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Thermogravimetric analyses and catalytic behaviors of zirconia-supported nickel catalysts for carbon dioxide reforming of methane

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Abstract

Carbon dioxide reforming of methane has been performed over zirconia-supported nickel catalysts. Temperature-programmed surface reactions (TPSR) with CH_4 and CO_2 have also been investigated over the catalysts by means of thermogravimetric analysis technique to explore the behavior of carbon formation during the reaction. The effect of the modification of the zirconia support on supported Ni catalysts reveals that the ceria-doped zirconia support exhibits high catalyst stability against high temperature aging test as well as high resistance to coke formation. Moreover, simultaneous alteration of the support and Ni surface of Ni/ZrO_2 with a Ce modifier and a Ca promoter led to a high performance catalyst, $Ni-Ca/Ce-ZrO_2$, revealing high activity as well as high stability in the CO_2 reforming of methane.

Keywords: CO_2 reforming of methane; Cerium-zirconia support; Nickel catalyst; Thermogravimetry

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1. Introduction

Carbon dioxide reforming of methane (Eq. (1)) to produce synthesis gas is becoming an attractive and challenging subject for the chemical utilization of natural gas and carbon dioxide, which are substances intimately related to greenhouse effect and energy resources [1]:

$$CO_2 + CH_4 \rightleftarrows 2H_2 + 2CO \quad (\Delta H^\circ_{298} = +247\,\mathrm{kJ/mol}) \qquad (1)$$

The major commercial interest in the CO_2 reforming originates from the demand for the production of liquid hydrocarbons and oxygenates, e.g., acetic acid, formaldehyde, and oxoalcohols since this reaction gives synthesis gas with a low H_2/CO ratio [2].

Considerable efforts have been devoted to the development of high performance nickel-based catalysts [3–10]. However, the coke formation over nickel catalysts during the CO_2 reforming was known to be more serious than for any other reforming reactions [4]. It has been observed that the nature of support and promoter to be adopted for the reforming catalyst affects greatly the catalytic performance in the CO_2 reforming [5]. One of key points in developing effective nickel-based catalyst is to find a suitable support [11]. Zirconia and metal-modified zirconia are good candidates as catalyst support for the CO_2 reforming because of unique chemical properties and high stability under oxidizing and reducing atmospheres [12,13]. Ross and co-workers have reported the development of a new Pt/ZrO_2 catalyst with excellent performance [14]. However, Lercher et al. have failed to apply Ni/ZrO_2 catalyst with high Ni loading to the same reaction due to a serious plug of the reactor by coke [15]. In contrast, we have successfully performed the carbon dioxide reforming of methane on Ni/ZrO_2 catalysts with high nickel loading at 1023 K for 30 h in spite of giving birth to a large amount of carbon deposition [16]. In addition, Xu and co-workers [17] have reported that Ni/ZrO_2 catalyst prepared by impregnation of ultra-fine $Zr(OH)_4$ particles with nickel nitrate exhibits high and stable activity for the CO_2 reforming. However, the modification of the catalyst system is still required for much improvement of the catalyst stability because in these cases the stable activity was obtained only under diluted reaction conditions or using diluted catalyst. We report here on thermogravimetric and catalytic behaviors of ZrO_2-supported Ni catalysts to seek catalyst suitable for the CO_2 reforming.

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2. Experimental

The zirconia support (Analytic Pure, Strem Chemicals) was calcined at 1173 K for 8 h prior to its use. Its specific surface area is 28 m^2/g. The Ni/ZrO_2 catalysts with the nickel content of 2.5–23 wt% were prepared by a incipient wetness method using $Ni(NO_3)\cdot 6H_2O$ as a Ni precursor on the zirconia support. After impregnation, samples were dried overnight at 373 K and subsequently calcined in air at 773 K for 4 h.

The modification of zirconia support by alkaline earth or rare earth metal was carried out by sol–gel method using the mixture of zirconyl chloride and the corresponding foreign metal salt of Ca, Mg, Ce, or La. The atomic ratio of zirconium to promoter is 5:1. The modified zirconia support was calcined at 1173 K for 8 h in air. The supported nickel catalysts with 13 wt% Ni were prepared by impregnation of the modified zirconia with the solution of nickel nitrate or a mixed solution of nickel nitrate and nitrate salts of alkaline-earth metals. The catalyst samples were calcined at 773 K for 4 h in air. Ca-promoted Ni catalysts supported on ceria-doped zirconia (Ni-Ca/Ce-ZrO_2) were prepared by molten-salt method described elsewhere [7,8]. The nickel content is 5 wt%. The catalyst samples were calcined at 500 °C for 4 h in air. The molar ratio of Ca to (Ni + Ca) is varied from 0 to 0.75.

