SURFACE EFFECTS OF COPPER ON DEPOSIT FORMATION FROM JET FUEL RANGE HYDROCARBONS

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Introduction

The formation of carbonaceous deposit on metallic surface of the fuel system from heated jet fuel is a major concern in the development of advanced jet aircraft where the fuel is used as the primary coolant and can reach temperatures up to 540 °C [1]. Recent studies regarding the thermal stability of jet fuels mostly focus on the homogeneous pyrolytic degradation of jet fuels and model compounds [2]. Limited studies show that at low temperatures (< 300 °C) copper was the most deleterious element promoting the deposit formation, probably due to the catalysis of oxidation reactions by oxides of copper [3]. At high temperatures and pressures (450 °C, 1500 psig) in a batch reactor copper displayed some activity with incipient formation of carbon filaments [4].

The principal objective of this work is to study the copper surface effects on deposit formation from JP-8 jet fuel and its model compounds (n-dodecane and Norpar 13) in batch and flow reactors. The deposit morphology and composition of reaction products are compared to those obtained with a nickel surface [5].

Experimental

In batch reactor experiments, n-Dodecane (Aldrich, > 99%) was isothermally heated to 450 °C in quartz lined stainless steel tubing reactors in a fluidized sand bath. A 5 ml sample was used for all the tests [4].

In flow reactor experiments, Norpar-13, a mixture of C11-C15 n-alkanes, or jet fuel was pumped into a reactor system (Chemical Data System, CDS model 803), mixed with ultra-high purity N_2, and then preheated to 250 °C in the valve oven. The preheated mixture of fuel and N_2 was heated and reacted in a 5 mL 316 stainless steel tubular reactor. Further details about the flow reactor system can be found elsewhere [5].

In both batch and flow reactor experiments, 25 μ thick copper foils (99.995 %, Goodfellow, UK) were cut into coupons and inserted into the reactor before reaction. The coupons were cleaned with acetone in an ultrasonic bath before reaction. After reaction, they were rinsed with hexane, dried at 120 °C in an vacuum oven, and weighed for further characterization. Morphologies of deposits were examined with an ISI ABT SX-40A scanning electron microscope (SEM). Deposit on metal coupons was also analyzed with a Bio-Rad 175 FTIR spectrometer (Micro-FTIR) equipped with UMA 500 microscope to obtain the reflective FTIR spectra.

Results and Discussion

In the batch reactor, after 1 hour reaction of n-dodecane at 450 °C, fibrous deposit was observed on Cu coupons by SEM. Some of the fibers had a varying diameter along the length which terminate with pointed ends. The fibers were usually 5-6 μm long, and 0.3 - 0.4 μm wide. No Cu particles were spotted at the tip of these fibers. Micrographs indicated that the main mass of the copper particle was at one end of the fiber or in the middle when bi-directional growth took place. After 3 and 5 hours of reaction, the deposit was seen as a bulky featureless layer, with some large particulates buried within the layer.

In the flow reactor, Norpar 13 was heated to 550 °C, 500 psig at a flow rate of 2 mL/min for 5 hours. Only a small amount of deposit was formed on Cu coupons. The deposit was seen as a smooth, featureless layer with a few particulate regions of deposit scattered on top of this layer. No fibrous deposit was observed under these conditions which led to large amounts of filamentous carbon deposit formed on nickel coupons [5].

In flow reactor experiments with JP-8 fuel at 625°C, 500 psig, heavy deposition occurred on the copper coupons after 5 h with no visible deposit on the reactor walls. The metal coupons became very brittle after the reaction. The SEM micrographs showed colonies of deposit aggregates on the copper surface. These deposit aggregates contained fibrous structures with pointed ends, similar to those obtained in the batch reactor experiments. The fibers appeared to be fused together. Using X-ray mapping of a polished pellet exposing the cross section of the copper/deposit interface, Cu particles were found to be distributed in the deposit. Cu signal was detected along the fibers, rather than concentrated at their tips. Using nickel coupons under the same conditions, very small amount of deposit was formed; no filamentous carbon was observed.

The FTIR spectra of the deposit on Cu coupons from 1 h reaction with n-dodecane did not show any C-H peaks. However, as the reaction time increased from 3 to 5 hours, the C-H peaks appeared and the ratio of the peak intensities in the $3100 - 2970$ cm^{-1} range to those in the $2970 - 2750$ cm^{-1} increased, indicating an increase in the aromaticity of the deposit with the increasing time from 3 to 5 h. A similar trend was also observed for the deposit on nickel coupons.

The FTIR spectra of the deposit formed on copper coupons in the flow reactor from JP-8 fuel show a strong aromatic C-H band and less intense bands for aliphatic C-H groups.

There are clear differences between the effects of copper and nickel surfaces on deposit formation from n-dodecane in a batch reactor and from Norpar-13 and JP-8 in a flow reactor, as summarized below:

• incipient fibrous deposit from n-dodecane on copper in a batch reactor; long induction period for filamentous carbon formation on nickel under the same conditions.

• no fibrous deposit from Norpar-13 on copper in a flow reactor; extensive filamentous carbon formation on nickel.

• fibrous deposit from JP-8 fuel on copper; no filamentous carbon on nickel.

• decreasing diameter of fibers formed on copper in the direction of growth; constant diameter of individual filaments on nickel.

These differences suggest that fibrous deposit formation on copper surfaces follow a different mechanism from that widely accepted for filamentous carbon formation on the surfaces of transition metals such as nickel. It appears that the formation of fibrous deposits on copper surfaces involves the surface diffusion of polynuclear aromatic hydrocarbons (PAH) as deposit precursors. This is in contrast to the bulk diffusion of small dissociated hydrocarbon species through the metal particles to produce filamentous carbon [6,7].

Although the JP-8 jet fuel consists mostly of n-alkanes (60%wt), it contains high concentrations of alkylbenzenes (16%wt). It is known that, upon thermal stressing, alkylbenzenes produce PAH much more readily than n-alkanes and alkylcyclohexanes [8]. It has been also shown that alkylbenzenes are produced from heating n-alkanes in the batch reactor [2]. The formation of fibrous deposits on copper from n-dodecane and jet fuel decomposition can be attributed to the formation of PAH in high concentrations. Heating Norpar-13 in the flow reactor does not produce much PAH, and no deposits are observed on copper coupons. The changing diameter and fused states of fibers formed on copper surfaces also suggest that a surface diffusion step, rather than bulk diffusion, is involved in the formation of these fibers.

It is reported in the literature that Cu is not active in forming conventional filamentous carbon because Cu is unable to dissociatively decompose the hydrocarbon species, which is considered as the first step to form the precursors to filamentous carbon [7]. Under thermal stressing conditions used in this study characterized by high pressure and heavier reactants, the formation of PAH is promoted in the batch reactor from n-dodecane and in the flow reactor from JP-8 jet fuel, to produce alternative precursors to various deposits, including fibrous deposits, resembling filamentous carbon. Filamentous carbon formation on Cu surface from PAH has also been reported recently in the literature by Setlur et al. [9].

Conclusions

There are differences in the activity of Cu and Ni surfaces towards carbon deposit formation from jet fuel and model compounds during pyrolysis. Fibrous deposit formation from thermal stressing of jet fuel on Cu surface proceeds with a surface diffusion mechanism which involves PAH as precursors to the deposits.

Acknowledgments

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