-UHR microscopes worked under 200 kV accelerated voltage with a point-to-point resolution of 0.18 nm.

3. Results and discussion

3.1. Catalysts characterisation

XRD pattern of the fresh catalysts (Ni/SiC and Ni/Al_2O_3) show the complete reduction of the nickel oxide into its corresponding nickel metal. The specific surface area of the catalyst was only slightly modified after deposition of the nickel which indicates that no pore plugging was occurred.

The nickel dispersion on SiC was measured by statistical TEM from more than 400 particles and the representative image is presented in Fig. 1A. The average Ni particle size deduced from the statistical TEM analysis was centered between 4 and 8 nm. Taken into account the relatively low specific surface area and the chemical inertness of the SiC-based support the dispersion was excellence. The high dispersion of the nickel phase on the SiC surface was attributed to the presence of an oxygen-containing (SiO_2–SiO_xC_y) surface layer on the SiC surface which provides a natural wash-coat for anchoring and dispersing the deposited metal particles. Such oxygen-containing layer on the topmost surface of the SiC can be clearly viewved by the high-resolution TEM micrograph in Fig. 1B. The HR-TEM micrograph also evidences the presence of a large number of stacking faults along the (1 1 1) growth axis of the ceramic material.

3.2. Pure CO_2 reforming of methane

The catalytic results obtained in the CO_2 reforming are presented in Fig. 2 as a function of time on stream. The CH_4 conversion was slightly high at the beginning of the test on the SiC-based catalyst and then, a rapid deactivation was observed as a function of time on stream during the first hours of test before reaching a steady-state at around 80% after 20 h on stream. After that, it is noteworthy that almost no deactivation was observed on the catalyst after more than 70 h on stream indicated that the active sites were still accessible to the reactants and no further active site loss where observed. The stability was attributed to the presence of meso- and macropores within the SiC support which were not easily blocked by the carbonaceous residues which were formed during the course of the reaction. The deactivation observed at the beginning of the reaction will be discussed below on the basis of the characterisation results.

On the other hand, Ni supported on alumina catalyst led to a slow but irreversible deactivation with time on stream. The continuous deactivation rate observed on the alumina catalyst was

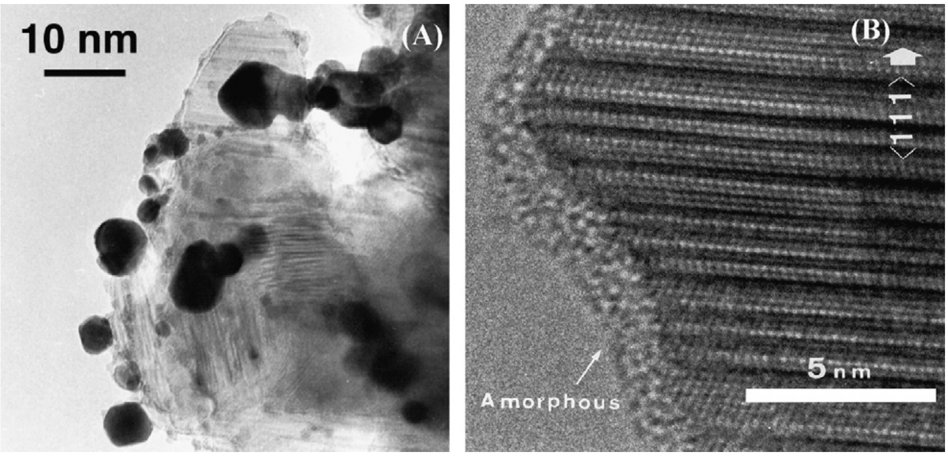

Fig. 1. (A) Representative TEM micrograph of the nickel particle on the SiC surface with an average particle size ranged between 4 and 6 nm, and (B) high-resolution TEM micrograph showing the presence of a thin amorphous layer (SiO_2–SiO_xC_y) on the SiC surface which plays a role of a natural wash-coat for the active phase anchorage.

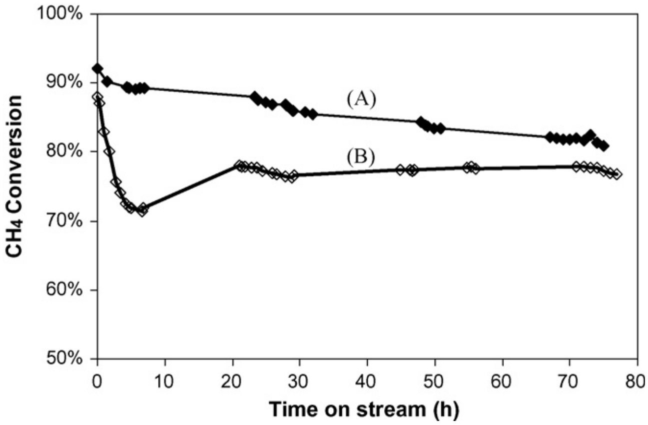

Fig. 2. The CH_4 conversion of the pure CO_2 reforming of methane on the 5% Ni-based catalyst with the different supports: (A) alumina support and (B) β-SiC support. Reaction conditions: CO_2-to-CH_4 ratio of 1, reaction temperature set at 900 °C, atmospheric pressure.