For CO_2 reforming of methane, catalytic measurements were conducted in a fixed-bed quartz tubular reactor with inner diameter of 4 mm at atmospheric pressure. The reactant gas stream consisted of CH_4 and CO_2 with a molar ratio of 1:1. The reactant feed was controlled via mass flow controllers at the flow rate, typically 50 $cm^3\,min^{-1}$. A catalyst sample (18–25 mesh) of 50 mg was diluted with quartz sand particle (15–20 mesh) of 250 mg, and then was charged into the reactor. Prior to each catalytic measurement, the catalyst was reduced in 5% H_2–N_2 (v/v) at 973 K for 2 h. Effluent gases from the reactor were analyzed by a gas chromatograph (Chrompack CP9001) equipped with a thermal conductivity detector (TCD).

SEM (Jeol, JSM 840) measurements were conducted to observe carbon formation of Ni-Ca/Ce-ZrO_2 catalyst before and after reaction.

Thermogravimetric analyses (TGA) of carbon deposition and removal were performed on an Intelligent Gravimetric Analyser (Hiden, IGA-002) under atmosphere of $CH_4 + CO_2$ + He (1:1:3), CH_4 + He (1:4), or CO_2 + He (1:4), which is denoted as a volume ratio in the parenthesis. In all experiments, about 50 mg catalyst was loaded on a quartz basket as a sample holder that was placed in a gravimetric chamber. In each case, total flow rate was 50 $cm^3\,min^{-1}$. The calcined samples were first reduced at 973 K for 2 h in a 5% H_2/N_2 flow and then purged with helium until the weight reaches a constant value. The weight change together with temperature and each gas flow were recorded at 1 s interval by a PC with data acquisition software supplied by Hiden Co. (England).

3. Results and discussion

In this work, catalyst design based on zirconia support for the CO_2 reforming sequentially proceeded in the following steps: the modification of ZrO_2 support, the selection of a promoter on active Ni species, and simultaneous alteration of the support and Ni surface.

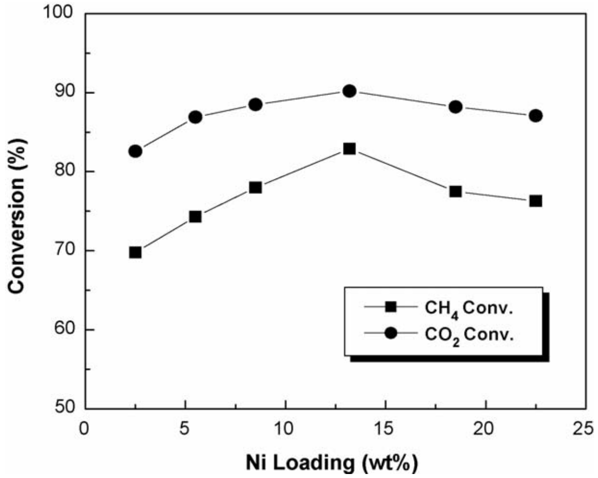

Fig. 1. Effect of Ni loading on catalytic activities of Ni/ZrO_2 catalysts in the CO_2 reforming of methane. *Notations*: $X(CH_4)$ for methane conversion and $X(CO_2)$ for carbon dioxide conversion. *Reaction conditions*: T = 1023 K, $CH_4/CO_2/N_2$ = 1:1:3, P = 1 atm, GHSV = 60,000 cm^3/(h g-cat).

Catalytic activities in terms of the conversions of methane, $X(CH_4)$, and carbon dioxide, $X(CO_2)$, were measured at 1023 K over a series of Ni/ZrO_2 catalysts with the nickel content of 2.5–23 wt% (Fig. 1). Among the catalysts, 13% Ni/ZrO_2 catalyst exhibits the highest activity even though a large amount of carbon is deposited on catalyst surface during the reaction, which might be attributed to the participation of carbon species as a reaction intermediate in the CO_2 reforming. In all cases, CO_2 conversion is higher than CH_4 conversion as a result of contribution of reverse water gas shift (RWGS) reaction at reaction temperature. As previously reported, when long-term tests were performed over Ni/ZrO_2 catalysts with high nickel loading, their catalytic activities were fairly stable at 1023 K for 30 h without significant catalyst deactivation [16].

