ARTICLE IN PRESS

Catalysis Today xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Origin and reactivity of active and inactive carbon formed during DRM over Ni/$Ce_{0.38}Zr_{0.62}O_{2-\delta}$ studied by transient isotopic techniques

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ARTICLE INFO

Keywords:
Dry reforming of methane
Transient isothermal hydrogenation (TIH) of carbon
SSITKA
DRM mechanism
Ceria-zirconia supported Ni

ABSTRACT

The role of $Ce_{0.38}Zr_{0.62}O_{2-\delta}$ redox support and that of reactants CH_4 and CO_2 in the carbon-path of dry reforming of methane (DRM) at 750 °C over a 3 wt% Ni/$Ce_{0.38}Zr_{0.62}O_{2-\delta}$ catalyst were investigated. In particular, meticulously designed SSITKA and other transient isotopic experiments were conducted in an attempt to provide conclusive answers to important issues related to the improvement of $CeZrO_2$-supported Ni DRM catalyst design, namely: (i) the extent of CO_2 and CH_4 contribution to inactive "carbon" deposition, (ii) the participation and to what extent of support lattice oxygen in the DRM, (iii) differences in the amount ($\mu mol\ g^{-1}$) and reactivity of the "carbon" formed between methane decomposition (CH_4/He) and DRM reactions, (iv) the possible participation of CO_2 and to what extent in the gasification of "carbon" to form CO and (v) the ability of hydrogen gas product towards gasification of the "carbon" formed during DRM. It was shown that a large reservoir of support's lattice oxygen (beyond the surface monolayer) participates in the carbon-path towards the formation of CO and which is considered largely responsible for the relatively low amount (0.3 wt%) of *inactive* "carbon" deposition after 20 h on stream (44.2 vol% CH_4, $CH_4/CO_2 = 1$). It was found that the CH_4 and CO_2 activation routes contribute equally to the formation of inactive "carbon" after DRM at 750 °C (5%CH_4, $CH_4/CO_2 = 1$) and the structural characteristics of "carbon" appear very similar according to temperature-programmed oxidation (TPO). The surface coverage of *active* carbon that truly participates in the formation of CO and which is associated with the CO_2 activation route was found to be very small ($\theta_C = 0.006$ or 0.6%) and remains practically constant for up to 2 h on TOS. On the other hand, a pool of *inactive* reversibly adsorbed CO_2 was measured, which was found to increase up to 2 h of TOS ($\theta_{CO2} = 0.017$ or 1.7%). The latter is suggested to be linked to catalyst's deactivation to a small extent only. It was also shown that the rate of *inactive* "carbon" accumulation seems to be influenced by the reaction of it with the hydrogen gas product.

1. Introduction

Dry (use of carbon dioxide) reforming of methane (DRM) has gathered a growing interest in the field of heterogeneous catalysis related to syngas (CO/H_2) production in recent years [1–3]. The DRM reaction (Eq. (1)) holds much promise for efficiently converting CH_4 and CO_2 into syngas, which can be further used for the synthesis of alkanes, alkenes and oxygenates (platform chemicals of modern industry) via established Fischer-Tropsch [4] or methanol synthesis processes [5]. Methane and CO_2 can be sourced efficiently on a large scale either from fossil and industrial sources (e.g. CO_2-rich natural gas and concentrated CO_2 emissions in ammonia synthesis processes) or by anaerobic digestion of various organic substrates in a somewhat more renewable and sustainable manner (ca. biogas formation).

$$CH_4 + CO_2 \leftrightarrow 2H_2 + 2CO \qquad (1)$$

Much research effort has been devoted towards identifying a suitable catalyst that can perform DRM with high activity, selectivity and long-term stability with TOS. Noble metal nanoparticles (in particular Ru and Rh) dispersed over appropriate metal oxide supports are stable and highly active [1,6,7] but they represent an unlikely solution for large-scale industrial applications due to their prohibitively high price. Supported transition metals, such as Co and especially Ni [3,8,9], represent a viable and economically acceptable alternative. However, supported transition metal catalysts suffer from fast and extensive accumulation of "carbon" over their surface and consequent deactivation or excessive pressure drop across the catalytic bed. Catalyst durability can be improved with efficient suppression of "carbon" deposition, which can be achieved by tuning various design

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http://dx.doi.org/10.1016/j.cattod.2017.03.057
Received 4 November 2016; Received in revised form 11 March 2017; Accepted 27 March 2017

