DEVELOPMENT AND MODIFICATION OF LOW NICKEL CONTENT CATALYSTS FOR DRY REFORMING OF METHANE

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Summary

Both the Ca Voi Xanh (Blue Whale) gas field in Vietnam and biogas produced in Germany possess comparable high contents of CO_2. For further processing, in both cases it is important to find a way to handle the concomitant CO_2. One option is the direct production of synthesis gas - a mixture of CO and H_2. Accordingly, low content (2.5wt%) but active Ni catalysts supported on Mg-Al mixed oxides were developed and studied for methane dry reforming reaction (DRM). The main scope of this investigation was to design an active catalyst and modify it to avoid quick deactivation caused by coking. The samples in this study were characterised by N_2 physisorption (BET) and X-ray diffraction (XRD). The results revealed that our Ni/MgAlO$_x$ catalysts show high surface area and good Ni dispersion. Such properties contribute to the high activity of the catalysts already at 500°C. Modification with La^{3+} significantly increases the resistance toward carbon formation due to its ability for C gasification. Such La.Ni/MgAlO$_x$ type catalyst also shows high and stable DRM activity over at least 60 hours with low carbon accumulation at high weight hourly space velocity (WHSV = 170L/(g$_{cat}$·h)) compared to state-of-art.

Key words: *Dry reforming of methane, carbon dioxide, low content nickel catalyst, lanthanum, coking resistivity.*

1. Introduction

The global energy demand is growing rapidly, and about 88% of this demand is met at present time by fossil fuels [1]. However, this causes serious environmental problems such as air pollution beside fast depletion of resources. Henceforth, during the recent years, many European countries - especially Germany, Denmark, Austria and Sweden - have been focusing their interest in biogas production because biogas is considered as a sustainable energy source which has a large potential for reducing greenhouse gas emissions [1]. Germany is one of the largest biogas-producing countries utilising available organic wastes, by-products and energy crops [2]. The total biogas potential in Germany is calculated by the Federal Agricultural Research Centre (FAL) as 24 billion m^3 per year [2]. The final composition of biogas is 50 - 75vol% CH_4, 25 - 45vol% CO_2, 2 - 7vol% H_2O and less than 1vol% is O_2, N_2, NH_3 and H_2S [3]. Interestingly, in 2011 Vietnam discovered the Ca Voi Xanh gas field with a large reserve of about 150 billion m^3 available for power generation and industrial purposes [4]. This Vietnamese gas has a high content of CO_2 (~ 30vol%) which is comparable with the biogas in Germany, and in both cases it is important to find a way to handle the concomitant CO_2 [4]. There are several possibilities to reduce total CO_2 emissions into the atmosphere. One of them is to develop different technologies to capture and utilise CO_2 to produce valuable chemicals from it. One possible CO_2 utilisation might be the reaction with methane towards synthesis gas (H_2, CO), which is among the most important starting materials in large-scale chemical syntheses. At present, synthesis gas is the main source for H_2 production via steam reforming [5, 6]. However, both the evaporation of great quantities of water and the endothermic reaction itself are very energy demanding as well as the upstream CO_2 removal and downstream CO removal [7]. Another alternative and cheaper way would be CO_2 reforming of methane (Equation 1, [8]), which has been proposed as one of the most promising technologies for utilisation of these two gases to produce synthesis gas [9].

$$CO_2 + CH_4 \rightarrow 2CO + 2H_2 \qquad \Delta H_{298} = 247 kJ/mol \qquad (1)$$

The syngas can be used in already existing industrial processes for chemical synthesis depending on the reaction conditions and the catalyst (Figure 1 [10]).

