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Chemical Engineering Science 61 (2006) 4207–4219

Chemical
Engineering Science

www.elsevier.com/locate/ces

Contributions of heterogeneous and homogeneous chemistry in the catalytic partial oxidation of octane isomers and mixtures on rhodium coated foams

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Received 21 December 2005; received in revised form 1 February 2006; accepted 2 February 2006
Available online 23 March 2006

Abstract

Catalytic partial oxidation experiments with *n*-octane, 2,2,4-trimethylpentane (*i*-octane), and an *n*-octane:*i*-octane (1:1) mixture were performed on 80 and 45 ppi Rh-coated α-alumina foam supports at 2, 4, and 6 SLPM total flow rate in order to explore the effects of chemical structure for single components and binary mixtures on fuel reactivity and product distribution. When reacted as single components, the conversion of *i*-octane is greater than *n*-octane at $C/O > 1.1$ (both fuel conversions are 100% for $C/O < 1.1$). However, when reacted in an equimolar mixture, the conversion of *n*-octane is greater than *i*-octane. All three fuels give high selectivity to syngas (H_2 and CO) on 80 ppi supports for $C/O < 1$. For $C/O > 1$, *n*-octane produces high selectivity to ethylene while *i*-octane makes *i*-butylene and almost no ethylene. The fuel mixture produces these species proportional to the mole fractions of *n*-octane and *i*-octane within the reacting mixture. Increasing the support pore diameter decreases the selectivity to syngas and increases H_2O and olefin selectivity.

The reforming of all three fuels is modeled using detailed chemistry by decoupling the heterogeneous and homogeneous chemistry in a two-zone plug flow model. Detailed homogeneous reaction mechanisms with several thousand elementary reactions steps and several hundred species are used to simulate experimentally observed olefin selectivities for all three fuels on 80 and 45 ppi monoliths at 2, 4, and 6 SLPM quite well. These results support the hypothesis that a majority of the observed olefins are made through gas-phase chemistry.

Keywords: Partial oxidation; Rhodium; Octane; Syngas; Olefins; Reactor modeling; Reaction engineering; Catalysis

1. Introduction

Catalytic partial oxidation (CPO) is a process by which valuable chemicals can be autothermally generated from hydrocarbon feedstocks at millisecond contact times. Specifically, a CPO reactor can be tuned to produce high selectivity to syngas ($H_2 + CO$) or olefins (ethylene, propylene, etc.) when liquid hydrocarbons are used as fuel (Krummenacher et al., 2003; O'Connor et al., 2001). Hydrogen can be used to power fuel cells, and olefins are the biggest commodities produced in the chemical industry with approximately 100 million tons of ethylene produced annually (Sundaram et al., 2001; Zimmermann and Walzl, 2002). Hydrogen is produced industrially through steam reforming, and olefins are made via steam cracking. Both processes are highly endothermic and require large amounts of energy from externally fired heaters to drive the reaction. Consequently, residence times on the order of one second are required for both methods. CPO is a viable alternative to these processes for making H_2 or olefins because residence times are dramatically decreased from one second to approximately 10 ms and thermal efficiency is increased by eliminating the need for external furnaces because the overall reaction is exothermic and self-sustaining.

For use in a transportation fuel cell application, H_2 will likely be reformed from distributed liquid fuels like gasoline or diesel. Olefins will be made from refinery sources like naptha (Sundaram et al., 2001; Zimmermann and Walzl, 2002). These chemical feedstocks are complicated mixtures that typically contain linear and branched hydrocarbons as well as aromatic compounds. By comparing the reaction of different classes of compounds individually and in binary mixtures in a CPO reactor, we can begin to assemble an idea of how the actual

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0009-2509/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.ces.2006.02.010

distributed fuels will perform and what contribution each component makes to the overall reaction.

The motivation for this work is threefold. First, a direct comparison of the CPO of *n*-octane, 2,2,4-trimethylpentane (*i*-octane), and an equimolar mixture of *n*-octane and *i*-octane is performed in order to explore the effects that branching has on fuel reactivity and product distribution when isomers are reacted as single components and as a binary mixture. These two fuels were chosen because they are model components of gasoline, and they have the same chemical formula but very different chemical structures. Previous work on binary mixtures of linear alkanes where the components have different molecular weights has argued that the specific C/O ratio for each component (local C/O ratio) and diffusive flux are important parameters for fuel conversion (Subramanian et al., 2004). These variables are eliminated in this work because *n*-octane and *i*-octane have the same chemical formula (C_8H_{18}). For this analysis, the most important parameter to consider when comparing the competitive and non-competitive conversion of these isomers is the structural differences between a straight-chain and a highly branched alkane. Previous work on the CPO of heavy alkanes shows that straight-chain hydrocarbons like decane and hexadecane produce the highest olefin selectivity to ethylene (Krummenacher et al., 2003), while branched and cyclic hydrocarbons like *i*-octane and cyclohexane produce high selectivities to branched and cyclic olefins like *i*-butylene and cyclohexene (O'Connor et al., 2001). Comparing the olefin selectivities resulting from the reaction of a binary mixture of octane isomers to the single components will aid in the analysis of the reaction pathways required for olefin generation.

