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Monolithic $Ni_5Ga_3/SiO_2/Al_2O_3$/Al-fiber catalyst for CO_2 hydrogenation to methanol at ambient pressure

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ABSTRACT

A series of Ni_5Ga_3/m-SiO_2/Al_2O_3/Al-fiber (m = 0, 0.5, 1.0, 3.0 and 5.0 wt%) catalysts have been developed for CO_2 hydrogenation to methanol at ambient pressure. Microfibrous-structured SiO_2/Al_2O_3/Al-fiber supports are obtained though endogenous growth of free-standing boehmite (AlOOH) nanosheets onto a three-dimensional (3D) network of 60 μm-Al-fiber thin felt with the aid of steam-only hydrothermal oxidation reaction between Al metal and H_2O ($2\,Al + 4H_2O \rightarrow 2\,AlOOH + 3H_2$), followed by calcination and SiO_2-modification using silica sol. The bimetallic Ni_5Ga_3 nanoparticles are then placed onto the pore surface of as-obtained SiO_2/Al_2O_3/Al-fiber support by co-impregnation method using Ni and Ga nitrates as precursors followed by reduction in H_2 at 630 °C. The promising Ni_5Ga_3/1-SiO_2/Al_2O_3/Al-fiber catalyst is capable of converting 2.3% CO_2 into CH_3OH with a high selectivity of 86.7% as well as 10.3%/3.0% selectivities to CO/CH_4 at 210 °C, for a feed of $CO_2/H_2/N_2$ (2/6/1, molar ratio). Such microfibrous-structured catalyst design combines the promising catalytic performance of Ni_5Ga_3 with the enhanced heat transfer and high permeability of the Al_2O_3/Al-fiber support. The effect of SiO_2 loading on the formation of Ni_5Ga_3 alloy nanoparticles is also discussed.

1. Introduction

Global warming and ocean acidification caused by excessive CO_2 emission are two of the most vital global environmental problems in the 21 st century [1,2]. Therefore, developing high efficiency catalytic process for CO_2 transformation into high value-added chemical products has become an urgent and significant issue to mitigate these threats. Among the various transformations, CO_2-to-methanol is an ideal candidate because methanol can not only be used as a clean fuel substitute, but also be a promising platform molecule [3–5]. At present, advanced unit operation of chemical engineering enables methanol conversion into many chemicals, such as high-octane gasoline by MTG (methanol to gasoline), lower olefins by MTO (methanol to olefins), and aromatics by MTA (methanol to aromatics [4,5]. Seasonably, the concept of "methanol economy" is proposed by Olah et al. [3], which manifests the importance both in the environment protection for reducing CO_2 emissions and in the industry due to the flexible applications of methanol.

The synthesis of methanol (CH_3OH) from CO_2 and H_2 (i.e., $CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$) attracts considerable attentions from academic researches and commercial applications. Notably, CO_2 molecule is extremely inert, and this reaction is exothermic with standard enthalpy of $-49.3\,kJ\ mol^{-1}$. Hence, it is imperative, on the side of catalysis, to open up the high-performance catalysts to accelerate the kinetics of this reaction, and on the other side of reaction engineering, to effectively control the catalyst bed temperature to prevent its temperature rising that will provoke the undesired reactions.

Great efforts have been made in the hydrogenation of CO_2 to methanol [6,7]. Cu-based catalysts are recommended to be the most effective catalysts for the CO_2 hydrogenation to methanol [8,9]. For example, the $Cu/ZnO/Al_2O_3$ catalyst was used to convert syngas mixtures ($H_2/CO_2/CO$) into methanol at 5–10 MPa and 200–300 °C on an industrial scale [10]. Recently, a ZnO-ZrO_2 solid solution catalyst [11] was synthesized by co-precipitation method, and showed the methanol selectivity of 86–91% at a CO_2 conversion of higher than 10% under the reaction conditions of 5.0 MPa, gas hourly space velocity (GHSV) of 24,000 L $kg^{-1}\ h^{-1}$, H_2/CO_2 molar ratio of 3/1 to 4/1, and reaction temperature of 315 to 320 °C. However, these catalysts require high pressure (i.e., 5–10 MPa). Since high pressure has a high capital requirement and increases safety hazards, it is particularly desirable to develop an efficient catalyst that can yield a high production rate of CH_3OH from CO_2 hydrogenation at low or ambient pressure. Recently, an intermetallic compound Ni_5Ga_3 was reported to be catalytically active with a yield of 0.24 mol[methanol] mol^{-1}[active metal] h^{-1} and

