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Thermodynamic properties and pyrolysis performances of hydrocarbon-fuel-based nanofluids containing palladium nanoparticles

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ABSTRACT

Three different kinds of palladium nanoparticles (Pd NPs) 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 average diameters of Pd NPs are 1–3 nm. The Pd NPs can be well-dispersed in decalin and kerosene. The properties of the kerosene-based nanofluids, such as viscosities, thermal conductivities and stabilities are determined. The pyrolysis of decalin-based nanofluids containing Pd NPs is carried out in a batch reactor from 440 to 470 °C. The order of the catalytic ability for three Pd NPs is: Pd@N > Pd@S&N > Pd@S. The catalytic abilities of Pd NPs for pyrolysis of decalin are ascribed to the combined effects of Pd and its ligands. Based on GC analysis results, the major gaseous products are found to be methane, ethane, ethylene, propane and propylene. The liquid products contain aromatic, cycloalkene, cycloalkane, and chain hydrocarbons. The amount of chain hydrocarbons is small at different reaction temperatures, which means ring-opening reaction is difficult to occur during the pyrolysis of decalin. The formation of aromatic results from the dehydrogenation and condensation of cycloalkene induced by the secondary reaction at relatively high temperatures. For a comprehensive evaluation of the thermal conductivity, stability and catalytic ability, Pd@S&N is the most potential additive for the hydrocarbon fuel to prepare an advanced propellant with high stability, thermal conductivity and cooling ability.

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1. Introduction

Aerodynamic heating becomes extremely severe when the flight speed of aircraft reaches or exceeds Mach 5. The uncooled surface would exceed 3000 °C when the speed reaches Mach 8 [1]. Using liquid hydrocarbon fuels as both propellants and coolants is considered to be one of the most effective techniques for the thermal protection of advanced aircrafts. Hydrocarbon fuels circulate through the cooling passages located on the hot wall surface to absorb the waste heat before they are injected into the combustion chamber. The fuels decompose into small molecules through endothermic reactions during the cooling process, and it is known as regenerative cooling. The heat sink (cooling ability) 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. Because of the catalytic ability of nanoparticles for the cracking and combustion of hydrocarbons, the hydrocarbon fuel-based nanofluids have been investigated widely [2,3] for the potential application in the aircraft.

Nanofluid is a new class of fluids by dispersing nanometer-sized materials into base fluids [4–7]. The thermal conductivity of nanofluid is effectively enhanced compared to those of the base fluid, so it can be used as a novel coolant in the heat exchangers, such as electronics cooling, nuclear systems cooling and regenerative microchannel cooling in the hypersonic aircrafts [8–10]. Due to the high surface energy of nanoparticles, it is easy for them to coagulate and difficult to disperse in the base fluids [11,12]. This result limits the application of nanofluids. The surfactants have always been employed to modify the surfaces of the metal nanoparticles to improve its dispersity in nonpolar solvents [13]. In the practical application of nanofluids, the coagulations of nanoparticles are inevitable. The agglomeration of nanoparticles results in not only the settlement on the inner face of microchannels but also

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decreasing of thermal conductivity of nanofluids. The heat transfer efficiency would decrease to a certain extent. So, the investigation on stability is a key issue that influences the properties of nanofluids for application, and it is important to study and analyze the dispersion stability of nanofluids under various conditions including in static container and flowing channel.

Palladium is usually used as catalyst for C-H olefination, Suzuki cross-coupling reaction, dehydrogenation reaction etc. [14–16]. It is supposed to enhance the pyrolysis conversion and heat sink of hydrocarbon fuels, which is very meaningful for the engine of hypersonic aircraft. So, three different kinds of palladium nanoparticles (Pd NPs) modified by octadecanethiol, octadecylamine, and mixture of them have been prepared and characterized detailedly in our previous work [17], which are simply marked as Pd@S, Pd@N and Pd@S&N in turn. These nanoparticles show good catalytic activity in a flowing reactor.

