

View Article Online View Journal

# **RSC Advances**

This article can be cited before page numbers have been issued, to do this please use: Q. Liu, F. Gu, Z. Zhong, G. Xu and F. Su, *RSC Adv.*, 2016, DOI: 10.1039/C5RA28057E.



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This Accepted Manuscript will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the <u>Ethical guidelines</u> still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



www.rsc.org/advances

# Anti-sintering ZrO<sub>2</sub>-modified Ni/a-Al<sub>2</sub>O<sub>3</sub> catalyst for CO methanation

Qing Liu<sup>a</sup>, Fangna Gu<sup>a,\*</sup>, Ziyi Zhong<sup>b</sup>, Guangwen Xu<sup>a</sup>, Fabing Su<sup>a,\*</sup>

<sup>a</sup> State Key Laboratory of Multiphase Complex Systems, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China

<sup>b</sup> Institute of Chemical Engineering and Sciences, A\*star, 1 Pesek Road, Jurong Island 627833,

Singapore

\*Corresponding author. Tel.: +86-10-82544850; Fax: +86-10-82544851. *E-mail address:* <u>fngu@ipe.ac.cn</u> (F. Gu); <u>fbsu@ipe.ac.cn</u> (F. Su).

# Abstract

To obviously reduce sintering behavior of Ni particles in Ni/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalysts during CO methanation reaction, ZrO<sub>2</sub> was deposited onto the Ni/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalyst surface by a modified impregnation method. It was observed that the ZrO<sub>2</sub>-modified catalyst with proper amount of ZrO<sub>2</sub> showed enhanced catalytic activity due to the increased H<sub>2</sub> uptake and Ni dispersion. During the 103h-lifetime test, the ZrO<sub>2</sub>-modified catalyst exhibited higher stability and anti-sintering performance than the unmodified one, because the partial coverage of ZrO<sub>2</sub> particles could effectively prevent Ni particles from sintering during the reaction at high temperatures. The findings obtained in this study should be conducive to the design and development of supported metal catalysts for high temperature reactions with enhanced the stability.

# 1. Introduction

In the last several decades, CO methanation reaction from syngas (CO +  $3H_2 \rightarrow CH_4 + H_2O$ ) has attracted intensive attention from both academia and industry.<sup>1,2</sup> In this reaction, the syngas can be obtained via gasification reaction of coal or biomass, and Ni/y-Al<sub>2</sub>O<sub>3</sub> catalysts are often employed due to their relatively high activity and low cost.<sup>3,4</sup> However, these catalysts often suffer from Ni sintering during the methanation process because of its strongly exothermic nature<sup>5,6</sup> as well as the presence of water vapor, which is one of the byproducts of methanation and can accelerate the Ni particle sintering.<sup>7,8</sup> In addition, the surface acidity of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support easily causes coking formation on the catalyst Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts, and the phase transformation of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> during the high temperature reaction process can lead to the fast deactivation due to collapse of the pore structure and burying of the Ni particles. Therefore, considering the above drawbacks of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support, some researchers paid their attentions to more stable, acid-free and inert  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> support.<sup>9,10</sup> Although, partial success has been achieved, the Ni sintering of Ni/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalysts seems to be more serious due to the low surface area of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> support and the weak interaction between NiO species and the support.<sup>9,10</sup> Hence, the anti-sintering property of Ni/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalyst should be further improved.

Various approaches have been employed to stabilize metal particles, e.g., by adding inorganic oxide via chemical vapor deposition, atomic layer deposition, encapsulating with dendrimer, grafting, or formation of the well-defined cavities or channels, such as core–shell and ordered mesoporous structures.<sup>11-14</sup> However, there are still some drawbacks for these methods, such as the poor control on the shell thickness, the need of special equipment as well as the associated high cost, limiting their wide and large-scale application. ZrO<sub>2</sub> is an inorganic oxide having high thermal stability as well as chemical inertness, and having been reported as the efficient promoter<sup>15-17</sup> or

3

**RSC Advances Accepted Manuscript** 

support<sup>18,19</sup> in the catalysts for methanation reaction. However, the sintering-resistance of these catalysts is usually far from ideal except for the ones with ordered mesoporous structure.<sup>17,18</sup> Therefore, improving the anti-sintering property of the catalysts prepared by the conventional methods is in demand.

Recently, several reports showed that the construction of an oxide-on-metal surface structure can enhance both the catalytic activity and stability of metal catalysts dramatically, because they not only combine the function of the metal nanoparticles, but also bring unique collective and synergetic catalytic properties compared to the uncovered metal catalysts.<sup>20-22</sup> Following the previous work on the catalysts with specific oxide-on-metal structures in our group for CO methanation,<sup>14,15</sup> the ZrO<sub>2</sub>-modified Ni/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalysts were prepared by a modified impregnation method in this work. To the best of our knowledge, there is no report in the literature for such route for CO methanation reaction. In addition, in order to obtain a deep insight into the interrelationship among the structure, activity and stability, we investigated the catalytic performances of the catalysts and characterized their structures. It is found that the ZrO<sub>2</sub> nanoparticles can distribute over the surface of the catalyst and even partially cover some Ni particles, which can restrain the growth of the Ni particles and result in enhanced stability in the lifetime test.