Please cite this article as: Vasiliades, M.A., Catalysis Today (2017), http://dx.doi.org/10.1016/j.cattod.2017.03.057

parameters, such as the use of chemical promoters (e.g. Mg, K or Ca) [10–12] and suitable metal oxide supports having an appropriate concentration of oxygen vacant sites [13–17]. For the latter design parameter, nickel is dispersed over metal oxides possessing high oxygen mobility [13,14,17]. This not only decreases significantly the “carbon” deposition rate but also mitigates sintering of metallic nickel [2]. In particular, ceria-zirconia and ceria-praseodymia solid solutions have been reported to exhibit significant improvements in reducing carbon formation on the catalyst surface, as well as improved catalyst stability compared to non-reducible metal oxides (e.g. γ-Al_2O_3 and SiO_2) [6,13,14,16–21]. Recent research investigations on NiCo/$Ce_{1-x}Zr_xO_{2-\delta}$ catalysts examined in the DRM reaction has notably demonstrated that “carbon” deposition could be prevented over timescales lasting several hundred hours [18].

Fundamental insights into the reaction mechanism of DRM over supported metal catalysts have been recently reviewed [3]. One of the slow elementary reaction steps from the dissociation of adsorbed CH_4-s to the formation of CH_x-s and CH_xO-s intermediates on the metal surface is the rate-limiting step. The nature of active sites for CO_2 chemisorption and dissociation into CO-s and O-s depends on the nature of the metal and metal oxide support [3]. Oxygen vacancies seem to play a vital role for the reduction of CO_2 to CO [22] over reducible metal oxide supports as the present investigation also suggests. Bobin et al. [23] have investigated essential mechanistic steps of DRM over doped ceria-zirconia-supported metals (Ni + Ru, Pt) using transient kinetic methods (TAP, SSITKA). They concluded that an easy dissociation of CO_2 on reduced sites of support followed by a fast oxygen transfer along the surface/domain boundaries to metal sites occurs, where CH_x-s derived from methane react to form CO and H_2. Strongly bound carbonates were found to be spectator species. In a recent work regarding the effect of Ni particle size on the rates of important elementary reaction steps of DRM on Ni/Al_2O_3 [24], it was concluded that the increase of O-s (derived from the dissociation of CO_2) per active site on the Ni surface may enhance oxidation of CH_x-s to CH_xO-s and in turn its decomposition to CO and H_2. Thus, oxidation of CH_x-s than their further dissociation to surface carbon whiskers is considered as a key step for the development of a “carbon”-free DRM catalytic system.

“Carbon” formation is well accepted as the primary reason for the deactivation of dry reforming Ni-based catalytic systems. The quantification of the relative importance of each of the “carbon” formation routes, namely, the Boudouard reaction ($2\ CO \leftrightarrow CO_2 + C$) and that of methane decomposition have recently been investigated in some detail using various transient kinetic and isotopic techniques [13,14,23,25].

In the present work, important fundamental questions regarding the role of $Ce_{0.38}Zr_{0.62}O_{2-\delta}$ support and that of reactants in the carbon-path of dry reforming of methane performed on a 3 wt% Ni/$Ce_{0.38}Zr_{0.62}O_{2-\delta}$ catalyst are addressed directly with meticulously designed SSITKA and other transient isotopic experiments. In particular, the following are addressed:

- What is the extent of CO_2 or CH_4 contribution to the “carbon” deposition pathway?
- Does lattice oxygen participate in the catalytic DRM reaction?
- Does the “carbon” formed via CH_4 decomposition alone differ from that formed during DRM reaction?
- Does CO_2 participate in the gasification of “carbon” to produce CO?
- Are labile oxygen species of the $Ce_{0.38}Zr_{0.62}O_{2-\delta}$ reducible support the only species involved in the gasification of *inactive* “carbon” or does hydrogen possess a similar ability?