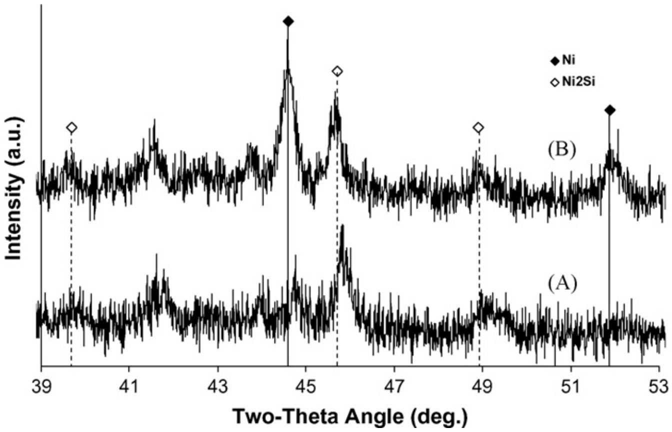

Fig. 3. XRD patterns of the Ni/β-SiC catalysts after CO_2 reforming reaction: (A) without oxidative pretreatment and (B) with oxygen pretreatment (combined reforming) and tested under pure CO_2 reforming conditions.

attributed to the active sites encapsulation by carbonaceous residues or by secondary reaction between the nickel phase and the alumina support leading to the formation of a new phase with lower activity.

The XRD patterns of the spent SiC-based catalyst are presented in Fig. 3 and show diffraction lines corresponding to the $NiSi_2$ phase whereas the diffraction lines belong to the nickel metal were significantly lowered. It was expected that during the course of the reaction part of the Ni was reacted with the support surface leading to the formation of $NiSi_2$ which is probably less active for the CO_2 reforming of methane compared to that of Ni. The formation of $NiSi_2$ has already been observed by different authors in the literature on the SiC-based catalyst at temperature ranged from 800 to 1000 °C. The formation of the $NiSi_2$ phase on the SiC-based catalyst during the course of the reaction was expected to be responsible for the sharp deactivation observed at the beginning of the test.

TEM micrographs of the catalyst after reaction are presented in Fig. 4A and clearly evidence the formation of carbon nanofilaments on the alumina-based catalyst and represent one of the modes of deactivation. This result has already been reported in the literature [17]. On the contrary, it is noteworthy that on the SiC-based catalyst, almost no carbon filaments were observed (Fig. 4B) and thus highlighted the higher resistance towards deactivation of the catalyst. It was expected that carbon nanofilaments growth process was low on SiC and thus, part of it was rapidly burn-off by the CO_2 in the feed resulting to a low amount of carbonaceous species on the spent catalyst. The low rate of carbon nanofilaments formation on the SiC-based catalyst remains unclear for the moment and work is on going to get more insight about the metal–support interaction and its influence on the carbon nanofilaments growth rate on the SiC support.

3.3. *Influence of the oxygen pretreatment on the CO_2 reforming of methane on Ni/SiC*

A new activation method was used in order to improve the catalytic stability of the Ni/SiC catalyst: instead of CO_2 and CH_4 alone a small amount of oxygen was added to the feed at the beginning of the test. The methane conversion in such a combined reforming process was extremely high at the beginning of the test and was reached about 95% (Fig. 5). It is noteworthy that activation-test carried out in the presence of CH_4, CO_2 and trace amount of O_2 leads to a highly active and stable catalyst and no deactivation was observed during the first 40 h on stream contrary to the same test carried out without trace amount of O_2 in the feed. The oxygen presence in the feed seems to inhibit in a significant manner the deactivation of the catalyst during the starting period as observed with the catalyst runed in the absence of oxygen. In addition, the most interesting feature is that when the oxygen flow was switch-off after 40 h on stream the CO_2 reforming activity was remained relatively high compared to that was observed without

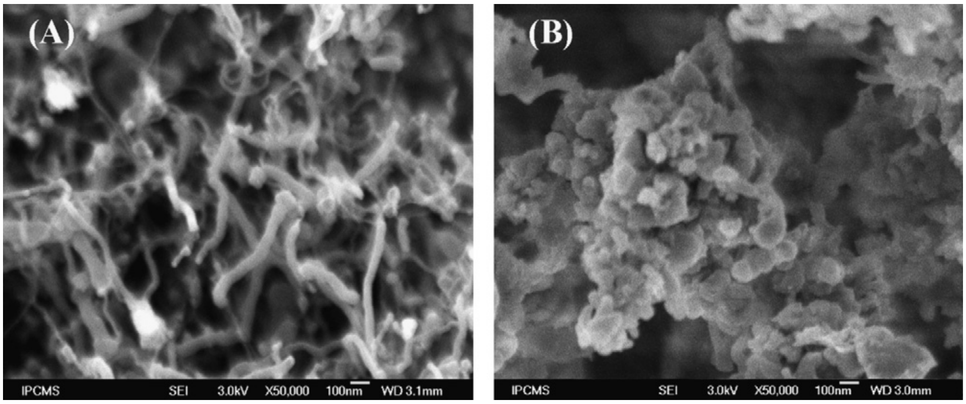

Fig. 4. SEM photos of the Ni-based spend catalysts after CO_2 reforming reaction with different supports: (A) alumina support and (B) β-SiC support. The high amount of carbon filaments formed on the alumina-based catalyst was expected to be responsible for the continuous deactivation of the catalyst.

