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Ceria-supported nickel borate as a sulfur-tolerant catalyst for autothermal reforming of a proxy jet fuel

Lei Liu^a, Liang Hong^{a,b,*}

^a Department of Chemical and Biomolecular Engineering, National University of Singapore, 4 Engineering Drive 4, Singapore 117576, Singapore ^b Institute of Materials Research and Engineering, Singapore

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ABSTRACT

Catalytic reforming of liquid hydrocarbons to produce H_2 -enriched fuel in an auxiliary power unit is essential to the operation of fuel cell on board. This study explored ceria-supported nickel borate $[Ni_3(BO_3)_2]$ catalyst for conducting the above reaction under autothermal reforming (ATR) condition. In the present catalytic system operating at 750 °C and under purge stream of feed, nickel borate undergoes partial degradation whose degree depends on the type of support used to release catalytically reactive tiny Ni⁰ metal crystallite and B_2O_3 . To achieve a high fuel conversion (>95%), it is crucial to maintain a dominant ratio of nickel borate versus Ni⁰ nanocrystallites as the reactive site. Typically, more than 90% nickel borate remains on the Y-doped ceria (CYO) while almost all nickel borate degrade to Ni⁰ and B_2O_3 on the Gd-doped ceria (CGO) after 24 h ATR of the proxy fuel comprising dodecane, naphthalene (10 wt%) and thiophene (containing 100 pm S). In consequence, the former catalyst shows a higher fuel conversion of fuel molecules, which provides smaller hydrocarbon species for the reforming on Ni⁰ crystallites, and promotes sulfur tolerance of Ni⁰ crystallites to a large extent on CYO according to the XPS and NMR characterizations.

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1. Introduction

The fuel processor that supplies the mixtures of H_2 and CO (reformat) through catalytic reforming of liquid hydrocarbons, such as diesel, kerosene and jet fuel or ethanol, glycerol and biodiesel, has been proposed as an auxiliary power unit for fuel cell stacks on board [1,2]. As the catalytic autothermal reforming (ATR) offers an energy-saving path to produce the reformat [3], exploration of thermally stable, coking-resistant and sulfur-tolerant reforming catalysts is imperative to advance the on-board fuel processor technology [4]. It has been known that sulfur tolerance is the most challenging amid other requirements for a desired catalyst to undertake ATR of jet fuel [5]. This is because jet fuels produced from hydrodesulfurization [6] normally contain 500–3000 ppm sulfur. Further desulfurizing through adsorption treatments [7,8] could lower the sulfur contents down to below 100 ppm. Although

http://dx.doi.org/10.1016/j.cattod.2015.07.047 0920-5861/© 2015 Elsevier B.V. All rights reserved. catalytic reforming for small-scale hydrogen production has option to use fuels from sulfur-free sources, e.g. F-T hydrocarbon fuel or trans-esterification of vegetable oils or ethanol from fermentation, the low-sulfur jet fuels still have lower costs. Accordingly, attempts to improve sulfur tolerance of the supported-Ni catalytic system have led to various advances. These accomplishments include introduction of co-catalytic components to modify the Ni⁰ crystallite catalytic site as well as varying the doping structure of metal oxide supports. Regarding the modification of Ni⁰, noble metals (M = Pt, Rh, Ru) are often employed to form bimetallic catalytic sites with a M/Ni mass ratio from 1/20 to 1/10 [9-13] because the noble metals, in particular Rh, possess better sulfur tolerance than Ni. Besides the costly noble metals, transition or rare earth metals (such as Co, Mo, Re or La) have also been found to improve sulfur tolerance through their participation in the Ni reforming catalytic sites [14,15]. Alternatively, modification of catalyst support has been undertaken as well recently through properly doping ceria [16,17] and alumina [18–20], which enhances sulfur tolerance of the supported catalytic site. In a word, as sulfur poisoning takes place through the adsorption of hydrogen sulfide (H₂S) on Ni⁰ crystallites, tuning the Lewis acidity of the metallic site to repress its affinity with sulfur has been conducted by either integrating a metal







^{*} Corresponding author at: Department of Chemical and Biomolecular Engineering, National University of Singapore, 4 Engineering Drive 4, Singapore 117576, Singapore.

