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Effects of calcination temperature of electrospun fibrous Ni/Al_2O_3 catalysts on the dry reforming of methane

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ABSTRACT

The effects of calcination temperature on catalyst properties were studied on fibrous Ni/Al_2O_3 catalysts prepared by electrospinning, utilizing its high thermal and structural stability. The average Ni particle size was increased up to 27.1 nm as calcination temperature was increased from 700 to 1000 °C due to the increased $NiAl_2O_4$ crystal size, which also caused the higher reduction temperature required according to temperature-programmed reduction results and the lower catalytic activity in the dry reforming of methane. Interestingly, a higher reduction temperature resulted in more and uniform Ni particles instead of catalyst aggregation. It might be the reason that the high reduction temperature thermodynamically promoted Ni nucleation on the $NiAl_2O_4$ surface to initiate Ni precipitation from ceramic bulk. The catalytic activity in the dry reforming of methane confirms the reduction temperature effect.

1. Introduction

Calcination is an important step of catalyst preparation to turn catalyst precursors into catalysts or metal oxides (e.g. NiO), which can be reduced in situ to metal catalysts to perform catalytic reactions. The calcination temperature greatly determines the catalyst properties and subsequent catalytic performance.

A high calcination temperature can cause catalyst particles to sinter and therefore to loss catalytic activity [1,2]. However, the high calcination temperature increases the interaction between catalyst particles and support [3]. A strong interaction can be beneficial for achieving high coking-resistance and catalytic activity [4,5]. Moreover, the high calcination temperature is required to form some catalysts with special characteristics. For example, Ni nanocatalyst is exsolved from $La_{0.8}Sr_{0.2}Cr_{0.82}Ni_{0.18}O_{3-\delta}$ perovskite ceramic during reduction [6]; Ni nanocatalyst is formed in situ during the reduction of $NiAl_2O_4$ spinel ceramic [7]. These nanocatalysts exhibit high dispersion and the strong interaction with the support while the spinel and perovskite phases are only formed at high calcination temperatures (e.g. 700–900 °C) [8,9]. Accordingly, it is necessary to study the effects of calcination temperature on catalyst properties to optimize preparation process.

$NiAl_2O_4$ catalyst precursors can be prepared by either an impregnation process or a wet-chemical synthesis process. There is a limited amount of $NiAl_2O_4$ formed on Al_2O_3 support surface during the impregnation process [10]. The catalysts prepared by the wet-chemical synthesis process readily aggregate during the calcination at high temperatures [11,12]. The catalyst aggregation can increase mass transfer resistance and even make some catalyst particles inaccessible for catalytic reactions, which results in the complication of catalyst calcination temperature effect on catalytic performance. Furthermore, if catalysts are calcined at a lower temperature than the reaction temperature [13], the subsequent sintering of the catalysts during the reaction will mask the effects of calcination temperature. Therefore, a catalyst with a stable structure is highly desired to study the effects of calcination temperature on catalyst dispersion, the catalyst/support interaction and catalytic performance.

In this study, we found that fibrous Ni/Al_2O_3 catalysts prepared by an electrospinning process retained the fibrous structure at a calcination temperature of 1000 °C because the fibrous structure has high resistance to sintering. Utilizing the structure-stable fibrous catalysts, this study will investigate the effects of calcination temperature on the properties of electrospun fibrous Ni/Al_2O_3 catalysts, including crystallinity, microstructure, particle size, reducibility and finally catalytic performance during the dry reforming of methane. The effect of reduction temperature on catalyst properties will also be studied. To our knowledge, it has not been reported previously.