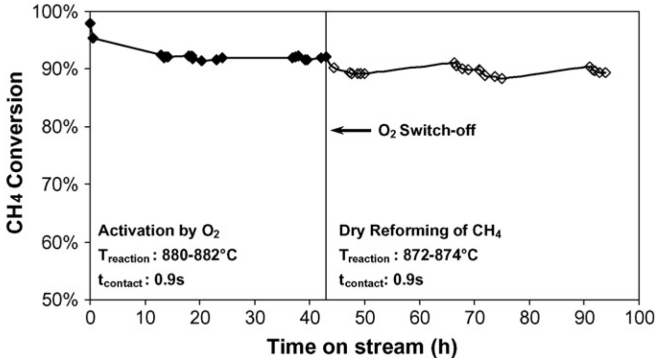

Fig. 5. The CH_4 conversion of the CO_2 reforming of methane on 5%Ni/β-SiC with the oxygen pretreatment and after switch-off the oxygen supply keeping the reaction conditions unchanged. Apparently, the presence of the trace amount of oxygen during the starting period allows the avoidance of the $NiSi_2$ phase which was linked with the catalyst deactivation.

oxygen activation, i.e. 90 instead of <80%, keeping other reaction conditions similar. The CO_2 reforming activity, expressed in terms of conversion, was remained extremely stable with time on stream as no deactivation was observed for the whole duration of the test which was lasted for almost 100 h (Fig. 5). It is expected that pretreatment in the presence of a small amount of oxygen has led to a modification of the active phase nature during the starting period which in turn, improve the CO_2 reforming activity of the Ni/SiC catalyst.

X-ray diffraction analysis was carried out on such catalyst in order to get more insight about the crystalline phases present after the tests in the presence and absence of trace amount of oxygen during the activation period. On the catalyst formed directly in the presence of a mixture of CH_4 and CO_2 the diffraction lines corresponding to the Ni metal were relatively weak compared to those of the $NiSi_2$ phase (Fig. 3A). It is noteworthy that this later was not observed on the freshly reduced catalyst. The loss of the reforming activity was attributed to the formation of the $NiSi_2$ phase which exhibits a lower reforming activity. On the same catalyst, activated in the presence of a mixture of CO_2/O_2 and CH_4, the diffraction lines corresponding to the Ni phase were much higher compared to those of the $NiSi_2$ phase (Fig. 3B). Apparently, the presence of a small amount of oxygen during the activation period seems to favor the Ni phase maintain at the detriment of the $NiSi_2$ phase formation with probably lower the reforming catalytic activity. It is seemed that the $NiSi_2$ phase was steadily formed during the starting period as the switching-off of the oxygen supply after 40 h on stream did not led to any further deactivation compared to that was observed on the Ni/SiC catalyst activated in the absence of oxygen.

It is noteworthy that TEM analysis carried out on the Ni/SiC after activation in the presence of a small amount of oxygen followed by a relatively long period under CO_2 and CH_4 shows no presence of carbon nanofilaments contrary to that was observed on the same catalyst but activated directly under a mixture of CO_2 and CH_4. Apparently, the formation of carbon nanofilaments could be linked to the presence of the $NiSi_2$ phase which was formed at the beginning of the reaction. The absence of carbon nanofilaments could also be advanced to explain the catalytic activity improvement observed in this case. However, no clear and unique explanation accounting for the observed catalytic results has been developed yet for the moment and work is on going to get more insight about the operated mechanism.

4. Conclusions

SiC with medium surface area and open pore structure, i.e. meso- and macropores, can be efficiently employed as catalyst support for the CO_2 reforming of methane to yield synthesis gas. However, the catalyst exhibits an induction period during which a slow decrease of the CH_4 conversion was observed before reaching a steady-state for the rest of the test. The deactivation slope observed at the beginning of the test was attributed to the formation of the $NiSi_2$ phase with probably lower the reforming activity before reaching a steady-state. The pretreatment of the catalyst by a mixture of CO_2 and O_2 led to a significant improvement of the catalytic activity for the CO_2 reforming compared to that was observed on the same catalyst without oxygen pre-activation, i.e. 90 instead of <80%. The reforming activity remains unchanged after switching-off the O_2 supply which indicate that the active phase nature yielding high CO–H_2 products can be effectively formed by an activation period in the presence of trace amount of O_2 in the feed. The improvement in the CO_2 reforming activity after oxygen pretreatment was attributed to be due to the inhibition of the $NiSi_2$ formation which displays a lower catalytic activity compared to that of metallic nickel according to the XRD analysis. The pretreatment under a trace amount of O_2 also led to a complete inhibition of the carbon nanofilaments on the catalyst. In the direct activation, without O_2, a small amount of carbon nanofilaments was observed.

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