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The kinetics of decalin ring opening over a Ir/H-Beta catalyst

Ali H. Alzaid, Kevin J. Smith*

Department of Chemical and Biological Engineering, University of British Columbia, 2360 East Mall, Vancouver, BC V6T 1Z3, Canada

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ABSTRACT

The selective ring opening of decalin over Pd/H-Y-30, Ir/H-Beta-300 and Ir/H-Beta-25 catalysts, measured in a stirred, batch reactor at 350 °C and 3 MPa H_2, showed that Ir/H-Beta-25 ($SiO_2/Al_2O_3 = 25$) had the highest activity and yield of ring-opened products. The effect of temperature (275–350 °C) and pressure (3–6 MPa) on the activity and product selectivity was further investigated over the Ir/H-Beta-25 catalyst. The highest ring-opened product yield (53 mol%) was obtained at a decalin conversion of 90 mol% at 325 °C and 6 MPa H_2. A Langmuir–Hinshelwood kinetic model, that assumed a bifunctional catalytic process in which hydrogenation and dehydrogenation reactions occurred on metal sites and isomerization, ring-opening and cracking occurred on acid sites, was successfully applied to the data. The model included the effect of catalyst deactivation associated with the catalyst acid sites. Activation energies estimated from the model parameters showed that the ring opening of isomers had the lowest activation energy (141 kJ/mol), whereas cracking had the highest (159 kJ/mol).

1. Introduction

The Canadian oilsands are a strategic source of energy supply for North America with established reserves of 169.9 billion barrels and potential reserves of 300 billion barrels [1]. The 2011 daily production of 1.7 million barrels/day is expected to increase to 2.5 million barrels/day in 2015 and 5.3 million barrels/day in 2030 [2]. Although the synthetic crude oil (SCO) derived from oilsands bitumen has low S content and zero residue, the high cycloparaffinic and aromatic content causes processing difficulties [3–5]. The heavy gas oil (HGO) derived from bitumen has a cycloparaffin and aromatic content of more than 90% compared to 60% in conventional paraffinic HGO [6]. The aromatic and cycloparaffinic content of HGO can be reduced using commercially proven hydrogenation technologies. However, the cetane number improvement by aromatic saturation is insufficient to enhance the quality of HGO significantly [3,7,8]. Other commercially proven technologies such as hydrocracking can be used to saturate the aromatics and reduce the number of ring structures. However, hydrocracking produces lower carbon number paraffins which have low cetane number [9]. Consequently, the optimum process to improve SCO quality is selective ring opening of cycloparaffins without a reduction in the product carbon number.

Many studies have explored selective ring opening using different supported and unsupported catalysts and model reactants including decalin [10–17], tetralin [18,19] and naphthalene [20,21]. McVicker et al. [22] examined different metal (Pt, Ir, Ru, Ni) and metal supported catalysts, and concluded that Ir was the most active and selective metal for ring opening of both five- and six-membered ring naphthenes. However, ring opening of six-membered ring naphthenes is much slower and less selective than with five-membered ring naphthenes. In order to improve six-membered ring opening, isomerization to five-membered rings with minimal branching is required. This can be achieved by optimizing the catalyst acidity and metal/acid properties using acidic supports, such as zeolites.

Corma et al. [17] investigated several medium-sized pore zeolites (ZSM-5, MCM-22, ITQ-2), large pore zeolites (USY, Beta), ultra-large pore zeolites (UTD-1) and mesoporous zeolites (MCM-41) for the hydrocracking of decalin and tetralin. Among all the zeolites tested, Beta zeolites had the lowest amount of cracked products and low naphthalene and coke yields with high selectivity to ring opened products. The superiority of Beta zeolites for selective ring opening reactions was also confirmed by Kubicka et al. [12]. Based on these studies, Ir supported on H-Beta should be an efficient catalyst for selective ring opening, a catalyst formulation that had not been reported in the open literature until the recent report by Kubicka et al. [10].

The mechanism of selective ring-opening is thought to start with aromatic ring saturation, followed by isomerization, ring opening and eventually cracking [10–14,16,22,23]. However, there remains some debate as to the role of the catalyst metallic and acidic

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* Corresponding author. Tel.: +1 604 822 3601; fax: +1 604 822 6003.
E-mail addresses: kjs@mail.ubc.ca, kjs@chbe.ubc.ca (K.J. Smith).

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functions in each of the reaction steps. Kinetic studies allow one to identify the relative rate of each reaction step and hence the relative importance of different catalyst properties in determining the selectivity for the desired ring-opened products.

In the present study, we compare the ring-opening of decalin over Ir/H-Beta catalysts and a Pd/H-Y catalyst that had been studied previously [21]. Higher conversion and ring-opening selectivity were obtained over the Ir/H-Beta catalyst with a low SiO_2/Al_2O_3 ratio (high acidity). The effect of reaction temperature and pressure on the ring opened product yield was further investigated over this catalyst. A Langmuir–Hinshelwood (L–H) kinetic model for the ring opening of decalin, based on the model proposed by Kubicka et al. [16] but modified to include the effect of catalyst deactivation, was applied to the experimental data. Decalin was used as model reactant so as to eliminate ring saturation and focus on the ring opening reactions. The reaction was performed in a stirred batch reactor as it is most efficient for studying reaction kinetics.