2. Experimental

2.1. Catalyst preparation

Fibrous catalysts were prepared by an electrospinning process. A mixture of H_2O/C_2H_5OH with a weight ratio of 4:1 was used as a solvent. Polyvinylpyrrolidone (PVP, molecular weight 1.3×10^6 by Light scattering) was added to the solvent to adjust solution viscosity and form a

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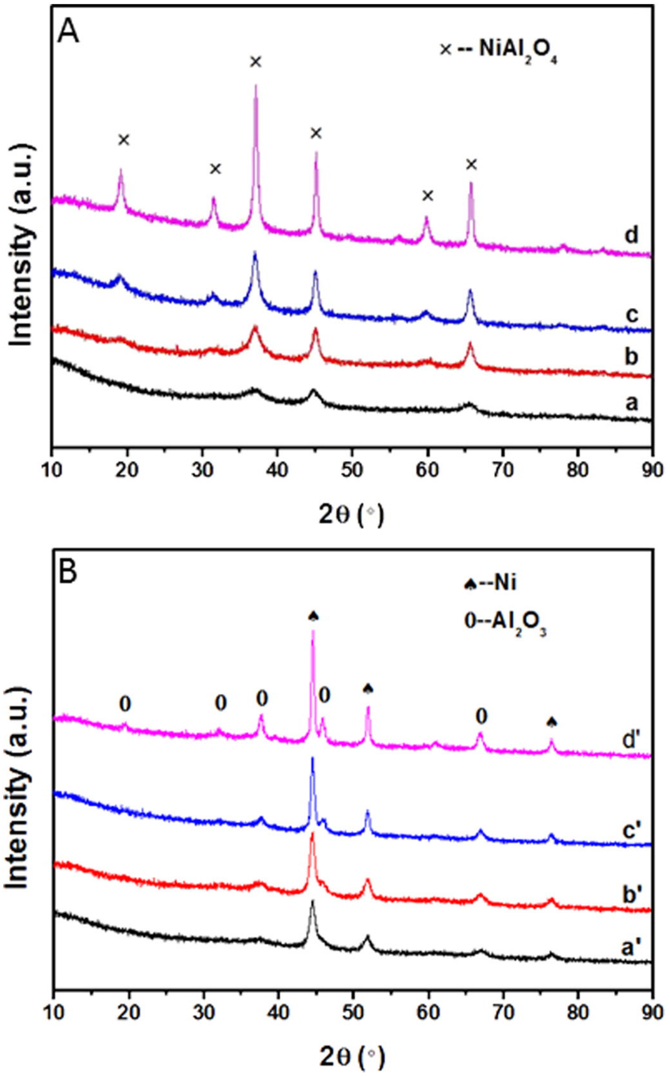

Fig. 1. XRD patterns of the Ni/Al_2O_3 catalysts before (A) and after (B) reduction at 750 °C for 1 h at different calcination temperatures: a, a′ - 700 °C; b, b′ - 800 °C; c, c′ - 900 °C; d, d′ - 1000 °C.

spinnable solution. The PVP weight ratio in the solution was 15%. $Ni(NO_3)_2\cdot 6H_2O$ (>99%) and $Al(NO_3)_3\cdot 9H_2O$ (≥98%) were dissolved in the solution to form a catalyst precursor solution. The Ni content of Ni/Al_2O_3 catalyst is 19.2 wt% in this study. 5.622 g of $Ni(NO_3)_2\cdot 6H_2O$ and 17.707 g of $Al(NO_3)_3\cdot 9H_2O$ (≥98%) were added into 40 g of the PVP solution. All chemicals were purchased from Sigma Aldrich Australia.

Electrospinning was conducted using an electrospinning device (NABOND-NEU) with an electric field of 2.4 kV/cm between a syringe tip and an aluminium foil collector. The feeding rate of the solution was 0.5 ml/min. The as-spun fibre mat was collected from the collector and then dried at 55 °C. The fibre composite was calcined in air at 700, 800, 900 and 1000 °C, respectively, to be turned into ceramic fibres.