2. Experimental

2.1. Catalyst preparation

The $Ce_{0.38}Zr_{0.62}O_{2-\delta}$ mixed metal oxide support (CeO_2:ZrO_2 = 80:20 w/w) was prepared after 1 g of cerium(III) nitrate hexahydrate (Fluka, p.a.) and zirconium(IV) oxynitrate hydrate (Sigma Aldrich, > 99% purity) in the appropriate ratio were dissolved in 1 mL of ultrapure water and mixed with 1 mL of propionic acid (Merck, > 99% purity) and 30 mL of ethylene glycol (Merck, > 99% purity). The solution was transferred to a PTFE-clad autoclave and aged for 200 min at 180 °C. The precipitated solid was separated from the solution by 15-min centrifugation at 9000 rpm, washed with ultrapure water and ethanol and dried overnight in a laboratory drier at 70 °C. After drying, the material was calcined for 4 h at 400 °C in air (heating ramp of 5 °C min^{-1}). The supported nickel (3 wt%) catalyst was prepared after using the homogeneous deposition-precipitation method. During synthesis, 0.318 g of nickel nitrate hexahydrate (Merck, p.a.), 2.1 g of $Ce_{0.38}Zr_{0.62}O_{2-\delta}$ powder and 1.68 g of urea (Merck, p.a.) were dispersed in 100 mL of ultrapure water. One drop of concentrated HNO_3 was then added to decrease the initial pH value below 3. The suspension was heated in a slow and controlled manner from room temperature to 90 °C and maintained under reflux for 22 h. Subsequently, the suspension was filtered, washed with ethanol and water and then dried overnight in air at 70 °C. The resulting solid was then calcined for 4 h at 750 °C in air before storage (3 wt% Ni/$Ce_{0.38}Zr_{0.62}O_{2-\delta}$).

2.2. Catalyst characterization

X-ray powder diffraction spectra were recorded on a PANalytical X'pert PRO diffractometer using Cu Kα radiation (λ = 0.15406 nm). The scanned 2θ range was between 20 and 85° with 0.034° increment and 100 s dwell time at each increment. Unit cell size (α) was calculated according to the relationship: $a = \frac{\lambda}{2} \times \frac{\sqrt{h^2+k^2+l^2}}{\sin\theta}$, which holds for the ceria cubic (or ceria-zirconia pseudo-cubic) system [26]; λ is the X-ray irradiation wavelength and θ the apex position of (*hkl*) reflection with *h*, *k* and *l* being the Miller indices of the (*hkl*) crystal plane. The Scherrer equation (K = 0.9) and the (111) diffraction peak of $Ce_{0.38}Zr_{0.62}O_{2-\delta}$ solid were used for the calculation of its mean primary crystal size. The required FWHM and 2θ values, belonging to the reflection from the (111) crystal plane of the solid support were obtained by fitting the corresponding signal with Pearson VII function in Origin 8.1 software.

The BET specific surface area (SSA, $m^2\ g^{-1}$), total pore volume (V_p, $cm^3\ g^{-1}$) and average pore size (d_p, nm) of the supported Ni catalyst were determined using N_2 adsorption/desorption isotherms measured at −196 °C (Micromeritics, model TriStar II 3020). The sample was degassed before measurements using a SmartPrep degasser (Micromeritics) in N_2 stream at elevated temperature (60 min at 90 °C followed by 240 min at 180 °C).

The amount of reducible Ce ($Ce^{4+} \rightarrow Ce^{3+}$) in the $Ce_{0.38}Zr_{0.62}O_{2-\delta}$ mixed metal oxide was determined by the H_2-TPR technique (AutoChem II 2920, Micromeritics). During the experiment, 100 mg of supported Ni was positioned inside the quartz tube and pretreated in 10 vol% O_2/He at 500 °C for 20 min. After sample cooling to 50 °C, it was degassed in Ar for 30 min. TPR analysis was performed between 50 and 750 °C using 25 mL min^{-1} of 5 vol% H_2/Ar and a heating rate of 10 °C min^{-1}. The extent of CeO_2 reduction in the $Ce_{0.38}Zr_{0.62}O_{2-\delta}$ mixed metal oxide was calculated based on the amount of consumed H_2 during the H_2-TPR experiment after subtracting the equivalent amount corresponding to complete reduction of NiO.

Nickel dispersion was evaluated by using the H_2-TPD technique. The supported Ni catalyst was first reduced in 5 vol% H_2/Ar gas stream for 30 min at 750 °C. The gas flow was then switched to Ar and the temperature was increased to 780 °C and maintained for 20 min to desorb H_2. The sample was then cooled to 30 °C in Ar flow and H_2 pulses were injected to the sample. After pulsing, the sample was degassed in Ar at the same temperature for 20 min, followed by a temperature ramp to 800 °C. The low-temperature H_2 desorption peak was used for nickel dispersion estimation (Ni_s-H stoichiometry of 1:1 was assumed).