Heat-sink enhancement of decalin and aviation kerosene prepared as nanofluids with palladium nanoparticles

Lei Yue [a], Xiaoxing Lu [a], Hai Chi [a], Yongsheng Guo [a,*], Li Xu [a], Wenjun Fang [a,*], Yu Li [b], Shenlin Hu [b]

[a] Department of Chemistry, Zhejiang University, Hangzhou 310027, China
[b] Science and Technology on Scramjet Laboratory, The 31st Research Institute of CASIC, Beijing 10074, China

HIGHLIGHTS

- Surface-modified Pd nanoparticles were synthesized with diameters of 1–3 nm.
- Nanofluids were prepared with Pd NPs and decalin/kerosene.
- An electrically heated apparatus for cracking of fuel-based nanofluids was built.
- Heat sink was enhanced for cracking of decalin/kerosene prepared as a nanofluid.

ARTICLE INFO

ABSTRACT

Three different kinds of palladium nanoparticles modified by octadecanethiol, octadecylamine, and mixture of them have been prepared, which are simply marked as Pd@S, Pd@N and Pd@S&N in turn. The nanoparticles are characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), and thermo-gravimetric analysis (TGA). It follows that the average diameters of the nanoparticles are 1–3 nm. Pd@S shows noncrystalline structure, while Pd@N and Pd@S&N show face-center cubic (fcc) structure. These palladium nanoparticles can be well-dispersed in decalin, and then the nanofluids composed of decalin and palladium nanoparticles are prepared, which can be regarded as pseudohomogeneous systems. The cracking of each nanofluid containing 500 ppm Pd is performed under supercritical conditions (3.5 MPa, 600–750 °C) of decalin with a mass flow rate of 1 g/s in an electrically heated tube reactor which simulates a single passage in a practical heat exchanger. The cracking results indicate that these nanoparticles exhibit catalytic activity to a certain extent, and the activity of Pd@N nanoparticles is better than that of Pd@S or Pd@S&N. At 750 °C, the conversion of decalin is raised from 70.31 wt% of thermal cracking to 73.21 wt% with the existence of Pd@S, while that raised to 80.54 wt% with Pd@S&N and even raised to 91.85 wt% with Pd@N. The heat sink of nanofluids is effectively enhanced, and the nanofluid containing Pd@N shows the highest value, which reaches 3.50 MJ/kg and is increased by 0.29 MJ/kg in comparison with the heat sink of thermal cracking at 750 °C. The cracking of aviation kerosene containing Pd nanoparticles is then performed, the results of which confirm the feasibility of practical application of Pd nanoparticles to hydrocarbon fuels.

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1. Introduction

Hypersonic aircrafts have been attracting a great deal of attention in recent years [1–3]. Aerodynamic heating becomes extremely severe when the flight speed of aircraft reaches or exceeds Mach 5. Using liquid hydrocarbon fuels as both propellants and coolants is usually considered to be one of the most effective techniques for the thermal protection of advanced aircrafts [4,5].

The heat sink of a liquid hydrocarbon fuel, which comes from the physical heat and cracking reactions, has to be designed to meet the endothermic requirement. The catalytic cracking of hydrocarbon fuels proves to be a significant technique in cooling aircrafts due to the higher heat sink in comparison with the thermal cracking [6–8].

Palladium is usually used as catalyst for C–H olefination, Suzuki cross-coupling reaction, dehydrogenation reaction [9–11]. It is supposed to enhance the cracking conversion and heat sink of hydrocarbon fuels. Unfortunately, heterogeneous catalysis by packing metal powder or metal oxide into the reactor leads to small contact areas and high heat resistance resulting from coke deposition over metal surface. Noble metal nanoparticles (NPs) are widely studied owing to their unique optical, electronic, physical and catalytic properties [12–14]. Nanofluids composed of

hydrocarbon fuels as base fluids and NPs with outstanding catalytic property can be treated as pseudohomogeneous systems, which have good dispersion stability, appropriate thermal conductivity and viscosity [15–17]. Hence, the nanofluids might be used as a promising coolant for hypersonic aircrafts to overcome the drawbacks of heterogeneous catalyst systems.

In order to simulate the actual regenerative cooling-channel, electrically heated tube experiments have usually been carried out, and a much high heat flux flows through the tube reactor in this kind of apparatus than in that heated by furnace. Linne et al. [18] evaluated the heat transfer and thermal stability of JP-7, and Siegemeier et al. [19] investigated the coking and heat transfer of five hydrocarbon fuels. Liu et al. [20] studied the hydraulic and thermal effects of coke deposition during pyrolysis of hydrocarbon fuels. Generally, it is recognized that the experimental data obtained from electrically heated tube reactors with a higher heat flux are valuable and authentic to the practical aircrafts.

In this work, decalin is chosen as the model hydrocarbon fuel due to its high density and thermal stability, which is often found in jet fuels [21–23]. Three different kinds of Pd NPs are synthesized by the Brust–Schiffrin method [24] and the Leff method [25]. An electrically heated tube experimental system is built. A series of cracking reactions of decalin- and kerosene-based nanofluids under different operation conditions are carried out to verify the catalytic ability of the nanoparticles. These original investigations are expected to provide detailed information to prepare an advanced hydrocarbon fuel as both propellant and coolant with an excellent value of heat sink.