#### 2. Experimental

## 2.1. Catalyst preparation

Nickel (II) nitrate hexahydrate (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) and ethanol were analytical grade (Sinopharm Chemical Reagent Co. Ltd., China). Zirconium *n*-butoxide (Zr(OBu)<sub>4</sub>) (purity 80 wt% in n-butanol) was used without further treatment (Sigma-Aldrich). The  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> was obtained by calcination of the commercial  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (purity >95% GongYiHuaYu Alumina Co. Ltd., China, 300 m<sup>2</sup> g<sup>-1</sup>) at

4

# 2.1.1. Preparation of NiO/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalyst

The NiO/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalyst was prepared by the wet impregnation method according to our previous report.<sup>14</sup> Typically, 0.39 g Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O was dissolved in 20 mL deionized water, followed with addition of 1.00 g of the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> powder, then the slurry was kept under vigorous stirring at room temperature overnight. After evaporation of the liquid at 80 °C, the sample was calcined at 400 °C for 2 h in air. The obtained NiO/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalyst was denoted as 10NA with a NiO loading of 10 wt%.

## 2.1.2. Preparation of $ZrO_2$ -modified NiO/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalyst

 $ZrO_2$ -modified NiO/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalyst was prepared by the modified impregnation method after the above procedure. Typically, for each cycle, 1.00 g 10NA was immersed in a Zr(OBu)<sub>4</sub> ethanol solution (5 mL 0.05 M) for 1 min in a sand core funnel to allow adsorption of Zr(OBu)<sub>4</sub> onto the 10NA. After filtrated and washed twice with anhydrous ethanol, 5 mL 0.1 M ethanol aqueous solution was added sequentially within 1 min to initiate the reaction of the pre-adsorbed Zr(OBu)<sub>4</sub> with H<sub>2</sub>O to form the desired ZrO<sub>2</sub> precursor. The substrates were then dried at 100 °C in air. Such a modification cycle (Scheme 1) could be repeated for several times to achieve the desired amount of ZrO<sub>2</sub>. The obtained samples were finally calcined at 400 °C for 2 h and denoted as 10NA@ZrO<sub>2</sub>-x (x = 5, 10 and 15), where x represents the cycle times. In addition, the bulk ZrO<sub>2</sub> was obtained through the calcination of the hydrolyzed Zr(OBu)<sub>4</sub> under the same calcination condition as 10NA.



Scheme 1. Illustration of the one impregnation cycle of the ZrO<sub>2</sub>-modified Ni/Al<sub>2</sub>O<sub>3</sub> catalyst.

# 2.2. Catalysts characterization

Published on 15 February 2016. Downloaded by New York University on 16/02/2016 23:24:17.

 $N_2$  adsorption was measured at -196 °C (Quantachrome surface area & pore size analyzer NOVA 3200e) and degassed at 200 °C for 4 h under vacuum. The specific surface area was determined according to the Brunauer-Emmett-Teller (BET) method. PANalytical X'Pert PRO MPD was used to record the X-ray diffraction (XRD) patterns with the Cu K $\alpha$  radiation ( $\lambda = 1.5418$  Å) at 40 kV and 40 mA. Quantachrome chemBET pulsar TPR/TPD was used to record both H<sub>2</sub> temperature-programmed reduction  $(H_2$ -TPR) and  $H_2$  temperature-programmed desorption (H<sub>2</sub>-TPD) profiles. Similar with our previous report,  $^{13}$  0.05 g sample was used in the H<sub>2</sub>-TPR measurement. After being heated from room temperature to 200 °C at 10 °C min<sup>-1</sup> and maintained for 1 h in a He flow, the sample was cooled to room temperature and followed by heating to 1000 °C at 10 °C min<sup>-1</sup> in the 10 vol % H<sub>2</sub>/Ar flow (30 mL min<sup>-1</sup>). In the H<sub>2</sub>-TPD measurement, 0.2 g catalyst was used and reduced in situ in the H<sub>2</sub>/Ar flow at 650 °C for 2 h, then the sample was cooled to room temperature and saturated with  $H_2$  for 1 h. After being flushing with Ar for 1 h, the sample was heated to 600 °C at 10 °C min<sup>-1</sup> in the Ar flow (30 mL min<sup>-1</sup>). The signal was detected using a thermal conductivity detector (TCD). The dispersion of Ni was calculated using the method described in our previous work.<sup>13</sup> The morphology of the samples was observed by scanning electron microscopy (SEM) equipped with energy-dispersive X-ray spectroscopy (EDS) (JSM-6700F, JEOL, Japan) and transmission electron microscopy (TEM) (JEM-2010F, JEOL,

#### **RSC Advances**

Japan) under a working voltage of 200 kV. The surface chemical composition of the reduced catalysts was measured using X-ray photoelectron spectroscopy (XPS) test conducted on a VG ESCALAB 250 spectrometer (Thermo Electron, U.K.) with a non-monochromatized Al K $\alpha$  X-Ray source (1486 eV). In addition, the exact composition of the catalysts was determined by using a Thermo Scientific iCAP 6300 inductively coupled plasma atomic emission spectrometry (ICP-AES). Moreover, thermogravimetric (TG) analysis was conducted on a Seiko Instruments EXSTAR TG/DTA 6300 in the temperature range of room temperature to 1000 °C (10 °C min<sup>-1</sup>) in air.

