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ScienceDirect

Journal of Catalysis 251 (2007) 374–387

JOURNAL OF CATALYSIS

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Carbon deposited on Ni/Ce–Zr–O isooctane autothermal reforming catalysts

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Received 7 May 2007; revised 20 July 2007; accepted 27 July 2007

Abstract

On-board reforming of liquid fuels is attractive for fuel-cell-powered auxiliary power unit (APU) applications in heavy-duty vehicles. However, a technology barrier is catalyst deactivation due to carbon deposition. In this work, we studied carbon identification and the effect of nickel loading on carbon growth during isooctane autothermal reforming (iC_8-ATR) over Ni-supported Ce–Zr–O (Ni/CZO) catalysts. The crystallographic phase, type, deposition amount, and morphologies of deposited carbon were characterized by X-ray diffraction (XRD), thermogravimetric analysis (TGA), X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM). Two types of carbon, coating and filamentous, were identified by SEM, with binding energies of 281.6 and 284.5 eV in C1s XPS spectra and oxidation temperatures of 392 and 572 °C in TGA curves, respectively. Both coating and filamentous carbon were X-ray amorphous for nickel loadings $\leqslant 5\%$, even though deposited carbon reached up to 60.2%. Over the entire nickel loading range of 1–15%, with corresponding nickel crystal sizes of 30–103 nm, the coating carbon formation rates were low ($0.04\ \mathrm{g/m^2_{Ni}\ h}$) and independent of nickel particle size. The growth rates of filamentous carbon increased with increasing nickel particle size. Filamentous carbon growth may require not only a critical nickel particle size, but also a certain minimum number of nickel particles per unit support area. The results suggest a strategy for inhibiting the growth of filamentous carbon on Ni/CZO catalysts during autothermal reforming of liquid fuels.

Keywords: Carbon; Nickel; Cerium zirconium oxide; Isooctane; Autothermal reforming; Thermogravimetric analysis; X-ray photoelectron spectroscopy; Scanning electron microscopy

1. Introduction

The desire for increased fuel economy and decreased CO_2 emissions are two important driving factors in the development of more efficient vehicles that emit less greenhouse gases. Fuel cell vehicles possibly could address these problems, but these have not yet been commercialized. A hybrid system consisting of a conventional internal combustion engine (ICE) for propulsion and a fuel cell-powered auxiliary power unit (APU), which replaces the ICE under heavy NO_x and CO emissions conditions (low speed and idling operations), could be a promising choice due to higher energy efficiency and lower emissions [1]. The APU is a combination of a fuel cell and an on-board hydrogen generation system using gasoline or diesel fuel. Catalytic autothermal reforming (ATR) is an attractive option for hydrogen generation due to its low cost, simplicity, and better energy efficiency compared with steam reforming or partial oxidation. Unlike proton-exchange membrane (PEM) fuel cells, in which CO acts as an anode catalyst poison and thus water–gas shift and preferential oxidation units are required, solid oxide fuel cells (SOFCs) can operate with mixtures of H_2 and CO and are of interest to the military and the trucking industry for on-board fuel cell-powered APU applications. Nickel-based catalysts have been the catalyst of choice for steam reforming to produce hydrogen due to their good activity and long-term stability [2]. The formation of carbon deposits during reaction, however, is one of the main causes of catalyst deactivation during hydrocarbon reforming. Sulfur is also a catalyst poison and is present in many fuels, but may not be a major problem in the future as sulfur-free or very low sulfur fuels become available. Unlike sulfur, carbon deposition is a problem caused by intrinsic properties of the catalyst (e.g., structure, formulation,

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0021-9517/$ – see front matter
doi:10.1016/j.jcat.2007.07.031

preparation), but can be controlled to some extent by reaction conditions (e.g., type of fuel, steam to carbon ratio, oxygen to carbon ratio, temperature).

Extensive studies have been devoted to carbon deposition during methane reforming on nickel-based catalysts. The main foci have been the identification of carbon type and morphology, nucleation and growth mechanisms, the influence of reaction conditions and catalyst structure, and modifications to reduce carbon formation. Graphitic carbon on a nickel surface was first reported by Dent et al. [3]. Rostrup-Nielsen et al. identified carbon deposits on nickel catalysts in form of filaments [4], and subsequent studies confirmed this observation [5–8]. Additional studies have revealed a variety of types, morphologies, and chemistries of carbon deposited on nickel catalysts depending on the reaction conditions and carbon sources used [2,6,9–12]. The generally accepted mechanism for carbon filament formation is bulk diffusion of carbon through nickel particles to form metastable carbide intermediates at the end of the filaments [2,6,7,11,13,14]; however, an alternative mechanism for the growth of filamentous carbon, via surface diffusion of carbon to the edges of nickel particles, has been demonstrated recently [15–18].

