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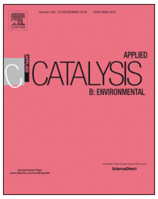

Mechanism of carbon deposits removal from supported Ni catalysts

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ABSTRACT

Catalyst deactivation due to carbon deposition is a major issue in all reforming technologies. Because of the significant economic cost of catalyst replacement, catalyst regeneration is increasingly attracting attention. The regeneration mechanism of Ni catalysts, with respect to carbon removal, was investigated on support materials prepared by one-pot synthesis. The supports were classified based on their redox functionality: Al_2O_3, $MgAl_2O_4$ show no redox properties in contrast to $MgFe_{0.09}Al_{1.91}O_4$ and $CeZrO_2$ that have redox functionality.

A Temporal Analysis of Products (TAP) setup was used to investigate the isothermal regeneration mechanism of Ni catalysts at 993 K by O_2. Different mechanisms were distinguished depending on the redox functionality of the support material. Two consecutive steps occur on the support that have no redox properties (Al_2O_3 and $MgAl_2O_4$): metallic Ni is oxidized to form NiO (oxidation step), resulting in an initial local temperature increase of 50–60 K in total, enabling metal particle migration to carbon that was initially separated from the metal and subsequent oxidation through NiO lattice oxygen (reduction step). On the other hand, the mechanism of carbon removal by O_2 from Ni catalysts on supports with redox properties does not require particle migration. Two parallel contributions are proposed: 1) Ni metal is oxidized to form NiO, where after lattice oxygen of NiO is used for the oxidation of carbon that is deposited upon the metals, 2) carbon oxidation through lattice oxygen that is provided by the support. No dependency of the carbon gasification mechanism on the exposed fraction of the metal (particle size in the nanoscale) or on the structure of the deposited carbon was concluded.

1. Introduction

Syngas is a building block for chemical industry and it is the product of all the reforming technologies [1]. One of the main challenges, common to reforming processes, as well as to methanation and steam cracking of hydrocarbons [2,3], is carbon formation [4]. In catalytic reforming, it will lead to catalyst deactivation and thus process shutdown, resulting in a major economic cost [5].

Catalyst regeneration is eventually required, by removing all carbon species through gasification [6,7]. Oxygen is one of the gases most often used for gasification [8] in order to infer type and location of carbon species on the catalyst, while there are also studies on carbon gasification by CO_2, H_2O and H_2 [9–13]. The rate of carbon gasification is a function of its structure [14], location [15] and of the nature of the catalyst present [16–18]. Temperature programmed (TP) techniques are important for carbon species characterization [19,20]. However, isothermal studies are also required in order to understand and model the kinetics [7].

Different mechanisms for catalyst regeneration from carbon deposits have been proposed since the 1930s, including increased adsorption of the oxidizing gas (CO_2 or H_2O) [21] and mobility of valence electrons from the catalyst lattice to carbon [22]. Wood [23] suggested that particularly for alkali metal catalysts, a liquid film that wets the carbon surface is formed. The molten catalyst layer, which is an oxygen deficient compound, attacks during gasification the carbon surface. Other available mechanisms in literature include: 1) carbon bulk diffusion that was suggested in the 1980s, where carbon is transported through the metal particle to the region where the gasification reaction takes place [9,4], 2) oxygen/hydrogen spillover, where metal-activated oxygen/hydrogen migrates over a considerable distance on the support towards the deposited carbon species to remove them [10], and 3) the redox mechanism, where the catalyst provides lattice oxygen to carbon (reduction step) and is then oxidized by a gas phase oxidizer (O_2, CO_2, H_2O; oxidation step) [24,25]. A fourth mechanism has recently been proposed, which includes mobility of the active metal particles [13] towards the carbon deposits, when O_2 is used as gasification agent due

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to the exothermicity of the reactions (Eqs. (1) and (2)). Then, the deposited carbon is removed via the redox mechanism.

$$C+O_2 \rightleftarrows CO_2 \quad \Delta_r H^0_{298K} = -393.5\,\text{kJ.mol}^{-1} \tag{1}$$

$$C+{}^{1}\!/_{2} \rightleftarrows O_2\,CO \quad \Delta_r H^0_{298K} = -110.5\,\text{kJ.mol}^{-1} \tag{2}$$

The mobility of metal particles on graphite under O_2 and CO_2 atmosphere was evidenced in 1964 [26]. Later, McKee used hot stage optical microscopy to demonstrate mobility of catalytic particles with channeling on graphite [27]. Transition metal particles may engage in transport through the layers of carbon deposits during carbon gasification by O_2 [28–30]. The atoms of solid surfaces become mobile due to thermal energy at temperatures well below the melting point. The mobility temperature of various metal and metal oxide particles dispersed on graphite was investigated by Baker [31]. By comparing this specific temperature with the melting point of different particles (Ag, Au, Cu, Ni, Pd, Co, Fe, Pt, …), Baker found that the mobility temperature coincided with the Tammann temperature of these materials. In a recent review [32], Lobo and Carabineiro compared the several available mechanisms in literature for carbon gasification. They indicated the success of the carbon bulk diffusion mechanism in explaining the observed kinetic and geometry effects.

There have been many attempts to reach a concluding mechanism for catalyst regeneration from carbon deposits, but so far no unambiguous conclusion has been reached. The present work aims at elucidating this question by means of dedicated isothermal regeneration experiments on Ni reforming catalysts. Different parameters are varied: support material, exposed fraction of the active metals at the nanoscale, structure of the deposited carbon and type of active metal. A transient technique, Temporal Analysis of Products (TAP), is used to investigate the isothermal carbon species gasification process using oxygen as regeneration agent. The TAP reactor is an important tool for investigating heterogeneous reactions, particularly reactions on industrial catalysts. 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 reaction mechanism [33–35].