# 2.3. Catalytic measurement

The catalysts (20–40 mesh) were reduced at 650 °C in pure H<sub>2</sub> (100 mL min<sup>-1</sup>) for 2 h and then cooled to the starting reaction temperature in H<sub>2</sub> in a fixed-bed quartz tubular reactor (10 mm I.D.) at 0.1 MPa. Then the mixed H<sub>2</sub> and CO as well as N<sub>2</sub> (as an internal standard) (H<sub>2</sub>/CO/N<sub>2</sub> = 3/1/1) were introduced into the reactor at a weight hourly space velocity (WHSV) of 30000 mL g<sup>-1</sup> h<sup>-1</sup>. The inlet and outlet gases were analyzed on line by Micro GC 3000A (Agilent Technologies) with a TCD detector. The lifetime test of CO methanation was performed at 500 °C, 0.1 MPa, 60000 mL g<sup>-1</sup> h<sup>-1</sup>. Hydrothermal treatment for catalysts aging was also carried out in a fixed bed quartz tube reactor under 0.1 MPa.<sup>17</sup> Prior to the treatment, the catalyst (10NA and 10NA@ZrO<sub>2</sub>-5) was reduced at 650 °C in pure H<sub>2</sub> for 1 h and then subjected to 90 vol% H<sub>2</sub>O/H<sub>2</sub> at 650 °C for 8 h. After being cooled to room temperature in pure H<sub>2</sub>, the obtained samples were denoted as 10NA-HT and 10NA@ZrO<sub>2</sub>-5-HT, respectively. The CO conversion, CH<sub>4</sub> selectivity and yield are defined as follows:<sup>13</sup>

CO conversion: 
$$X_{CO}(\%) = \frac{F_{CO,in} - F_{CO,out}}{F_{CO,in}} \times 100$$

CH<sub>4</sub> selectivity: 
$$S_{CH_4}(\%) = \frac{F_{CH_4,out}}{F_{CO,in} - F_{CO,out}} \times 100$$
  
CH<sub>4</sub> yield:  $Y_{CH_4}(\%) = \frac{X_{CO} \times S_{CH_4}}{100} = \frac{F_{CH_4,out}}{F_{CO,in}} \times 100$ 

Here, X is the conversion of CO, S is the selectivity of CH<sub>4</sub>, Y is the yield of CH<sub>4</sub>,  $F_{i, in}$  and  $F_{i, out}$  are the volume flow rates of species *i* (*i*=CO or CH<sub>4</sub>) at the inlet and outlet.

## 3. Results and discussion

#### 3.1. Characterization of the catalysts

All the calcined samples show the similar N<sub>2</sub> adsorption-desorption isotherms with Type IV isotherms and H4 hysteresis loops (Fig. 1A), suggesting the textural structure still remains after the incorporation of ZrO<sub>2</sub> into 10NA. After reduction at 650 °C for 1 h, there is no obvious change in their isotherms (Fig. 1B), and the hysteresis loops of the samples locate at  $P/P_0 = 0.75-1.0$ , indicating the pores are from the aggradation of nanoparticles.<sup>9</sup> Table 1 lists the surface areas of the calcined and reduced samples. Overall, the reduced samples have the lower surface areas than the calcined ones, and the surface areas of 10NA@ZrO<sub>2</sub>-x samples are slightly increased with the increase of the ZrO<sub>2</sub> amount, because the small ZrO<sub>2</sub> nanoparticles can make the surface of the catalyst much coarser. In addition, the exact compositions of the above catalysts are determined by ICP-AES and listed in Table 1. The ZrO<sub>2</sub> loading varies from 3.10 to 12.05 wt%, and the real Ni loading of 10NA@ZrO<sub>2</sub> is slightly lower than 10 wt% due to the addition of ZrO<sub>2</sub> to 10NA.

Fig. 2 shows the morphology and XRD patterns of the 650°C-reduced catalysts. In 10NA, the Ni nanoparticles are highly dispersed over the support with the average Ni size of 10.3 nm (Fig. 2a), which is consistent with the result of XRD in Table 1.  $ZrO_2$  nanocrystallites can be easily identified in the TEM images due to the obvious contrast difference between  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub>. It is seen that