However, dry reforming is not yet commercialised due to the fast deactivation of the catalyst by carbon formation. Many efforts have been made to search for an active and stable catalyst. Nickel-based catalysts showed

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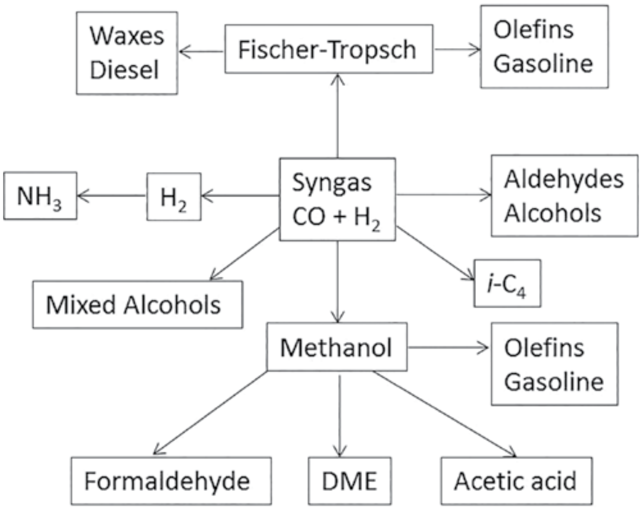


Figure 1. *Selection of options to use syngas and methanol for products adapted [10]*

to be promising candidates but they tend to form Ni aggregates and then unreactive carbon easily forms on the surface leading to deactivation [11]. There are several approaches in the reduction of carbon deposition of Ni-based catalysts; the first is to decrease the particle size of the nickel and to improve its dispersion by supporting it on high-surface area supports [12, 13]. The second is to alter the acidity and basicity of the supports and the third is to apply different specific methods of catalyst preparation [14]. Liu et al. found that the method of preparation of different Ni loadings supported on MCM-41 has an effect on the activity and stability of the catalyst [15]. Supporting 7wt% of Ni on SiC monolithic foam resulted in an excellent activity (95%) and stability over 100 hours at 800°C [16]. Also Al_2O_3 and MgO were used recently as supports to prepare Ni-based catalysts for dry reforming. Zhang et al. studied a series of Ni/MgO-Al_2O_3 catalysts prepared by a simple two-step hydrothermal method. It was confirmed that Ni/MgO-Al_2O_3 (15wt% Ni) catalyst afforded 52% CH_4 conversion with excellent stability during reaction at comparatively high space velocity (6×10^5 $cm^3 \cdot g_{cat}^{-1} \cdot h^{-1}$) and lower reaction temperature (650°C) [17]. It seems that the addition of Al_2O_3 to MgO contributes to the formation of an $MgAl_2O_4$ phase, which is stable and could effectively increase the CO_2 adsorption due to the increased amount of basic sites on the catalyst surface. Kathiraser et al. investigated the behaviour of Ni particles supported on $LaAlO_3$-Al_2O_3 which were stable and active over 30 hours due to the formation of $NiAl_2O_4$ spinel structure [18]. Liu et al. investigated the activity of La-promoted catalysts which was higher than for non-promoted hydrotalcite derived catalyst [19]. From the previous research, we decided to prepare Ni supported on basic hydrotalcite precursors and to investigate the effect of La addition on the stability of such catalysts against coke deposition in DRM.

2. Materials and methods

2.1. Catalyst preparation

Mg-Al mixed oxides (calcined Mg-Al hydrotalcite, Pural MG, Sasol) supported Ni catalysts were prepared by wet impregnation. Mg-Al hydrotalcite precursor possesses the Mg/Al ratio ~1.0 (data from ICP-OES and AAS measurement). $Ni(NO_3)_2 \cdot 6H_2O$ (Alfa Aesar) and $La(NO_3)_3 \cdot 6H_2O$ (ABCR GmbH) were used as precursors for Ni^{2+} and La^{3+}. Prior to impregnation, the hydrotalcite precursor was calcined at 800°C for 6 hours in air to obtain the bare supports which are denoted as $MgAlO_x$. The calculated amounts of Ni and La precursors were dissolved together in deionised water and then the support was put into the solution and the slurry was stirred. Samples were then dried overnight and calcined at 800°C for 6 hours in static air. The final catalysts are abbreviated as Ni/$MgAlO_x$ and La.Ni/$MgAlO_x$. The nominal content of Ni in all supported Ni-containing catalysts was 2.5wt%.

