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Shorter Communication

Kinetic studies of the partial oxidation of isooctane for hydrogen production over a nickel–alumina catalyst

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Abstract

The kinetics of the catalytic partial oxidation of isooctane for hydrogen (H_2) production over a stable Ni/γ-Al_2O_3 catalyst was investigated at atmospheric pressure in the temperature range of 863–913 K, ratio of weight of catalyst to the molar feed rate of isooctane (W/F^{o}_{iC8}) in the range of 7.09–30.89 kg mol^{-1}, and molar feed ratio O_2/i-C_8H_{18} of 4.0 in a 12.7 mm diameter Inconel micro-reactor housed in an electrically controlled furnace. The developed rate models were based on the Langmuir–Hinshelwood–Hougen–Watson (LHHW) and Eley–Rideal (ER) formulations. Out of the 18 models developed, 10 were eliminated due to poor predictive efficiency. A LHHW mechanism requiring the dissociative adsorption of isooctane and molecular adsorption of oxygen on a single site was the most likely pathway for the partial oxidation of isooctane. The reaction order of 1.5 indicates a strong coverage of nickel by isooctane.

Keywords: Isooctane; Gasoline; Partial oxidation; Nickel-based catalyst; Kinetics

1. Introduction

The use of catalytic converters to control vehicle exhaust emissions is well known (Heck and Farrauto, 2002). However, increasingly stringent legislation has led to consideration of alternative means of reducing emissions. Of these measures, the use of fuel cells appears to be very promising and has seen remarkable progress in the past decade because of an increasing need to improve energy efficiency as well as to address environmental concerns (Krumpelt et al., 2003). The polymer electrolyte membrane fuel cell (PEMFC) is a potential candidate for direct electricity production from hydrogen for transportation applications and also for distributed and portable power generation. Also, hydrogen is projected to be one of the primary energy sources in the 21st century (Sabacchi et al., 2002). Its combustion and oxidation is pollution free and supplies sufficient energy for transportation and other applications. However, the absence of a viable hydrogen storage option and a hydrogen marketing infrastructure, at least in the near term, necessitate the search for an appropriate fuel (Ahmed et al., 1999). Petroleum-derived fuels such as gasoline are attractive sources of hydrogen because of their existing production, distribution, and retailing infrastructure. Also, gasoline has a much higher energy density and larger hydrogen content compared to methanol and ethanol (Zhu et al., 2004; Moon et al., 2004), which are also considered as good sources for hydrogen. The conversion of hydrocarbons to hydrogen can be carried out using one of three major techniques: steam reforming, partial oxidation and autothermal reforming. The major by-product CO_2 can be captured and sequestered prior to hydrogen use. Partial oxidation is chosen for this study for the reasons that: (i) the reaction is exothermic, making it much more energy-efficient than steam reforming; (e.g. $C_8H_{18} + 4(O_2 + 3.76N_2) \leftrightarrows 8CO + 9H_2 + 15.04N_2$; $\Delta H^{o}_{298} = -6.60 \times 10^5$ J/mol, (ii) a smaller reformer can be used to achieve a high conversion of the hydrocarbon selectively in favor of the production of H_2 at short contact times; and (iii) the partial oxidation setup is more compact and mechanically simpler than the steam reforming, since no additional heating is required (Li et al., 2000). The development of an efficient partial oxidation reformer for the production of hydrogen from

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liquid hydrocarbon fuels such as gasoline is very challenging. It requires the development of a stable catalyst for the process. It also requires detailed thermodynamic and kinetic information about the reaction and such information is presently scant (Springmann et al., 2002). In aprevious study (Ibrahim et al., 2006), we obtained a stable performance for a Ni/γ-Al_2O_3 catalyst for the production of hydrogen by the partial oxidation of isooctane.

Thus, the objective of the present study is to develop a mechanistic based kinetic model to describe the catalytic partial oxidation of isooctane to produce hydrogen using this stable Ni/Al_2O_3 catalyst. The developed models are based essentially on the LHHW and ER hypotheses and these were cross-examined with actual experimental kinetic data. The results are presented in this communication.