RSC Advances Accepted Manuscript

some  $ZrO_2$  particles are distributed on the surface of the catalysts (Fig. 2b-c), and even cover the dominating surface at higher  $ZrO_2$  loadings (Fig. 2d). The coverage of  $ZrO_2$  species are expected to improve the interaction between NiO and the support, and restrain the growth of the Ni particles during the reduction and catalytic reaction at high temperatures. Actually, the average Ni particle sizes are about 7.2, 7.5 and 7.0 nm in 10NA@ZrO<sub>2</sub>-5 (Fig. 2b), 10NA@ZrO<sub>2</sub>-10 (Fig. 2c) and 10NA@ZrO<sub>2</sub>-15 (Fig. 2d), respectively, which is smaller in size compared to that of 10NA. Fig. 2e shows the HRTEM image of the reduced  $10NA@ZrO_2-15$ , which reveals more information on the distribution of  $ZrO_2$  particles. The observed lattice spacing of ca. 0.20 nm corresponds to the Ni (111) plane,<sup>13</sup> and the ones at ca. 0.26 and 0.30 nm to the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (104) plane and the tetragonal  $ZrO_2$  (t- $ZrO_2$ ) (011) plane, respectively. Clearly, the  $ZrO_2$  species covers part of the catalyst surface, which should include some Ni particles, while the rest Ni particles are distributed among the  $ZrO_2$ particles. Furthermore, the results of the elemental mappings and EDS of the reduced 10NA@ZrO<sub>2</sub>-15 confirm that both Zr and Ni elements are well dispersed across the whole Al<sub>2</sub>O<sub>3</sub> support (Fig. 3). In Fig. 2f, the observed peaks at 25.6, 35.2, 43.4 and 57.9° correspond to (012), (104), (113), and (116) planes of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (JCPDS 01-082-1468), while those at 44.5, 51.8 and 76.6° to (111), (200) and (220) planes of metallic Ni (JCPDS 01-070-1849). After the ZrO<sub>2</sub> addition, new diffraction peaks at 30.3, 50.4 and 60.2° are observed in the XRD patterns, which correspond to (011), (112) and (121) planes of t-ZrO<sub>2</sub> (JCPDS 00-050-1089), while the ones at 28.2 and  $31.5^{\circ}$ attributing to (-111) and (111) planes of monoclinic ZrO<sub>2</sub> (m-ZrO<sub>2</sub>). Clearly, the mixed crystal phases of  $ZrO_2$  exist in the reduced catalysts. Furthermore, the Ni particle sizes are calculated using the Debye-Scherrer equation and listed in Table 1. Overall, the Ni particle sizes of the ZrO<sub>2</sub>-modified catalysts are smaller than that of 10NA, and the Ni particle size calculated through XRD is consistent with that estimated from TEM, which confirms that the steric hindrance of  $ZrO_2$ 

9

RSC Advances Accepted Manuscript

can restrict the sintering of the Ni particles during the reduction process at high temperature.

Fig. 4A presents the H<sub>2</sub>-TPR profiles of the catalysts as well as the bulk ZrO<sub>2</sub>. It should be pointed out that there is no any reduction peak for ZrO<sub>2</sub>, and hence all the hydrogen consuming peaks of the catalysts are attributed to the NiO reduction. There are three reduction peaks at about 305, 362 and 524 °C in the profile of 10NA, which corresponds to NiO with weak (305 and 362 °C) or middle (524 °C) interactions with the support.<sup>3</sup> The reduction peaks at low temperature are disappeared after the ZrO<sub>2</sub> addition, and shifted to high temperature range (475 and 616 °C), because the NiO species is covered partially by ZrO<sub>2</sub> particles, which significantly increases the difficulty of the reduction of NiO species.<sup>3</sup>

Fig. 4B shows the H<sub>2</sub>-TPD profiles of all the catalysts and the bulk ZrO<sub>2</sub>. There is a negligible H<sub>2</sub> adsorption peak for ZrO<sub>2</sub>, which is quite similar to the results in the literature,<sup>15</sup> and thus all the hydrogen desorption peaks in the H<sub>2</sub>-TPD profiles of the catalysts can be contributed to the Ni species. The H<sub>2</sub>-TPD profile of 10NA shows two main H<sub>2</sub> desorption peaks at around 153 and 296 °C. After the ZrO<sub>2</sub> addition, there is an obvious increment in the integrated area of the low-temperature peak (153 °C) as compared with that of 10NA; Meanwhile, the peak at 296 °C is disappeared, indicating the presence of more highly-dispersed Ni atoms.<sup>3</sup> However, the intensity of the H<sub>2</sub> desorption peak decreases gradually with the increase of the ZrO<sub>2</sub> addition due to the coverage of some exposed Ni particles by excess ZrO<sub>2</sub>. The hydrogen uptakes and Ni dispersion of the catalysts are listed in Table 1. The modification of ZrO<sub>2</sub> is beneficial for enhancing the hydrogen uptakes and Ni dispersion of 6.5%. In addition, we notice that the Ni dispersion of 10NA@ZrO<sub>2</sub>-5 is almost 2 times higher than that of 10NA, which is contradictory to the fact that their Ni particle size difference is considerable small (1.5 nm). This may be understood from the

RSC Advances Accepted Manuscript

results of H<sub>2</sub>-TPR, in detail, there is a stronger interaction between Ni species and support in 10NA@ZrO<sub>2</sub>-5 than that in 10NA (Fig. 4A). Thus the sintering degree of Ni particle in the former should be lower during the 650°C-reduction process, resulting in the formation of more exposed surface active Ni atoms with high density of surface defects,<sup>13</sup> and much improved Ni dispersion. However, for 10NA@ZrO<sub>2</sub>-10 and 10NA@ZrO<sub>2</sub>-15, the excess ZrO<sub>2</sub> has the negative effect on H<sub>2</sub> uptake because of the severe coverage of Ni species. In all, only the proper amount of ZrO<sub>2</sub> can lead to the improved dispersion of Ni particle in this work.