E-mail address: chehongl@nus.edu.sg (L. Hong).

having softer Lewis acidity, e.g. Rh and Re, with Ni metal or modifying the catalyst supports to enhance the reactivity of lattice oxygen on surface, which plays the sulfur scavenging role [21].

As to the strategy to adjust the Lewis acidity of Ni⁰ catalytic site with the aim of reducing its affinity to coke and sulfur, integration of an electron-deficient chemical species with Ni⁰ [22,18] could also work to different extents. Along this line, boron as a typical example could increase Lewis acidity of Ni atom when both are covalently bonded. Experimentally, dispersing a dilute B₂O₃ in NiO [23] or mixing of boric acid with NiO has been carried out [24], from which the resulting mixtures are subjected to hydrogen reduction. Similarly, chemical reduction of a nickel salt in aqueous medium [25] also helped to realize the purpose. Contrary to this methodology, we explored nickel borate as a cocatalyst of the Ni⁰ catalytic site rather than polar Ni-B species to carry out ATR of a proxy fuel in the present study. Nickel meta-borate (NiBO₂) was first prepared, through the in situ formation of it on a doped ceria support, as the precursor of catalyst. The supported NiBO₂ was then transformed to the real catalytic site, consisting of nickel borate [Ni₃(BO₃)₂] and Ni⁰ crystallites, under the ATR condition. It was observed that only a small amount of Ni⁰ crystallites were released from the uniformly distributed Ni₃(BO₃)₂ on Y-doped ceria, implying a high distribution of nanocrystallites over the surface. Furthermore, the doping composition of the ceria support strongly influences the degradation of nickel borate, resulting in Ni⁰ and B₂O₃. Briefly, nickel borate itself is the source of the Ni⁰ catalytic site as well as a cocatalyst for Ni⁰. The cocatalytic role includes stabilizing a high distribution of Ni⁰ crystallites and impeding the attack of sulfur to the Ni⁰ site in the ATR of the surrogate jet fuel, comprising alkane, aromatic and organosulfur compounds.

2. Experimental

2.1. Preparation of the nickel borate on the doped ceria support

All chemicals used in the preparation are of analytical grade. Ceria (Ce), gadolinium (III)-doped ceria (CGO) and yttrium (III)doped ceria (CYO) were prepared by the modified Pechini method [26]. A doping level of 10% by mole is kept in the preparation of both CGO and CYO. In a typical protocol, an aqueous solution of the metal nitrate salts, $(Ce(NO)_3 \cdot 6H_2O)$, and $Gd(NO)_3 \cdot 6H_2O$ or $Y(NO)_3 \cdot 6H_2O$, with the determined stoichiometry was prepared. It was followed by introducing glycine and citric acid into the above solution, using the molar ratio of the metal ions to the two functional groups (-COOH+NH₂)=0.154 and that of citric acid to glycine = 0.05. In addition, the resulting solution was controlled to have an approximate concentration of 20 wt% and then mixed with 0.8 portion (by volume) of ethylene glycol. After homogenizing, the mixture was thickened at 200 °C by stirring until a gel was obtained. The gel was then subjected to pyrolysis at 400 °C for 2 h and calcined at 600 °C in air for another 2 h to allow the growth of crystal phase. The as-prepared ceria powder (Ce, CGO or CYO) of 2 g was dispersed in an aqueous solution of Ni(NO₃)₂ (100 ml, 0.07 M) to prepare a uniform slurry. To this slurry a NaBH₄ solution (0.21 M, 100 ml) was introduced dropwise under stirring. The slurry was stirred overnight at room temperature to produce nickel metaborate, Ni(BO₂)₂, which has been validated by both XPS and NMR. The precipitate was separated by filtration and washed using deionized water and ethanol, respectively. After that, the powder was vacuum dried at 60 °C and compressed to pellets, which were then crushed and sieved to collect granules with sizes of 0.5-1 mm. The three ceria-supported powders, viz. the catalyst precursors, were labeled by NiBO/Ce, NiBO/CGO and NiBO/CYO, in which the nickel content is about 15% by weight. A Ni $(BO_2)_2$ powder without ceria was also prepared as the control sample. In addition, a control was made by the impregnation approach: an appropriate amount of CYO was dispersed by mechanical stirring in the Ni(NO₃)₂ aqueous solution (0.07 M, 100 ml) for 2 h. After that, the resulting slurry was subjected to vaporization at 60 °C. The solid left was calcined in air at 600 °C for 3 h to generate the CYO-supported NiO denoted by Ni/CYO.

