



Tuning the metal-support interaction in catalysts for highly efficient methane dry reforming reaction



Fagen Wang^{a,b,*}, Leilei Xu^b, Jian Zhang^b, Yu Zhao^c, Hui Li^c, He Xing Li^c, Kai Wu^{d,e}, Guo Qin Xu^{a,b,d,*}, Wei Chen^{a,b,d,f,*}

^a Laboratory of Energy and Environment Interface Engineering, National University of Singapore Suzhou Research Institute, 377 Linquan Street, Suzhou 215123, China

^b Department of Chemistry, National University of Singapore, 3 Science Drive 3, 117543, Singapore

^c Department of Chemistry, Shanghai Normal University, Shanghai 200234, PR China

^d Singapore-Peking University Research Centre for a Sustainable Low-Carbon Future, 1CREATE Way, #15-01 CREATE Tower, 138602, Singapore

^e BNLMs, SKLSCUSS, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, PR China

^f Department of Physics, National University of Singapore, 2 Science Drive 3, 117543, Singapore

ARTICLE INFO

Article history:

Received 9 March 2015

Received in revised form 3 June 2015

Accepted 2 July 2015

Available online 9 July 2015

Keywords:

Metal-support interaction

Methane dry reforming

Ir/Ce_{0.9}Pr_{0.1}O₂ catalyst

ABSTRACT

The metal-support interaction of Ir/Ce_{0.9}Pr_{0.1}O₂ catalyst is tuned by adopting different preparation techniques of deposition–precipitation (DP), co-precipitation (CP) and sequential precipitation (SP) to control the locations of Ir, improving catalytic performance in methane dry reforming reaction. Ir/Ce_{0.9}Pr_{0.1}O₂-DP catalyst shows the highest catalytic performance and stability due to the unembedded Ir nanoparticles on catalyst surfaces, followed by Ir/Ce_{0.9}Pr_{0.1}O₂-SP and Ir/Ce_{0.9}Pr_{0.1}O₂-CP catalysts in which Ir species are either partially or fully embedded in Ce-Pr-O mixed oxides. Our results clearly demonstrate that the metal-support interaction plays important roles in controlling the catalyst sintering and carbonaceous deposition.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Although fossil fuels provide more than 80% of global energy resources, their non-sustainable and non-renewable nature may limit the future economic development. The predictable fossil fuels depletion calls for great efforts to explore innovative and more efficient ways in using this natural resource. As one of the largest reserves on Earth, methane can be converted to syngas and C₂ hydrocarbons through steam reforming, partial oxidation and oxidative coupling [1]. Owing to the strong bond strength of C–H (434 kJ/mol), the activation of methane requires high temperature, implying a high energy input [2]. Thus methane utilization and conversion at a relatively low temperature becomes a great challenge and a hot topic for research.

On the other hand, the combustion of fossil fuels produces abundant CO₂, which contributes to global warming. Reducing CO₂

emission has been receiving much attention in recent years. One approach is carbon capture and sequestration, and the other is CO₂ transformation into value-added chemicals [3]. For the latter, dry reforming of methane (DRM) represents one promising way to simultaneously convert greenhouse gases of methane and CO₂ to syngas, which can further be used as feedstock for long chain hydrocarbons production through Fischer–Tropsch synthesis [4].

Great efforts have been devoted to developing catalysts for DRM, mainly consisting of transition and noble metals [1,4–9]. Among these metals, Ni catalyst shows high performance for methane conversion due to its excellent C–H breaking capacity. However, severe coke formation and Ni nanoparticles sintering were found to cause catalyst deactivation [10]. The size of Ni nanoparticles was reported to have a significant effect on the coke formation. Small Ni nanoparticles (<5 nm) were recently synthesized for DRM to minimize coke [11]. Noble metal catalysts exhibit a better performance for DRM reaction compared to Ni catalysts [12,13]. Under the conditions of stoichiometric feedstock and atmospheric pressure, high conversions of methane and CO₂ were achieved over Ru, Rh, and Ir [11]. Although the noble metal catalysts are used for DRM, the supports of catalysts were found to be critical in coke formation. Heavy coke deposition was observed on irreducible oxides [14,15], while much less extent was seen on reducible oxides [9,16].

* Corresponding authors at: Laboratory of Energy and Environment Interface Engineering, National University of Singapore Suzhou Research Institute, 377 Linquan Street, Suzhou 215123, China. Fax: +65 6779 1691.

E-mail addresses: fagen.wang@gmail.com (F. Wang), chmxugq@nus.edu.sg (G.Q. Xu), chmcw@nus.edu.sg (W. Chen).