The XPS spectra of the reduced 10NA and 10NA@ZrO<sub>2</sub>-5 catalysts are shown in Fig. 5. The reduced 10NA catalyst shows the metallic Ni (Ni<sup>0</sup>) peak at around 852.3 eV, the peaks at 855.8 and 861.5 eV are assigned to the Ni oxide states (Ni<sup>2+</sup>) because catalysts were oxidized in air during the sample transfer and preparation (Fig. 5a).<sup>16</sup> After addition of ZrO<sub>2</sub>, there is no obvious change of the Ni<sup>0</sup> binding energy, indicating ZrO<sub>2</sub> species is a structure promoter rather than the electron promoter in the 10NA@ZrO<sub>2</sub>-x catalysts for CO methanation. The similar Ni<sup>0</sup>/(Ni<sup>0</sup>+Ni<sup>2+</sup>) of the two catalysts indicates the similar reducibility of Ni spices in the different catalysts. The O 1s spectra are displayed in Fig. 5b. There is only one peak in the O 1s spectra of 10NA, while two kinds of oxygen species can be observed in 10NA@ZrO<sub>2</sub>-5. The low binding energy peak was assigned to the surface lattice oxygen (O<sub>1</sub>), and the other is the chemisorbed oxygen (O<sub>11</sub>)<sup>18</sup> which is the typical characteristic of ZrO<sub>2</sub>. The adsorbed oxygen of 10NA@ZrO<sub>2</sub>-5 can supply more oxygen vacancies which are favorable for eliminating deposited carbon and improving the stability of the catalyst.

#### 3.2. Catalytic performances of the catalysts

The CO methanation reaction was carried out in the temperature range of 260–440 °C at 0.1 MPa,  $30000 \text{ mL g}^{-1} \text{ h}^{-1}$ , and the results are shown in Fig. 6a–c. For 10NA, the CO conversion increases

11

with the increase of the reaction temperature and reaches the maximum of 87% at 440 °C; at the same time, the CH<sub>4</sub> selectivity drops with the rise of the temperature due to the side reactions such as water-gas shift and inversed methane CO<sub>2</sub> reforming reaction.<sup>23</sup> It can be seen that the addition of ZrO<sub>2</sub> considerably improves the catalytic activities, and 10NA@ZrO<sub>2</sub>-5 shows the best catalytic performance, whose CO conversion and CH<sub>4</sub> yield can reach 94% and 74% respectively at 400 °C. However, excess ZrO<sub>2</sub> is adverse for the catalytic performance, and the activities of 10NA@ZrO<sub>2</sub>-x (x = 10 and 15) decrease with the further increase of the ZrO<sub>2</sub> loading. The order of the activity of the different catalysts is consistent with that of the H<sub>2</sub> uptake, which is similar to the literature results.<sup>3,24</sup> It should be pointed out that the order of CH<sub>4</sub> selectivity of the different catalysts is opposite with their order of CO conversion, indicating the side reactions can also be significantly enhanced in the presence of the more active catalysts. In all, only the proper amount of ZrO<sub>2</sub> can remarkably enhance the CO methanation, and the excess ZrO<sub>2</sub> has the adverse effect on it due to the coverage of the active sites.

Published on 15 February 2016. Downloaded by New York University on 16/02/2016 23:24:17.

In order to evaluate the lifetime of the catalyst in a short time in laboratory, a 103h-lifetime test of 10NA@ZrO<sub>2</sub>-5 was carried out at high temperature and WHSV (500 °C, 60000 mL g<sup>-1</sup> h<sup>-1</sup>, 0.1 MPa), and 10NA was also evaluated as a comparison (Fig. 6d–f). During the test, the CO conversion and CH<sub>4</sub> yield over 10NA are decreased by 17.8% and 13.1%, respectively, although the CH<sub>4</sub> selectivity (Fig. 6e) is still comparable. On the contrary, the CO conversion and CH<sub>4</sub> yield over 10NA@ZrO<sub>2</sub>-5 show the decrement of 6.7% and 5.5%, respectively. Clearly, 10NA@ZrO<sub>2</sub>-5 exhibits a better stability especially at high temperature and WHSV. In Fig. 7, it can be seen that in the spent 10NA (Fig. 7A) and 10NA@ZrO<sub>2</sub>-5 (Fig. 7B), the Ni nanoparticle size is 12.2–25.1 and 7.0–12.5 nm, respectively. Compared with the aforementioned TEM images of the reduced catalysts (Fig. 2), the anti-sintering of Ni particle on 10NA@ZrO<sub>2</sub>-5 is significant. At the same time, the

#### **RSC Advances**

average Ni particle size of the spent 10NA calculated from XRD pattern is 17.2 nm, while that of the spent 10NA@ZrO<sub>2</sub>-5 is 9.5 nm, only slightly larger than that of the reduced catalysts (Table 1), further confirming the anti-sintering property of 10NA@ZrO<sub>2</sub>-5. We believe that the anti-sintering performance can be further improved through optimization of the amount of ZrO<sub>2</sub>. Moreover, the amount of carbon deposited on the spent catalysts can be measured by TG analysis, and the result is presented in Fig. 7D. The TG curves of the samples exhibit a rise in the temperature range of 200 to 430 °C, which results from the oxidation of the metallic Ni.<sup>25</sup> Furthermore, the decrement of mass loss percentage of the spent 10NA catalyst is larger than that of 10NA@ZrO<sub>2</sub>-5, indicating a higher resistance of 10NA@ZrO<sub>2</sub>-5 to coke formation. The TEM image of the spent 10NA catalyst further confirms the existence of the filamentous carbon. However, the amount of the deposited carbon of the two catalysts is close, suggesting that coke may be not the main factor of deactivation. In short, the sintering of Ni particles leads to the decrease of the activity of 10NA in the lifetime test, and 10NA@ZrO<sub>2</sub>-5 exhibits high catalytic activity and stability as well as much improved resistance to Ni sintering.

