INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 43 (2018) 17726–17736

Available online at www.sciencedirect.com

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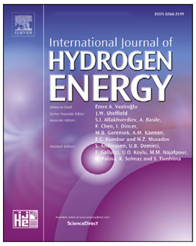
journal homepage: www.elsevier.com/locate/he



Promotion effect of proton-conducting oxide $BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$ on the catalytic activity of Ni towards ammonia synthesis from hydrogen and nitrogen

John Humphreys [a], *Rong Lan* [a,c], *Dongwei Du* [a], *Wei Xu* [a], *Shanwen Tao* [a,b,*]

[a] *School of Engineering, University of Warwick, Coventry, CV4 7AL, UK*
[b] *Department of Chemical Engineering, Monash University, Clayton, Victoria, 3800, Australia*
[c] *Faculty of Engineering, Environment & Computing, Coventry University, Coventry, CV1 5FB, UK*

A R T I C L E I N F O

Article history:
Received 26 April 2018
Received in revised form
30 July 2018
Accepted 1 August 2018
Available online 23 August 2018

Keywords:
Renewable hydrogen
Ammonia synthesis
Catalysis
Proton conductor
Nickel catalyst
Catalyst promoter

A B S T R A C T

In this report, for the first time, it has been observed that proton-conducting oxide $BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$ (BZCY) has significant promotion effect on the catalytic activity of Ni towards ammonia synthesis from hydrogen and nitrogen. Renewable hydrogen can be used for ammonia synthesis to save CO_2 emission. By investigating the operating parameters of the reaction the optimal conditions for this catalyst were identified. It was found that at 620 °C with a total flow rate of 200 mL min^{-1} and a H_2/N_2 mol ratio of 3, an activity of approximately 250 μmol g^{-1} h^{-1} can be achieved. This is ten times larger than that for the unpromoted Ni catalyst under the same conditions although the stability of both catalysts in the presence of steam was not good. The specific activity of Ni supported on proton-conducting oxide BZCY is approximately 72 times higher than that of Ni supported on non-proton conductor $MgO-CeO_2$. These promotion effects were suspected to be due to the proton conducting nature of the support. Therefore it is proposed that the use of proton conducting support materials with highly active ammonia synthesis catalysts such as Ru and Fe will provide improved activity of at lower temperatures.

Introduction

Ammonia, due to its important use as a fertiliser is mass produced at approximately 150 million tons per annum [1]. That fact that ammonia fertilisers have supported approximately 27% of the world's population over the last century confirms its importance, with the development of the high temperature Haber-Bosch process being considered one of the most important chemical processes of the last 100 years [2]. In this process, ammonia is produced from H_2 and N_2 under high temperature and high pressure. About 50% of the hydrogen produced in the world is used for ammonia production [3]. In addition, CO_2 emitted from the ammonia industry is equivalent to 0.77% of the world total CO_2 emission because the

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[*] *Corresponding author*. School of Engineering, University of Warwick, Coventry, CV4 7AL, UK.
E-mail address: S.Tao.1@warwick.ac.uk (S. Tao).

https://doi.org/10.1016/j.ijhydene.2018.08.002

source of hydrogen is mainly from steam-reforming of natural gas [3,4]. This green-house gas emission can be significantly reduced if the source of hydrogen can be changed to be provided through renewable sources such as hydro-electricity, wind or solar energy. Hydrogen from the electrolysis of water (hydroelectricity) was used for low-carbon ammonia production through Haber-Bosch process in Norway [5]. A Dutch company Proton Venture is developing de-centralised ammonia production technology using renewable electricity as the energy source [6]. Therefore synthesis of ammonia from renewable hydrogen could be a complementary part of hydrogen economy [3,7–11].

The Haber-Bosch process is very important in chemical industry. This led to Fritz Haber being awarded the Nobel Prize in 1918 and with Carl Bosch also receiving the award in 1931. Gerhard Etrl also won the Nobel Prize in Chemistry in 2007 for his contributions towards the understanding of the surface chemistry of iron catalyst [12]. Industrially promoted fused iron catalysts are used in the Haber-Bosch process with promoters including potassium, barium and aluminium oxides [13–18]. As well as iron, supported ruthenium has attracted a large amount of research interest as an ammonia synthesis catalyst with carbon supported ruthenium currently employed in the Kellogg advanced ammonia process (KAAP) [19]. Due to the cost of ruthenium, it is supported on a range of materials in order to be used in the ammonia synthesis process. These supports often also fill the role of promoter with very high activities recently reported for Ru/HT-C12A7:e$^-$ [20], Ru/Y_5Si_2 [21], and Ru/MgO [22] supports. In 2013 Wang Z et al. [23] reported the use of perovskite material $BaZrO_3$ as a catalyst support for the ammonia synthesis reaction at high pressure and intermediate temperature when ruthenium was used as the catalyst.