2. Theory

Initially, an empirical, irreversible fixed feed molar ratio power law rate model was developed as shown in Eq. (1).

$$r_A = k_0 e^{(-E/RT)} C_A^m. \tag{1}$$

Then, different mechanistic models based on LHHW and ER mechanisms were proposed. The overall reaction considered in the development of all models is given in Eq. (2).

$$C_8H_{18} + 4O_2 \longleftrightarrow 8CO + 9H_2 \quad \Delta H^o_{298} = -660\,\text{kJ mol}^{-1}. \tag{2}$$

The discrimination between rival models was based on predictive efficiency (i.e., the average absolute deviation (AAD%) between predicted and experimental results) and the similarity in activation energy values between the model and the power law model. Other supporting criteria such as residue analysis and chemical common sense were also used where appropriate. The development of these two classical mechanisms was based on the assumptions that: (1) the rate-determining step (RDS) could be controlled by the surface reaction step, adsorption step or desorption step; (2) there is the presence of uniformly energetic adsorption sites; and (3) there is monolayer coverage. The only differing assumption between LHHW and ER mechanisms was the use of a dual site mechanism for the reaction in the former case and a single site mechanism in the latter case. Sixteen LHHW and two ER models were proposed and tested. All the rate models, and the assumptions used in their derivation are given in Table 1(a–c).

3. Experimental

3.1. Catalyst selection

The catalyst used in this work was a 3% Ni/γ-Al_2O_3 catalyst prepared by the precipitation method. This catalyst showed good activity and stability in terms of isooctane conversion and hydrogen selectivity. Details of preparation, characterization and performance evaluation of this catalyst are given elsewhere (Ibrahim et al., 2006).

3.1.1. Experimental apparatus and analysis

An Inconel fixed bed reactor (i.d. = 12.7 mm) housed in a furnace with a single heating zone was used for catalyst performance evaluation. Liquid isooctane was introduced by a syringe pump (kd Scientific-200) while the gas flows were metered and regulated by an Aalborg digital flow controller (DFC-26). The air to isooctane molar ratio was 12.0. The catalyst bed temperature was measured by means of a sliding thermocouple dipped inside the catalyst bed. The diluent used in the catalyst bed was α-Al_2O_3 having the same particle size as the catalyst (150 μm). Pure α-Al_2O_3 (150 μm) was used in the preheating zone and the section after the catalyst bed. The total catalyst bed height was 70 mm. The exit product from the reactor was separated into permanent gases and liquid condensate by passing first through a condenser and then a gas/liquid separator. The gases were analyzed with an on-line gas chromatograph (HP-6890, Agilent Technologies) equipped with a TCD using Haysep and Molsieve columns (Alltech Associates) for complete gas product separation. The unreacted isooctane was analyzed with a GC-MS (HP-6890/5073, HP) using a 30 m GS-GasPro column (J&W Scientific).

4. Kinetic studies

Experimental kinetic data were collected at atmospheric pressure; temperatures of 863, 883, 903 and 913 K; and W/F^o_{iC8} of 255.6, 198.0, 162.0 and 136.8 kg-cat s kg-iC_8^{-1}. In order to approach plug flow conditions, and minimize backmixing and channeling, certain operating criteria as prescribed by Froment and Bischoff (Froment and Bischoff, 1990) were used. These were that the ratio of catalyst bed length to catalyst particle diameter (L/D_p) was 350 and the ratio of the inside diameter of reactor to particle diameter (D/D_p) was 63.5. Catalyst particle size of 150 μm and feed flow rate of 390 mL min^{-1} were used to eliminate pore and external diffusional limitations, respectively. The pressure drop along the reactor was calculated for the particle size used and found to be insignificant ($< 5 \times 10^3$ Pa) at the highest reaction temperature.

5. Results and discussion

5.1. Heat and mass transport limitations

It is well known that intrinsic kinetic data can only be obtained in the absence of heat and mass transport resistances. Theoretical criteria were used to determine whether there were any effects of interparticle and intraparticle heat and mass transport limitations on the rate of reaction at 913 K.

5.1.1. Heat transport effects

Internal pore heat transfer resistance was estimated using the Prater analysis given by

$$\Delta T_{\max,\text{particle}} = \frac{D_{\text{eff}}(C_{As} - C_{Ac})(-\Delta H_r)}{k_{\text{eff}}}, \tag{3}$$