Journal of Energy Chemistry xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Journal of Energy Chemistry

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

http://www.journals.elsevier.com/journal-of-energy-chemistry/

Core-shell structured Ru-Ni@SiO_2: Active for partial oxidation of methane with tunable H_2/CO ratio

Q1 Yixuan Dou[a], Yijun Pang[a], Lingli Gu[a], Yifan Ding[a], Wu Jiang[a], Xinzhen Feng[a], Weijie Ji[a,*], Chak-Tong Au[b]

[a] Key Laboratory of Mesoscopic Chemistry, MOE, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210023, Jiangsu, China
[b] Department of Chemistry, Hong Kong Baptist University, Kowloon Tong, Hong Kong, China

ARTICLE INFO

Article history:
Received 23 April 2017
Revised 21 June 2017
Accepted 12 July 2017
Available online xxx

Keywords:
Ruthenium
Nicolet
Bimetallic
Core-shell structure
Partial oxidation of methane

ABSTRACT

This study demonstrated that a Ru-Ni bimetallic core-shell catalyst (0.6%Ru-Ni)@SiO_2 with a proper surface Ru concentration is superior in achieving better catalytic activity and tunable H_2/CO ratio at a comparatively lower reaction temperature (700 °C). Compared to the impregnation method, the hydrothermal approach leads to a highly uniform Ru distribution throughout the core particles. Uniform Ru distribution would result in a proper surface Ru concentration as well as more direct Ru-Ni interaction, accounting for better catalyst performance. Enriched surface Ru species hinders surface carbon deposition, but also declines overall activity and H_2/CO ratio, meanwhile likely enhances Ni oxidation to certain degree under the applied reaction conditions. Over the current (*m*%Ru-Ni)@SiO_2 catalyst, the formation of fibrous carbon species is suppressed, which accounts for good stability of catalyst within a TOS of 10 h.

1. Introduction

Energy crisis is still a vital problem worldwide [1,2], methane is one of the most important fossil energies due to its abundant reserves, and can be produced from decay or organic fermentation [3]. Several routes have been employed to convert methane to value-added chemicals [4–6]. Among the most widely studied technologies, CH_4 conversion to syngas (mixture of H_2 and CO) involves reforming and partial oxidation such as steam (H_2O) reforming (SRM), dry (CO_2) reforming (DRM), and partial oxidation of methane (POM) [7–9]. The POM usually has a H_2/CO ratio close to 2 favorable for Fischer–Tropsch synthesis and methanol synthesis [10]. In addition, SRM and DRM are highly endothermic reactions, while POM is mildly exothermic and therefore an energy-saving reaction. POM also undergoes rapidly and requires a smaller reactor [11,12].

Two kinds of catalysts are wildly used in POM, one is the noble metal-based catalyst (Rh, Ru, Ir, Pt, or Pd) [13,14], and the other is the first-row transition metal-based catalyst (Ni, Co, and Cu) [15,16]. The latter kind is known to deactivate quickly because of serious carbon deposition, while the former kind is more active and less sensitive to coke formation in POM, but unfortunately too expensive to be widely used in practice [17]. Nevertheless, bimetallic catalysts could offer an optimal solution, where catalysts mainly comprise base metal with a small fraction of noble metal, showing promising performance in both activity and durability [18]. It was reported that addition of Ru to the Ni-based catalysts showed enhanced activity and improved coke deposition in DRM and/or SRM [19,20]. However, catalyst deactivation arising from sintering of metal constituent together with quick carbon deposition is the major issues that limit life of metal particles. Many approaches have been tried to address the issues. Applying mesoporous materials with which the fine metal particles are localized in the mesopores is a common way for catalyst design [21]. On the other hand, the core-shell structured catalysts presented excellent performances in high temperature reactions, for instances, Ni@SiO_2 catalyst in SRM [22] and POM [23], and Fe@SiO_2 in ammonia decomposition [24]. Due to shell isolation and core-shell interaction, the core metal particles are not only sintering-resistant but anti-coking as well.

Our previous investigations indicated that the core-shell structured Fe, Co, and Ni catalysts are active and durable for NH_3 decomposition and POM [25–27], for example, the bimetallic Co–Ni nanoparticles showed better catalytic performance than the monometallic Ni in POM. Therefore, in the present study, we developed the bimetallic Ru-Ni core-shell structured catalysts with a tunable Ru/Ni ratio and different Ru addition. The obtained materials were applied for POM, and showed superior performance

---

[*] Corresponding author.
E-mail addresses: jiwjnju@yahoo.com, jiwj@nju.edu.cn (W. Ji).

http://dx.doi.org/10.1016/j.jechem.2017.07.011
2095-4956/© 2017 Published by Elsevier B.V. and Science Press.

