Applied Catalysis A: General 490 (2015) 80–92

Contents lists available at ScienceDirect

Applied Catalysis A: General

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

Effect of interactions between Ni and Mo on catalytic properties of a bimetallic Ni-Mo/Al_2O_3 propane reforming catalyst

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ARTICLE INFO

Article history:
Received 5 September 2014
Received in revised form 26 October 2014
Accepted 2 November 2014
Available online 11 November 2014

Keywords:
Hydrogen production
Steam reforming
Ni-Mo catalysts

ABSTRACT

The effect of promoting a 15 wt.% Ni/Al_2O_3 catalyst with small amounts of Mo (0.1 and 0.5 wt.%) to produce H_2 via propane oxidative steam reforming was investigated. Activity and stability experiments run at 450 °C showed that the 0.1 wt.% Mo-promoted catalyst had higher propane conversion, higher H_2 yields and showed superior performance in terms of resisting deactivation by coking. Different characterization techniques show that the impact on activity, selectivity and stability are driven by an electronic effect of Mo on Ni, even with such small amounts. For example, oxygen storage capacity measurements revealed higher oxygen mobility over the promoted catalyst surface. This high O_2 mobility led to higher gasification rates of carbonaceous species, leading to higher H_2 yields and preventing coking of the catalyst. In-situ DRIFTS experiments also showed that the addition of Mo affected the stability of adsorbed reaction intermediates on the catalyst surface. Higher CO yields over the Mo-promoted catalyst resulted from weak adsorption or rapid desorption of CO in the presence of these small amounts of Mo. These changes in intermediate species stabilities affected some pathways in the general propane oxidative steam reforming scheme. Weak adsorption of CO also decreased the amount further oxidized to CO_2 while the increased oxidation of CHx species lowered the amount hydrogenated to CH_4.

1. Introduction

Because of its common storage and existing infrastructure, propane is a potential candidate as a hydrogen carrier. Early studies included research on total combustion and during the 1990s significant amounts of research were published which focused on propane reforming (mainly steam reforming) as a process to supply hydrogen [1]. Autothermal reforming has also been investigated, where the reactor combines endothermic steam reforming with exothermic oxidation reactions, via the addition of small amounts of O_2 [2].

For many years, nickel has been the most suitable metal for steam reforming of propane as far as cost effectiveness is concerned. Usually nickel is supported on alumina, magnesia, zirconia and/or ceria [3–6]. These supports provide high crush strength and stability. However, coke formation is still a major problem associated with nickel catalysts. Filamentous carbon is formed at the surface of the metal particle by consecutive formation, diffusion and dissolution of carbon [7]. As the coke is produced, the degradation of the catalyst is accelerated until the catalyst is deactivated by coking and continuation of catalyzed reforming becomes impossible. To improve the stability of the Ni-based catalyst and its resistance to coking, many researchers have considered adding another metal to Ni to form a bimetallic structure on the same support, as well as adding small amounts of O_2 to be fed with steam and propane [8–12].

The benefit of adding a metal to a monometallic catalyst is driven by the structural interaction between the two metals, or between the metals and the support within the new bimetallic catalyst. Generally, these structural interactions may be of a textural nature affecting the physical properties of the Ni catalyst such as metal dispersion or metal crystal surface area [13–15] or they may be of an electronic nature, changing electronic densities of different catalyst components, and hence affecting the adsorption and chemical interactions of these components with different reaction intermediates [16,17]. Although these interactions may be established at the onset of the reaction [4,6,18,19], the nature of these interactions may change during time on stream.

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http://dx.doi.org/10.1016/j.apcata.2014.11.002
0926-860X/

Mo-Ni catalysts have been extensively studied in the literature as active and stable hydrodesulphurization catalysts [20,21]. In these catalyst formulations, the Mo loading is greater than that of Ni, since Mo is the primary desulphurization metal, while Ni is added as a promoter. More recently, a number of studies have evaluated Ni-Mo catalysts for reactions other than desulphurization, especially those that have Ni as the main reactant-activation metal [22–27]. Although in most of these studies the resistance of Ni-Mo catalysts to coking during hydrocarbon reforming has been observed, an agreed upon explanation of the role of Mo has not been established, especially for very low Mo loadings (<0.5 wt.%) [16,17]. Moreover, in many studies the addition of Mo to Ni had a negative impact on catalyst activity [28–30], while none discussed the effect of Ni-Mo catalysts on the selectivity to different steam reforming (SR) or oxidative steam reforming (OSR) reaction products. The objective of this study was to investigate the effect of adding small amounts of Mo to a 15 wt.% Ni/Al_2O_3 propane reforming catalyst. Different characterization techniques were applied to understand the nature of the effects (textural and electronic) with the addition of small amounts of Mo (0.1–1 wt.%) on the Ni catalyst, and to explain the changes and improvements in the catalytic properties based on these.

