



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



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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 H₂, showed that Ir/H-Beta-25 (SiO₂/Al₂O₃ = 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 H₂. 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).

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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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