



Carbon gasification from Fe–Ni catalysts after methane dry reforming



Stavros Alexandros Theofanidis, Rakesh Batchu, Vladimir V. Galvita*, Hilde Poelman, Guy B. Marin

Laboratory for Chemical Technology, Ghent University, Technologiepark 914, B-9052 Ghent, Belgium

ARTICLE INFO

Article history:

Received 14 September 2015

Received in revised form

30 November 2015

Accepted 2 December 2015

Available online 7 December 2015

Keywords:

Fe–Ni catalyst

Catalyst regeneration

Carbon gasification mechanism

Methane dry reforming

In situ XRD

TAP reactor

ABSTRACT

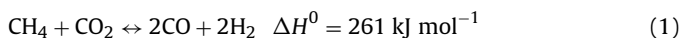
Carbon species removal was studied from a Fe–Ni catalyst supported on MgAl₂O₄ after methane dry reforming at 1023 K, atmospheric pressure and a CH₄/CO₂ molar ratio of 1:1. The deactivated and regenerated catalysts were characterized using X-ray photoelectron spectroscopy (XPS), Raman spectroscopy and energy-dispersive X-ray spectroscopy (EDX)-STEM mapping. The catalyst regeneration was studied by CO₂ and O₂ temperature programmed oxidation (TPO) and by operando time-resolved X-ray diffraction (XRD). A transient response technique, Temporal analysis of products (TAP), was applied to investigate the isothermal carbon species gasification.

Two different types of carbon species, graphitic and amorphous, were present after reaction. CO₂ oxidation could remove part of the carbon species, although EDX-STEM mapping showed the presence of carbon species located far from active metals phase even after CO₂-TPO at 1123 K. Carbon species removal by CO₂ involves two contributions: (1) the dissociation of CO₂ over Ni followed by the oxidation of carbon species by surface oxygen; (2) Fe oxidation by CO₂ and subsequent carbon species oxidation by Fe oxide lattice oxygen. The oxidation of carbon species by O₂ was identified from temperature programmed and isothermal experiments as a process including two processes: (1) oxidation of surface carbon by lattice oxygen and (2) particles migration to carbon species deposited far from active metals and subsequent oxidation through lattice oxygen of the iron and/or nickel oxides. The contribution of oxygen spillover in carbon gasification was considered to be negligible.

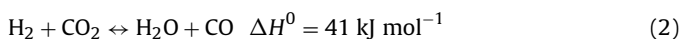
© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Methane dry reforming (DRM) has been a subject of several studies for a long time [1]. The H₂/CO ratio from DRM is more favorable for Fischer-Tropsch and methanol synthesis than the ratio obtained from classical steam reforming [2]. Moreover, DRM has the lowest operating cost among these processes and offers the additional advantage of converting CO₂ into valuable chemicals:

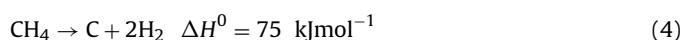


Side reactions of importance include the reverse water gas shift:



However, dry reforming technologies have the inherent disadvantage of rapid catalyst deactivation due to carbon deposition, i.e., coke [3]. Carbon deposition can originate either from the methane

decomposition reaction (Eq. (4)) or from CO disproportionation [4] (Eq. (3)):



Carbon formation on metals from hydrocarbons decomposition is a complex process which includes surface catalysis and solid state reactions. Lobo and Trimm in 1971 [5–7] suggested a mechanism for steady-state carbon deposition on Ni catalysts. They suggested that the carbon atoms migrate through the Ni surface, upon which the hydrocarbon decomposition takes place, towards the active growth regions (carbides) where the process of carbon growth (nucleation) takes place [6]. The carbide phase decomposes at some stage to give graphite. Molecular mass and chemical structure of these carbon species may vary depending on the reaction type, conditions and catalyst [3,8,9]. Similarly, the carbon species deposited during DRM vary in morphology and may be carbidic, amorphous, graphene-like, graphitic, filamentous [4,10–13].