# 3.3. Hydrothermal stability of the catalysts

Recently, researchers have reported that  $H_2O^{26}$  and OH anions (NaOH in water)<sup>27</sup> could significantly enhanced the activity and selectivity of Ni based catalysts for C-O bond hydrogenolysis of lignin model compounds and organosolv lignin. Considering water is one of the byproducts in CO methanation and additional steam in the feed gas is an often used strategy to avoid the generation of hot spots in the catalyst bed and to reduce carbon deposition in industry,<sup>9,17,28</sup> the hydrothermal stability of 10NA@ZrO<sub>2</sub>-5 was examined, and that of 10NA was also carried out as the reference. Fig. 8 shows the catalytic properties of 10NA@ZrO<sub>2</sub>-5-HT and

RSC Advances Accepted Manuscript

10NA-HT after the hydrothermal treatment. Compared with the fresh catalysts in Fig. 6, 10NA@ZrO<sub>2</sub>-5-HT shows comparable catalytic activity and selectivity; while the activity of 10NA-HT decreases drastically, suggesting that the introduction of proper amount of  $ZrO_2$  is useful to stabilize Ni particles on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> support. In addition, the Ni particle sizes of the two hydrothermally treated catalysts were also estimated using XRD analysis (Fig. 9). The Ni particle size grows from 10.3 (Table 1) to 25.3 nm in 10NA-HT, which is even larger than that of the spent 10NA catalyst (17.2 nm); while the change in 10NA@ZrO<sub>2</sub>-5-HT is from 8.8 (Table 1) to 12.8 nm, which further indicates the superior anti-sintering property of 10NA@ZrO<sub>2</sub>-5. In addition, there is no obvious change of crystallization of ZrO<sub>2</sub> during the hydrothermal treatment.

## 3.4. Schematic diagram of the catalysts

Combing and considering all the above results, a schematic diagram illustrating the preparation process and the structure-property relationship of  $ZrO_2$ -modified Ni/Al<sub>2</sub>O<sub>3</sub> catalyst is depicted and shown in Fig. 10. The calcined 10NA successively adsorbs  $Zr(OBu)_4$  and H<sub>2</sub>O during the preparation process, and amorphous  $ZrO_2$  (*a*- $ZrO_2$ , XRD pattern not shown here) is obtained after the hydrolysis of  $Zr(OBu)_4$  and the calcination (Fig. 10a–b). After reduction, tetragonal and monoclinic phases of  $ZrO_2$  (*t*- $ZrO_2$  and *m*- $ZrO_2$ ) will be formed, and the  $ZrO_2$  particles that are interspersed among the nickel species can act as a physical barrier to restrict the growth of the Ni particles and enhance the anti-sintering of the Ni species at high temperatures. However, the excess  $ZrO_2$  may be beneficial to the improved stability, but it has adverse effect on the catalytic activity due to the coverage of some exposed Ni atoms.

#### 4. Conclusions

#### **RSC Advances**

 $ZrO_2$ -modified Ni/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalysts were prepared by a modified impregnation method and used for CO methanation to produce synthetic natural gas. Compared to the unmodified catalyst, the 10NA@ZrO<sub>2</sub>-5 catalyst shows superior catalytic activity, coinciding with its large H<sub>2</sub> uptake and high Ni dispersion. In a 103h-lifetime test conducted under the conditions at 500 °C, 0.1 MPa and 60000 mL g<sup>-1</sup> h<sup>-1</sup>, 10NA@ZrO<sub>2</sub>-5 displays a high stability and resistance to Ni sintering. Further characterizations indicate that in the preparation process, ZrO<sub>2</sub> particles are formed and interspersed among the nickel particles to restrain the growth of the Ni particles during the reduction and catalytic reaction at high temperatures, resulting in the high stability in the lifetime test. It is expected that this approach for catalyst preparation can be widely applied in the metal-based catalysts to enhance their anti-sintering performance in some high-temperature reactions.

#### Acknowledgements

The authors gratefully acknowledge the supports from the National High Technology Research and Development Program 863 (No. SS2015AA050502), the Fund of State Key Laboratory of Multiphase complex systems (No. MPCS-2015-A-06), the National Natural Science Foundation of China (No. 21476238), the National Basic Research Program (No. 2014CB744306), the Open Research Fund of State Key Laboratory of Multiphase Complex Systems (No. MPCS-2014-D-03) and "Strategic Priority Research Program" of the Chinese Academy of Sciences (Nos. XDA07010100 and XDA07010200). Z. Zhong (Zhong\_ziyi@ices.a-star.edu.sg) works in Institute of Chemical Engineering in Singapore, and also holds an adjunct associate professor position in the School of Chemical & Biomedical Engineering, Nanyang Technological University (NTU) in Singapore.