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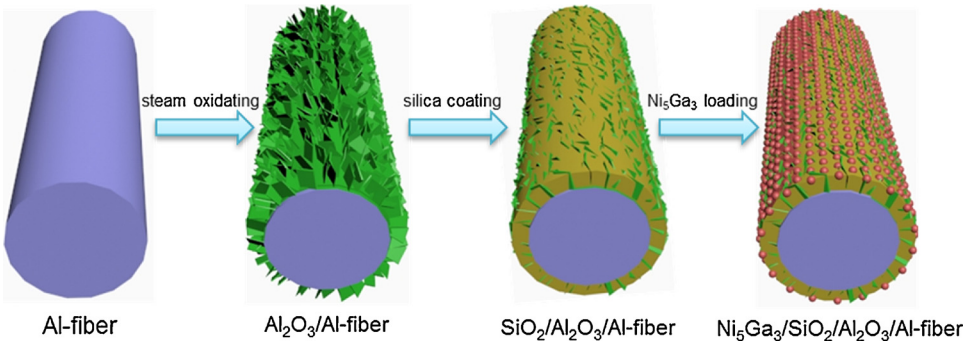

Scheme 1. Fabrication strategy of the Ni_5Ga_3/*m*-SiO_2/Al_2O_3/Al-fiber catalysts.

a considerable higher methanol selectivity than Cu/ZnO/Al_2O_3 at ambient pressure [12,13]. It was also proposed as a superior alternative to the traditional Cu/ZnO/Al_2O_3 catalyst. It should be noted that the methanol selectivity for this catalyst is very sensitive to the catalyst bed temperature, and a slight fluctuation of bed temperature causes great variation in methanol selectivity. However, exothermicity of the CO_2-to-methanol reaction easily causes the temperature rising in the catalyst bed, thereby lowering the methanol selectivity. A promising protocol to address this issue is to render a new approach to combine the superior catalytic activity/selectivity of Ni_5Ga_3 for the CO_2-to-methanol reaction with the enhanced heat transfer of the catalyst support to timely dissipate the reaction heat.

It is well known that the monolithic metal substrate is characterized with high heat/mass transfer and permeability, which is qualified to design and tailor the catalysts for strongly exo-/endothermic and/or high-throughput reactions [14–18]. Moreover, in our previous studies on the strongly exothermic syngas methanation reaction, both experimental and computational fluid dynamics results showed that the metal-foam-structured Ni catalysts achieved much lower bed temperature rising and more homogeneous bed temperature distribution than the particulate Ni/Al_2O_3 catalysts [15,16]. Delighted by the high catalytic performance of Ni_5Ga_3 [12,13] and the enhanced heat/mass transfer of Al_2O_3/Al-fiber substrates [14,17,18], we develop a monolithic $Ni_5Ga_3/SiO_2/Al_2O_3$/Al-fiber catalyst to achieve a unique combination of high activity/selectivity with enhanced heat transfer for methanol synthesis from CO_2 hydrogenation at ambient pressure. This catalyst is flexibly obtainable via direct incipient wetness co-impregnation of a mixed aqueous solution of nickel and gallium nitrates onto the silica-modified thin-felt Al_2O_3/Al-fiber substrate (60 μm diameter), followed by reduction at 630 °C in H_2 flow. Benefitting from the combination of high catalytic performance of Ni_5Ga_3 nanoparticles and high heat transfer of Al_2O_3/Al-fiber, this catalyst delivers a promising methanol productivity of 19.1 g kg_{cat}^{-1} h^{-1} (corresponding to 2.3% CO_2 conversion) with methanol selectivity of 86.7% at 210 °C for a feed of $CO_2/H_2/N_2$ molar ratio of 2/6/1 using a GHSV of 3000 L kg^{-1} h^{-1}.