2. Experimental

2.1. Catalyst preparation

Three catalysts were synthesized as part of the present study: Ir/H-Beta-25, Ir/H-Beta-300, and Pd/H-Y-30. The metal content of each catalyst was 2 wt%. The SiO_2/Al_2O_3 molar ratio of each of the two H-Beta zeolites and the H–Y zeolite was 25, 300 and 30, respectively. NH_4-Beta-25 (CP814E), H-Beta-300 (CP811C-300) and H-Y-30 (CBV720) zeolites were obtained from Zeolyst International. The ammonium form of the Beta-25 zeolite was transformed to H-form using a step calcination process, whereby the zeolite was heated to 120 °C at a rate of 10 °C/min, held at 120 °C for 2 h, and then heated to 500 °C at the same rate of 10 °C/min and finally held at 500 °C for 5 h. The calcination was performed in stagnant air in a muffle furnace.

$IrCl_3 \cdot xH_2O$ (52 wt% Ir) and $PdCl_2$ (≥99.9%) precursors were obtained from Pressure Chemical Company and Sigma–Aldrich, respectively. The supports H-Beta-300 (5.79 g), H-Beta-25 (6.18 g) and H-Y-30 (4.16 g) were impregnated with aqueous solutions of 0.31 M Ir^{3+}, 0.13 M Ir^{3+} and 0.40 M Pd^{2+}, respectively. Each solution was prepared from the corresponding precursor salt to obtain the desired Ir and Pd loading of 2 wt% by incipient wetness impregnation of the supports. After impregnation, the catalysts were aged for 24 h and then calcined in a muffle furnace in air at 500 °C for 3 h [24]. No catalyst reduction was performed since the catalysts were readily reduced in situ during the reactor heat-up and stabilization periods.

2.2. Catalyst characterization

Temperature-programmed reduction (TPR) of the calcined catalysts was performed using a Micromeritics Autochem II 2920 unit. The catalyst (0.1 g) was placed in a glass u-tube and pre-treated in 50 ml (STP)/min He while heating to 300 °C at a rate of 20 °C/min and holding the final temperature for 2 h. After cooling to ambient temperature in a He flow of 50 ml (STP)/min, the sample was heated at a rate of 10 °C/min to a final temperature of 500 °C in a 30 ml (STP)/min flow of 10% H_2 in Ar for the TPR analysis, holding the final temperature for 1 h.

The same Micromeritics Autochem II 2920 unit was used to determine the CO uptake of the reduced catalysts by pulsed chemisorption. After cooling to ambient temperature in a He flow of 50 ml (STP)/min after the TPR analysis, the catalyst sample was repeatedly injected with CO pulses from a 20 ml (STP)/min 10% CO in He flow, until there was no further CO uptake by the sample, as indicated by a thermal conductivity detector (TCD). The CO uptake was used to calculate the metal dispersion assuming a CO:Metal adsorption stoichiometry of 1:1.

The total BET surface area, pore volume, and average pore size of the reduced catalysts were measured using a Micromeritics ASAP 2020 Accelerated Surface Area and Porosimetry analyzer. The catalyst sample was placed in a glass tube, degassed at 1.33 kPa/s while heating at a rate of 10 °C/min until 300 °C and 0.04 kPa. The temperature was then held at 300 °C for 240 min. Subsequently the sample was transferred to the analysis section to analyze the BET surface area by N_2 adsorption at 77 K.

The elemental carbon analysis of the fresh and used catalysts was performed using a Perkin-Elmer 2400 Series II CHNS/O analyzer. The used catalyst was recovered from the reaction product using vacuum filtration, washed with acetone, vacuum filtered, and dried before analysis.

2.3. Catalytic activity measurements

The catalytic reaction was performed in a stirred, 300 ml autoclave, batch reactor operated at temperatures of 275, 300, 325 and 350 °C and pressures of 3, 5 and 6 MPa at each temperature. Internal and external diffusion effects were suppressed by using a catalyst particle size of <63 μm and a stirrer speed of 1500 rpm, as suggested by Kubicka et al. [12]. At the start of each experiment, the reactor was charged with 100 ml of decalin (mixture of cis + trans-anhydrous, ≥99%, Sigma–Aldrich) and 0.5 g of catalyst. The reactor was then sealed and purged with N_2 for 15 min to remove air from the system, followed by purging with H_2 for 15 min. Subsequently the reactor was pressurized with H_2 at ambient temperature and heated to the required temperature such that after heat-up, the reactor was at the required operating pressure. During the reaction, liquid samples (0.1 ml) were collected periodically. The first sample was collected 45 min from the start of the heat-up period so that the reactor temperature had stabilized. In the first hour of operation at the required temperature, a sample was collected every 15 min. Subsequent liquid samples were collected every hour, up to 5 h reaction time. The liquid samples were analyzed by gas chromatography using a Shimadzu QP-2010S GC/MS equipped with a Restek RTX5 30M × 0.25 mm capillary column. In addition, representative gas samples were collected and analyzed using a gas chromatograph. The results indicated minimal amounts of cracked products in the gas phase compared to the liquid phase. Therefore, the products present in the gas phase were not included in the analysis that follows. The experimental reproducibility was confirmed by repeating selected experiments and the results obtained showed a variation coefficient of ±2% in the measured decalin conversion.

Although the feed consisted of cis- and trans-decalin only, the reaction resulted in more than 200 products identified by GC–MS analysis. A similar number of products has been reported in previous studies [11,16]. To simplify the discussion and development of the reaction kinetics, the products were grouped according to structural similarities. Five major groups were identified: decalin (D) which consisted of both cis- and trans-decalin; skeletal isomers of decalin (I) consisting of all products with 10 carbon atoms and two cyclic rings; ring-opened products (R) consisting of all products with 10 carbon atoms and one or no cyclic rings; cracked products (C) consisting of all products with less than 10 carbon atoms; and finally heavy products (HP) consisting of all products with more than 10 carbon atoms [16]. The repeatability of the product distribution analysis was confirmed by repeated injection of the same sample and the variance coefficient was found to be <± 1%.