# References

- 1. C. H. Bartholomew, Appl. Catal. A Gen., 2001, 212, 17-60.
- 2. A. M. Cao, R. W. Lu and G. Veser, Phys. Chem. Chem. Phys., 2010, 12, 13499-13510.
- D. C. Hu, J. J. Gao, Y. Ping, L. H. Jia, P. Gunawan, Z. Y. Zhong, G. W. Xu, F. N. Gu and F.
   B. Su, *Ind. Eng. Chem. Res.*, 2012, **51**, 4875-4886.
- 4. J. J. Gao, Q. Liu, F. N. Gu, B. Liu, Z. Y. Zhong and F. B. Su, *RSC Adv.*, 2015, **5**, 22759-22776.
- J. J. Gao, Y. L. Wang, Y. Ping, D. C. Hu, G. W. Xu, F. N. Gu and F. B. Su, *RSC Adv.*, 2012, 2, 2358-2368.
- 6. W. R. Kang and K. B. Lee, *Korean J. Chem. Eng.*, 2013, **30**, 1386-1394.
- 7. S. Kawi, Y. Kathiraser, J. Ni, U. Oemar, Z. Li and E. T. Saw, *ChemSusChem* 2015, **8**, 3556-3575.
- 8. J. Kopyscinski, T. J. Schildhauer and S. M. A. Biollaz, *Fuel*, 2010, **89**, 1763-1783.
- Y. J. Liu, J. J. Gao, Q. Liu, F. N. Gu, X. P. Lu, L. H. Jia, G. W. Xu, Z. Y. Zhong and F. B. Su, *RSC Adv.*, 2015, 5, 7539-7546.
- J. J. Gao, C. M. Jia, M. J. Zhang, F. N. Gu, G. W. Xu and F. B. Su, *Catal. Sci. Technol.*, 2013, 3, 2009-2015.
- 11. S. R. Li and J. L. Gong, Chem. Soc. Rev., 2014, 43, 7245-7256.
- H. Liu, C. Y. Guan, X. Li, L. Y. Cheng, J. B. Zhao, N. H. Xue and W. P. Ding, ChemCatChem 2013, 5, 3904-3909.
- Q. Liu, J. J. Gao, F. N. Gu, X. P. Lu, Y. J. Liu, H. F. Li, Z. Y. Zhong, B. Liu, G. W. Xu and F.
   B. Su, J. Catal., 2015, 326, 127-138.
- 14. Q. Liu, J. J. Gao, M. J. Zhang, H. F. Li, F. N. Gu, G. W. Xu, Z. Y. Zhong and F. B. Su, RSC

*Adv.*, 2014, **4**, 16094-16103.

- Q. Liu, F. N. Gu, J. J. Gao, H. F. Li, G. W. Xu and F. B. Su, J. Energy Chem., 2014, 23, 761-770.
- 16. F. H. Meng, Z. Li, F. K. Ji and M. H. Li, Int. J. Hydrogen Energy, 2015, 40, 8833-8843.
- Q. Liu, F. N. Gu, X. Y. Wang, G. J. Jin, H. F. Li, F. Gao, Z. Y. Zhong, G. W. Xu and F. B. Su, *RSC Adv.*, 2015, 5, 84186-84194.
- X. Y. Wang, Q. Liu, J. X. Jiang, G. J. Jin, H. F. Li, F. N. Gu, G. W. Xu, Z. Y. Zhong and F. B.
   Su, *Catal. Sci. Technol.*, 2015, DOI: 10.1039/C5CY01482D.
- W. Y. Teoh, D. E. Doronkin, G. K. Beh, J. A. H. Dreyer and J. D. Grunwaldt, *J. Catal.*, 2015, 326, 182-193.
- J. Zhang, M. Ibrahim, V. Collière, H. Asakura, T. Tanaka, K. Teramura, K. Philippot and N. Yan, J. Mol. Catal. A Chem., 2016, DOI: <u>http://dx.doi.org/10.1016/j.molcata.2016.01.014</u>.
- N. A. Mashayekhi, Y. Y. Wu, M. C. Kung and H. H. Kung, *Chem. Commun.*, 2012, 48, 10096-10098.
- 22. G. D. Li and Z. Y. Tang, *Nanoscale*, 2014, **6**, 3995-4011.
- J. R. Rostrup-Nielsen, K. Pedersen and J. Sehested, *Appl. Catal. A Gen.*, 2007, 330, 134-138.
- A. M. Zhao, W. Y. Ying, H. T. Zhang, H. F. Ma and D. Y. Fang, J. Nat. Gas Chem., 2012, 21, 170-177.
- 25. H. Y. Ma, L. Zeng, H. Tian, D. Li, X. Wang, X. Y. Li and J. L. Gong, *Appl. Catal., B Environ.*, 2016, **181**, 321-331.
- J. Zhang, J. Teo, X. Chen, H. Asakura, T. Tanaka, K. Teramura and N. Yan, ACS Catal., 2014, 4, 1574-1583.