2. Materials and methods

2.1. Materials

Potassium tetrachloropalladate (II) (K_2PdCl_4, mass fraction 98 wt%), tetraoctylammonium bromide (TOAB, 98 wt%), octadecanethiol ($C_{18}H_{37}SH$, 97 wt%), octadecylamine ($C_{18}H_{37}NH_2$ 97 wt%) and decalin ($C_{10}H_{18}$, 99 wt%) were obtained from Aladdin Chemical Reagent Co., China. Toluene (C_7H_8, 99.5 wt%) and sodium borohydride ($NaBH_4$, 96 wt%) were purchased from Sinopharm Chemical Reagent Co., China. Aviation kerosene is provided by China National Petroleum Corporation.

2.2. Preparation of palladium nanoparticles

K_2PdCl_4 was dissolved in water, and TOAB was dissolved in toluene. Both of the solutions were mixed by sonication in a three-necked bottle. The two-phase mixtures were stirred until $PdCl_4^{2-}$ was transferred to the toluene phase. During the stirring process, the orange water phase was gradually changed to colorless, while the toluene phase changed to be deep red. The toluene phase was then separated from water phase, and octadecanethiol or octadecylamine was added in a mole ratio of $Pd:C_{18}H_{37}SH = 2:1$ or $Pd:C_{18}H_{37}NH_2 = 1:12$. $NaBH_4$ was dissolved in water as a reducing agent, and was added dropwise into the toluene phase. After the deep red became black in the toluene phase, the solvent was removed by rotary evaporation, and the black powders of Pd@S or Pd@N were obtained after they were washed with ethanol for three times. With the prepared Pd@N nanoparticles in the toluene phase, octadecanethiol was added under stirring overnight, and the mole ratio was controlled to be $Pd:C_{18}H_{37}SH = 4:1$. The solvent toluene was then removed by rotary evaporation, and the black powder of Pd@S&N was washed with ethanol for three times.

The Pd NPs could be well-dispersed in the nonpolar solvents such as decalin, cyclohexane and dodecane. These three kinds of Pd NPs, Pd@S, Pd@N and Pd@S&N were dried by vacuum oven, and reserved for characterization and property measurements.

2.3. Characterization of palladium nanoparticles

A thermo X-ray diffractometer (XRD) (Bruker AXS, Germany) was used to characterize the crystal structures. The XRD data were collected using Cu Kα radiation (γ = 1.5405 Å), and the scanning angle was set from 10° to 80° with the rate of 5 deg/min. The morphology and size of Pd@S, Pd@N and Pd@S&N were investigated by employing a transmission electron microscopy (TEM) (HT7700, Japan) with an operating voltage of 100 kV. The relative contents of the organic ligands and metal were measured by thermo-gravimetric analysis (TGA) (Q50, USA). The temperature range of TGA was set from 25 to 700 °C, and the heating rate was 10 °C/min. The TGA operation was performed under nitrogen atmosphere.

2.4. Cracking of decalin-based nanofluids

Cracking reactions of the decalin-based nanofluids were carried out to investigate the catalytic effects of these three kinds of Pd NPs. Cracking of decalin with corresponding ligands were also performed to confirm the catalytic effects of Pd in the nanofluids. Since the contents of Pd in these three kinds of NPs are different, the addition quantity of Pd is controlled to be 0.05 wt%. On the basis of TGA data, the addition quantities of NPs and ligands are calculated, and listed in Table S1 of Supplementary Material. A simplified scheme of cracking apparatus is presented in Fig. 1. It is mainly composed of five systems: a, feeding system; b, electrically heated reaction system; c, cooling system; d, gas–liquid separation system; e, data measurement and acquisition system.

Before each run of the cracking experiment, nitrogen was blown into the channel for 10 min to exhaust the inside air. The sample of decalin or its nanofluid was pumped into the channel at a constant mass flow rate of 1 g/s with a high-pressure pump (P500, China). The outlet pressure was controlled by a back pressure valve at 3.5 MPa to ensure the fuel under its supercritical condition. A direct current power supply provided a given current passing through the channel to raise the temperature quickly to a target value. The cracked fuel flowed into the cooling system and was quenched to the room temperature. The gaseous and liquid products were then separated by a gas–liquid separator.

The test channels were made of nickel GH3128 with heated length 1000 mm, outside diameter 3 mm, and wall thickness 1 mm. Several K-type thermocouples (TC) with outside diameter of 0.2 mm were welded on the channel to measure the wall temperature. The outlet fuel temperature was measured by a K-type TC with outside diameter of 3 mm.

Under a given cracking condition, each test was performed three times to prove the repeatability and to evaluate the uncertainty.

2.5. Cracking of kerosene-based nanofluids

On the basis of the practice to decalin-based nanofluids, the kerosene-based nanofluids with Pd NPs were prepared and the cracking performances were similarly carried out. The aviation kerosene is composed of 16.5 wt% chain alkanes, 79.0 wt% cycloalkanes and 4.5 wt% aromatics.

2.6. Analysis of cracking products

The gaseous products were analyzed by gas chromatography (GC) (9790, China). The content of hydrogen was determined by GC equipped with a stainless steel column and a thermal conductivity detector (TCD). The column temperature was kept constant