2.2. Catalyst characterisation

Nitrogen physisorption method served for calculating the specific surface area and pore volume according to the BET theory. The measurements were performed on a Micromeritics ASAP 2010 apparatus (Micromeritics GmbH, Aachen, Germany) at -196°C. The samples were degassed at 200°C in vacuum for 4 hours before the analysis.

XRD powder patterns were recorded either on a Panalytical X'Pert diffractometer equipped with a X'celerator detector or on a Panalytical Empyrean diffractometer equipped with a PIXcel 3D detector system using Cu Kα1/α2 radiation (40kV, 40mA) in both cases. Cu beta-radiation was excluded by using nickel filter foil. Cu Kα2 radiation contribution was removed arithmetically using the Panalytical HighScore Plus software package. Peak positions and profile were fitted with Pseudo-Voigt function using the WinXPow software package (Stoe). Phase identification was done by using the PDF-2 database of the International Center of Diffraction Data (ICDD).

2.3. Catalyst tests

DRM was carried out in a fixed-bed continuous flow quartz reactor (ambient pressure, WHSV = 100 or 170L/(g_{cat}·h); T = 500 - 780°C). All volumetric flow rates given in this study are related to 25°C and atmospheric pressure. After in-situ pre-reduction in H_2 (700°C, 100% H_2, 50mL/min) for 1.5 hours, temperature was adjusted and maintained for 8 or 60 hours and the reactant mixture (45vol% CH_4, 45vol% CO_2, 10vol% He) was fed to the reactor. Helium was used as internal standard for volume change determination in reaction. The gas compositions were then analysed by an on-line gas chromatograph (Agilent 6890) equipped with flame ionisation detector (HP Plot Q capillary, 15m × 0.53mm × 40µm) and thermal conductivity detector (carboxene packed, 4.572m × 3.175mm) for analysis of hydrocarbons and permanent gases, respectively. Pure components were used as reference for peak identification and calibration. Carbon balances were calculated from gas products and reached more than 95% in this work. Conversions (X) and H_2/CO ratio were calculated using the formulas given below:

3. Results and discussion

$$X_{CH_4}\,(\%) = \frac{moles\ of\ converted\ CH_4 \times 100\%}{moles\ of\ CH_4\ in\ feed}$$

$$X_{CO_2}\,(\%) = \frac{moles\ of\ CO_2\ converted \times 100\%}{moles\ of\ CO_2\ in\ feed}$$

$$H_2/CO\ ratio = \frac{moles\ of\ H_2\ produced}{moles\ of\ CO\ produced}$$

3.1. Characterisation of the catalysts

The crystallographic structure patterns of the MgO-Al_2O_3 mixed oxides, as the support material, and the corresponding Ni-containing catalysts were determined by XRD. Figure 2 represents the spinel structure formation of $MgAl_2O_4$ (ICDD file No. 00-021-1152) in the support with reflections at 2θ = 19.5°, 31.3°, 37°, 45° and 59°. This spinel phase is favoured when calcining the Mg-Al hydrotalcite precursor at high temperature [20]. Besides, periclase (the cubic form of magnesium oxide, ICDD file No. 01-071-1176) is also observed with broad reflections at about 2θ = 43° and 63°. This phase is probably created due to the unity ratio of Mg:Al in the hydrotalcite precursor, which is higher than that of mentioned $MgAl_2O_4$ (0.5), leading to the formation of MgO species. XRD patterns of Ni containing samples (Ni/$MgAlO_x$ and La.Ni/$MgAlO_x$) expose almost no additional reflections of Ni^{2+}- containing species compared to the corresponding support. This suggests the formation of well-dispersed Ni^{2+} species on the surface or diffusion into the bulk of support, adapting those mentioned structures of MgO-Al_2O_3 mixed oxides forming solid solutions or spinel. This behaviour is predominant when low content of impregnated species and high calcination temperature were applied during the preparation [21].

The textural parameters of the calcined Ni samples and the support are summarised in Table 1. Compared to the pure support $MgAlO_x$, impregnated catalysts (with La^{3+} and/or Ni^{2+}) show lower specific surface areas. However, La.Ni/$MgAlO_x$ shows significantly less specific surface area (S_{BET}) and pore volume than Ni/$MgAlO_x$. By that, the accessibility of the support surface, the pore system and even the Ni^{2+} atoms were decreased.

