

# Isooctane decomposition and carbon deposition over ceria–zirconia supported nickel catalysts

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## ABSTRACT

Catalytic decomposition of hydrocarbons is a major contributor to carbon formation during hydrocarbon reforming. This work investigates the effects of temperature and hydrocarbon decomposition intermediates on carbon deposition during catalytic isooctane decomposition over ceria–zirconia supported nickel. The carbon deposition rate and hydrocarbon concentrations were monitored in real-time via thermogravimetry and FT-IR spectroscopy. Carbon-deposited catalysts were characterized by temperature-programmed oxidation (TPO) and scanning electron microscopy (SEM). Carbon deposition rate, morphology, and quantity were strongly dependent on decomposition temperature ( $T$ ); three distinct decomposition temperature regimes were identified, i.e.  $T \leq 575^\circ\text{C}$ ,  $575^\circ\text{C} < T < 725^\circ\text{C}$ , and  $T \geq 725^\circ\text{C}$ . Gaussian deconvolution of TPO data and carefully designed oxidation experiments indicated the presence of different types of carbon: coating, filamentous, and pyrolytic carbon. Catalytic and homogeneous decomposition of isooctane, propene, and methane suggest that smaller hydrocarbon fragments, typically formed during reforming of large hydrocarbon molecules, play an important role in carbon deposition. Specifically, low-temperature decomposition of isooctane into olefins, such as propene or isobutene, leads to the formation of both coating and filamentous carbon deposits. At high temperatures, decomposition of acetylene and methane leads to the formation of significant quantities of coating and pyrolytic carbon deposits in addition to filamentous deposits.

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## 1. Introduction

Reforming and decomposition of liquid hydrocarbons (LHCs) to  $\text{H}_2$ -rich gas are active areas of research [1,2]; such  $\text{H}_2$ -production techniques have also attracted interest in transportation applications [3,4]. Nickel (Ni) is a promising alternative to precious metal reforming catalysts due to its lower cost, and because it activates the carbon–hydrogen bond readily. Recently, extensive efforts have been devoted to Ni-catalyzed reforming of LHCs [1], including steam reforming (SR) [1,4–7], partial oxidation (POX) [1,4,8,9], and autothermal reforming (ATR) [1,4,10–16]. Nickel-based solid oxide fuel cell (SOFC) anodes have also received attention for their use as direct internal-reforming systems [17–21], particularly for automotive auxiliary power units (APUs) [22]. Fuel flexibility is desirable for such applications; nickel anode catalysts can operate with fuels such as  $\text{H}_2$ , CO,  $\text{CH}_4$  [17,19,20], and LHCs [23].

A key challenge to operating Ni-catalyzed hydrocarbon reformers is avoiding carbon deposition [1,3,4,18–20,23,24] while sustaining high  $\text{H}_2$  yield and stable anode performance [25]. It is well known that Ni-based catalysts are prone to deactivation due to carbon deposition [26,27]. There is an extensive body of literature addressing carbon nucleation, growth, and morphologies during reforming of methane or light hydrocarbons [1,27–32]. Various strategies for carbon mitigation have been developed, including modifications of catalyst formulations [1,4,27,29,33], mainly via stabilizing [34] or reducing Ni particle size [29,31,33,35], using bimetallic catalysts [7,16,36,37] to promote surface properties of Ni catalysts [29,33,38] or forming surface Ni–metal alloys [5,6,21,31,39–41], modifying the support [1,34,35,42–44], pre-reforming [45], and others [46,47]. Among the formulation modifications of Ni-containing catalysts or SOFC anodes, promotion by ceria [20,33,43] and surface Au–Ni alloying [48] appeared to be the most effective as these methods led to remarkable carbon-tolerance and enhanced performance in direct reforming of methane in SOFCs [20,24]. As a result, nearly carbon-deposition-free operation could be achieved even with low steam to methane ratios [43,48]. Studies indicated that the role of ceria [49] in mitigating carbon formation is attributed to the redox properties of ceria [44,50] promoting oxygen mobility [49,51,52] or, alternatively, is

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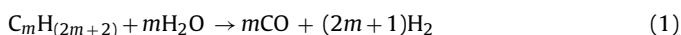
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**Table 1**  
Infrared band assignment of the species during isooctane decomposition.

Compound	Centered IR band (cm <sup>-1</sup> )	Characteristic vibration
Isooctane	1215/1176	Tert-butyl C–C skeletal
Isobutene	888	C–H out-of-plane bend for vinylidene C=CH <sub>2</sub>
Propylene	912	C–H out-of-plane bend for vinyl CH=CH <sub>2</sub>
Ethylene	1888	CH <sub>2</sub> wag for combination of ( $\nu_7 + \nu_8$ )
Acetylene	730	Alkyne C–H bend
Methane	1303	C–H bend
Benzene	673	C–H out-of-plane bend for aromatic ring

attributed to the strong interaction between ceria and active Ni [49,53,54].

The design of reforming catalysts with increased stability can be challenging, due to the numerous reactions and intermediate products involved. The reforming pathway, e.g. steam reforming, is generally described in literature as Eq. (1).