To examine coking and decoking characteristics of Ni/ZrO_2 catalysts during the CO_2 reforming, the behaviors of carbon deposition and removal on the catalysts were investigated by temperature-programmed surface reaction (TPSR) mode using TGA technique. Fig. 2 shows typical profiles of the weight change occurring on 13% Ni/ZrO_2 catalyst in TPSR sequences. The data were normalized in terms of the weight of the reduced catalyst. In first TPSR curve, the carbon formation can be divided into three stages: (a) induction period, (b) acceleration in coking rate, and (c) a decrease in coking rate. Integrated carbon deposition on the catalyst starts at 695 K and the amount of carbon steeply increases up to 880 K, and then tended to be constant (Fig. 2(a)). The appearance of a plateau in the curve is probably due to reaction equilibrium between coking and carbon removal. The degree of carbon deposition on Ni/ZrO_2 catalyst is obviously higher than those of other catalysts, e.g., Ni/α-Al_2O_3, Ni/SiO_2, Ni/MgO, and Ni/La_2O_3, which were reported by Wang et al. [18]. A differential curve of the first TPSR shows only one symmetrical peak, indicating that one kind of carbon species is formed on the freshly reduced catalyst

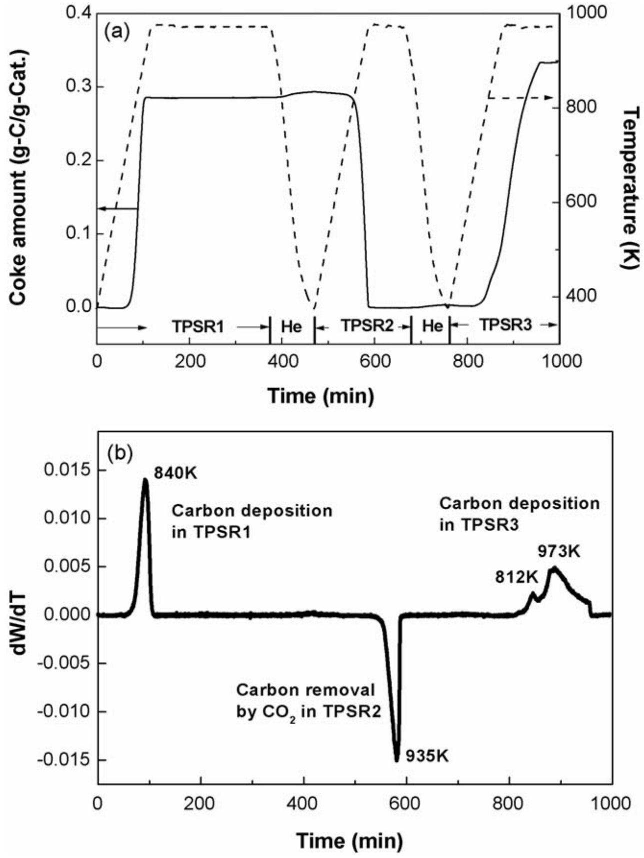

Fig. 2. TGA profiles of carbon deposition and removal over 13 wt% Ni/ZrO_2 catalyst during subsequent TPSR processes: (a) TGA profiles and (b) differential curves of (a). *Test conditions*: $P = 1$ atm, heating rate = 5 K/min, total flow rate = 50 $cm^3\ min^{-1}$, $CH_4/CO_2/He$ = 1:1:3 for TPSR1, CO_2/He = 1:4 for TPSR2, $CH_4/CO_2/N_2$ = 1:1:3 for TPSR3.

(Fig. 2(b)). The maximum peak temperature (T_{max}) for carbon deposition is centered at 840 K. No significant weight change appeared even when the catalyst is further exposed to the reactant stream with $CH_4 + CO_2 + He$ (1:1:3) at 973 K for 6 h after the TPSR operation, revealing that carbon formation reaches a steady state (data not shown). From the second TPSR with $CO_2 + He$ stream, it was observed that the deposited carbon could quickly and completely be removed by CO_2 in the temperature range of 835–925 K. Correspondingly, the appearance of a sharp reverse peak in a differential curve of the second TPSR due to the weight loss by removing carbon points out that the deposited carbon is reactive to CO_2 at temperatures higher than 840 K (Fig. 2(b)). The third TPSR profile with $CH_4 + CO_2 + He$ (1:1:3) shows rather different characteristic from the first TPSR profile. The amount of the deposited carbon in the third TPSR sequence increases by 10% comparing with that of the first TPSR. Carbon formation in the third TPSR sequence starts at 680 K and proceeds even when the temperature reaches at 973 K. Moreover, there are at least two T_{max} peaks for carbon deposition, 812 and 973 K, respectively, and the amplitude of higher T_{max} peak is larger than that of lower T_{max} peak. The origin of this different characteristic on coking may be ascribed to the change of surface state according to CO_2 treatment of the coked surface.