Secondly, the effect of the monolith support is explored. Previous experiments on butane, *i*-octane and *n*-decane have shown that increasing the pore diameter increases selectivity to olefins and combustion products and decreases syngas selectivity (Bodke et al., 1998; Krummenacher and Schmidt, 2004; O'Connor et al., 2001). Increasing the pore size increases the extent of homogeneous chemistry because the ratio of surface area to volume is decreased. A detailed examination of the dependence of product distribution on pore size gives further insight as to which products are made heterogeneously and which are formed homogeneously in the CPO system.

Finally, the CPO of octane isomers and mixtures is modeled in order to demonstrate that this process can be accurately described by combining heterogeneous and homogeneous chemistry. Previous research has demonstrated that ethylene can be produced with 70% selectivity from the reaction of ethane with O_2 on noble metal coated ceramic foam monoliths (Huff and Schmidt, 1993). It was first thought that ethylene was formed heterogeneously from ethane, and a surface reaction mechanism was developed to describe the reaction of ethane on Pt foams (Huff and Schmidt, 1996). Recent experimental and theoretical work on the oxidative dehydrogenation of ethane on $Pt/\gamma\text{-}Al_2O_3$ catalysts has shown that ethylene is primarily produced through gas-phase reactions and suggests that the catalyst is critical in initiating gas-phase reactions by heterogeneously oxidizing the fuel to CO, CO_2, and H_2O and generating the heat that drives the homogeneous reactions that produce ethylene (Beretta et al., 2000, 2001a,b). Simulations of these experiments that integrate heterogeneous and homogeneous chemistry agree with this relationship between surface and gas-phase chemistry (Donsi et al., 2004, 2005; Huff et al., 2000). These ideas on the CPO of ethane are extended to the development of a model for the reaction of octane isomers. A two-zone model is developed by which H_2, CO, H_2O, and CO_2 are assumed to form through heterogeneous reactions between absorbed fuel and O_2 in the first zone at the entrance of the catalytic bed. Olefins and other hydrocarbons are then formed downstream in a second zone through homogeneous (O_2-free) pyrolysis of unreacted fuel. These two reaction pathways are combined to accurately predict fuel conversion and product distribution for all three fuels studied at total flow rates from 2 to 6 standard liters per minute (SLPM) on 45 and 80 pores per linear inch (ppi) supports.

2. Experimental method

The fuels used in these experiments are HPLC grade ($>99\%$ purity) *n*-octane, *i*-octane, and *n*-octane:*i*-octane (1:1). The reactor is a quartz tube with an inner diameter of 19 mm. A detailed sketch of the reactor setup has been provided elsewhere (Krummenacher et al., 2003; Williams and Schmidt, 2006). The fuel is delivered to the reactor through a low flow automotive fuel injector from a 136 kPa (5 psig) pressurized liquid fuel tank. The fuel injector sprays a conical dispersion of droplets onto the wall of the tube creating a thin film of fuel that is vaporized by heating the walls of the tube with a Variac-controlled resistive heating tape. High purity O_2 and N_2 are delivered separately to the reactor through calibrated mass flow controllers. The fuel, O_2, and N_2 mix in this arrangement such that homogeneous auto-ignition of the fuel is avoided upstream of the catalyst (Krummenacher et al., 2003). The total flow rate of fuel and air to the reactor is varied between 2 and 6 SLPM corresponding to residence times on the order of 5 to 15 ms at average catalyst back-face temperatures between 800 and 1000 °C. The feed stoichiometry is given as the carbon to oxygen ratio (C/O), and is defined as the moles of carbon atoms divided by the moles of oxygen atoms in the feed. By this definition, the stoichiometric feed composition for partial oxidation is at $C/O = 1.0$.

The experimental system is controlled by a personal computer with a program written in LabView. The software regulates the N_2 and O_2 mass flow controllers and the automotive fuel injector. The software also reads and stores the temperatures from chromel–alumel K-type thermocouples located at the back-face of the catalyst and in the upstream mixing zone. The products are analyzed with an HP5890 gas chromatography (GC) instrument fitted with a GS-GasPro 60 m capillary column and a thermal conductivity detector. Liquid nitrogen is used to cool the GC oven to an initial temperature of $-80\,°C$ so that all products can be analyzed using a single separation column. The resulting carbon and hydrogen atom balances typically close to within $\pm 5\%$.

The catalyst support structures are cylindrical α-alumina macroporous ceramic foam monoliths of 18 mm diameter and