



Highly dispersed Rh-, Pt-, Ru/Ce_{0.75}Zr_{0.25}O_{2-δ} catalysts prepared by sorption-hydrolytic deposition for diesel fuel reforming to syngas

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ABSTRACT

Three noble metal catalysts (Rh-, Pt-, Ru/Ce_{0.75}Zr_{0.25}O_{2-δ}) for reforming of hydrocarbons were studied in steam and autothermal process conditions. Each catalyst was prepared by sorption-hydrolytic deposition with a metal loading of 0.1 mmol/g. The main idea of this technical approach was to form a solution of “metal complex + alkaline agent” that was metastable at given conditions (temperature, concentrations) with respect to homogeneous metal hydroxide precipitation, due to the kinetic inertness of the metal complexes for ligand exchange. As the support surface accelerated heterogeneous nucleation and growth of metal hydroxide particles, addition of the support to the reagent mixture initiated the hydrolysis which led to uniform depositing of 1–2 nm metal particles over the support surface. The Rh-based catalyst synthesized surpassed the Ru- and Pt-based catalysts in activity and stability in that under the experimental conditions, complete *n*-hexadecane conversion and equilibrium reformat product distribution were observed for 1-wt. % Rh/Ce_{0.75}Zr_{0.25}O_{2-δ} for 17 h. This catalyst also showed competitive performance in autothermal reforming of diesel fuel providing stable operation for 9 h.

1. Introduction

In recent decades, the development of new technologies for on-site power generation has attracted considerable attention [1,2]. Among commercially available auxiliary power units of 1-kW scale, solid oxide fuel cell (SOFC) based systems are considered as the most effective for electricity generation. Compared with thermoelectric, gasoline and diesel generators, SOFC-based systems of similar mass and volume demonstrate higher efficiency, along with silent and reliable operation.

Diesel fuel is an attractive source of hydrocarbons due to its high energy density, widespread availability and mature distribution infrastructure. In recent years, a number of papers have been published on studies of steam and autothermal reforming, and partial oxidation of diesel fuel to produce hydrogen gas for SOFC operation [3–13]. Being a complex blend of C₁₀–C₂₄ hydrocarbons, including aromatic compounds, diesel fuel is difficult to reform into syngas, because of accompanying side reactions resulting in undesired coke formation. The latter results from both catalytic and homogeneous thermoc cracking reactions that produce light hydrocarbons, such as ethylene, easily converted to carbon [14–16].

To avoid undesirable homogeneous non-catalytic reactions, numerous engineering solutions have been proposed, including various types of injectors, ultrasonic atomizers, and special evaporation and mixing chambers for homogenizing the reaction mixture prior to the catalytic process [15–17]. Catalysts shaped in ceramic or metallic honeycomb blocks, foams, wire meshes, or microchannel plates supporting an active component layer provide low pressure drop and effective heat and mass transfer. Numerous types of catalysts have been studied to improve the performance of diesel reforming. Rh, Ru, Pt and Ni, their bimetallic compositions together with various transition metals supported on individual or mixed Zr-, Ce-, Gd-, La-, and Al-oxides have been designed as active catalyst components. Perovskite and pyrochlore structures have also been widely studied [20–27]. Among others, precious metals on ion-conducting supports have shown the highest activity, stability and, therefore, durability in diesel reforming. In addition to carbon deposition, catalyst deactivation may be caused by sintering of the supported metal particles at the high temperatures of the diesel reforming process, resulting in a decreased reforming rate for the slow-reacting diesel components, such as aromatic compounds, promoting coke formation and further accelerating catalyst

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deactivation.

Ion-conducting oxide supports for diesel reforming catalysts usually have low specific surface area making the deposition of the required amount of highly dispersed metal particles difficult using currently available preparation techniques (e.g. adsorption, impregnation, incipient wetness impregnation, and deposition-precipitation). The problem is especially complex for wire mesh, foam or honeycomb supports, resulting in insufficiently high reforming activity and durability.

In this paper, composite oxide $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_{2-\delta}$ supported Rh, Ru and Pt catalysts synthesized using a novel preparation technique were studied for steam reforming (SR) of *n*-hexadecane (HD) used as a diesel surrogate, and autothermal reforming (ATR) of HD and conventional diesel fuel, the type of “summer” Euro-5 (SD). The catalytic activity was tested using a micro-reactor setup. Transmission Electron Microscopy (TEM), BET, temperature-programmed oxidation (TPO), X-ray photoelectron spectroscopy (XPS) and CO chemisorption techniques were used for catalyst characterization and coke formation studies.

2. Experimental

2.1. Catalyst preparation

Composite oxide $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_{2-\delta}$ (CZ) was purchased from Ecoalliance Ltd. (Russia), prepared by direct precipitation as described in detail elsewhere [28]. Solutions of Ce^{3+} and ZrO^{2+} nitrates were combined in fixed proportions resulting in concentrations of components totaling 0.1 g cm^{-3} . The composite oxide was precipitated from the solution by adding 25% aqueous ammonia dropwise under permanent stirring. The mixture was held at 100°C and atmospheric pressure for 120 h. Thereafter, the precipitate was filtered and repulped in isopropanol. The resulting slurry was dried at 100°C for 12 h and calcined at 500°C for 2 h, and then at 800°C for 1 h. The synthesized CZ material was crushed in an agate mortar with the 0.2–0.5 mm fraction separated for further catalyst synthesis. The CZ BET surface area was $69 \text{ m}^2 \text{ g}^{-1}$.