Please cite this article as: Y. Dou et al., Core-shell structured Ru-Ni@SiO_2: Active for partial oxidation of methane with tunable H_2/CO ratio, Journal of Energy Chemistry (2017), http://dx.doi.org/10.1016/j.jechem.2017.07.011

through optimization of catalyst constitution/structure as well as operating parameters.

2. Experimental

2.1. Catalyst preparation

2.1.1. Precursor of (m%Ru-Ni)O_x

Certain amount of $RuCl_3$ solution ($0.015\,mol\,L^{-1}$) was mixed with deionized water, according to different Ru/Ni molar ratios. Cetyl trimithyl ammonium bromide (CTAB) of 0.05 g, polyvinylpyrrolidone (PVP) of 0.28 g, and $Ni(NO_3)_2{\cdot}6H_2O$ of 1.0 g were added into the above mixture and the resulting solution was stirred for 1 h at room temperature (RT). And then urea of 0.4 g was added under stirring. The solution was transferred into a Teflon-lined autoclave (100 mL) and subjected to a hydrothermal treatment at 120 °C for 48 h. When the autoclave was cooled down to RT, the precipitate was collected by centrifugation, washed with deionized water three times and ethanol one time, dried at 80 °C for 4 h and calcined in a static air at 500 °C for 3 h. The Ru/Ni molar ratio in the precursor of (*m*%Ru-Ni)O_x was measured to be 0.6% and 2% by ICP-AES.

2.1.2. Precursor of NiO

The preparation procedures were similar to those adopted in preparing the precursor of (*m*%Ru-Ni)O_x, except that neither $RuCl_3$ solution nor CTAB was added. Urea of 1.6 g was used. The hydrothermal temperature and time was changed to 160 °C and 18 h.

2.1.3. Precursor of (m%Ru/Ni)O_x

NiO nanoparticles of 0.36 g was added into anhydrous ethanol of 50 mL. The suspension was sonicated for 1 h, and then certain amount of $RuCl_3$ aqueous solution ($0.015\,mol\,L^{-1}$) was added into the suspension under sonication for another 15 min. The resulting mixture was stirred at RT for 11 h, and mildly evaporated at 80 °C in a rotary evaporator. The solids were calcined in a static air at 500 °C for 3 h.

2.1.4. Encapsulation of oxide precursor

A certain amount of oxide precursor [NiO, (*m*%Ru-Ni)O_x, or (*m*%Ru/Ni)O_x] was dispersed into anhydrous ethanol of 50 mL, and the suspension was sonicated for 30 min. Then concentrated ammonia solution (25–28 wt%) of 5 mL was added under sonication for another 30 min. TEOS of 50 µL was introduced upon 60-min sonication. The obtained material was centrifuged and washed with deionized water, dried at 80 °C for 6 h and calcined in a static air at 500 °C for 3 h.

The catalyst names have been unified throughout the text. Before hydrogen reduction, the precursors derived through hydrothermal and impregnation routes are denoted as (*m*%Ru-Ni)O_x@SiO_2 and (*m*%Ru/Ni)O_x@SiO_2 respectively; after hydrogen reduction, the corresponding fresh catalysts are denoted as (*m*%Ru-Ni)@SiO_2 and (*m*%Ru/Ni)@SiO_2 respectively. In both cases, *m*% represents the molar ratio of Ru to Ni in percentage.