3.2. Catalyst performance

Blank tests without catalyst or with Ni/$MgAlO_x$ without pretreatment by H_2 reduction exposed no conversion of CH_4 or CO_2 in the temperature range of 500 - 800°C. First, this proves the essential role of Ni metal as the active sites for DRM. Besides, tests on catalytic methane thermal cracking were also conducted on both catalysts. This is one of the known reactions responsible for coke formation during DRM (Equation 2). However, no remarkable conversion was obtained except small carbon deposition on the spent catalyst.

$$CH_4 \rightarrow C + 2H_2 \qquad (2)$$

$$2CO \rightarrow CO_2 + C \qquad (3)$$

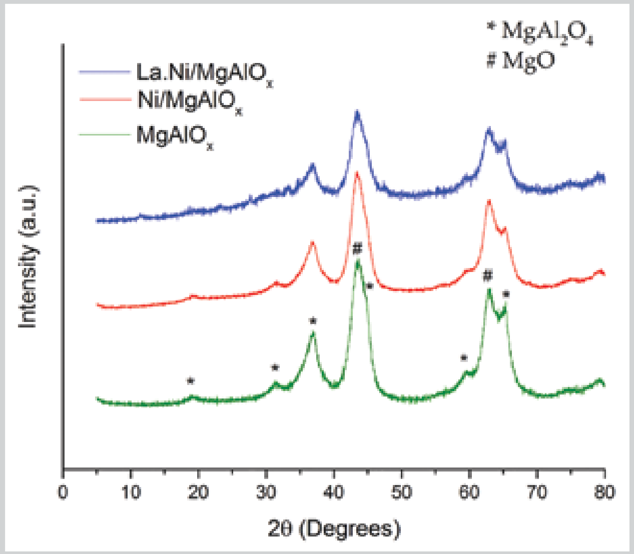


Figure 2. *XRD patterns of support $MgAlO_x$ and catalysts derived therefrom by impregnation*

Table 1. *Textural properties of calcined catalysts and the support*

Catalyst	**S_{BET} (m^2/g)**	**Total pore volume (cm^3/g)**
$MgAlO_x$	180	0.24
Ni/$MgAlO_x$	174	0.40
La.Ni/$MgAlO_x$	118	0.27

DRM performance tests of pre-reduced Ni/$MgAlO_x$ at different temperatures in the range of 500 - 780°C were investigated with the same feed composition and WHSV (100L/(g_{cat}·h)). Figure 3 discloses that the performance regarding the CH_4 and CO_2 conversions is close to thermodynamic equilibrium at corresponding reaction temperatures [22]. It is well understood that DRM is only effective at high temperature due to its highly endothermic nature [22]. According to literature, the DRM reaction could be thermodynamically beneficial above 647°C [8]. Some investigations concluded that the catalysts might be active in DRM already at lower temperature (400°C [23] or 450°C [24]). However, therein WHSV was lower, the content of active species was higher or noble metals were added which offered more beneficial conditions for high reaction rates than this study. Compared to some remarkable literature results regarding Ni catalyst systems (Table 2) and also other studies [14], Ni/$MgAlO_x$ of this study shows promising potential for DRM by activating the reaction at mild condition (low temperature and high WHSV) even with low Ni content. This high activity probably is in accordance with high surface of the catalyst (Table 1) and good dispersion of Ni (XRD). Below 650°C, CO formation via CO_2 by reverse water gas shift reaction (RWGS, Equation 4, [8]) is expected to get predominant [22].