2. Experimental methods

2.1. Support and catalyst preparation

2.1.1. Support preparation

One-pot synthesis by co-precipitation was applied for the support materials: Al_2O_3, $MgAl_2O_4$, $MgFe_xAl_{2-x}O_4$ (x = 0.09) and $CeZrO_2$. The precursors, $Al(NO_3)_3{\cdot}9H_2O$ (98.5%, Sigma-Aldrich®), $Mg(NO_3)_2{\cdot}6H_2O$ (99%, Sigma-Aldrich®), $Fe(NO_3)_3{\cdot}9H_2O$ (99.99+%, Sigma-Aldrich®), $Ce(NO_3)_3{\cdot}6H_2O$ and ZrN_2O_7 were dissolved in water. A precipitating agent, NH_4OH (ACS reagent, 28.0 − 30.0% NH_3 basis), was added to adjust the pH to 10, at 333 K, forming thecorresponding hydroxides (Eq. (3)). The produced precipitate containing the hydroxides was filtered, dried at 393 K for 12 h, and subsequently calcined in air at 1023 K for 4 h, leading to the formation of the oxide support materials.

$$M(NO_3)_x + NH_4OH \rightleftarrows M(OH)_x + xNH_4NO_3 \tag{3}$$

where M = Al, Mg, Ce, Fe.

The supports were chosen according to their different properties and can be ranked in two categories, supports with and without redox properties. Al_2O_3 and $MgAl_2O_4$ show no or little oxygen mobility compared to $MgFe_xAl_{2-x}O_4$ [36,37] and $CeZrO_2$ [38,39].

2.1.2. Catalyst preparation

Monometallic 9 wt%Ni catalysts were prepared by incipient wetness impregnation on the aforementioned supports (Al_2O_3, $MgAl_2O_4$, $MgFe_xAl_{2-x}O_4$ and $CeZrO_2$) using an aqueous solution of $Ni(NO_3)_2{\cdot}6H_2O$ (99.99+ %, Sigma-Aldrich®). The catalysts were dried at 393 K for 12 h and subsequently calcined in air at 1023 K for 4 h, resulting in "as-prepared" catalysts. Also, a 1 wt% Rh sample was synthesized on a $MgAl_2O_4$ support for comparison purposes.

2.2. Support and catalyst characterization

The Brunauer-Emmett-Teller (BET) surface area of each sample was determined by N_2 adsorption at 77 K (five point BET method using Tristar Micromeritics) after outgassing the sample at 473 K for 2 h. The bulk chemical composition of support and as-prepared catalysts was determined by means of inductively coupled plasma atomic emission spectroscopy (ICP-AES, ICAP 6500, Thermo Scientific). The samples were mineralized by acid fusion.

2.3. Catalyst coking protocol

The coking of the catalyst was performed 1) at atmospheric pressure in a quartz reactor with an internal diameter of 9 mm, which was housed inside an electric furnace and 2) by pulsing CH_4 in the TAP reactor set-up.

For the experiments performed in the quartz reactor, the purpose was to deposit carbon on the catalysts prior to carbon gasification. DRM at 1023 K was chosen as a reforming reaction to coke the catalysts in a continuous flow experiment, where the CH_4/CO_2 ratio was equal to 2/1. The temperature of the catalyst bed was measured with N-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 calibrated Bronkhorst mass flow controllers. Prior to each coking experiment, the fresh sample was reduced in a 1 N mL·s^{-1} flow of 30 vol%H_2/Ar at 1123 K for 30 min and then the flow was switched to Ar for 30 min.

Transient measurements were performed in a TAP-3E reactor (Mithra Technologies, St. Louis, USA) equipped with an Extrel Quadrupole Mass Spectrometer (QMS). The details of the TAP reactor can be found in [33]. For the experiments, 20 mg ($250 < d_{particle} < 500$ µm catalyst fraction) of the catalyst was placed in a quartz microreactor (I.D = 4 mm and ∼2 mm bed length), which was located between two inert beds of quartz particles with the same sieved fraction. The temperature of the catalyst was measured by a K-type thermocouple housed inside the catalytic zone. The following procedure was applied for coking the catalysts by pulsing CH_4 in the TAP reactor set-up (Fig. S1): (a) the samples were pre-reduced in a continuous flow setup using a quartz reactor under flow of 1 mL s^{-1} of 30 vol% H_2/Ar at 1123 K, using a heating ramp of 15 K min^{-1} and a dwell time of 30 min at 1123 K. The catalysts were cooled down under Ar flow and then immediately placed in the TAP reactor, named as "reduced". (b) H_2 pulses were initially applied, after placing the catalyst in the TAP reactor, to ensure that it was fully reduced. (c) A series of CH_4 pulses, diluted in Ar, (approximately 10^{-7} mol/pulse) were used isothermally at 993 K for coking (carbon deposition) of the catalysts, yielding an "coked catalyst" state. Ar was used as internal standard. H_2, CH_4, H_2O, CO, O_2, Ar and CO_2 responses were monitored at amu signals of respectively 2, 16, 18, 28, 32, 40 and 44 by QMS. Data were recorded with millisecond time resolution in each pulse. A correction was applied to remove contributions from unavoidable interference with fragmentation peaks of other gases. The average amount of CH_4 that was pulsed during catalyst coking was $4{\cdot}10^{-5}$ mol. The nature of the deposited carbon during CH_4 pulsing in the TAP reactor set-up is discussed in § 3.4.

2.4. Characterization of carbon deposits

The coked catalysts under continuous flow were used for carbon characterization through Raman spectroscopy and HRTEM. Raman analysis of the samples was performed on a RXN1 Raman instrument (Kaiser Optical Systems) fitted with a 532 nm laser operating at 40 mW.