In literatures [1,9,17], the bi-functional mechanism is well accepted for DRM over catalysts supported on the reducible oxides. Methane is activated on the active metal to form adsorbed H and CH_x intermediates while CO_2 binds on the support to produce carbonates or dissociate into CO and O. The CH_x intermediates react with the carbonates or the dissociated O at the metal-support boundaries, resulting in CO and formate species. The formate is subsequently decomposed to CO and OH group, which further reacts with the CH_x to yield CO and H_2 . From this reaction pathway, it is clear that the properties of active metals and supports, and their synergies are vital for DRM catalytic performances. Noble metals like Pt and Ir were shown to be highly active in methane activation [16,17]. Ceria and ceria-based mixed oxides are excellent support candidates for CO_2 activation through oxygen vacancies. These supports like CeO_2 , $\text{Ce}_{1-x}\text{Zr}_x\text{O}_{2-\delta}$ and $\text{Ce}_{1-x}\text{Pr}_x\text{O}_{2-\delta}$ have abilities to store and release oxygen (oxygen storage capacity, OSC) [18–20], which is very beneficial for coke gasification [20]. The interaction between metal and ceria not only promotes OSC to further coke elimination [10], and also strengthens catalyst structure to mitigate sintering of active metal [21]. Therefore, the coupling of noble metals with ceria-based mixed oxides may allow us to design promising catalysts for DRM [20,22,23].

In our previous study, it was found that Ir/ $\text{Ce}_{0.9}\text{Pr}_{0.1}\text{O}_2$ catalyst greatly enhanced the activity and stability for high temperature ethanol steam reforming reaction, which was contributed from the doping of PrO_x promoted the redox property of ceria by creating more surface oxygen vacancies and improved the thermal stability of ceria by partially avoiding sintering. Considering the high reaction temperature and the similar causes for catalysts deactivation in ethanol steam reforming and DRM reactions, Ir/ $\text{Ce}_{0.9}\text{Pr}_{0.1}\text{O}_2$ catalysts were synthesized to develop highly efficient catalysts for DRM reaction in this work. It is wished that the enhanced OSC would reduce coke deposition and the promoted metal-support interaction might prevent active metal sintering. The metal-support interaction was tuned by different preparation methods to position Ir species at different locations in the catalysts. It was revealed that the highest conversions of methane and carbon dioxide reached 60% and 75%, respectively, at a space velocity of 18,000 mL/(g h) over the catalyst prepared by deposition precipitation. The performance was maintained for at least 200 h at 1023 K. No obvious coke deposits and Ir sintering can be found on the used samples.

2. Experimental

2.1. Catalysts preparation

Ir/ $\text{Ce}_{0.9}\text{Pr}_{0.1}\text{O}_2$ -DP catalyst (noted as Ir/CePr-DP) was synthesized by deposition-precipitation (DP). A homogeneous mixture of $\text{CO}(\text{NH}_2)_2$ (2.08 mol/L), $\text{Ce}(\text{NO}_3)_3$ (0.040 mol/L) and $\text{Pr}(\text{NO}_3)_3$ (0.0044 mol/L) was heated to 363 K and stirred for 5 h. After filtration and washing, the precipitates were dried at 373 K overnight and calcined at 673 K for 4 h to form $\text{Ce}_{0.9}\text{Pr}_{0.1}\text{O}_2$ -DP support. This support (1.0 g) was mixed with H_2IrCl_6 solution (0.0078 mol/L, 14 mL) in 400 mL water at 338 K, followed by dropping Na_2CO_3 (aq., 0.20 mol/L, 100 mL). After filtration and washing, the powders were dried at 373 K overnight and calcined at 1023 K for 4 h.

Ir/ $\text{Ce}_{0.9}\text{Pr}_{0.1}\text{O}_2$ -CP catalyst (noted as Ir/CePr-CP) was prepared by co-precipitation (CP). A mixture of $\text{Ce}(\text{NO}_3)_3$ (0.040 mol/L), $\text{Pr}(\text{NO}_3)_3$ (0.044 mol/L) and H_2IrCl_6 (8.54×10^{-4} mol/L) was gradually added to Na_2CO_3 (aq., 0.2 mol/L, 300 mL) at 338 K under vigorous stirring. After aged for 3 h, the precipitate was filtrated and washed. The obtained powders were dried at 373 K overnight and calcined at 1023 K for 4 h. $\text{Ce}_{0.9}\text{Pr}_{0.1}\text{O}_2$ -CP support was prepared in the same way without H_2IrCl_6 .