- H. Konnerth, J. Zhang, D. Ma, M. H. G. Prechtl and N. Yan, *Chem. Eng. Sci.*, 2015, **123**, 155-163.
- G. J. Jin, F. N. Gu, Q. Liu, X. Y. Wang, L. H. Jia, G. W. Xu, Z. Y. Zhong and F. B. Su, *RSC Adv.*, 2016, 6, 9631-9639.

# Table and Figure Captions

 Table 1 Physical and chemical properties of the samples.

- Fig. 1. N<sub>2</sub> adsorption isotherms of the calcined (A) and reduced (B) samples: (a) 10NA, (b) 10NA@ZrO<sub>2</sub>-5, (c) 10NA@ZrO<sub>2</sub>-10, and (d) 10NA@ZrO<sub>2</sub>-15 (For clarity, the isotherm of 10NA, 10NA@ZrO<sub>2</sub>-5, 10NA@ZrO<sub>2</sub>-10 and 10NA@ZrO<sub>2</sub>-15 was vertically shifted for 80, 55, 35 and 0 cm<sup>3</sup> g<sup>-1</sup>, respectively).
- **Fig. 2.** TEM images of the reduced samples: (a) 10NA, (b) 10NA@ZrO<sub>2</sub>-5, (c) 10NA@ZrO<sub>2</sub>-10, and (d and e) 10NA@ZrO<sub>2</sub>-15; and XRD patterns of the reduced catalysts (f).
- Fig. 3. SEM image of the reduced 10NA@ZrO<sub>2</sub>-15 (a), elemental mapping images of O (b), Al (c), Ni (d), and Zr (e); Energy-dispersive X-ray spectroscopy (EDS) analysis of this sample (f).
- Fig. 4. H<sub>2</sub>-TPR profiles (A) and H<sub>2</sub>-TPD profiles (B) of the catalysts: (a) 10NA, (b) 10NA@ZrO<sub>2</sub>-5, (c) 10NA@ZrO<sub>2</sub>-10, (d) 10NA@ZrO<sub>2</sub>-15 and (e) ZrO<sub>2</sub>.
- Fig. 5. XPS spectra of the reduced catalysts: (a) Ni 2p and (b) O 1s.
- Fig. 6. Catalytic properties of the catalysts: (a) CO conversion, (b) CH<sub>4</sub> selectivity, and (c) CH<sub>4</sub> yield; and lifetime test of 10NA and 10NA@ZrO<sub>2</sub>-5 catalysts: (a) CO conversion, (b) CH<sub>4</sub> selectivity, and (c) CH<sub>4</sub> yield.
- Fig. 7. TEM images of the spent samples: (A) 10NA, and (B) 10NA@ZrO<sub>2</sub>-5; XRD patterns of the spent catalysts (C): (a) 10NA, and (b) 10NA@ZrO<sub>2</sub>-5; and TG curves of the spent catalysts in air (D) (Inset: TEM image confirming the carbon filament).
- **Fig. 8.** Catalytic properties of the catalysts after hydrothermal treatment: (a) CO conversion, (b) CH<sub>4</sub> selectivity, and (c) CH<sub>4</sub> yield.
- Fig. 9. XRD patterns of the catalysts after hydrothermal treatment.
- Fig. 10. Schematic diagram illustrating the preparation of the ZrO<sub>2</sub>-modified Ni/α-Al<sub>2</sub>O<sub>3</sub> catalyst: (a)

the calcined 10NA, (b) the calcined 10NA@ZrO2-15, and (c) the reduced 10NA@ZrO2-15

(Note: *a*, *t* and *m* is the abbreviation of amorphous, tetragonal and monoclinic, respectively.)

Catalysts	$S_{\rm BET}^{a} ({ m m}^2 { m g}^{-1})$		NiO content	ZrO <sub>2</sub> content	Ni particle size (nm)		$H_2$ uptake	$D^{e}$
	Calcined	Reduced	(wt%) <sup>b</sup>	$(wt\%)^b$	XRD <sup>c</sup>	TEM <sup>d</sup>	$(\mu mol g^{-1})$	(%)
10NA	25	12	_	_	10.3	10.3	23.9	3.6
10NA@ZrO <sub>2</sub> -5	27	17	9.53	3.10	8.8	7.2	44.0	6.5
10NA@ZrO <sub>2</sub> -10	29	19	9.10	7.21	9.3	7.5	33.1	4.9
10NA@ZrO <sub>2</sub> -15	30	21	8.35	12.05	9.2	7.0	23.0	3.4

Table 1

<sup>a</sup> Surface area of the sample derived from BET equation.

<sup>b</sup> The exact composition of the calcined catalysts was determined by ICP-AES.

<sup>c</sup> Particle size estimated from the XRD diffraction peak ( $2\theta = 44.6$ ) using the Debye-Scherrer equation.

<sup>d</sup> Average particle size estimated from the TEM images.

<sup>e</sup> Ni dispersion calculated from the H<sub>2</sub>-TPR and H<sub>2</sub>-TPD results.



Fig. 1



Fig. 2





24



Fig. 4



Fig. 5



Fig. 6



Fig. 7



Fig. 8



Fig. 9



Fig. 10

# **Graphical Abstract**

The  $ZrO_2$ -modified Ni/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalysts prepared by a modified impregnation method show obvious enhancement of Ni anti-sintering because of the special distribution of  $ZrO_2$  nanoparticles on the surface of the catalyst.