The reaction to produce ammonia from hydrogen is shown below [19].

$$N_2 + 3H_2 \leftrightarrow 2NH_3 \ (\Delta H^o = -46.1\ kJ\ mol^{-1}) \quad (1)$$

Although this reaction is exothermic and favours high pressure and low temperature the ammonia formation rate at these conditions is extremely low even though an ammonia equilibrium concentration of close to 100% is theoretically possible. For this reason, the Haber-Bosch process is carried out at temperatures between 400 °C and 500 °C at pressures close to 200 bar.

It is commonly accepted that the rate limiting step for the ammonia synthesis reaction is the dissociative adsorption of nitrogen although the reaction could also be limited by the N binding energy due to the Sabatier principle [24]. This is shown in Eqs (2)–(8) below:

$$N_2 +^* \leftrightarrow N_2^* \quad (2)$$

$$N_2^* +^* \leftrightarrow 2N^* \quad (3)$$

This dissociated nitrogen reacts with dissociated hydrogen on the catalyst surface to form ammonia. The dissociative adsorption of hydrogen and the surface reactions are shown below where * represents the catalyst active site:

$$H_2 + 2^* \leftrightarrow 2H^* \quad (4)$$

$$H^* + N^* \leftrightarrow NH^* +^* \quad (5)$$

$$NH^* + H^* \leftrightarrow NH_2^* +^* \quad (6)$$

$$NH_2^* + H^* \leftrightarrow NH_3^* +^* \quad (7)$$

$$NH_3^* \leftrightarrow NH_3 +^* \quad (8)$$

It can be seen from this that if the dissociative adsorption of hydrogen is favoured on the catalyst surface then there will be less active sites for the rate limiting step therefore reducing activity. It has been reported that reduce dinitrogen will be feasible upon addition of protons and electrons similar to the mechanism of ammonia production by nitrogenases. This has been described in detail in an excellent review [25].

Recently, it was discovered that ammonia could be produced from hydrogen and nitrogen in an electrochemical cell [7,26–35]. This led Vasileiou E et al. [36,37] to achieve the electrochemical synthesis of ammonia using a proton conducting electrolyte. They achieved this by using $BaCe_{0.2}Zr_{0.7}Y_{0.1}O_{2.9}$ as the electrolyte with Ni–$BaCe_{0.2}Zr_{0.7}Y_{0.1}O_{2.9}$ used as the cathode and anode. When they performed the experiment with no applied voltage they discovered that ammonia was also produced through the catalysed reaction of H_2 and N_2 fed to the cell. Although the catalytic activity of the Ni–$BaCe_{0.2}Zr_{0.7}Y_{0.1}O_{2.9}$ material was noted no further investigation was done. In this paper, the effects of a similar proton conducting electrolyte on the catalytic activity towards ammonia synthesis, were investigated with the use of a Ni catalyst. $BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$ (BZCY) was chosen due to its excellent proton conductivity [38,39]. Ni-BZCY has been investigated as membrane materials for hydrogen separation using the proton conduction of BZCY [40,41]. By using a proton conducting support, it is proposed that the dissociated hydrogen on the catalyst active sites will be transferred to the proton conducting support, therefore freeing active sites for the dissociative adsorption of nitrogen. Through this increase in active sites, it is expected that the catalyst activity will be greatly increased. In this study, the catalytic activity of Ni and Ni supported on BZCY or MgO–CeO_2 are investigated. It was found that proton-conducting oxide BZCY has promotion effects on the catalytic activity towards ammonia synthesis.

Experimental

Materials and preparation method

In order to synthesise the $BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$ (BZCY) perovskite catalyst support a solid state reaction was employed. Firstly stoichiometric amounts of $BaCO_3$ (99% alfa), ZrO_2 (99% alfa), CeO_2 (99.5% Alfa) and Y_2O_3 (99.9% Alfa) were weighed and mixed using a pestle and mortar. The resulting mixture was then wet ground in isopropyl alcohol for 12 h. After drying at 80 °C the mixture was then fired at 1000 °C for 3 h with a heating and cooling rate of 5 °C min^{-1}. After this NiO (99% Alfa) was added to the $BaZr_{0.1}Ce_{0.7}Y_{0.2}O_3$