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In-situ hydrogasification/regeneration of NiAl-hydrotalcite derived catalyst in the reaction of CO_2 reforming of methane: A versatile approach to catalyst recycling

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ABSTRACT

A novel approach describing the *in-situ* regeneration of NiAl hydroalcite derived catalyst between two cycle reaction systems of CO_2 reforming of methane, also known as dry reforming of methane (DRM) is described herein. The catalyst was initially prepared by co-precipitation method at pH = 11 and calcined at 450 °C for 6 h. The obtained material was characterized using X-ray diffraction (XRD) spectroscopy, Fourier transform infrared (FTIR) spectroscopy, Brunauer-Emmett-Teller (BET), atomic absorption spectroscopy (AAS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), thermogravimetry (TG/ATD) and temperature programmed reduction (TPR-H_2) techniques. Following treatment of our catalyst under DRM conditions, the catalyst was subjected to *in-situ* hydrogasification conditions to promote regeneration followed by a second DRM cycle. An increase of 15.7% in the conversion of CH_4 and 17.3% in the conversion of CO_2 was attained, while the ratio of resulting H_2/CO augmented by 14%. The ratio of H_2 consumed over the course of two hours hydrogasification, to that generated over ten hours of DRM, was 9.6%. The small particle sizes of resulting Ni° species as well as their high stability were both key factors contributing to the increase in the amount of H_2/CO produced prior to and after regeneration.

1. Introduction

The development of efficient and recyclable catalysts which can be utilized to effect diverse range of chemical transformations had attracted the attention of many environmental and green chemists over the past decades. Recently, a number of research groups reported the utilization of various catalysts such as those derived from NiAl hydrotalcites (NiAl-HT) for the process of dry reforming of methane [1,2], a chemical procedure that converts two main greenhouse gases, namely methane and carbon dioxide to produce syngas in excellent conversion yields. However, the formation of coke on the surface of the catalyst limits the role of continuously utilizing such metal complexes over prolonged period of times; thus, the reaction yield degrades and the overall process becomes inefficient [3].

Compared to steam reforming of methane, DRM reaction was found to produce equimolar amounts of H_2 and CO gas [4]. The resulting syngas can play an important role in the Fisher-Tropsh synthesis [5], a key procedure for the production of a variety of hydrocarbons used as precursors to gain access to other useful chemical derivatives. When blasted with a source of steam, syngas can react with water at high temperatures to generate methanol in good yields [6]. The inclusion of Zeolites [7], supported catalysts and other mixed oxides such as Al_2O_3, ZrO_2 and CeO_2 was also found to play a positive role in the smooth transformation of DRM reaction [8,9].

The incorporation of noble metals such as Ru, Rh and Pt as catalysts for DRM reaction was also investigated by other scientists; although the transformation was remarkably efficient, the high cost of such metals in conjunction with their limited

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availability rendered the scientific community to limit the exploitation of such materials [5,10].

Hydrotalcite (HT) like compounds, also named layered double hydroxides (LDH), are anionic clays, their structure is based on a mixture of divalent and trivalent metal cations occupying randomly the centers of coplanar edge-sharing $M(OH)_6$ octahedra. $\mathbf{[M_{1-x}^{2+}\ M_x^{3+}\ (OH)_{2}]^{x+}[A^{n-}{}_{x/n}]\ m\ H_2O}$ is the general formula of hydrotalcite where A^{n-} represent interlayer anions (CO_3^{2-}, NO_3^-, Cl^-, OH^-) or organic anions and n^- is the charge in interlayer ion; x and m are the fraction constants [11]. This class of materials is characterized by their low density and high surface area. Numerous works studied the influence of thermal decomposition effect on the stability and catalytic activity of these materials [11,12]. The thermal stability of hydrotalcites depends on their method of synthesis, the ratio M^{2+}/M^{3+} and the nature of incorporated metals (M^{2+}, M^{3+}). The thermal decomposition temperature of hydrotalcite (loss of LDH structure) can be initiated at different temperatures ranging from 300 °C to 500 °C [13]. The higher thermal treatment induces dehydratation, dehydroxylation and loss of compensation inter-anions, thus, forming mixed oxides with redox and/or basic properties [14,15]. Furthermore, the oxides derived from hydrotalcites show small particle sizes, large surface areas, homogenous inter-dispersion of metallic phase and a better resistance to sintering compared to other supported catalysts [11,13].

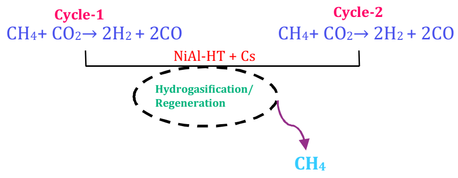
Previously, Fredersdorff reported an elegant process for coal gasification to produce methane gas [16]; Iwasyk and co-workers also reported that reaction of elemental carbon and hydrogen in the presence of nickel or cobalt catalyst, at elevated temperatures, *i.e.*, 527 °C, produces methane gas in good conversion yields [17]. Inspired by Le Châtelier's principle and with this information in hand [18], we envisaged that pausing the DRM process for a short period of time, and subsequently introducing a short reaction cycle to convert the elemental carbon residing on the surface of the hydrotalcite derived catalyst, should result in the formation of methane gas; thus regenerating the catalyst in order to initiate a second DRM cycle (Scheme 1).