Several ways have been examined in order to inhibit or control the deactivation originating from carbon species deposition. Higher dispersion of the active metals on the support surface [14],

* Corresponding author. Fax: +32 93311759.

E-mail address: Vladimir.Galvita@UGent.be (V.V. Galvita).

increase of catalyst basicity to achieve a higher activation rate of mildly acidic CO₂ [15,16] and addition of materials that offer an oxygen reservoir through their redox behavior [17–20] have been investigated. Sadykov et al. [21] used CeO₂ as an oxygen reservoir material for DRM and showed that the oxygen mobility of CeO₂ can be increased by incorporation of rare earth metals (La, Gd and Pr) as dopants. They found that catalytic activity is correlated with oxygen near the surface and/or bulk mobility for elimination of deposited carbon species. Theofanidis et al. [22] on the other hand used Fe₂O₃ as promoter for a Ni/MgAl₂O₄ catalyst because of its good redox properties [23]. They found lower amounts of deposited carbon after methane dry reforming on Fe-modified samples in comparison with pure Ni/MgAl₂O₄. This was attributed to FeO_x formation during DRM reaction and subsequent oxidation of carbon by lattice oxygen [24–26]. Zhang and Verykios [16] showed that Ni/La₂O₃ activity increases after 2–5 h time-on-stream (TOS). This study revealed a CO₂ pool, stored in the form of La₂O₂CO₃.

However, despite all the different ways to reduce carbon deposition, carbon accumulation during reforming reactions remains an issue. Eventually, catalyst regeneration is required, by removing all carbon species by gasification [27,28]. There are many reports in literature proposing different mechanisms for catalytic carbon gasification. Some of the mechanisms that are mentioned are: (1) carbon bulk diffusion, where carbon is transported through the metal particle to the region where the gasification reaction takes place [6,29,30], (2) oxygen spillover where metal-activated oxygen may migrate over a considerable distance over the support towards the deposited carbon species and oxidizing them [31,32] and (3) the redox mechanism, where the catalyst provides oxygen towards carbon (reduction step) and is itself oxidized by the gas phase (oxidation step) [33–35]. Figueiredo and Trimm in 1975 [29] studied the gasification of carbon deposits on Ni foil and supported Ni catalysts. They found a zero reaction order for carbon gasification by steam, concluding that the reaction is controlled by the diffusion of carbon through Ni. Machida et al. [36] used CeO₂ as an active catalyst for soot oxidation concluding to two possible reaction pathways: (i) soot oxidation by adsorbed superoxide species (O₂⁻) at the three-phase boundary (catalyst, carbon and gas) and (ii) soot oxidation by active lattice oxygen at the CeO₂/soot interface.

The rate of gasification depends on the structure of the carbon [37], its location [11] and on the nature of the catalysts present [10,38,39]. One important method for carbon species characterization is temperature programmed (TP) techniques [40,41]. However, isothermal studies are also required in order to understand the kinetics [28]. Oxygen is one of the gases most often used [42] to infer type and location of carbon species on the catalyst while there are also studies on carbon gasification by CO₂, H₂O and H₂ [4,29,31,43]. Among the latter, the mechanism according to which carbon species are oxidized by CO₂, as well as, the differences between CO₂ and O₂ carbon species removal await clarification. In view of the promising results on Fe–Ni/MgAl₂O₄ [22] regarding reduced carbon species deposition, this material was used for further investigation of carbon removal. The questions raised are addressed by performing X-ray diffraction (XRD) characterization of used Fe–Ni/MgAl₂O₄ catalysts, both in situ during O₂ temperature-programmed oxidation (TPO), as well as operando by coupling in situ XRD with MS. Further, for first time to our knowledge a transient response technique, Temporal Analysis of Products (TAP), has been used to investigate the isothermal carbon species gasification process. The latter is recognized as an important experimental method for heterogeneous catalytic reaction studies. A TAP pulse response experiment consists of injecting a very small amount of gas, typically nanomoles per pulse, into a tubular fixed bed reactor that is kept under vacuum. The time-dependent exit flow rate of each gas is detected by a mass spectrometer. The high time resolution of the TAP technique allows detection

of short-(millisecond time scale) and/or long-lived (>1 s) reaction intermediates, which helps to formulate the mechanism of reaction [44,45].