In this work, the hydrocarbon-fuel-based nanofluids containing Pd NPs were prepared. The viscosity, thermal conductivity and thermal stability of the kerosene-based nanofluids were investigated, along with the pyrolysis performance of decalin-based nanofluids in a batch reactor from 440 to 470 °C. The results are expected to provide the fundamental information for the application of nanofluids with Pd NPs as a novel coolant in the cooling systems.

2. Experimental

2.1. Materials

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

2.2. Preparation of Pd nanoparticles

The preparation process and characterization of Pd NPs was described in detail in the previous work [17]. In brief, K_2PdCl_4 was dissolved in water, and TOAB was dissolved in toluene. The two-phase mixtures were stirred until $PdCl_4^{2-}$ was transferred to the toluene phase. 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. 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 washed with ethanol for three times. With the prepared Pd@N nanoparticles in the toluene phase, octadecanethiol was added, 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.

2.3. Preparation of nanofluids

A series of nanofluids were prepared by dispersing different mass fractions of Pd NPs into kerosene and decalin as the base fluid. The samples were homogenized by means of ultrasonic method for 1 h to ensure good dispersion of the nanoparticles in the base fluid. The nanofluids were observed to be black with various degrees.

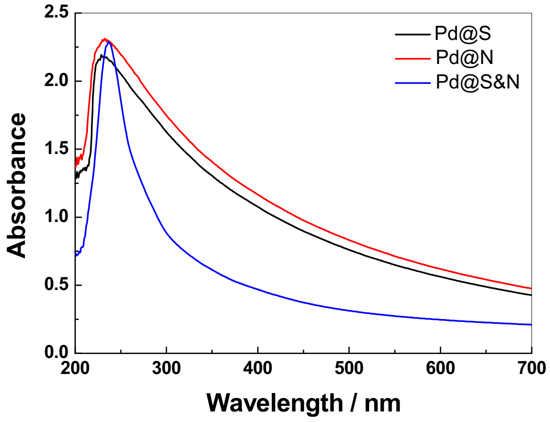

Fig. 1. UV-vis spectra of different Pd nanoparticles dispersed in kerosene.

2.4. Measurement on viscosity and thermal conductivity of nanofluids

The viscosities were measured by using an Anton Paar AMVn viscometer at the temperature $T = (298.15–323.15)$ K and pressure $p = 0.1$ MPa. The precision of the efflux time was ± 0.001 s, and the apparatus could keep the temperature varying within ± 0.01 K. The combined uncertainty of the viscosity measurement is ± 0.005 mPa·s. Each test was performed three times to obtain the mean viscosity value of nanofluid.

The thermal conductivities were measured by using a KD2 transient calorimeter at the temperature $T = (298.15, 303.15, 308.15)$ K and pressure $p = 0.1$ MPa. The relative standard deviation of the thermal conductivity measurements was evaluated to be less than 2%. The experimental values were reported by averaging the values of three duplicate tests.

2.5. Measurement on stability of nanofluids

The nanoparticles are observed to coagulate under different conditions. As the concentration of suspension has a linear relation with absorbance, Ultra violet-Visible spectrophotometer (UV1770, Shimadzu Corporation, Kyoto, Japan) measurements have been used to quantitatively characterize the concentration variations of nanoparticles in the nanofluids from 200 to 700 nm. All the tested samples were diluted 10 times with the base fluids. As shown in Fig. 1, the nanofluids containing Pd NPs show an obvious absorption peak at the wavelength about 220 nm depending on the size of NPs [18]. If the initial concentration of nanofluids is considered to be one, the relative content of nanoparticles in nanofluids after settlement for a certain time can be calculated according to the variation of absorbance peak area.

2.5.1. Stability of nanofluids at room temperature and atmospheric pressure

Nanofluids containing Pd NPs with a mass fraction of 0.1% were reserved in bacterial bottles. A small amount of sample was removed from the bottles for the spectroscopic analyses once a month.

2.5.2. Thermal stability of nanofluids in flowing equipment

The 0.1 wt% Pd nanofluids were pumped into a microchannel (Φ 3×0.5) with a volume flow of 1 mL/min. The outlet pressure was controlled by a back pressure valve at 3.5 MPa. Then the channel was heated to a given temperature ranging from 180 to 350 °C. The samples collected at the exit of the systems were analyzed by UV

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