Catalysis Today 207 (2013) 13–20

Contents lists available at SciVerse ScienceDirect

Catalysis Today

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

Diesel steam reforming: Comparison of two nickel aluminate catalysts prepared by wet-impregnation and co-precipitation

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ARTICLE INFO

Article history:
Received 6 March 2012
Received in revised form
24 September 2012
Accepted 25 September 2012
Available online 3 November 2012

Keywords:
Co-precipitation
Wet impregnation
Nickel catalyst
Diesel steam reforming

ABSTRACT

γ-Al_2O_3 supported Ni–Al spinel catalysts, prepared by co-precipitation and wet impregnation, were produced, analysed and tested on commercial diesel steam reforming. The study of the preparation method's effect on the catalytic activity, builds on a previously patented Ni–Al spinel ($NiAl_2O_4$) catalyst supported on alumina (Al_2O_3) and yttria-stabilized zirconia (YSZ). This non-noble metal-based $NiAl_2O_4/Al_2O_3$–YSZ catalyst demonstrated high activity for commercial diesel and biodiesel steam reforming.

Diesel steam reforming experiments were performed in a fixed-bed reactor setup, with a proprietary diesel–water emulsion mixture at 760 °C. The two tested catalytic formulations yielded the same overall conversion while the products obtained were significantly different. Thus, the catalyst produced via the co-precipitation method (Copr) (a) suffered rapid deactivation from carbon deposition; (b) produced 5 times more methane than the catalyst produced via the wet impregnation method (Impr) and (c) showed a decreasing hydrogen production. The Impr catalyst exhibited a higher stability for diesel steam reforming with no signs of carbon formation or activity loss. The difference between Impr and Copr catalyst activities is related to the Ni-aluminates dispersion: located on the surface for the Impr catalyst, whereas located in the bulk of the Copr catalyst.

In order to correlate their activities to their physicochemical properties, both new catalytic formulations presented in this work were characterized before and after steam reforming tests, using scanning electron microscopy (SEM), X-ray diffraction (XRD) as well as temperature programmed reduction (TPR).

1. Introduction

The increasing deployment and use of fuel cells in various applications are driven by our society's need for innovative energy production methods. Hydrogen is an ideal fuel for fuel cells, thus making it an invaluable energy source with increasing demand.

Liquid fuels, derived from either fossil or renewable sources, represent an attractive source of hydrogen since their distribution infrastructure is readily available. Steam reforming is the most effective method to produce hydrogen from liquid hydrocarbons with a high yield [1].

Although steam reforming of methane/natural gas to produce hydrogen is a well-defined and mature technology, liquid fuel reforming still encounters significant scientific and technological challenges. The financial burden of the catalysts and the lack of precise knowledge of the deactivation pathways are two critical issues associated with this hydrogen production method. These challenges have led to a massive interest for the development of cheap, active, poison-resistant and renewable catalysts.

Noble-metal-based catalysts (Pt, Rh, Pd) are more efficient because of their long-term activity and coke resistance, but their cost is prohibitive [2–4]. Nickel-based catalysts appear to be a good alternative but suffer rapid deactivation due to carbon and sulphur poisoning. Coking appears in 3 ways: (1) the diffusion of carbon into active metal crystal causing its detachment, then carbon filament growth from the detached metal (whisker carbon), (2) hydrocarbon cracking at high temperatures (pyrolytic carbon), (3) polymerisation of hydrocarbons (encapsulating carbon) [1,5]. Wang et al. [6], reported that coking is due to the support acidity, while Li et al. [7], attributed this problem to the nickel particle size, especially for those larger than 12 μm.

We have previously reported that a nickel–alumina, supported on alumina and yttria-stabilized zirconia catalyst ($NiAl_2O_4/Al_2O_3$–YSZ) [8–10], prepared by wet-impregnation, demonstrates a high diesel conversion and a noticeable poison resistance when compared with the traditional Ni/Al_2O_3–YSZ catalyst. This catalyst remains stable for more than 14 h of laboratory testing, at H_2O/C molar ratios as low as 1.9 without any significant carbon deposition. Although the catalyst is extremely efficient for diesel and biodiesel steam reforming, questions remain concerning possible interactions between the active metal and support.

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http://dx.doi.org/10.1016/j.cattod.2012.09.017

In addition to the catalytic metal used, the production method also has an impact on the catalyst's performance. Several studies [11–13], reported that one of the most important parameters is the preparation procedures of the catalyst. It is known that the catalytic activity and selectivity are strongly affected by several physico-chemical features such as total surface area, total pore volume and metal distribution.

Both wet impregnation and co-precipitation methods are reported in the literature for Ni–Al_2O_3 catalyst preparation [7,14]. Impregnation is the procedure of adding a precursor of the active phase to a solid support, which is then dried to remove the imbibed solvent. The second method is based on forming a crystalline precipitate via three steps: supersaturation, nucleation and growth. The occurrence of these steps is controlled by the temperature and pH of the dispersion [12].

Aksoylu et al. [14], compared a Ni/Al_2O_3 catalyst prepared by co-precipitation and impregnation. They demonstrated that, in a carbon monoxide hydrogenation reaction, the co-precipitated catalyst produced higher hydrocarbon levels attributed to a higher level of metal–support interaction. The authors also noticed that co-precipitation catalyst had a homogeneous Ni distribution and suffered from lower specific surface loss than the impregnated catalyst. Work by Liu et al. [15], also showed that the co-precipitated catalyst used for Cu/ZrO_2 catalyst preparation provides higher surface, and better nickel distribution than the impregnation method, leading to lower carbon deposition.