2. Experimental methods

The 15 wt.% Ni/Al_2O_3 (15Ni) catalyst was prepared using a wet impregnation method. A calculation using the support surface area and Ni atomic radius suggests that 15 wt.% is the amount of Ni required to form a monolayer of the support surface. Commercial γ-Al_2O_3, in the form of a 3 micron powder, with a surface area of 80–120 m^2/g and 99.97% metal basis, was purchased from Alfa Aesar. After drying the required amount of support overnight, the calculated amount of $Ni(NO_3)_2{\cdot}6H_2O$, used as the Ni precursor (also obtained from Alfa Aesar), was added to the Al_2O_3 powder and mixed in deionized water. After mixing, water was evaporated by heating and stirring the mixture until a paste-like mixture was obtained. The paste was dried overnight, and then the catalyst was crushed and sieved to obtain 35-45 mesh particles. The 15 wt.% Ni-X wt.% Mo/γ-Al_2O_3 bimetallic catalyst was prepared using a co-impregnation method. In this method, $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (supplied by Alfa Aesar) was used as the Mo precursor, and was dissolved with the $Ni(NO_3)_2{\cdot}6H_2O$. Following the same evaporation and drying procedure of the 15Ni catalyst, 35–45 mesh particles of the bimetallic catalyst were obtained. The freshly prepared catalysts were then calcined at 700 °C for 3 h. Three Mo-based samples were prepared: 15 wt.% Ni–0.1 wt.% Mo/γ-Al_2O_3 (0.1Mo), 15 wt.% Ni–0.5 wt.% Mo/γ-Al_2O_3 (0.5Mo) and 15 wt.% Ni-1 wt.% Mo/γ-Al_2O_3 (1Mo, which was used only in TPR experiments).

H_2-TPR experiments were run using a 0.3 mm ID quartz reactor, filled with 200 mg from the same catalyst batches, after calcination in the furnace with air circulation for 3 h at 700 °C. The temperature was ramped from room temperature to 950 °C at a rate of 3 °C/min. At 300 °C a stream of 5% H_2 in N_2 was introduced. H_2O produced via the reduction was removed using a silica gel trap before reaching the GC. H_2 concentrations were measured using an Agilent 3000 micro GC equipped with a TCD.

XRD patterns were compared for the non-promoted 15Ni catalyst and two Mo-promoted catalysts; 0.1Mo and 0.5Mo. XRD patterns were measured first for fresh catalysts after calcination in an external oven at 700 °C, and then after reduction by H_2 at 750 °C. Also, in order to identify patterns resulting from the support, XRD patterns were obtained from pure γ-Al_2O_3 calcined at 700 °C. A BrukerAXS D8 Advance diffractometer using a Bragg-Brentano geometry with Ni-filtered Cu Kα radiation of λ = 1.5425 Å was used. Spectra were collected for a 2θ range of 15–80° using a step size of 0.02° and a count time of 1 second.

H_2 chemisorption was measured for three reduced catalysts (15Ni, 0.1Mo and 0.5Mo) to calculate Ni dispersions as well as Ni crystallite size. Measurements were performed in a Hiden CatLab reactor using a dynamic flow technique to measure H_2 chemisorption uptake at room temperature. Prior to each run the catalyst was reduced under a H_2 stream at 750 °C. The reactor was then cooled down under He and pulses of a H_2/He stream were injected through the catalyst bed. H_2 uptakes were measured using a Hiden QIC mass spectrometer until no further H_2 uptake was detected.

Oxygen storage capacity (OSC) measurements were performed in a Hiden CatLab reactor. 50 mg of fresh pre-calcined catalyst at 700 °C for 3 h was placed in a tube reactor of 4 mm ID. The catalyst was first reduced in a 5% H_2 in He stream at 750 °C for 30 min. Then the temperature was cooled to room temperature and the reactor was flushed with pure He. A dynamic flow technique was used to measure O_2 uptake at room temperature. In this method, pulses of a 1 vol% O_2/He were injected through the catalyst bed and O_2 uptakes were measured using a Hiden QIC mass spectrometer until no further O_2 uptake was detected. The same procedure was repeated to measure O_2 uptake at 400 °C.

In-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) experiments were performed in a Nicolet Nexus spectrometer, equipped with a MCT detector and a KBr beam splitter. 100 mg of pre-reduced powder catalyst was placed in a small cylindrical ceramic cell. The maximum cell temperature that could be reached was 400 °C, controlled using a Thermo Scientific-Cal 9500P temperature controller. Prior to each run, background normalization of the spectra was performed by subtracting the spectrum recorded in a flow of He at the reaction temperature. In all experiments, the spectra were averaged over 50 scans in the mid IR range (600–4000 cm^{-1}) to a nominal 4 cm^{-1} resolution. Scans were taken every minute until no change between spectra was observed. The reaction gases were then stopped and only He was flowed as desorption spectra were collected. Spectra were collected and analyzed using OMNIC computer software.

Activity and selectivity of different catalysts for propane steam reforming were tested in a standard laboratory fixed bed reactor setup composed of three main parts; the reactant delivery system, the reactor and the analytical system. Gases were supplied by Praxair. Propane had a quality grade of 99.5%, with a sulfur content less than 1 ppmw, while O_2, H_2 and N_2 had quality grades of 99.99%. Flow rates of the different gases were controlled by mass flow controllers. A Brooks 5850E mass flow controller was used to control the flow rate of propane, while Unit UFC 1000 mass controllers were used to control flow rates of the other gases. The specified amount of steam was generated by delivering deionized water to a vaporizer through a KDS model 200 syringe pump manufactured by KD Scientific. The vaporizer consists of an 18″ long, 1/8″ OD stainless steel tube, wrapped in heating tape. To ensure complete vaporization of the water, the vaporizer temperature was set and maintained at 230 °C. The gases mix with steam in the vaporizer before entering the reactor from the top.

The reactor was installed inside a vertical tube furnace and consisted of a quartz tube 555 mm long with an ID of 9.9 mm and wall thickness of 2 mm, where the catalyst bed sat on a quartz frit located 220 mm from the top of the reactor, in the middle of the isothermal zone of the reactor. A K-type thermocouple was installed inside the furnace, just beside the catalyst bed, to control the furnace temperature, while the catalyst bed temperature was measured using a quartz sheathed micro K-type thermocouple located just above the bed. The hot product stream entered a condenser, where the water was removed. The non-condensable gas products exited the condenser to the GC for compositional analysis.