Catalysts were prepared by sorption-hydrolytic deposition as described in [29] that contained Pt, Ru and Rh deposited on CZ particles in the amount of 0.1 mmol/g (1 wt.% Ru and Rh, 1.9 wt.% Pt), denoted further as Ru/CZ, Rh/CZ and Pt/CZ, respectively. The main idea of this technical approach is to form a solution of “metal complex + alkaline agent” which is metastable at given conditions (temperature, concentrations) in respect to homogeneous metal hydroxide precipitation. This is due to the kinetic inertness of the metal complexes for ligand exchange [30]. As the support surface accelerates heterogeneous nucleation and growth of metal hydroxide particles [31], addition of a support to the reagent mixture initiates hydrolysis which leads to uniform depositing of the metals over the support surface.

For this purpose, a solution of metal chloride (RuCl_3 , RhCl_3 or H_2PtCl_4) was mixed with Na_2CO_3 in a molar ratio of $\text{Na}/\text{Cl} = 1$. The mixture was then brought into contact with the aqueous suspension of the CZ support. The deposition was performed at 5°C for Pt, 60°C for Ru and 75°C for Rh. After the end of the deposition procedure (i.e., when no reaction of the solution with NaBH_4 was observed), the samples were thoroughly rinsed with hot water by decanting, dried and reduced in hydrogen flow at 250°C for 30 min. The BET specific surface area of the prepared catalysts was close to that of the CZ support ($69 \text{ m}^2 \text{ g}^{-1}$).

For comparison purpose, 1 wt.%Rh supported on CZ was prepared by typical incipient wetness impregnation technique. This catalyst is further denoted as Rh/CZ(WI).

2.2. Catalyst characterization

The BET specific surface area (S_{BET}) of the support, as-prepared and used catalysts was determined from the complete nitrogen adsorption isotherms at -196°C using an ASAP 2400 sorptometer (Micromeritics,

USA).

The dispersion of the metal particles supported on the CZ, their specific surface area and mean size were evaluated using pulse chemisorption of CO in H_2 at 20°C . Prior to the CO chemisorption measurements, the catalysts were reduced in a hydrogen flow at 350°C for 30 min. The technique of pulse titration of the metal surface was adopted from [32,33].

The X-ray diffraction (XRD) patterns were obtained on a diffractometer X'tra (Thermo Scientific, Switzerland) using monochromatic $\text{CuK}\alpha$ radiation ($\lambda = 154.18 \text{ pm}$). The measurements were carried out in the 2θ range of $15\text{--}80^\circ$ with a step of 0.05° and 5.0 s sampling time. The ICDD PDF-2 database was used for the phase composition analysis. The Rietveld refinement with quantitative phase analysis was performed using TOPAS v4.3 software. The sizes of the coherent scattering regions (D_{XRD}) were calculated by line broadening analysis according to the Scherrer equation.

To quantify the carbon formation during steam reforming of HD and autothermal reforming of SD, the used catalysts were studied by TPO using a TG209 F1 LibraThermo microbalance instrument (Netzsch, Germany). The feed gas, 0.6 vol. % O_2 in He, flowed at $70 \text{ cm}^3 \text{ min}^{-1}$. The temperature was raised linearly from 30 to 900°C at a rate of $10^\circ\text{C min}^{-1}$. The outlet CO_2 concentration was monitored on-line using a QMC-200 mass-spectrometer (Stanford Research Systems, USA).

X-ray photoelectron spectroscopy (XPS) was applied to determine surface composition of the as-prepared and used catalysts. The XPS measurements were carried out using an ES-300 photoelectron spectrometer (KRATOS Analytical, U.K.) with $\text{MgK}\alpha$ irradiation. Before the measurements, the catalyst samples were reduced at 250°C in H_2 (667 Pa) for 2 h in the preparation chamber of the spectrometer. The power of the X-ray was no more than 80 W to avoid X-ray damage of the catalyst surface. The spectra were calibrated by Ce3d U^m line with binding energy of 916.7 eV. The XP spectra were processed with a proprietary in-house XPS-Calc program, which has been tested on a number of systems [34,35]. The Shirley-model was used for subtraction of the inelastic photoelectron background. The spectra were fitted by Gauss–Lorentz or Doniach–Sunjic functions.

The transmission electron microscopy (TEM) images of the as-prepared and used catalysts were obtained using a JEOL JEM 2010 electron microscope with 1.4 \AA resolution at 200 kV (JEOL Ltd., Japan). The interplanar spacing was analyzed, and the particles composition was determined using the JCPDS-ICDD database.

Detailed characterization by XPS and TEM was performed only for the Rh/CZ catalyst which had superior catalytic performance, as discussed in Sections 3.2–3.4, below.

2.3. Catalytic activity measurements

The reactions of *n*-hexadecane (Komponent-Reaktiv LLC, Russia) steam reforming, autothermal reforming of HD and SD were performed in a fixed-bed continuous-flow U-shaped quartz reactor (ID: 7 mm, catalyst bed length: 12 mm) at atmospheric pressure in the temperature range of $550\text{--}650^\circ\text{C}$. In all the experiments, 0.5 g of the catalyst was placed in the reactor together with a 50 mm piece of copper foam at the reactor inlet used as an evaporator at 450°C . The 130 mm space between the evaporator and the catalyst bed was filled with 1–2 mm quartz pellets homogenizing the reactants mixture. The fuels were fed via a capillary into the evaporator. The evaporated water from a steam generator together with the nitrogen carrier gas was supplied via a heated capillary to the evaporator and mixed with the vaporized fuel. Air was fed via a coaxially positioned capillary close to the catalyst bed. The reaction temperature was measured by a K-type thermocouple in the middle of the catalyst bed.

Prior to the experiment, the catalyst was reduced inside the reactor in a mixture of 10 vol. % H_2 in Ar at a heating rate of 6°C min^{-1} up to 600°C . The temperature was then changed to 550 or 650°C , and the reaction mixtures were fed to the reactor. The mixture compositions

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