Chen and Wang [16,17], also studied the influence of the preparation method on Ni/$Ce_{0.75}Zr_{0.25}O_2$ catalyst structure and performance for CH_4—CO_2 reforming; they both concluded that more active metal cations enter the support lattice with the co-precipitation method. Chen et al. [17], related the active metal cation content of the lattice to the resistance of the catalyst to carbon deposition; they showed that the incorporation of the active metal in the solid solution provides stronger metal–support interactions, and accelerating the catalytic steps, thus leading to a more active catalyst. However, Wang et al. [6], attributed the higher catalytic activity of the co-precipitated catalysts to their higher specific surface and pore volume than the ones prepared by wet impregnation.

In this paper, two Ni–Al/Al_2O_3 catalysts, prepared respectively by co-precipitation and wet impregnation techniques, are compared in order to correlate the catalytic activity with the catalyst properties. The results will contribute to the optimization and eventual commercialization of the catalyst.

The catalyst's physical and chemical properties are examined before and after diesel steam reforming tests, by several characterization techniques, including scanning electron microscopy (SEM), X-ray diffraction (XRD), and various temperature programmed analyses. The characterization was performed before and after diesel steam reforming tests.

2. Materials and methods

2.1. Catalyst preparation

Nickel–alumina catalysts of 5% weight Ni loading were prepared by co-precipitation and wet-impregnation methods, according to methods similar to those reported in literatures [11,12] and will be referred to as Copr and Impr, respectively.

Impr-Ni–Al catalyst on an alumina support was prepared by adding an aqueous nickel nitrate ($Ni(NO_3)_2{\cdot}7H_2O$, Alfa Aesar) solution to gamma-alumina (γ-Al_2O_3, specific surface = 185 $m^2\ g^{-1}$, Alfa Aesar) suspended powder. The detailed procedure is presented in Fig. 1.

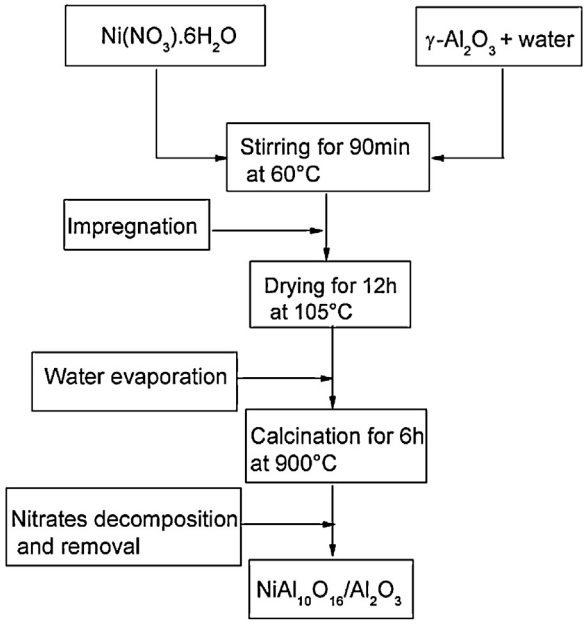

Fig. 1. Typical procedure for Impr-Ni–Al catalyst processing using the wet impregnation method.

The co-precipitation method, used to prepare the Copr-Ni–Al catalyst, involved mixing $Ni(NO_3)_2{\cdot}7H_2O$ and aluminium nitrate ($Al(NO_3)_3{\cdot}9H_2O$, Alfa Aesar) precursor solutions. A solid precipitate was then formed by adjusting pH and temperature. A detailed process flow chart for Copr-Ni–Al catalyst preparation is presented in Fig. 2.

2.2. Catalyst characterization

The catalysts were first examined using SEM before and after reforming tests, using a Hitachi S-4700 field emission gun (FEG) and energy-dispersive X-ray spectroscopy (EDXS) with an Oxford EDXS detector and ultra-thin ATW2 window. Fresh catalyst samples were deposited on carbon double-face tape for SEM and EDXS analysis, and were replaced by silicon supports for used catalysts in order to analyse carbon deposition. The particle size distributions of both fresh and used catalysts were characterized and compared using Laser diffraction (Malvern Mastersizer 2000).

X-ray diffraction analysis (XRD) was also conducted on both fresh and used catalysts. To perform this analysis, each catalyst powder was first mixed with Paratone Oil to obtain a sample with a paste-like consistency. Then, it was cut to approximately 0.3 mm × 0.3 mm × 0.3 mm, placed on a steel needle and mounted on a Bruker APEX DUO X-ray diffractometer. Then, 6 correlated runs with Phi Scan of 360° and exposure times of 360 s were collected with the Cu micro-focus anode (λ = 1.54184 Å) with the CCD APEX II detector at distance of 150 mm. The acquisition was handled with the XRW2 Eva Bruker software to produce the X-ray powder pattern from ~7 to 80 degrees 2θ range. The pattern was treated with Diffrac Eva version 2.0 from Bruker and the matching was performed using the International Center for Diffraction Data (ICDD®) PDF-2 (2011) Release.

Specific surface area was determined using the multipoint Brunauer, Emmet and Teller (BET) method. Nitrogen adsorption was measured using an Accelerated Surface Area and Porosimetry System (ASAP 2020, Micrometrics).

Thermogravimetric analysis (TG) was also performed, using a Setsys 24 Setaram. In the TGA experiments, the sample was heated in 20%O_2/argon from 20 to 1000 °C at 10 °C/min.