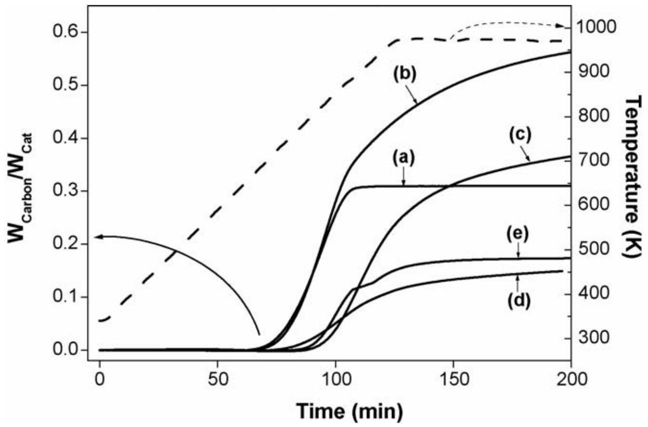

Fig. 3. TGA results of TPSR in CH_4–CO_2–He over Ni/ZrO_2 and Ni/modified-ZrO_2 catalysts with 13 wt% Ni loading: (a) Ni/ZrO_2, (b) Ni/Mg–ZrO_2, (c) Ni/La–ZrO_2, (d) Ni/Ce–ZrO_2, and (e) Ni-Ca/Ce-ZrO_2 *Analysis conditions*: 20 vol.% CH_4–20 vol.% CO_2–60 vol.% He; flow rate, 50 $cm^3\ min^{-1}$; heating rate, 5 K/min.

For Ni/ZrO_2 catalysts with high Ni loading, the carbon species deposited on catalyst surface at an initial stage of the reaction are characterized to play a role as a reaction intermediate in the reaction. However, the modification of the catalyst system is still required for much improvement of the catalyst stability because its stable activity can be obtained only under diluted reaction conditions.

The effect of the modification of the zirconia support on supported Ni catalysts reveals that the ceria-doped zirconia support exhibits high catalyst stability against high temperature aging test as well as high resistance on coke formation. According to TPSR of CH_4 and CO_2 coupled with TGA (Fig. 3), the modification of a zirconia support with ceria reveals the most profound effect for coke resistance of catalyst among modifiers tested in this work. On the other hand, alkaline-earth promoters on Ni surface exhibit better activity as well as stability than those of Ni/ZrO_2 catalyst [19]. Based on the above results, a new catalyst system, Ni-Ca/Ce-ZrO_2 was adopted for high performance reforming catalyst. This catalyst showed strong coke resistance in TPSR profile using a mixture of $CH_4 + CO_2 + He$ (1:1:3), almost comparable with that of Ni/Ce-ZrO_2. It is noted that these TPSR experiments are useful for confirming coke resistance of catalyst in a wide range of reaction temperature and temperature dependence of reforming catalysts on the coke formation.

Accumulation of coke on the nickel catalysts ultimately induces catalyst deactivation due to a subsequent coverage of inactive carbon species onto catalyst surface. Considering the Ni loading effect on coke formation a decrease in Ni loading is needed for lowering the degree of coke formation and obtaining more stable activity during the reaction. The proper combination of modifier and promoter on Ni/ZrO_2 catalyst can circumvent the activity loss even under undiluted reaction conditions or at low Ni loading. Fig. 4 compares methane conversions of Ni/ZrO_2 and modified Ni/ZrO_2 catalysts at 993 K using an equimolar mixture of CH_4 and CO_2 without diluent gas. 5% Ni/ZrO_2 catalyst appears to be sufficiently active (CH_4 conversion, 86% on 1 h stream) at initial period of

