Applied Surface Science 416 (2017) 59–68

Contents lists available at ScienceDirect

Applied Surface Science

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

Full Length Article

Insight into the reaction mechanism of CO_2 activation for CH_4 reforming over NiO-MgO: A combination of DRIFTS and DFT study

Shiping Jiang, Yao Lu, Shengping Wang*, Yujun Zhao, Xinbin Ma

Key Laboratory for Green Chemical Technology, School of Chemical Engineering and Technology, Tianjin University, Collaborative Innovation Center of Chemical Science and Engineering, Tianjin 300072, China

ARTICLE INFO

Article history:
Received 16 February 2017
Received in revised form 16 April 2017
Accepted 18 April 2017
Available online 20 April 2017

Keywords:
Dry reforming
CO_2 activation
NiO-MgO
DRIFTS
DFT

ABSTRACT

The interaction mechanisms of dry reforming of methane, especially in the part of CO_2 activation on the reduced NiO-MgO catalyst, have been systematically investigated by in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and density functional theory (DFT) calculations. Based on the results, it is indicated that, what more favorable for CO generation is gaseous CO_2 reaction with deposited C intermediates, namely E-R type mechanism, rather than CO_2 direct dissociation to form CO and atomic O. In addition, with the help of H species, monodentate carbonate, which derives from the adsorbed CO_2 on the MgO surface, can be also activated and hydrogenated dissociation to generate CO.

1. Introduction

In recent decades, the utilization of greenhouse gases has become a more and more important research in governing global warming [1]. Dry (CO_2) reforming of methane (DRM), not only provides a pathway to reduce those natural gases, but fulfills a requirement of the Fischer-Tropsch synthesis, for producing industrially important syngas with a H_2/CO ratio $\leq$1 [2,3]. DRM is a strongly endothermic reaction, so from the point of coke resistance, noble metal catalysts possess excellent performance. However, owing to the limited availability of noble metal catalysts, nickel-based catalysts would be a suitable substitute in the industrial process of methane reforming, because of its outstanding activity, low cost and the abundant supplies [4–7]. Unfortunately, Ni-based catalysts are known to be easily deactivated by CO disproportionation and methane decomposition [8–10], therefore, more and more attention has been paid to the reduced NiO-MgO solid solutions, which significantly contributes to inhibiting carbon deposition [11,12]. It is the surface basicity and the small metal particle size that result in a high stability against metal sintering and a strong coking resistance of this catalyst [13]. Ruckenstein and Hu investigated and reported the prominent property of NiO-MgO solid solution catalysts for DRM [14–17]. They found that NiO-MgO catalysts, which were prepared simply by impregnation, exhibited approximate 100% conversion of CO_2, 95% selectivities to CO and H_2 as well as the noteworthy stability (120 h), within the range of certain NiO content from 4.8–50.0 wt%. Furthermore, Hu [18] proposed that, it was the special process of NiO reduction in NiO-MgO solid solution that contributed to its excellent performance of carbon resistance. They also concluded that NiO was isolated by MgO, which controlled the size of Ni particles in the reaction condition, and this was also the reason why the reduction of NiO was so difficult.

The mechanism of DRM over the noble metal catalysts has been extensively investigated. It is generally recognized that methane dissociates on the metal surface to generate the hydro-carbonate species and H_2 firstly. Nevertheless, activation mechanism of CO_2 is still under debate, depending on the reaction conditions and the nature of the support [5,19]. Generally, CO_2 is activated by formation of carbonates on the basic supports, which has been confirmed by Tsipouriari and Verykios [20]. It was observed that the activation of CO_2 over La_2O_3 was easier than Al_2O_3 through isotopic tracing techniques. This was due to the presence of $La_2O_2CO_3$ on the surface of La_2O_3. In addition, in the former research, CO_2 may react directly with adsorbed CH_x intermediates on the Rh surface to yield CO by an Eley-Rideal type model [21,22]; besides, activation of the CO_2 can also be achieved by the spillover hydrogen species on the γ-Al_2O_3 surface [23,24].

However, to the best of our knowledge, literatures for DRM over NiO-MgO catalyst mainly focus on the activity and stability, while

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* Corresponding author.
E-mail address: spwang@tju.edu.cn (S. Wang).

http://dx.doi.org/10.1016/j.apsusc.2017.04.142
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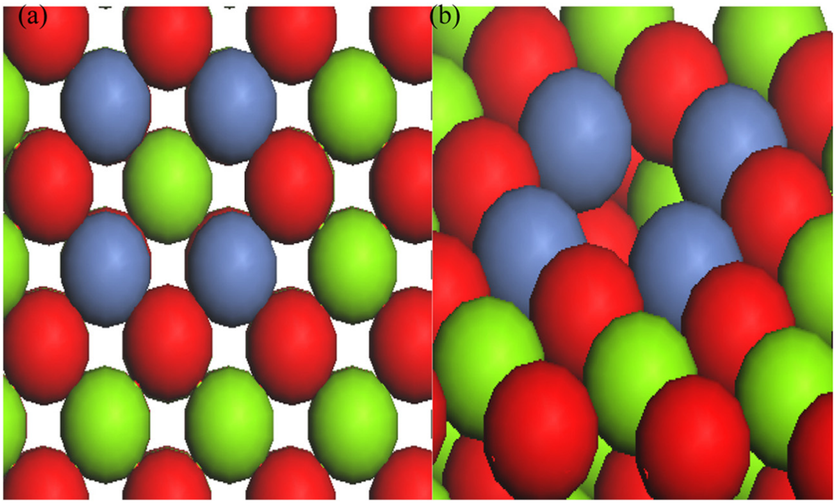