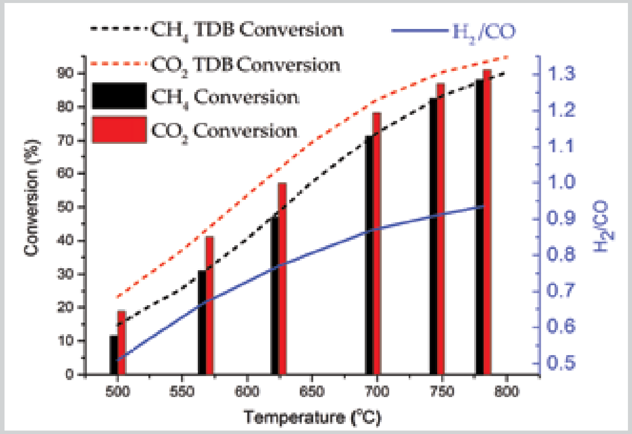


Figure 3. *Performance of Ni/$MgAlO_x$ in comparison with the thermodynamic balance (TDB) (1bar, CO_2/CH_4 = 1, WHSV = 100L/(g_{cat}·h)). Activity data were collected after 2 hours stabilisation at each temperature set point.*

$$CO_2 + H_2 \rightarrow CO + H_2O \quad \Delta H_{298} = 41kJ/mol \qquad (4)$$

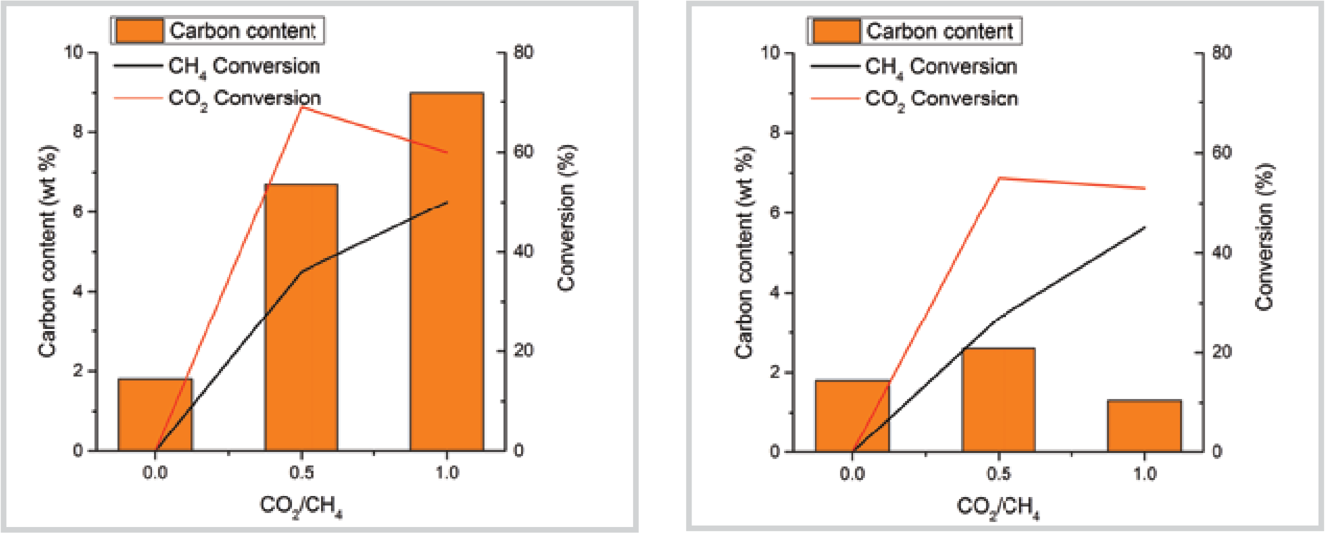
This reaction is less endothermic and thus more favourable at low temperature compared to DRM. This effect is seen clearly in Figure 3 which shows the effect of temperature on the H_2/CO ratio. The lower the reaction temperature, the lower the H_2/CO ratio and H_2 selectivity. Subsequently, H_2O forms as side product and the relative conversion ratio between CO_2 and CH_4 increases [22].