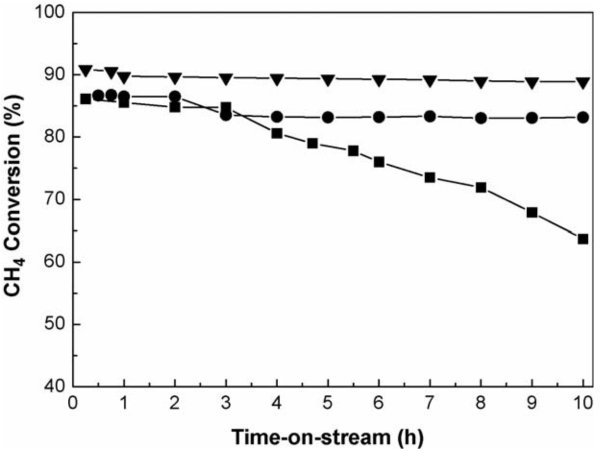

Fig. 4. Catalytic activities of Ni/ZrO_2 and Ni/modified-ZrO_2 catalysts with 5 wt% Ni loading. Ni-Ca/Ce-ZrO_2 *reaction conditions*: $T = 1023$ K, $CH_4/CO_2 = 1/1$, GHSV = 24,000 h^{-1}. *Symbols*: (■) Ni/ZrO_2, (●) Ni/Ce-ZrO_2, (▼) Ni-Ca (1:1)/Ce-ZrO_2.

reaction, but it is subjected to gradual catalyst deactivation due to partial coverage of inactive coke on active sites after 10 h. However, 5% Ni/Ce-ZrO_2 exhibits high activity and catalyst stability as compared with Ni/ZrO_2. Moreover, Ni-Ca/Ce-ZrO_2 reveals slightly but distinctively higher activity than that of Ni/Ce-ZrO_2. Its high activity reaches near equilibrium conversions of CH_4 without catalyst deactivation at 973 K.

For Ni-Ca/Ce-ZrO_2 catalysts, an increase of Ca to Ni molar ratio, Ca/(Ca + Ni), leads to a slight decrease in activity, while the coke resistance of the working catalyst is greatly improved with increasing its ratio (data not shown). Long-run test for the Ni-Ca/Ce-ZrO_2 catalyst with Ca/(Ni + Ca) = 0.75 has been performed at 1023 K for 120 h, as shown in Fig. 5. The catalytic activity gradually increases with time on stream during the first half of 120 h of reaction. High concentration of a calcium promoter on Ni-Ca/Ce-ZrO_2 catalyst hinders reduction of active nickel species as well as prevents coke formation in the CO_2 reforming of methane at the expense of initially rather low activity. However, it is reasonably thought that the catalyst surface is changed to be more active towards the reforming reaction as a result of gradual reduction of nickel during the reaction so that the activity gradually increases. Its activity reaches thermodynamic equilibrium after 60 h of reaction and then it tends to be quite stable towards further reaction. Essentially no significant catalyst deactivation is observed due to coke formation as well as thermal sintering even without the dilution of reactants for such a long reaction time. SEM image of the used catalyst after 120 h of reaction shows that there is no carbon filament on catalyst surface, indicating the excellent resistance on coke formation (Fig. 6). For the Ni-Ca/Ce-ZrO_2 catalyst, CO_2 conversion is always higher than methane conversion due to the formation of water via the reverse water gas shift reaction. In this work, the maximum possible conversions corresponding to thermodynamic equilibrium have been calculated by taking into account of the CO_2 reforming and the water gas shift reactions without consideration of other coking reactions. Interestingly, the steady-state activity of the catalyst after 60 h is quite consistent with equilibrium conversions under our conditions. This means that catalyst performance of the Ni-Ca/Ce-ZrO_2 system can exclude the carbon formation under the given reaction conditions.

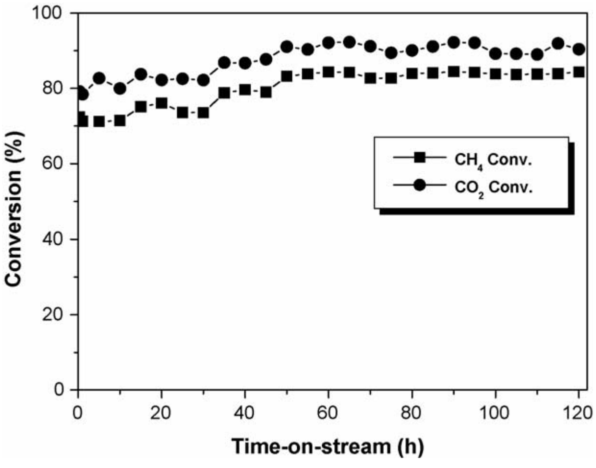

Fig. 5. Change in catalytic activity as a function of reaction time over of Ni-Ca (1:3)/Ce-ZrO_2 catalyst. *Reaction conditions*: $P = 0.1$ MPa, $CH_4/CO_2 = 1/1$, $T = 973$ K, GHSV = 60,000 cm^3/(h g-cat).