In this paper we demonstrate for the first time, an efficient *in-situ* procedure to regenerate Ni/Al hydrotalcite derived catalyst using hydrogasification to subsequently effect a second process of DRM reaction. To the best of our knowledge, *in-situ* regeneration of Ni/Al hydrotalcite derived catalysts using hydrogasification during the process of DRM has not been previously studied by other research groups.

2. Experimental

2.1. Catalyst preparation

NiAl-HT catalyst with ratio (Ni^{2+}/Al^{3+}) = 2 was prepared by co-precipitation method at pH = 11, starting from a solution containing appropriate amounts of nitrate salts of Ni^{2+} and Al^{3+}. Sodium carbonate solution was added drop-wise to the nitrate solution while pH was maintained constant by adding NaOH (1 M) under vigorous stirring at room temperature. The obtained slurry was hydrothermally treated at 60 °C for 24 h, washed several times with bi-distilled water until a neutral pH of the filtrate was obtained. Finally, the powder was dried in an oven at 80 °C overnight and calcined at 450 °C for 6 h with heating increments of 4 °C/min.



Scheme 1. Hydrogasification/Regeneration protocol for DRM.

2.2. Catalyst characterization

The chemical composition was established by atomic AAS using Spectro-Analytical Instruments Horiba Jobin–Yvon, Ultima2 spectrometer. X-ray diffraction (XRD) patterns were recorded with Siemens D-501 diffractometer using CuKα radiation in the 2θ range between 5 and 80°. Brunauer-Emmett-Teller (BET) analysis was carried out with a NOVA 2000e volumetric adsorption analyzer at −196 °C. Prior to measurement, the powder was degassed under vacuum at 150 °C for 2 h. Fourier transform infrared (FTIR) spectra were recorded with a Perkin Elmer spectrometer over 32 scans to improve the signal-to-noise ratio in the wavelength range (400–4000 cm^{-1}). The analysis was performed on *ca.* 4 mg of powder mixed with 100 mg of dried spectroscopic KBr pressed into pellets. Thermogravimetry (TG) and differential thermal analysis (DTA) were carried out with a Netzsch STA 409 PC/PG instrument using air as purge gas at temperature up to 850 °C with heating rate of 10 °C/min. Scanning electron microscopy (SEM) images of the products were recorded on a Hitachi S-4800 instrument equipped with a field emission filament using an acceleration voltage of 5 kV and a working distance of 10 mm. Temperature programmed reduction (TPR) profiles were determined using a TriStar 3000 V6.01A apparatus equipped with a TCD detector. Prior to TPR analysis, 20 mg of the catalyst was placed in a quartz tube reactor, flushed with Ar and incrementally heated to 120 °C for 2 h under continuous flow of Ar, then cooled to room temperature. TPR analysis of the catalyst was performed using 5% H_2 in Ar with a flow rate of 50 mL/min from room temperature to 950 °C; the temperature was raised with increments of 10 °C/min. To prevent the possibility of substance coalescence, Caballero's approach was applied during TPR analysis [19]. Transmission Electron Microscopy (TEM) was performed on Philips CM-200 operated at 200 kV. Raman spectroscopy was done on Witec spectrometer equipped with alpha-300 microscope using Ar ion laser; the analysis power was 0.5 MW.

2.3. DRM reaction and catalyst hydrogasification/regeneration

Catalytic activity measurements were carried out under atmospheric pressure in U-shaped tubular quartz reactor. Quartz wool was used as the catalyst bed. Prior to reaction, 100 mg of the obtained NiAl-HT catalyst was reduced *in-situ* under constant hydrogen flow at 650 °C for one hour. The reactor's temperature was then reduced to 500 °C and a stream gas mixture containing a molar ratio of 20/20/60 of $CH_4/CO_2/Ar$ was passed through the reactor under continuous flow, while the total flow rate was kept at 30 mL/min over the course of ten hours. The system temperature was then elevated to 700 °C for 30 h upon which a drastic treatment of the catalyst to force carbon deposition during DRM was performed; the temperature was then dropped to 500 °C for another 10 h. The outgoing gas generated from the reactor was analyzed by gas chromatography (GC) containing thermal conductivity detector (TCD) and carbosieve B columns (1w/8 inch, 100–200 mesh). The overall process was halted for 2 h during which the elemental carbon enriched catalyst, resulting from DRM reaction, underwent a regenerative hydrogasification cycle in the presence of hydrogen gas. The hydrogasification/regeneration process was performed *in-situ* at 650 °C for 2 h. A second cycle of DRM reaction was then initiated at 500 °C for another 10 h, using the same gas molar ratio and flow rate as mentioned earlier (Scheme 2).