2.2. Catalyst characterisation

The crystallinities of the ceramic fibres before and after reduction by 20 vol% H_2 in Ar for 1 h were identified using CuKα radiation with a Bruker D8 Advance diffractometer equipped with a LynxEye detector (Bruker-AXS, Karlsruhe, Germany) at a scan rate of 2°/min and a step size of 0.02°. The microstructure of fibrous catalysts was observed via a scanning electron microscopy (SEM, Zeiss Neon 40EsB FIBSEM). The catalyst reducibility was tested by the temperature-programmed reduction (TPR), which was carried out on a ChemBET3000 system (Quantachrome Instruments). 0.03 g of the Ni/Al_2O_3 catalyst was put into a U-tube sample cell and held by quartz wool. Before the test, the catalyst surface was cleaned by nitrogen at 250 °C. The sample cell was then cooled to room temperature for the test using 5% H_2 in N_2. The test was operated from room temperature to 1000 °C at a ramp rate of 10 °C/min.

2.3. Catalytic reforming test

The catalytic performance of the fibrous catalysts was tested for the dry reforming of methane. Firstly, the calcined ceramic fibre mat was crushed into flakes with sizes of about 500 μm and then loaded into a quartz tube reactor with an inner diameter of 10 mm, in which a quartz frit was set in the middle of the tube to hold the catalyst bed. The quartz reactor was vertically held in a furnace to be heated up to the desired temperatures. After the reduction by 20 vol% H_2 in Ar, the furnace temperature was set at the reaction temperature of 500 °C. The reactant gas of 10% CH_4 and 10% CO_2 balanced with Ar was introduced into the reactor to conduct reforming. Gas flow rates were controlled by mass flow controllers (Alicat Scientific). Gas chromatography (GC, Agilent 6890) was used to quantify product gas composition. After the reactions, the reactor was cooled down with a flow of Ar to avoid the oxidation of catalyst including carbon.

3. Results and discussions

3.1. Catalyst crystallinity

To investigate the effects of catalyst calcination temperature on catalyst properties, the electrospun fibre composites were calcined at different temperatures ranging from 700 to 1000 °C because $NiAl_2O_4$ formation normally starts at around 700 °C [8]. As shown in the XRD patterns in Fig. 1A, at the calcination temperature of 700 °C, the crystallinity of $NiAl_2O_4$ spinel is very low, which confirms that a high temperature is required to form $NiAl_2O_4$ spinel. The crystallinity was improved as the calcination temperature increased, resulting in increased crystal sizes. Correspondingly, the reduced catalysts showed the increased Ni crystal size with calcination temperature according to diffraction intensities in Fig. 1B. Calculated using the Scherrer Equation, the Ni crystal sizes after reduction at 750 °C are 8.8, 11.1, 17.8 and 18.1 nm, at the calcination temperatures of 700, 800, 900 and 1000 °C, respectively.

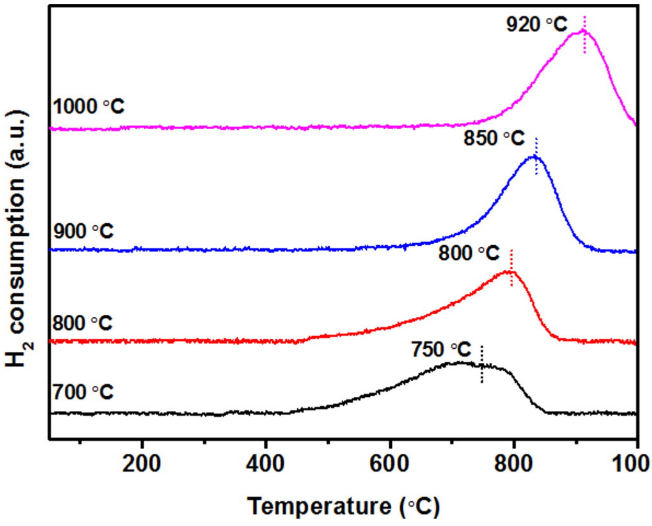

Fig. 2. TPR profiles of the catalysts calcined at different calcination temperatures.

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