Figure 4 shows the conversions of CH_4 and CO_2 as well as the amount of carbon deposition depending on the CO_2/CH_4 ratio for runs with Ni/$MgAlO_x$ and La.Ni/$MgAlO_x$. The carbon accumulation in DRM was examined on the spent catalysts after 8 hours on stream in terms of weight percentage. Typically a CO_2/CH_4 ratio of 1 is used for DRM, whereas the ratio of 0.5 is close to the composition of typical biogas as well as the gas content discovered in Ca Voi Xanh gas field. With both catalysts, increasing CO_2/CH_4 ratio from 0 to 1 enhances CH_4 conversion (from almost 0 to around 50%) due to the DRM reaction between both CH_4 and CO_2. The CO_2 conversion achieves a maximum (70%) at CO_2/CH_4 = 0.5 as the result of excess amount of CH_4 shifting DRM more to the production side.

It is well known that carbon deposition during DRM causes catalyst deactivation and reactor plugging [32]. Carbon formation is the result of side reactions including mainly methane decomposition (MD) above 550°C as well as Boudouard Reaction (BD) (Equation 3) below 700°C [22]. The carbon amount on spent Ni/$MgAlO_x$ varies proportionally with CH_4 conversion (Figure 4a). On the other hand, the thermal cracking of methane (CO_2/CH_4 = 0) exposes negligible carbon deposition on spent Ni/$MgAlO_x$, reflecting limited coking rate in case of CO_2 absence, which prevents CO formation in DRM and further disproportionation in BD reaction. Therefore, it can be proposed that both MD and BD reactions

Table 2. *Remarkable recent studies with Ni catalysts for DRM*

Catalyst	Ni content (wt%)	Space velocity	Reactants $CH_4:CO_2:N_2$(He)	T (°C)	X_{CH_4} (%)	X_{CO_2} (%)	Ref.
Ni/SBA-15	12.5	12,000h^{-1}	N/A	800	43	70	[25]
Ni/Mo/SBA-15-La_2O_3	5	12,000ml/(g_{cat}.h)	N/A	800	84	96	[26]
Ni-MgO-$Ce_{0.8}Zr_{0.2}O_2$	15	480,000h^{-1}	1:1:3	800	96	97	[27]
Ni/Ce-Al_2O_3	10	20,000ml/(g_{cat}·h)	N/A	800	80	90	[28]
Ni/MgO-Al_2O_3	12.6	30,000ml/(g_{cat}·h)	1:1:1	800	92	95	[29]
Ni-Co/MgO-ZrO_2	3% Ni, 3% Co	125,000ml/(g_{cat}·h)	N/A	750	80	85	[30]
Ni/SiO_2	0.35	19,000ml/(g_{Ni}·h)	9:9:2	800	42	55	[31]
Ni/$MgAlO_x$	**2.5**	**100,000ml/(g_{cat}·h)**	**9:9:2**	**780**	**83**	**90**	**This study**



(a) (b)

Figure 4. Performance of $Ni/MgAlO_x$ (a) and $La.Ni/MgAlO_x$ (b) at different CO_2/CH_4 ratios (1bar, 600°C, WHSV = 170L/(g_{cat}·h))

contribute to coke formation in DRM with different extent when changing the CO_2/CH_4 ratio. The occurrence of coke formation is as expected because the chosen reaction temperature (600°C) is in the thermodynamic range for both MD and BD [22].

La^{3+} addition to the catalyst results in slightly lower DRM activity (Figure 4b). This phenomenon can be explained by the lower surface area of $La.Ni/MgAlO_x$ compared to that of $Ni/MgAlO_x$ (Table 1). La^{3+} ions probably cover some Ni species in the preparation steps and prevent the active sites from being fully exposed to CH_4 and CO_2, lowering the conversion of those reactants. This behaviour was also seen elsewhere [33] on La-promoted $Ni/MgAl_2O_4$ which is similar to the catalyst formulation in this study. However, the La-promoted catalyst is significantly resistant toward coking in the DRM (Figure 4). This rare-earth metal oxide was also studied to eliminate the rapid coking in other reforming reactions (partial oxidation [34], steam reforming [33]). In this study, the tests without CO_2 (CO_2/CH_4 = 0) showed very low conversion for both catalysts and comparable carbon deposition. In DRM with $La.Ni/MgAlO_x$, the higher the CO_2 fraction in the feed, the lower the carbon deposition compared to that of $Ni/MgAlO_x$ under the same condition. This is a measure for the CO_2 activation in carbon gasification by La^{3+} species. Such activation was also discovered in other reforming reactions [33, 34]. Besides, both catalysts expose comparable CH_4 and CO_2 conversions as a function of CO_2/CH_4 ratio (Figures 4). However, the coke formation on $La.Ni/MgAlO_x$ is not proportional to the conversion as it was found on $Ni/MgAlO_x$. Therefore, CO_2 promotion by La^{3+} prevents the BD because carbon gasification is the reverse reaction of BD, and also removes the carbon species formed via methane thermal cracking. Regarding the reaction pathway, DRM occurs on both catalysts, but $La.Ni/MgAlO_x$ promotes additional steps that activate C gasification by CO_2 which was also proposed elsewhere [35]:

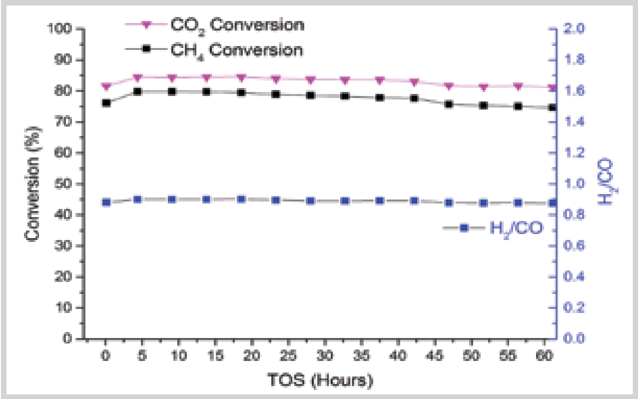


Figure 5. Catalytic performance of $La.Ni/MgAlO_x$ in long-term DRM (T = 750°C, p = 1 bar, CO_2/CH_4 = 1, WHSV = 170L/(g_{cat}·h)).

$$La_2O_3 + CO_2 \rightarrow La_2O_2CO_3$$

$$CH_4 + 5x^* \rightarrow CH_x^* + 4H^* \qquad (x^*)\text{: surface sites}$$

$$La_2O_2CO_3 + CH_x^* \rightarrow 2CO^* + La_2O_3 + x/2\ H_2$$

$$La_2O_2CO_3 + C \rightarrow 2CO + La_2O_3$$

Finally, a long-term DRM test was carried out with $La.Ni/MgAlO_x$ (Figure 5). The considerably high WHSV of 170L/(g_{cat}·h) compared to literature review [6] was helpful to verify the activity and stability of catalysts during reaction away from thermodynamic equilibrium. The conversions of CH_4 and CO_2 are slightly lower than the thermodynamic balance for CH_4 (83%) and CO_2 (90%) at the corresponding reaction temperature [22].

The catalyst did not deactivate over at least 60 hours on-stream, representing its good stability. During the reaction, CO_2 conversion is always higher than CH_4 conversion, illustrating the contribution of RWGS reaction, causing the H_2/CO ratio to be lower than unity. Negligible carbon deposition (< 2wt%) was measured after 60 hours on stream, reflecting the contribution of C gasification by CO_2 which is promoted by mentioned effect of La^{3+}.

4. Conclusions

The $MgAlO_x$ supported 2.5wt% Ni catalyst shows high activity at 500 - 780°C, revealing the possibility to operate the catalyst at low temperature even at high WHSV and low Ni content. At low temperature, the H_2/CO ratio is low due to the contribution of reverse water gas shift reaction which also creates H_2O as the side product. Compared to Ni/$MgAlO_x$, La.Ni/$MgAlO_x$ shows significantly higher coking resistance, both for CO_2/CH_4 ratio = 0.5 and 1, due to C gasification by CO_2. The obtained results indicate that for Ni/$MgAlO_x$ the coking rate is proportional to methane conversion, whereas this is not the case for La-modified catalyst. Most likely La^{3+} affects the CO_2 activation and gasification of carbonaceous deposits. La.Ni/$MgAlO_x$ also exposes high and stable DRM activity over at least 60 hours at high WHSV.

Acknowledgments

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