

# Microstructural Evolution of Nickel Nanoparticle Catalysts Supported on Gadolinium-Doped Ceria during Autothermal Reforming of Iso-Octane

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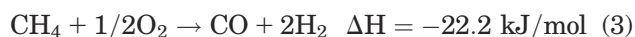
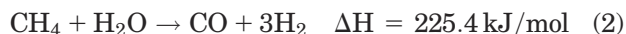
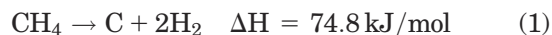
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The microstructure and composition of a nanoparticle Ni catalyst supported on gadolinium-doped ceria ( $\text{Ce}_{1-x}\text{Gd}_x\text{O}_{(4-x)/2}$ ) were studied using transmission electron microscopy (TEM), x-ray diffraction (XRD), and x-ray photoelectron spectroscopy (XPS). The support of the fresh catalyst exhibits a homogenous aggregation of crystalline grains, with sizes ranging between 20 nm and 50 nm. The crystalline structure of the fresh catalyst support is of the  $\text{CeO}_2$  phase, in which gadolinium atoms exist in a solid solution of  $\text{CeO}_2$ . Nickel in the fresh catalyst is highly dispersed and forms granular crystals that are 5–30 nm in size on the surface of the ceria support. The support of the used catalyst exhibits a bimodal distribution of grains in which smaller grains have similar structure and morphology as those in the fresh catalyst, while the larger sized grains appear dull and exhibit nonfaceted crystal morphology resulting either from the sintering of a number of  $\text{CeO}_2$  grains or by the occupation of highly defective crystals of  $\text{Ce}_2\text{O}_3$  and  $\text{CeO}$  phases. A thin amorphous layer of carbon also covers most of the larger grains in the used catalyst. The Ni particles could not be imaged by TEM in the used catalyst, but energy dispersive x-ray spectroscopy (EDX) detected their presence. The XPS analysis of the catalyst samples suggests the participation of lattice O atoms from the ceria support in the catalytic reaction. The XPS data also show the presence of carbonate species and a higher hydrocarbon concentration in the used catalyst.

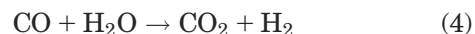
**Key words:** Autothermal reforming, ceria, nickel catalyst, gadolinium

## INTRODUCTION

The most promising method of supplying hydrogen to polymer electrolyte fuel cells (PEFCs) for automotive applications is the onboard processing of liquid fuels. Hydrogen can be produced from liquid fuels by (1) direct decomposition, (2) steam reforming, or (3) partial oxidation of the fuel.<sup>1</sup> For methane fuel, these reactions can be written as follows:



Analogous reactions can be written for long chain hydrocarbons. Carbon monoxide, CO, is a byproduct of reactions (2) and (3). In order to avoid Pt deactivation at the PEFC anode, CO concentration in the fuel processor must be below 10 ppm, and this is partially achieved via the water gas shift reaction (4):



The direct decomposition reaction (1) is endothermic and requires an external supply of energy; furthermore, it results in undesirable coke formation. Steam reforming (2) is also strongly endothermic and, as above, requires heat transfer to the reactor, making this reaction less attractive in an application that requires rapid start and fast dynamic response.<sup>1</sup> Partial oxidation (3) is exothermic, and can raise the gas

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