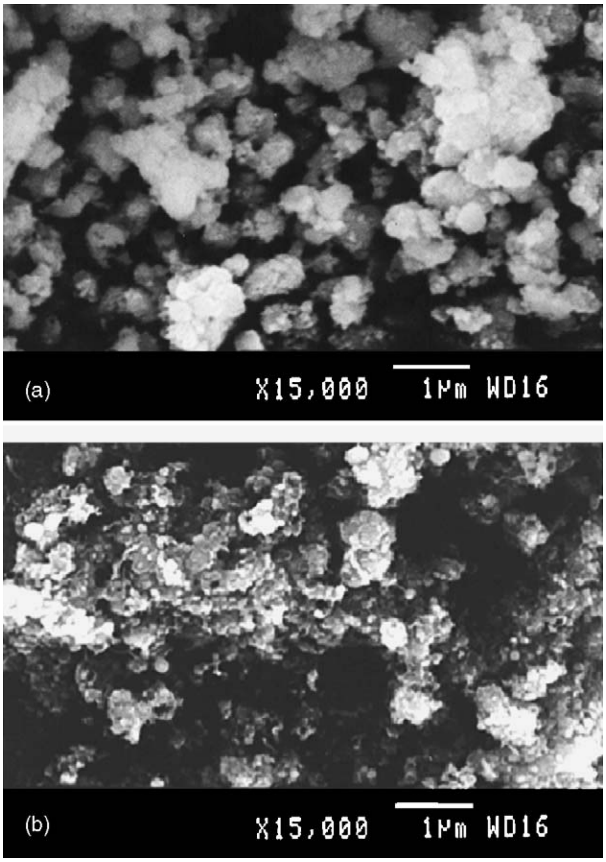

Fig. 6. SEM photographs of Ni-Ca (1:3)/Ce-ZrO_2 catalyst: (a) reduced sample and (b) used sample after the CO_2 reforming at 1023 K for 120 h.

The presence of ceria in this high performance catalyst appears to have beneficial effect on the catalyst performance such as improving the catalyst stability and enhancing concentration of the highly mobile oxygen species [20]. The role of ceria in the catalyst is generally assigned to form a thermally stable solid solution with zirconia and to give high capacity for oxygen storage [21]. This solid solution is identified as a tetragonal phase and shows high affinity for CO_2. High oxygen storage capacity of ceria is based on the ability to store and release reversibly a large amount of oxygen, responding to the reaction conditions. Ceria in the catalyst might be partially reduced under reductive condition like the CO_2 reforming, so that it is considered that the partially reduced ceria site produces active oxygen species by CO_2 dissociation [22], which reacts with the deposited carbon with the help of oxygen spillover from the support onto the Ni sites.

In addition to the role of ceria in Ni/Ce-ZrO_2 catalyst, it is found that the addition of Ca promoter gives pretty good promotional effect on catalyst stability due to its affinity towards CO_2 to form carbonate species and high activity of carbon gasification with CO_2. It has been reported that the presence of alkaline-earth promoters could offer several effects for the physicochemical properties of the reforming Ni catalyst [7,8,23–25], i.e., (a) an increase in electronic properties of the Ni clusters as well as their dimensions, (b) the modification of surface acidity of support, and (c) surface enrichment of CO_2 through the stabilization of surface carbonate species. Likewise, introduction of Ca onto Ni/Ce-ZrO_2 enhanced the formation of carbonate on the catalyst surface, suggesting that CO_2 may be activated through dissociation of the carbonate to release active oxygen species.

4. Conclusions

In this work, Ni-Ca/Ce-ZrO_2 was selected as a high performance catalyst for the CO_2 reforming of methane through simultaneous alteration of the support and Ni surface of Ni/ZrO_2. The reforming catalyst, Ni-Ca/Ce-ZrO_2 reveals high activity as well as high catalyst stability. The high catalyst stability is mainly ascribed to synergy effect of a Ca promoter and a Ce modifier for coke resistance and high temperature catalyst aging.

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