Studies of the relationship between carbon deposition and catalyst structure during hydrocarbon reforming have revealed that support modification and nickel crystallite size have significant effects on carbon formation [17,19,20]. Other efforts have investigated the improvement of carbon resistance by modifying the surface structure of Ni-based catalysts, using additives to form alloys [2,17,21–26] or to promote surface properties [27–29]. Sulfur passivation also has been demonstrated to inhibit the rate of carbon formation more than the rate of reforming [30]. Alloying is thought to inhibit carbon accumulation by decreasing the carbon deposition rate or increasing the carbon gasification rate [13,31]. Bulk carbon is not formed when the gasification rate is greater than the deposition rate [32]. Density functional theory (DFT) has shown that on a Ni–Sn alloy, the barrier to C–O bond formation (i.e., carbon gasification) is lower than the barrier for C–C bond formation (i.e., carbon deposition), in contrast with monometallic nickel, for which the two barriers are about the same [26]. Another method for inhibiting carbon formation is the use of basic supports or basic metal oxide promoters [2,33,34]. Commercial methane-reforming catalysts, in fact, are promoted by the addition of alkali and alkali earth, although this results in a decrease of reforming activity [2]. Recent efforts have been made to minimize carbon formation using rare earth oxides, especially CeO_2, as additives or catalyst supports [21,35,36]. The pronounced resistance of CeO_2 to carbon formation is attributed to improved carbon gasification rates [37–39]. In addition, in a methane dry-reforming study, nickel supported on mixed Ce–Zr–O proved beneficial for suppressing the formation of inactive carbon deposits [40].

The use of hydrocarbons heavier than methane presents an increased risk of carbon formation [41]. Due to the motivations discussed above, however, considerable attention has recently been paid to hydrogen production from liquid fuels via ATR [42] both for distributed electricity generation [43] and on-board vehicle applications [35,44,45]. Pt/CeO_2 is an active catalyst and shows robust resistance to carbon formation during ATR of liquid fuels [35,46,47]. Because platinum is expensive, ceria has poor thermal stability, and zirconia shows a high ability to inhibit carbon formation by promoting the gasification rate [48], a catalyst based on nickel- and zirconia-stabilized ceria should be promising for liquid fuel ATR [44,45,49]. But deactivation due to carbon deposition is a problem that still must be solved for the nickel-supported ceria–zirconia system, particularly at high nickel loadings [50]. Although a great deal about carbon formation during methane reforming has been learned, it remains to be seen whether the principles and strategies developed to reduce carbon deposition in that system can be applied to the reformation of liquid fuels. To prevent deactivation due to carbon deposition [26,45,50], it is necessary to identify the types of carbon formed and the relationship of carbon deposition and nickel loading. The current work presents a combined identification and characterization of carbon deposited on nickel-based ceria–zirconia catalysts of different nickel loadings during isooctane ATR. One of the objectives is to distinguish between carbon overlayers (“coating carbon”) and filamentous carbon; however, it is not the purpose of this work to study the detailed nature of nanotubes, such as identification of single-walled versus multiwalled nanotubes.

2. Experimental

2.1. Preparation of fresh NiO/Ce–Zr–O

The ceria–zirconia mixed oxide (CZO) with a composition of $Ce_{0.75}Zr_{0.25}O_2$ was synthesized by coprecipitating a mixed aqueous solution of $Ce(NO_3)_3$ and $ZrOCl_2$ salts using ammonium hydroxide as a precipitating agent. The precipitate was recovered by filtration and washed with deionized water, dried at 110 °C, and finally calcined at 600 °C in air for 2 h. Nickel oxide supported on CZO (NiO/CZO) with different nickel loadings was prepared by incipient wetness impregnation using an aqueous solution of nickel nitrate. After impregnation, the catalyst was dried at 110 °C and calcined at 600 °C in air for 1 h.

2.2. Autothermal reforming and carbon deposition

Carbon deposition was carried out during ATR of isooctane (iC_8-ATR) using approximately 80 mg of catalyst mixed with 240 mg of silica gel. The silica gel was calcined at 850 °C in air before use and was of the same particle size as the catalyst (60–80 mesh). The catalyst and diluent mixture was loaded into a $\frac{1}{2}$-inch-diameter quartz reactor tube and reduced in situ at 600 °C under a flow of 350 ml/min of 5% H_2 in N_2. The reduced catalyst, Ni/CZO, is designated *xx*Ni/CZO, where *xx* represents the weight percent nickel loaded on CZO, as shown in Table 1.

Various iC_8-ATR operations were run over Ni/CZO catalysts under different reaction protocols to investigate catalyst deactivation due to carbon deposition [50]. As shown in the iC_8-ATR protocol in Fig. 1, the reaction procedure in this work was started at 300 °C using a fuel flow rate of $\sim$0.14 g/min,