2.2. Structural characterizations

The crystalline structure of catalyst was determined by Xray diffractometry (XRD, SHIMADZU XRD-6000, Cu Kα radiation) using a scanning rate of 5 deg min⁻¹. The surface structures of the catalyst precursor were examined by the field-emission scanning electron spectroscopy (JEOL, JSM-6700F). The specific surface areas of various cerias and their corresponding supported catalyst precursor systems were gauged on a physicochemical absorber (Quantanchrome Autosorb-1 instrument) by applying the multipoint BET method after degassing at 300 °C for 3 h under N₂ purging. The temperature-programmed reduction (TPR) profile was measured on the same instrument by always loading a 50-mg sample, using a flow rate of $80 \text{ ml} \text{ min}^{-1}$ of sweep gas (5% H₂ in N₂), and a heating rate of 10 °C min⁻¹. The oxidation states of Ni, B and Ce in the catalyst precursor and the used catalyst were determined by the X-ray photoelectron spectroscopy (XPS, Kratos Axis HiS System) equipped with Al $K\alpha$ X-ray source (1486.6 eV) and the take-off angle of 90° with pass energy of 40 eV. C1s (284.6 eV) was used as the internal reference to calibrate the spectra obtained.

2.3. Evaluation of the ATR of a surrogate fuel

Approximately, 1 g catalyst (0.5–1 mm granules) was packed between two plugs of quartz wool at the center segment of a quartz tube reactor (1.2 m o.d., 1 cm i.d. and 40 cm long) to form a micro plug flow reactor (mPFR). It was placed in a thermostat-controlled vertical tube furnace. A diluted oxygen stream by combining synthetic air (O_2/N_2) and nitrogen was metered into the reactor through a mass flow controller (Alicat). The fuel stream comprising 90 wt% *n*-dodecane. 10 wt% naphthalene and 100 ppm S (from thiophene) and water were sent through two ISO-2000 isocratic pumps with desired delivery rates respectively to combine with the diluted oxygen stream. The mixture formulated from the above combination was directed to a mixer at 250 °C where vaporization of fuel and water takes place to form a feed stream. It was confirmed that nil pyrolysis of fuel happens during this vaporization process. The feed stream was directed into the mPFR to carry out the ATR reaction, for which the reaction conditions consist of fuel-supply rate = 0.02 ml min⁻¹, oxygen and steam supply rates: $O_2/C = 0.5$ and $H_2O/C = 3$ in molar ratio (where C is the carbon number of hydrocarbons), and GHSV = 10,000 h^{-1} at 1 atm. In a typical run, the mPFR was heated to $750 \,^{\circ}$ C in N₂ and then switched to superheated steam for 1 h to stabilize the packing density of catalyst bed before the feed stream was introduced into the reactor. The outlet stream from mPFR was passed through a cold trap to knock out condensable components if any and then connected to Shimadzu GC to analyze the composition. After completing the reaction, the inlet was switched to nitrogen to protect the catalyst until the mPFR was cooled down to room temperature. The fuel conversion, distribution of product gases and their yields were computed by the following equations using N₂ as internal standard.

$$Conversion = \frac{F_{total}(y_{CO} + y_{CO_2} + y_{CH_4})}{F_C \text{ in fuel}}$$
(1)

$$Yield = \frac{F_{total}y_p}{F_p \text{ in fuel}}$$
(2)

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