Ir/ $\text{Ce}_{0.9}\text{Pr}_{0.1}\text{O}_2$ -SP catalyst (noted as Ir/CePr-SP) was synthesized by sequential precipitation (SP). First, Na_2CO_3 (aq., 0.2 mol/L,

100 mL) was dropped to a mixture of $\text{Ce}(\text{NO}_3)_3$ (0.040 mol/L) and $\text{Pr}(\text{NO}_3)_3$ (0.0044 mol/L) at 338 K. Then, H_2IrCl_6 (0.0078 mol/L, 44 mL) was added and precipitated. After the suspension was filtrated, the obtained solid was dried at 373 K overnight and calcined at 1023 K for 4 h. $\text{Ce}_{0.9}\text{Pr}_{0.1}\text{O}_2$ -SP support preparation was followed the same method without H_2IrCl_6 .

2.2. Catalyst characterizations

The actual Ir loadings were analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES). Nitrogen adsorption-desorption isotherms were measured using a surface area and pore size analyzer (NOVA 2200e) at 77 K. Before the measurement, samples were degassed at 573 K for 3 h. The surface area was obtained with a multipoint BET analysis of the nitrogen adsorption isotherm.

X-ray diffraction (XRD) patterns of the samples were recorded using a PANalytical Empyrean DY 708 diffractometer with Cu radiation ($\text{Cu K}\alpha = 0.15406$ nm). The mean crystalline size was calculated based on the Scherrer equation.

Transmission electron microscopy (TEM) images were taken using JEOL 2010 operated at 200 kV. Specimens were prepared by ultrasonically suspending samples in ethanol. Droplets of the suspension were deposited on a thin carbon film supported on a standard copper grid.

X-ray photoelectron spectra (XPS) were recorded with an AMI-CUS spectrometer using Mg K α radiation. The charging effect was corrected by referencing the binding energy of C 1s at 284.6 eV. The spectra curves of Pr and Ir species were fitted using a Gaussian procedure due to the weak intensities and low contents, while raw data were used for the spectra of O, Ce and C.

Hydrogen temperature programmed reduction (H_2 -TPR) of fresh samples was conducted in a U-shaped reactor connected to a mass spectrometer (PrismaPlus). 100 mg samples were loaded and pretreated under flowing He (50 mL/min) at 573 K for 1 h. After cooling down at room temperature, a mixture of 10% H_2 /He (50 mL/min) was introduced through the samples to reach a steady state. The temperature was then increased to 1023 K at a rate of 5 K/min and the signal of H_2 ($m/e = 2$) was monitored by the mass spectrometer.

CO_2 temperature programmed desorption (CO_2 -TPD) was performed in the U-shaped reactor. The samples were pretreated by 10% H_2 /He (20 mL/min) at 673 K for 30 min. 5% CO_2 /He (20 mL/min) was then passed through at room temperature for 30 min. After purged by He (20 mL/min), the samples were heated to 1023 K with a rate of 5 K/min and the signal of CO_2 ($m/e = 44$) was monitored by the mass spectrometer (PrismaPlus).

CH_4 temperature programmed surface reaction (CH_4 -TPSR) was carried out in the U-type reactor. Fresh samples were reduced by 10% H_2 /He (20 mL/min) at 673 K for 30 min. After temperature was cooled down, 5% CH_4 /He (20 mL/min) was introduced to a stable state. Then the samples were heated to 1073 K at a rate of 5 K/min. The signals of CO_2 ($m/e = 44$), H_2O ($m/e = 18$), CH_4 ($m/e = 15$), CO ($m/e = 28$) and H_2 ($m/e = 2$) were measured.

$\text{CH}_4 + \text{CO}_2$ temperature programmed surface reaction (TPSR of $\text{CH}_4 + \text{CO}_2$) was run in the U-type reactor. Firstly, samples were heated to 673 K for reduction 30 min, and were treated by 5% CO_2 /He (20 mL/min) at room temperature for 30 min. Then, 5% CH_4 /He (20 mL/min) was switched to the samples. After CO_2 was purged, temperature was increased to 1073 K at 5 K/min. The signals of CO_2 ($m/e = 44$), H_2O ($m/e = 18$), CH_4 ($m/e = 15$), CO ($m/e = 28$) and H_2 ($m/e = 2$) were recorded.

Temperature programmed oxidation (TPO) of used catalysts was conducted in the U-type reactor. The used samples were initially heated to 573 K for 30 min under flowing He to eliminate possible contaminants. The samples were then heated from room

Download English Version:

<https://daneshyari.com/en/article/45269>

Download Persian Version:

<https://daneshyari.com/article/45269>

[Daneshyari.com](https://daneshyari.com)