2.2. Catalyst characterization

Transmission electron microscopy (TEM) images were taken on a JEOL JEM-1010 transmission electron microscope operated at 100 kV. The powder XRD patterns of samples were obtained by using a diffractometer (D8 Advance) operated at 40 kV and 40 mA with Co $K\alpha$ radiation ($\lambda = 1.62083$ nm) in 2θ range of 10°–110° at scan speed of $0.4088\,{}^{\circ}\,s^{-1}$ with a step size of 0.0167°. H_2-temperature-programmed reduction (H_2-TPR) was carried out on an instrument equipped with a thermal conductivity detector (TCD). Sample (ca. 15 mg) was pretreated at 200 °C in an Ar flow ($45\,mL\,min^{-1}$) for 2 h, followed by cooling down to 50 °C. Subsequently, the sample was switched to a reducing gas comprising 5 vol% H_2/Ar ($40\,mL\,min^{-1}$), and temperature was increased at a rate of $10\,{}^{\circ}C\,min^{-1}$ from 50 °C to 550 °C. Temperature-programmed oxidation (TPO) was performed using an on-line mass spectrometer (PrismaPlus TM QMG 220) to monitor the off-gas. Approximately 20 mg of spent catalyst was heated in a pure O_2 flow ($25\,mL\,min^{-1}$) from RT to 800 °C at a heating rate of $10\,{}^{\circ}C\,min^{-1}$. Under the condition applied (oxygen-rich environment), only CO_2 signal was detected. X-ray photoelectron spectroscopy (XPS) analysis was performed on a PHI 5000 Versaprobe system using monochromatic Al $K\alpha$ radiation (1486.6 eV). The sample was outgassed overnight at RT in an ultrahigh-vacuum chamber ($<5 \times 10^{-7}$ Pa). All binding energies were reference to the C 1*s* peak at 284.6 eV. BET surface areas and pore structures were measured using a NOVA-2020 material physical structure determinator. The Ru/Ni molar ratio of catalyst was measured over an ICP-Optima 5300DV series.

2.3. Activity evaluation

Catalyst of 50 mg (40–80 mesh) mixed with quartz chips of 0.5 g (20–40 mesh) was placed into a fixed-bed quartz tube reactor (length = 45 mm, external diameter = 8 mm, internal diameter = 4 mm) and evaluated for POM operated at atmospheric pressure. Before reaction, sample was pre-reduced in a flow of 5 vol% H_2-Ar ($50\,mL\,min^{-1}$) at 500 °C for 3 h and then cooled down to RT. After that the sample was switched to a reaction feed $CH_4/O_2/N_2 = 2/1/3$ (v/v/v) at a flow rate of $60\,mL\,min^{-1}$, giving a corresponding gas hourly space velocity (GHSV) of $72{,}000\,cm^3\,g^{-1}\,h^{-1}$. The off-gas was dehydrated by a cold-trap of concentrated H_2SO_4 and analyzed by an on-line GC (Agilent 6890N) equipped with a TCD and a packed TDX-01 column. A temperature-programmed analysis was employed: initial temperature was set to be 40 °C and kept at this temperature for 5 min, then the temperature was increased to 140 °C at a rate of $5\,{}^{\circ}C\,min^{-1}$ and kept at this temperature for 5 min.

3. Result and discussion

3.1. TEM

Fig. 1 shows the TEM images and core size distribution of (*m*%Ru-Ni)O_x@SiO_2 catalysts with different Ru/Ni molar ratios. Through statistical analysis of the randomly distributed 50–150 core particles, (0.1%Ru-Ni)O_x@SiO_2, (0.6%Ru-Ni)O_x@SiO_2, and (2%Ru-Ni)O_x@SiO_2 show an averaged core particle size of 15.9 ± 4.1 nm, 14.6 ± 3.0 nm, and 15.0 ± 2.5 nm, respectively. Change in Ru content has little influence on particle size of (*m*%Ru-Ni)O_x@SiO_2. However, the tendency of multi-particle encapsulation becomes obvious with increasing Ru content in the core particles, simply because RuO_2 has a higher potential of aggregation than NiO.

The multi-particle encapsulation could cause core particle emergence within a large microcapsule during the high-temperature reaction, and this is evident for the spent (2%Ru-Ni)@SiO_2 catalyst (Fig. 2). The mean core particle size in the used (2%Ru-Ni)@SiO_2 was increased to 23.5 ± 6.2 nm. Nevertheless, the presence of SiO_2 shell effectively suppresses the degree of core particle sintering, since if there is no SiO_2 shell protection, significant aggregation of naked metal nanoparticles would occur at a typical temperature required for POM.

Previous studies [26,28] indicated that without surfactant addition in SiO_2 encapsulation the micro-porosity (<2 nm) was mostly generated in the silica shell upon thermo-activation, and the resulting catalysts are highly active for NH_3 decomposition and POM. It was revealed that a small fraction of meso-porosity can also be

Please cite this article as: Y. Dou et al., Core-shell structured Ru-Ni@SiO_2: Active for partial oxidation of methane with tunable H_2/CO ratio, Journal of Energy Chemistry (2017), http://dx.doi.org/10.1016/j.jechem.2017.07.011