As the detailed mechanistic aspects of carbon deposition from LHCs are poorly understood, carbon mitigation strategies similar to those used in methane reforming have extensively been adopted [1,4–9,12,13,15,21,55–58]. Unlike methane reforming [32], the in situ study of carbon formation and growth during reforming of LHCs is a very difficult task. Carbon deposits present on post-reforming catalysts [59–61] represent accumulated carbon species, which result from the balance between carbon deposition, gasification, and oxidation [33]. This is particularly true when ceria is used as support or promoter as it can accelerate steam gasification [53,62]. Furthermore, previous studies indicated that significant amounts of light hydrocarbons (carbon numbers less than 5) are formed during reforming of LHCs [14,57], and under partial oxidation conditions [63]. These light hydrocarbons may play a significant role in final hydrogen production [14,64], and carbon deposition [13]. However, to our best knowledge, the relationship between smaller hydrocarbon intermediates and carbon deposition during reforming of LHCs is still poorly understood.

Thus this work investigated the effect of decomposition temperature and the role of decomposition fragments of isooctane on carbon deposition over ceria–zirconia supported Ni catalysts.

## 2. Experimental

### 2.1. Preparation of catalyst

The catalyst support material, ceria–zirconia mixed oxide (Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub>, denoted CZO), was prepared via the coprecipitation method by titrating 2 M ammonium hydroxide (Aldrich) aqueous solution into a mixed aqueous solution of Ce(NO<sub>3</sub>)<sub>2</sub> (Aldrich) and ZrOCl<sub>2</sub> (Aldrich) under constant stirring [59]. The suspension was stirred overnight, aged at room temperature, and then recovered by filtration and washed thoroughly with deionized water. The filter cake was then dried in an oven at 120 °C overnight and calcined at 600 °C in air for 2 h. Nickel loading was achieved via incipient wetness impregnation of the calcined support material by a nickel nitrate aqueous solution. The samples were then further calcined at 650 °C in air for 2 h to obtain NiO supported on CZO (NiO/CZO), followed by reduction in flowing H<sub>2</sub> at 850 °C, as described later in the decomposition section.

### 2.2. Catalyst characterization

BET surface area measurements were carried out by a single point method on a Quantachrome CHEMBET-3000. Ni dispersion was measured on a Micromeritics ASAP 2020 instrument by performing both CO and H<sub>2</sub> chemisorption at 35 °C. Ni dispersion was

calculated from the difference between total and weak adsorption volumes by assuming an adsorption stoichiometry of one CO molecule or one H atom corresponding to one exposed nickel surface atom. The unreduced 10 wt.% Ni/CZO catalyst (Ni/CZO) had a BET surface area of 37 ± 0.5 m<sup>2</sup> g<sup>-1</sup>. After H<sub>2</sub> reduction at 850 °C, the BET surface area decreased to 25 ± 0.5 m<sup>2</sup> g<sup>-1</sup>, indicating some sintering of either CZO support or nickel metal itself. Chemisorption data for the 10 wt.% Ni/CZO sample reduced at 600 °C showed a nickel dispersion of 1.6 ± 0.02% and nickel active surface area of 1.05 ± 0.03 m<sup>2</sup> g<sub>cat</sub><sup>-1</sup>, corresponding to an average nickel particle size of 63 ± 2 nm.

### 2.3. Isooctane decomposition

#### 2.3.1. Reactor system configuration

Isooctane decomposition reactions over Ni/CZO were carried out in the quartz furnace tube of a thermogravimetric analyzer (TA Q500). The composition of the effluent gas stream was monitored by a Nicolet 380 IR spectrometer. The predominant advantage of the combination of TGA and IR used in this work is the on-line acquisition of catalyst mass data and the corresponding concentration of reactant and products throughout the experiment. From this information, it is possible to identify the hydrocarbon(s) responsible for carbon deposition via interpretation of the IR spectra. The IR band assignments of isooctane and its decomposition products were determined using published NIST data and the spectral libraries that were included with the IR spectrometer. The representative vibrational peaks for each hydrocarbon are shown in Table 1. The integration of these peaks was used to represent the relative concentration of each compound.

Isooctane (99% reagent grade, Sigma–Aldrich) was introduced to the TGA reactor using a liquid/gas saturator at room temperature. Analysis of post-saturator isooctane concentration indicated that the isooctane concentration in the carrier gas flow could be effectively controlled by the carrier gas flow rate, while keeping all other saturator variables constant (saturator temperature and isooctane liquid level). The isooctane concentration was also confirmed using diffusion calculations for isooctane vapor-phase transport in nitrogen bubbles. The isooctane concentration was constant for all experiments, due to the constant TGA balance and sample gas flow rates.

#### 2.3.2. Homogeneous isooctane decomposition

Homogeneous isooctane pyrolysis was performed by flowing isooctane (4.1 vol.% in nitrogen) through the blank TGA reactor as the furnace cooled from 850 to 450 °C at a rate of 5 °C min<sup>-1</sup> in the absence of a catalyst. As the reactor cooled, IR spectra of the effluent gases were continuously acquired.

#### 2.3.3. Catalytic isooctane decomposition

Preliminary catalytic isooctane decomposition experiments were first conducted using catalysts with a wide range of Ni loading (2–10 wt.% Ni) in order to identify a metal loading that produced concentrations of decomposition products large enough to allow detection with the IR spectrometer. Low Ni loadings,

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