2. Experimental

2.1. Catalyst preparation

2.1.1. Synthesis of thin-felt Al_2O_3/Al-fiber substrate

Thin-felt three-dimensional (3D) microfibrous network structure consisting of 10 vol% 60 μm Al-fiber (Shanghai Xincai Net-structured Material Co. Ltd) was used as the substrate for endogenous growth of free-standing boehmite (AlOOH) nanosheets with the aid of steam-only hydrothermal oxidation reaction between Al metal and H_2O ($2\,Al + 4H_2O \rightarrow 2\,AlOOH + 3H_2$), as described elsewhere [17]. Firstly, circular Al-fiber chips were ultrasonically degreased in analytically pure acetone for 10 min, etched with 0.1 wt% NaOH aqueous solution at room temperature, and then thoroughly washed with deionized water for several times. Steam-only oxidation of Al-fiber proceeded in a quartz tube with vapor steam at 120 °C for 12 h, and the AlOOH/Al-fiber substrate was obtained. After calcining at 600 °C in air for 2 h, the AlOOH/Al-fiber was transformed into thin-felt Al_2O_3/Al-fiber substrate.

2.1.2. Synthesis of silica-modified thin-felt Al_2O_3/Al-fiber substrate

SiO_2 modifier was placed onto the as-obtained Al_2O_3/Al-fiber substrate by incipiently impregnating the Al_2O_3/Al-fiber into silica sol aqueous solution (the mother sol with 30 wt% SiO_2 was purchased from Sigma-Aldrich) with different SiO_2 loading, followed by calcining at 300 °C in air for 2 h to obtain the *m*-SiO_2/Al_2O_3/Al-fiber supports (SiO_2 nominal loading (*m*): 0, 0.5, 1.0, 3.0, and 5.0 wt%). The nominal loading of SiO_2 was calculated based on the Al_2O_3/Al-fiber substrate.

2.1.3. Preparation of thin-felt Ni_5Ga_3/*m*-SiO_2/Al_2O_3/Al-fiber catalyst

Preparation method of the Ni_5Ga_3/*m*-SiO_2/Al_2O_3/Al-fiber catalyst was adapted from the reported method [12,13]. The *m*-SiO_2/Al_2O_3/Al-fiber supports were incipiently co-impregnated into a mixed aqueous solution of nickel and gallium nitrates, followed by reduced at 630 °C in atmospheric pressure H_2 for 2 h, and the thin-felt Ni_5Ga_3/*m*-SiO_2/Al_2O_3/Al-fiber catalysts were obtained. The total Ni-Ga loading was 7.5 wt% with Ni/Ga nominal atomic ratio of 5/3. Nickel nitrate (≥99.8%, Sinopharm Chemical Reagent Co., Ltd) and gallium nitrate (99.99%, Aladdin) were directly used without further purification (Scheme 1).

For comparison, a particulate catalyst of Ni_5Ga_3/SiO_2 was also prepared by the same preparation method using pure SiO_2 powder (obtained by calcining silica sol at 300 °C in air for 2 h) as support.

2.2. Catalyst characterization

X-ray diffraction (XRD) patterns were obtained by a Rigaku Ultra IV diffractometer using Cu Kα radiation at 35 kV and 25 mA in the 2θ scanning range of 20–80 ° and at a scanning rate of 30° min^{-1}. The Ni/Ga atomic ratio in the catalyst was quantitatively determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) on a USA Thermo IRIS Intrepid II XSP ICP spectrometer. Scanning electron microscopy (SEM) images of the Al_2O_3/Al-fiber substrate, the 1-SiO_2/Al_2O_3/Al-fiber support and the Ni_5Ga_3/1-SiO_2/Al_2O_3/Al-fiber catalyst were obtained on a Hitachi S-4800 instrument. Transmission electron microscope (TEM) image of the Ni_5Ga_3/1-SiO_2/Al_2O_3/Al-fiber catalyst was obtained on a FEI TECNAI G^2 F30 instrument at 300 kV. The specific surface area (SSA) was determined using standard Brunauer-Emmett-Teller (BET) theory based on N_2 adsorption isotherm on a Belsorp max instrument at −196 °C. The pore size distribution and total pore volume were determined using the Barrett-Joyner-Halenda (BJH) method calculated by the adsorption isotherm.

H_2-temperature programmed reduction (H_2-TPR), NH_3-temperature programmed desorption (NH_3-TPD), and CO_2-temperature programmed desorption (CO_2-TPD) were performed on a TP 5080 multi-functional automatic adsorption instrument (Xianquan Industrial and Trading Co., Ltd) with a thermal conductivity detector (TCD) and an online mass