Fuel 222 (2018) 513–522

Contents lists available at ScienceDirect

Fuel

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

The effect of lanthanide promoters on NiInAl/SiO_2 catalyst for methanol synthesis

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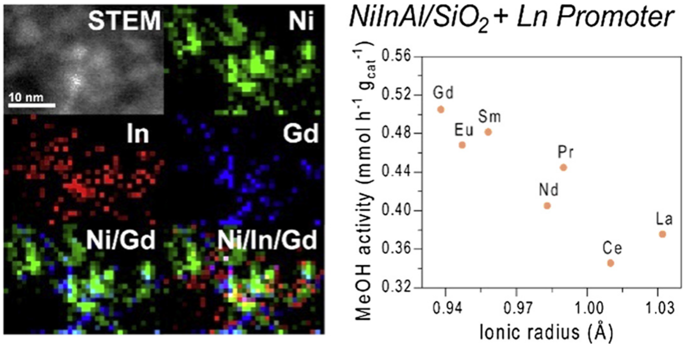
GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Lanthanides
Rare earth elements
Methanol synthesis
CO2 utilization
Nickel indium catalyst

ABSTRACT

The addition of lanthanides, or rare earth elements, as promoters to NiInAl/SiO_2 methanol synthesis catalysts was investigated. The promoters studied are the light rare earth elements (La to Gd) and all but La and Ce were shown to improve methanol synthesis activity. A comparison of the synthesis method for introduction of Pr as a promoter found that addition during the deposition-precipitation synthesis of the catalyst is superior to incipient wetness impregnation introduction after synthesis. The heaviest lanthanides tested (Sm, Eu, Gd) showed the greatest improvement in methanol synthesis activity and selectivity, with a concomitant decrease of CO produced. The Gd-promoted catalyst showed the greatest increase in methanol synthesis activity at 0.51 mmol $g_{cat}^{-1}\,h^{-1}$ which is a 27% increase over the catalyst with no promoter. Examination of the basic characteristics of the catalysts by CO_2 TPD and in situ FTIR revealed a negative correlation between basicity and methanol synthesis activity. FTIR methanol synthesis tests also revealed a larger proportion of the key intermediate, bidentate formate, with the addition of the Gd promoter. STEM micrographs and particle size distributions show that the incorporation of the Gd promoter results in smaller diameter metallic particles and higher resistance to sintering. EELS mapping revealed that the location of Ni and Gd correlates well with the metallic particles observed with STEM, and while the In is also found in these particles, small amounts are also observed to be dispersed outside of the particles.

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https://doi.org/10.1016/j.fuel.2018.02.185
Received 24 December 2017; Received in revised form 24 February 2018; Accepted 28 February 2018

1. Introduction

The release of carbon dioxide to the atmosphere remains a concern, not only in the context of climate effects and regulations, but also in terms of release of a potential feedstock. The use of CO_2 as a carbon source for gas to liquids conversion is a potential route for mitigation of its release while also providing a method for carbon recycling and value addition. Recently, we have synthesized a new family of methanol synthesis catalysts employing a phyllosilicate-derived nickel-indium-aluminum catalyst supported on SiO_2 (NIA catalyst) [1]. The phyllosilicate phase that is formed during synthesis contains nickel which is freed by partial decomposition of the phyllosilicate during reduction. The nickel then agglomerates with the other catalyst metal atoms on the surface to form mixed-metal particles. We now investigate the addition of lanthanide (Ln) promoters to NIA catalyst for their potential to increase methanol activity and selectivity while decreasing the output of CO due to the reverse water gas shift reaction.

As the simplest alcohol, methanol (CH_3OH) is used as a feedstock to produce several chemicals including formaldehyde, MTBE, DME, and acetic acid. It is also used in fuel blending and in methanol-to-olefins (MTO) and methanol-to-propylene (MTP) processes, with a 2015 global demand of 70 million metric tons [2]. Methanol is produced industrially from CO, CO_2, and H_2, typically using copper-based catalysts incorporating zinc and aluminum at 50–100 atm and temperatures of 230–300 °C [3,4]. The overall reactions for CH_3OH synthesis from CO, CO_2, and H_2 are described by R1 and R2. In addition to the methanol synthesis reactions, the reverse water gas shift reaction (R3) also occurs as well as the side reaction producing CH_4 (R4). Both reactions for methanol synthesis from CO or CO_2 are exothermic, which means that they are favored thermodynamically at low temperatures, but reaction kinetics favor higher temperatures so a balance is required. In our previous study, it was found that the methanol synthesis temperature range for NIA catalysts was ~50 °C higher than the copper-based catalysts, resulting in greater activity. The water gas shift reaction, shown here in reverse as R3, consumes the CO_2 and H_2 reactants to produce CO and H_2O which is typically an unwanted result.