Fig. 1. Top (a) and side (b) views of the Ni_4-MgO(100) solid solution. Red, green, and blue balls represent oxygen, magnesium, and nickel atoms, respectively, and throughout this paper. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the reaction mechanism involved is limited, especially in the part of CO_2 activation. For this reason we focused on studying the elementary steps and main pathway of dry reforming of CH_4 over NiO-MgO catalyst to have a more comprehensive understanding of this system.

Hence, in this paper, in order to look further into the fundamental insight about the mechanism and characteristics of the reduced NiO-MgO catalyst, in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and theoretical calculation have been carried out to have a more sophisticated and detailed description about the mechanism of CO_2 activation. CH_4 dissociation, CO_2 adsorption and hydrogenated dissociation, and the reaction pathways for the interaction of CO_2 were investigated, separately.

2. Experimental and computational details

2.1. Experimental

2.1.1. Catalyst preparation

NiO-MgO catalyst was prepared by conventional incipient impregnation. MgO support, was purchased from Sinopharm Chemical Reagent Co. Ltd. and was calcinated at 500 °C under static air for 5 h before use. $Ni(NO_3)_2{\cdot}6H_2O$ was purchased from Sinopharm Chemical Reagent Co. Ltd. and employed without further purification. The catalyst containing 20 wt% NiO in NiO-MgO catalyst was achieved via using aqueous solution of $Ni(NO_3)_2{\cdot}6H_2O$ impregnated onto the MgO support at room temperature, then the slurry was dried at 110 °C overnight and also calcinated at 500 °C under static air for 5 h.

2.1.2. In situ DRIFTS

Owing to the restriction that the DRIFTS cell could not be heated exceed 500 °C, all of the in situ DRIFT experiments were carried out at 500 °C, using about 50 mg catalyst. Prior to each test, the sample was reduced in 10 vol.% H_2/Ar mixture with a flow rate of 30 mL min^{-1} for 2 h and purged with He (20 mL min^{-1}) for additional 0.5 h at 500 °C. Then a flow of CH_4 (10 mL min^{-1}), CO_2 (10 mL min^{-1}) or the reaction mixture ($CH_4/CO_2 = 1$, F = 20 mL min^{-1}) was introduced into the DRIFTS cell at 500 °C. The spectra of the adsorbed species were obtained by subtraction of the initial spectrum registered after the reduction step. For all the spectra recorded, a 4-scan data accumulation was carried out at a resolution of 4 cm^{-1}.

2.1.3. Catalyst characterization

The structures and crystal phases of the prepared catalysts were examined by X-ray diffraction (XRD) patterns with a Rigaku D/max-2500 X-ray diffractometer from 10° to 90° with a scanning rate of 5°/min. The detailed morphological structures of samples were observed by transmission electron microscope (TEM) with a Tecnai G2 F20 instrument. H_2-temperature programmed reduction (H_2-TPR) was performed to measure the reducibility of the prepared catalysts. In H_2-TPR experiments, 100 mg sample was placed in the U-shaped quartz tube, followed by being heated from room temperature (RT) to 780 °C with a ramp of 10 °C/min in 10 vol.% H_2/Ar mixture (30 mL min^{-1}), and then exposed to H_2 for additional 0.5 h. The consumption of H_2 was recorded by a TCD.

2.1.4. Catalytic performance measurement

The catalytic performance of the catalyst for CO_2 reforming of methane was carried out in a fixed-bed quartz reactor with an inner diameter of 6 nm. The catalyst (50 mg) was reduced in situ under 10 vol.% H_2/Ar mixture with a flow rate of 30 mL min^{-1} at 500 °C for 2 h, then the feed gas was introduced ($CH_4/CO_2 = 1$, F = 20 mL min^{-1}) at 500 °C under 1 atm. Prior to DRIFT test, CO_2 reforming of methane was conducted with a consistent evaluation conditions in a fixed-bed reactor, CH_4 and CO_2 conversions were about 10% and 9%, respectively, so the in situ DRIFT experiments are feasible at 500 °C.

2.2. Computational details

2.2.1. Computational methods

The calculations were computed by using the Cambridge Sequential Total Energy Package (CASTEP) [25] in Materials Studio 6.1, where the generalized gradient approximation (GGA) corrected exchange correlation function was described with the Perdew-Burke-Ernzerhof (PBE) scheme. The cut-off for plane-wave expansion was set up to 340 eV. A 2 × 2 × 1 k-grid sampling was used for Brillouin-zones integration throughout the study. Furthermore, the transition state (TS) was located by using the complete LST/QST method. The convergence for structure optimization and TS search were 1.0×10^{-6} eV/atom for SCF, 1.0×10^{-5} eV/atom for energy, respectively. The chemisorption energy was calculated as follows:

$$Eabs = Ex/sub - Ex - Esub$$