2. Experimental methods

2.1. Catalyst preparation

2.1.1. Support preparation

The support material of MgAl₂O₄ was prepared by coprecipitation from an aqueous solution of Mg(NO₃)₂·6H₂O (99%, Sigma–Aldrich) and Al(NO₃)₃·9H₂O (98.5%, Sigma–Aldrich) (molar ratio Mg:Al = 1:2). A precipitating agent, NH₄OH (ACS reagent, 28.0–30.0% NH₃ basis) was added to adjust the pH to 10, at 333 K. The formed precipitate was filtered, dried at 393 K for 12 h and finally calcined in air at 1023 K for 4 h.

2.1.2. Catalyst preparation

8 wt% Ni–5 wt% Fe (named as “as-prepared Fe–Ni”) was prepared by incipient wetness impregnation on the support (MgAl₂O₄) using an aqueous solution of corresponding nitrates Ni(NO₃)₂·6H₂O (99.99 + %, Sigma–Aldrich) and Fe(NO₃)₃·9H₂O (99.99 + %, Sigma–Aldrich) [46]. The catalysts were dried at 393 K for 12 h and subsequently calcined in air at 1023 K for 4 h.

2.2. Catalyst characterization

The BET surface area of the catalyst was 84.7 ± 5.8 m²/g_{cat}. A more detailed characterization of the catalyst has been reported elsewhere [22]. The crystallographic phases of the materials were confirmed by ex-situ XRD measurements (Siemens Diffractometer Kristalloflex D5000, Cu K α radiation). The powder patterns were collected in a 2 θ range from 10° to 80° with a step of 0.02° and 30 s counting time per angle. XRD patterns of known compounds are referenced by their corresponding number in the powder diffraction file database.

High-resolution transmission electron microscopy (HRTEM) was used for structural analysis, while EDX yielded local chemical analysis. These techniques were implemented using a JEOL JEM-2200FS, Cs-corrected microscope operated at 200 kV, which was equipped with a Schottky-type field-emission gun (FEG) and EDX JEOL JED-2300D. All samples were deposited by immersion onto a lacey carbon film on a copper support grid.

XPS measurements were recorded with a S-Probe XPS spectrometer (VG, Surface Science Instruments), equipped with a monochromatized 450W Al K α source. The base pressure of the analysis chamber was below 2 × 10⁻⁷ Pa. Spectra were recorded with 200W source power. The analyzer axis made an angle of 45° with the specimen surface. Wide scan spectra were measured with a pass energy of 157 eV and a 0.2 eV step, while core levels were recorded with a step of 0.05 eV and a pass energy of 107.8 eV. Energy calibration to Al2p or C1s gave the same result, so the main intensity of C1s at 284.6 eV was used for alignment.

Raman analysis of the samples was performed on a RXN1 Raman spectrometer (Kaiser Optical Systems) fitted with a 532 nm laser operating at 40 mW.

2.3. Ageing of catalyst during DRM

The ageing of the catalyst was performed at atmospheric pressure in a quartz reactor with an internal diameter of 10 mm, which was housed inside an electric furnace. The temperature of the catalyst bed was measured with K-type thermocouples touching the outside and inside of the reactor at the position of the catalyst bed. The inlet gas flow rates were always maintained by means of

Download English Version:

<https://daneshyari.com/en/article/6499229>

Download Persian Version:

<https://daneshyari.com/article/6499229>

[Daneshyari.com](https://daneshyari.com)