In addition to the carbon source, in this case CO_2, hydrogen is also needed for methanol synthesis as shown in R1 and R2. The further development of renewable methods for H_2 production combined with carbon recycling via CO_2 use translates to a production of a renewable fuel or feedstock as methanol.

$$CO+2H_2 \rightarrow CH_3OH \quad (\Delta H= -90.4\ \text{kJ mol}^{-1}) \tag{R1}$$

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \quad (\Delta H= -49.2\ \text{kJ mol}^{-1}) \tag{R2}$$

$$CO_2 + H_2 \rightarrow CO + H_2O \quad (\Delta H= 41.2\ \text{kJ mol}^{-1}) \tag{R3}$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad (\Delta H= -200.6\ \text{kJ mol}^{-1}) \tag{R4}$$

In an effort to increase CH_3OH synthesis activity and inhibit the reverse water gas shift reaction, lanthanides were chosen as promoters for NIA catalysts due to their ability to enhance or diminish catalyst basicity. Studies on lanthanides (otherwise known as rare-earths) for methanol synthesis have shown that for various catalysts, their incorporation can improve activity and/or selectivity [5–9]. The lanthanides examined in this work are categorized as the light rare earth elements which include lanthanum, cerium, praseodymium, neodymium, samarium, europium, and gadolinium. Scandium is also included as a light rare earth element, but it is not included in this work.

2. Experimental

2.1. Materials

All materials were obtained from commercial sources. The silicon dioxide support (99.5%, 325 mesh), nickel(II) nitrate hexahydrate (99%), lanthanum(III) nitrate hexahydrate (99.99%), cerium(III) nitrate hexahydrate (99.99%), praseodymium(III) nitrate hexahydrate (99.9%), neodymium(III) nitrate hexahydrate (99.9%), europium(III) nitrate pentahydrate (99.9%), gadolinium (III) nitrate pentahydrate (99.99%), and sand (50–70 mesh) were provided by Sigma-Aldrich. Samarium(III) nitrate pentahydrate (99.9%) was obtained from Acros Organics. Indium(III) nitrate hydrate (99.999%) was provided by Alfa Aesar. Aluminum nitrate (99.9%) was provided by J.T. Baker. Sodium carbonate (Na_2CO_3, 99.5%) was provided by Fisher Scientific. Nitrogen (99.999%), helium (99.999%), hydrogen (99.999%), carbon dioxide (99.995%), and carbon monoxide (99.999%) were all provided by U.S. Welding.

2.2. Catalyst preparation

The deposition-precipitation method was used to prepare all catalysts, and the procedure used is similar to those described elsewhere [10–12]. A 100 mL solution of metal nitrates (nickel, indium, aluminum, and lanthanide) at the designated molar ratio was prepared in a room-temperature (~20 °C), stirred glass reactor to which the silica support was added. The pH was then raised to 10 by addition of a 1 M solution of sodium carbonate at a 0.3 mL min^{-1}, after which the pH was maintained for an aging period of thirty minutes by dropwise addition of sodium carbonate solution. Catalysts were subsequently filtered and rinsed three times using deionized water, followed by drying at 90 °C for ten hours. Catalysts were then ground to obtain particles no larger than 125 μm. All catalysts were calcined at 400 °C under dry air at a flowrate of 120 mL min^{-1}.

2.3. Physical and chemical characterization

Elemental analysis data for all catalysts was obtained using a PerkinElmer NexION 300S ICP-MS employing kinetic energy dispersion (KED) mode. A Quantachrome Instruments Quadrasorb-evo was used to obtain N_2 soprtion isotherms at −196 °C from which Brunauer-Emmett-Teller (BET) surface area, BJH (desorption) pore volume, and pore radius were calculated. Temperature programmed reduction (TPR) using H_2 and temperature programmed desorption (TPD) of CO_2 was recorded using a Quantachrome Instruments Autosorb iQ. TPR was performed on calcined samples in the temperature range of 40–1100 °C with a heating rate of 5 °C min^{-1} following outgassing at 200 °C in flowing He. TPD of CO_2 was performed on samples reduced in situ by flowing hydrogen at 390 °C for 120 min, followed by CO_2 at 30 °C for 120 min, then a final helium purge before measuring desorption from 30 to 350 °C at 5 °C min^{-1}. Scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS) analyses were performed using a 300 kV FEI Titan 80–300.

Fourier transform infrared spectroscopy (FTIR) studies were performed at atmospheric pressure using a Thermo Scientific Nicolet iS50 FTIR spectrometer employing a Praying Mantis device (Harrick Scientific) equipped with ZnSe windows, and MCT/A detector. Preceding tests, samples were reduced in situ at 390 °C under flowing H_2 for thirteen hours, followed by He at 100 mL min^{-1} for two hours to purge the H_2 from the chamber. FTIR TPD experiments were performed by first loading the surface of the catalysts with CO_2 by flowing the gas through the reaction chamber at 40 mL min^{-1} for six hours at 30 °C, after which the chamber was purged using He at 100 mL min^{-1} for two hours. TPD was then recorded in the range of 30–500 °C at a heating rate of 1 °C min^{-1} under flowing He (100 mL min^{-1}). Carbon monoxide temperature programmed adsorption (TPA) was conducted by flowing